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PREPARATION OF 1D-HYBRID ZnO/PVA NANO-FIBERS SYNTHESIZED BY ELECTRO-SPINNING

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1. INTRODUCTION

Electro-spinning is a very facile and feasible method for fabricating nanofibers. In addition to its simplicity and low cost, it is a versatile method to control the surface properties of nanostructures. Therefore this method is well suited for the fabrication of nanofibers. [1]

It is very efficient method for producing polymer fibers with special morphological properties. By using this process, nanofibers of smaller diameter could be produced, because of its large surface area to volume ratio. Recently, polymer nanofibers produced by electro-spinning were studied as materials for various applications such as medicine, wound dressing, tissue engineering or drug delivery etc. [2]

Nanofibers are typically formed using the process of electro-spinning, which involves applying a high voltage to an electrode in contact with the polymer solution. As the solution flows to the electrode, a high electric field deforms each drop of the polymer solution into a conical shape known as Taylor cone. Above a threshold limit, the electric forces overcome the surface tension of the solution and a fine, charged jet is ejected from electrode and ultimately nanofibers are deposited on grounded substrate. [3]

Luminescent nanofibers are a particular class of nanofibers. Thus the process of spinning fibers with the help of electrostatic force is known as electro-spinning which gives fibers with diameter below 100 nm are generally classified as nanofibers. There are various methods available to generate nanofibers but electrospinning is most suitable one among all methods. [4]

The basic set up of electro-spinning consists of three major components, which are, AC or DC high voltage power supply, plastic syringe, and collector is as shown in figure 1.



Fig.1 Basic set up of Electrospining

Under the influence of strong electrostatic field, charged polymer will be accelerated towards collector. [6]

Zinc oxide is an inorganic compound with the formula ZnO. ZnO is a white powder that is insoluble in water, and it is widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, lubricants [7], paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, and first-aid tapes. Although it occurs naturally as the mineral zincite, most zinc oxide is produced synthetically.ZnO is a wide-band gap semiconductor of the II-VI semiconductor group. This semiconductor has several favorable properties, including good transparency, high electron mobility, wide band gap, and strong room-temperature luminescence. Those properties are valuable in emerging applications for: transparent electrodes in liquid crystal displays, energy-saving or heat-protecting windows, and electronics as thin-film transistors and light-emitting diodes [8].

Several works has been done to fabricate the ZnOnanofibers by electro-spinning method which is shown in the following table 1:

SN	Material	Fiber Size	Polymer	Method Adopted	Ref
1	ZnO	150 nm	PVA	Electro-spinning	[9]
2	ZnO	200-300 nm	PANI	Electro-spinning	[10]
3	ZnO	200-400 nm	PVA	Electro-spinning	[11]
4	ZnO	150-300 nm	PVA	Electrospinning	[12]

EXPERIMENTAL

ZnO powder was prepared by the citric acid sol-gel method at 600 ° c for one hour. The precursor used Zinc nitrate (Zn (NO₃)₂. 6H₂O), Citric acid (C₆ H₈ O₇), all precursor are of AR grade and highly purified. First of all zinc nitrate were dissolve in double distilled water then citric acid and water taken in ratio of 1:2 it is used as a schelting agent. After vigorous stirring the solution kept on slow heating for the removal of water contained. During heating the black mass with powder precursors was obtained. Then material annealed at 600°C for 1 hour. After sintering white powder of ZnOwas obtained. The flow chart for the preparation of ZnO was as shown in figure 1.

The solution for electrospining prepared by mixing PVA in distilled water (1:12) along with ZnO particles, the solution was stirred for 2-3 h to obtain a homogeneous solution for electrospining. The following parameter are constant during nanofibers formation such as Flow rate for solution 1.0 ml/h, the tip to collector distance is 13 cm and applied voltage becomes 23 kV by using electrospining unit Super ES 1 purchased from IIT Kanpur.

As prepared Zn O was confirm by the XRD method using Rigakuminiflex II X-ray diffractometer with scan speed of 2.000°/min and Cu K α ($\lambda = 1.5406$ Å) radiation in the range 10–80°. The structural and morphological characteristics i.e., particle size and shape of particle sample was studied using a SEM analysis. The measurement was done using ZEISS EVO/18.



Fig.1: Flow chart for synthesis of ZnO

2. Result and discussion: XRD

As prepared ZnO samples crystal structure is confirmed by the XRD pattern matching with the standard JCPDS File number (36-1451) [13]. Fig. 2 shows the XRD pattern of the ZnO sample. All the peaks of ZnO are matching with the standard file. There are no diffraction peaks of other raw material or other impurities were present in the as prepared sample. According to Fig. 2 the sharp peak diffraction peaks shows that the powder sample has crystalline in nature. Moreover the miller indices of ZnO lattice calculated by using formula [14] as given in Table 2.



 Table 2

 Miller indices values of 7nO

while males values of ZhO.							
Material	20	θ	$\sin^2 \theta$	$\sin^2 \theta / \sin^2 \theta_{\min}$	$(\sin^2 \theta / \sin^2 \theta_{\min}) * 3$	$h^2 + k^2 + l^2$	h k l
	31.84	15.92	0.075163	1.000005	3.000016	3	111
	34.52	17.26	0.087949	1.170114	3.510341	4	200
	36.38	18.19	0.097354	1.29524	3.88572	4	200
ZnO	47.7	23.85	0.163338	2.173113	6.519339	6	211
	56.68	28.34	0.225133	2.995267	8.9858	9	221
	62.94	31.47	0.27229	3.622666	10.868	11	311

SEM analysis:

The as prepared nanofiber of ZnO with PVA is as shown in Fig. 3. The fibers are at random oriented and there exist many curvatures along the axis of fibers, which might be attributed to the asynchronous deposition of different parts of the electrospun fiber because of its own instabilities, such as whipping or non-symmetric wavering [15]. The random orientation of fibers is due to the repulsive electrostatic forces brought due to the induced surface charges. As we used the rotating collector for the collection of fibers there is slightly orientation of fibers alignment.



3. CONCLUSION:

We successfully prepared the ZnOnanofiber by using the Sol-gel method and successfully embedded in the PVA (Polyvinyl alcohol). With the help of the electrospining we have prepared the hybrid fiber of PVA/ZnO by maintaining the parameter of Espin for drawing nanofibers. Therefore we have concluded that the electrospining is one of the facile routes for the development of the metal oxide nonmaterial and electrospining is the effective technique for the fabrication of the 1D nonmaterial.

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BIO-GREEN SYNTHESIS OF Mn DOPED SnO₂ NANOPARTICLE THIN FILM

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ABSTRACT :

Herein Mn doped SnO_2 nanoparticles have been synthesized using simple, cost effective and ecofriendly biosynthesis method, in which remnant water (ideally kitchen waste) collected from soaked Bengal gram beans (Cicer arietinum L.) was used. This extract consists of different bio-molecules which acted as complexing as well as capping agents for synthesis of Mn-doped SnO_2 nanoparticles. The X-ray powder diffraction (XRD) and Field-emission scanning electron microscopy (FE-SEM) revealed uniform size distribution with the average size of 6 nm and confirmed the formation of rutile structure with space group (P42/mnm) and nanocrystalline nature of the products with spherical morphology. Further, the gas sensing properties of the materials have been studied in comparison with other gases. The reported gas sensing results are promising, which suggest that the Mn-dopant is a promising metal additives to fabricate low cost SnO_2 based sensor.

KEYWORDS: Biosynthesis, Gas Sensor, Mn-doped SnO₂.

PACS: 81, 89, 68

INTRODUCTION

SnO₂ has been extensively explored for different applications, such as gas sensors, ¹⁻³ transparent conducting electrodes,⁴ Li-ion battery anode materials^{5, 6} etc. The different properties needed for these applications have been achieved by synthesizing SnO₂ using different methods and by synthesizing different morphologies such as 1D SnO₂nanorod,⁷ SnO₂ nanosheets,⁸ SnO₂nanoflowers,⁹ etc. Apart from this, different dopants of noble metals (Pd, Au, Pt, and Ag)^{10, 11} considering the catalytic activity of noble metals have been investigated. Although they have been proven to be very effective for tuning and improving the materials properties, the high cost restricts their potential scope for practical applications. Thus, as an economic substitute, SnO₂ doped with transition metal ions such as Co, Mn, Fe, Ni, and Cr have been explored. These dopants cause smaller sizes and promote stabilization of the surface.

The metal doped SnO_2 nanoparticles have been synthesized using different physical and chemical roots, but this methods are either costly or make use of harmful chemicals. Thus, with a need for simple, economic and ecofriendly root for synthesis of metal doped SnO_2 nanoparticles, here in this work, Mn doped SnO_2 nanoparticles have been biosynthesized by completely green approach using remnant water (ideally kitchen waste) collected from soaked Bengal gram beans (*Cicer arietinum* L.).

EXPERIMENTAL

For typical synthesis of Mn-doped SnO₂ nanoparticles, 20 g of dry Bengal gram beans (*Cicer* arietinum L.) were soaked in 100 mL of DI water for 6 h at room temperature. Thereafter, the soaked seeds were removed and the extract was filtrated using a glass-fiber filter (GF/F) to be free from particulate matter. 10 mL of aqueous SnCl₄ (0.01 M) solution was added to 10 mL of the gram bean extract and diluted to 50 mL. To this solution, appropriate amount of MnCl₂ was added to have 5 wt% doping. The solution was centrifuged and the powder so obtained was calcined at 600 °C to remove the organic contaminants. This powder was then coated onto the glass substrates to form thin films using doctor blade method, annealed at 250 °C and was used for further characterizations and gas sensing application. The Mn-doped SnO₂ nanoparticles so produced were characterized for their preliminary structural and morphological properties. Gas sensing properties of the biosynthesized Mn-doped SnO₂ nanoparticles thin film was studied in detail and its sensitivity for NH₃ gas was investigated in this work.



FIGURE 1. Schematic of bio green synthesis of Mn doped SnO₂ nanoparticles

RESULT AND DISCUSSION

Synthesis Mechanism

When gram beans are soaked in de-ionized water for 6hrs, the cell walls undergo autolysis as a result the pectin molecules present in the cell wall get released in the extract.¹² Pectin molecules have a tendency to bind metal ions¹³ and thus, when tin ions are added to the extract, they get bound to the pectin molecules (Fig. 1.) This tin-hydroxide-pectin gel subsequently shrinks with increase in pH^{14} and inhibits the further growth of the nanoparticles. Thus, when calcined, very small sized nanoparticles with narrow size distribution are obtained.

Structural analysis

The biosynthesized nanocrystalline SnO₂ and Mn-doped SnO₂ nanoparticles were investigated using X-ray diffraction (XRD). The XRD spectra of SnO₂ and Mn-doped SnO₂ nanoparticles were recorded using Bruker D8 Advance X-ray diffractometer, using the 0.154 nm (Cu $_{K\alpha 1}$ radiation) wavelength of X-ray.



Figure 2.Rietveld refinement of biosynthesized Mn-doped SnO₂ nanoparticles.

The XRD spectra were further analysed using Rietveld refinement, shown in Figure 2. and the results are summarized in Table 1. The crystallite size of the synthesized nanoparticles was calculated using Scherrer's formula D=0.9 λ/β cos θ . Where 0.9 is a constant, λ is X-ray wavelength used and β is full width at half maxima for corresponding diffraction angle θ . The crystallite size and lattice strain calculated using Williamson hall method are given in Table 2.

TABLE 1. Parameters obtained from Rietveld refinement of pure and Mn doped SnO ₂ .						
Parameters	Pure SnO ₂	Mn-doped SnO ₂				
Diffractometer	Bruker	Bruker				
	D8 Advance	D8 Advance				
Radiation	CuKα ₁ (1.5406Å)	CuKα ₁ (1.5406Å)				
20 range	20-80	20-80				
Scan Step	0.02	0.02				
Peak Shape	Pseudo Voigt	Pseudo Voigt				
Chemical Formula	SnO ₂	$Sn_{0.95}Mn_{0.05}O_2$				
Space group	P 42/m n m	P 42/m n m				
a[Å]	4.74126	4.7402				
c[Å]	3.18912	3.1871				
V[Å]	71.69000	71.61643				
R _p	19.1	15.3				
R _{wp}	15.9	13.7				
R _f	4.89	4.61				
R _{exp}	12.38	10.52				

From the table 2 we can clearly see that with Mn doping the negative strain is induced into the crystal structure as the ionic radii of Mn (0.645\AA) is less than that of Sn (0.69\AA) and thus this strain resulted in decrease in size of the Mn-doped nanoparticles.

TABLE 2. Crystallite size and strain of pure and Mn doped SnO2							
Sample Crystallite size Strain							
	Scherrer's equation (nm)	W-H plot(nm)	W-H plot				
Pure SnO ₂	~6	~5.2	-0.00208				
Mn-SnO ₂	~5.8	~4.9	-0.00383				

Recent Advances in Nanotechnology

Morphological Analysis



Figure.3 FE-SEM image of biosynthesized (a) Pure and (b) Mn-doped SnO₂ nanoparticles

The morphology of the synthesized pure and Mn-doped SnO_2 nanoparticles was studied using Field emission scanning electron microscopy as shown in Figure 3. The FE-SEM image shows spherical morphology of the bio-synthesized pure and Mn-doped nanoparticle. The spherical grains are uniformly distributed with narrow size distribution throughout both the images.

Gas sensing



Figure4 Response of Mn-doped SnO₂ in the presence of 100ppm NH₃ gas at 200 °C operating temperature.

The gas response in the presence of 100 ppm NH_3 gas at 200°C operating temperature is shown in Figure 4. The response for 100ppm NH_3 gas is found to be 28% for pure SnO_2 and 46% for Mn-doped SnO_2 Nanoparticle thin film. The selectivity of the sensor was studied and is show in Figure 5. From figure 5.it can be clearly seen that the Mn-doped SnO_2 sensor is highly selective for NH_3 gas.



Figure 5 Selectivity of Mn-doped SnO₂ sensor for 100ppm gases at 200 °C operating temperature.

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SYNTHESIS AND PHOTO - LUMINESCENCE PROPERTIES OF BLUE EMITTING EUROPIUM DOPED CALCIUM CHLORO-BORATE PHOSPHOR SUITABLE FOR SOLID STATE LIGHTING APPLICATION

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ABSTRACT :

Solid state lighting (SSL) sources are emerging as a promising option due to several advantages along with energy saving such as high luminous efficiency, environment-friendliness, small volume, and long persistence.SSL refers to a type of lighting that utilizes light-emitting diodes (LEDs) as sources of illumination rather than electrical filaments or gas.

The intense blue emitting phosphor $Ca_2B_5O_9Cl:0.08Eu^{2+}$ with different concentration of Eu^{2+} is prepared by conventional solid state reaction method at1173K. The as-synthesized phosphor is crushed and sieved properly in order to get fine powder. The powder XRD pattern is recorded that is in good agreement with JCPDS card no.23-0859. The photoluminescence Emission (PL) and Excitation spectra (PLE) as well as SEM image is recorded. The as-synthesized phosphor shows intense blue emission at 452 nm. The PLE spectrum monitored at 452 nm emissionshows broad excitationband peaking at 365nm. CIE colour coordinates 1931 for the as-synthesized phosphor is recorded.

KEYWORDS: Solid state lighting (SSL), photoluminescence Emission (PL).

1. INTRODUCTION:

White LEDs are promising candidates to replace conventional incandescent and fluorescent lamps in the coming future due to their merits of a long operation life time, energy saving capabilities and high material stability [1].During past few years white LEDs fabricated using near ultraviolet LEDs coupled with red, green and blue phosphors have attracted much attention due to the advantages of color stability [2-3].This lead to the development of new phosphors with high quantum efficiencies for nUVLED applications. [4-9].

The luminescence in alkaline earth chloroborate has been reported at 298K by Peters and J. Baglio [10]. The dependence of luminescent properties of Eu^{2+} on host lattice cation and anion in alkaline earth haloborates $M_2B_5O_9X-Eu^{2+}$ at low temp (4.2K) has been extensively studied by A.Meijerink and G. Blasse [11]. The influence of the host lattice on the position of the lowest *4f65d* excited state is explained on the basis of a crystal field effect and nephelauxetic effect.

Nakamura et al reported the luminescence of sintered $Ca_2B_5O_9Cl:Eu^{2+}$ excited by UV-light [12]. The Eu^{2+} ions doped alkaline earth halo- borates $M_2B_5O_9X$ (M -Ca, Sr, Ba; X- Cl, Br) have gained special attention because of possible applications as storage phosphors for X-ray imaging and thermal neutron detection also. There are few reports on its possible application for white light emitting diodes [13]. In this paper we are reporting synthesis and luminescence properties of blue emitting phosphorCa₂B₅O₉Cl:0.08Eu²⁺.

2. EXPERIMENTAL:

 $Ca_2B_5O_9Cl:Eu^{2+}$ is prepared by conventional solid state reaction method in slightly reductive atmosphere produced by half burned charcoal at 1173K. The starting materials CaCO₃ (A.R.), CaCl₂ (5% excess), H_3BO_3 (10% excess) and Eu₂O₃ (99.99%) were mixed in stoichiometric proportions. The raw materials were mixed thoroughly in an agate mortar and then sintered at 1173K for 3 hours in reducing atmosphere produced by half burned charcoal. The obtained product is further grinded thoroughly to produce fine powder. The body colour of the phosphor so obtained is white.

3.RESULT AND DISCUSSION:

3.1 XRD analysis

Fig.1shows powder XRD pattern of $Ca_2B_5O_9Cl:xEu^{2+}$ recorded for structure confirmation.



Fig.1.The powder XRD pattern of as-synthesised Ca₂B₅O₉Cl:xEu²⁺

The powder XRD pattern is in good agreement with JCPDS card no.23-0859 indicating orthorhombic crystal structure with Pnn2 space group. The reported lattice constants are a=11.26(Å), b=11.33, (Å), c=6.3(Å). In this structure two different sites are available for the divalent cation. On both sites the cation is coordinated by six oxygen ions at an average distance of about 2.7 Å and by two halide ions at about 3.0 Å. The oxygen ions belong to borate groups. The site symmetry for the divalent cation is C1.



Fig.2. SEM images of Ca₂B₅O₉Cl:0.08Eu

Fig.2.represents the SEM images showing surface morphology of as-synthesised Ca₂B₅O₉Cl:0.08Eu²⁺ phosphor. These show the particles with irregular shape and the particle size ranging in 5-10µm. The acceptable percentage difference in ionic radii between doped and substituted ions must not exceed 30%. Since eight co-ordinated effective ionic radius of divalent Eu^{2+} ion (r = 1.25 Å) is closest to that of eight co-ordinated Ca^{2+} ions (r=1.12Å), it is believed that the Ca^{2+} sites are replaced by Eu^{2+} in this lattice[14-15].

3.2 Photoluminescence

The excited state $(4f^65d^1)$ energy of Eu^{2+} is strongly influenced by its ligand ions. Different host lattices doped with Eu^{2+} exhibit different luminescent characteristics. With increase in the crystal field strength the emission band shifts to longer wavelength side. P.Dorenbos compiled this for large number of inorganic compounds activated by $Eu^{2+}[16]$.



Fig.5.27: Fig.3.shows the PLE (a) and PL (b) curve for Ca₂B₅O₉Cl:xEu²⁺ for x=0.08.

In Ca₂B₅O₉Cl host Eu²⁺shows blue emission.Fig.3. showsthe PLE (a) and PL (b) curve for Ca₂B₅O₉Cl:xEu²⁺for x=0.08.The Photoluminescence excitation spectrum monitored at 452 nm shows broad band excitation peaking at 365 nm with a shoulder at 396 nm. This phosphor shows intense blue emission. The excitation band shows excellent spread in nUV region of the spectrum. This makes it potential candidate for near UV excited LED application.

The Emission spectrum monitored at 360 nm as well as 396 nm shows emission wavelength of 452 nm corresponding to $4f^{6}5d^{1}\rightarrow 4f^{7}$ transition of Eu²⁺ion. However the comparative intensity is less in later case.

Fig.4. represents the emission spectra of $Ca_2B_5O_9Cl:xEu^{2+}$ doped with different Eu^{2+} concentrations for the excitation wavelength 390nm. All of the emission spectra exhibit the similar profile with different relative intensities. The emission intensity increases initially with the increase of Eu^{2+} concentration and reaches to the maximum at x=0.08, then decreases due to the internal concentration quenching.



Fig.4. Emission spectra of Ca₂B₅O₉Cl:xEu²⁺for different 'x' values with excitation wavelength of 390nm

The concentration quenching mechanism is generally associated with energy transfer. The type of Non-radiative energy transfer process from one Eu^{2+} ion to another Eu^{2+} can be predicted by finding out the critical distance and on the basis of overlapping of excitation-emission spectrum. In this phosphor the activator is introduced solely on one crystallographic site (here Ca^{2+} site), the critical energy transfer distance (Rc) is approximately equal to twice the radius of a sphere with this volume. The critical energy transfer distance (Rc) can becalculated [17]. So in this case, V=789.54Å, N=4 and the critical doping concentration of Eu^{2+} in the $Ca_2B_5O_9Cl$: Eu^{2+} phosphor is determined to be 16.76Å. Since Rc is not less than 5 Å exchange interaction is not responsible for non- radiative energy transfer process from one Eu^{2+} ion to another Eu^{2+} ion in this host. In view of the emission and excitation spectra of $Ca_2B_5O_9Cl$: xEu^{2+} , the radiation re-absorption is unlikely to occur. As a result, the energy-transfer process of Eu^{2+} in $Ca_2B_5O_9Cl$: xEu^{2+} phosphor would be due to multi-polar interaction. Further it can be proved to be because of quadrupole–quadrupole interaction.

3.3 CIE colour coordinates

Fig.5.shows CIE colour co-ordinates1931for the as-synthesised phosphor is (0.145, 0.0368), indicating blue colour emission with FWHM of 37 nm.



Fig.5. CIE colour co-ordinates for the as-synthesised Ca₂B₅O₉Cl:0.08Eu²⁺

4. CONCLUSION

The blue emittingphosphor $Ca_2B_5O_9Cl:0.08Eu^{2+}$ is synthesized by conventional solid state reaction method. The powder XRD pattern is in good agreement with JCPDS card no. 23-0859. SEM images recorded show the particles with an irregular shape and the particle size ranging in 5-10µm. The as-synthesized phosphor shows intense blue emission at 452 nm. The PLE spectrum monitored at 452 nm emissionshows broad excitationband peaking at 365 nm with a shoulder at 396 nm. TheCIE 1931 color coordinates are (0.28, 0.56) for maximum emission intensity.

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VARIATION OF DAMPING LENGTH AND WAVELENGTH IN NORTH POLAR CORONAL HOLES OF SOLAR ATMOSPHERE

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ABSTRACT :

In the present paper, I would like to discuss about variation of damping length and wavelength in the region of $1.05R \odot$ to $1.35R \odot$ and in different cases like (i) Magnetic diffusivity only (ii) viscosity only and (iii) when both are present. It shows that Comparison of the fast and slow modes explicitly shows that the damping length as well as the wavelength for the fast-mode waves is much larger than those for the slow-mode waves.

INTRODUCTION:

The role of magnetohydrodynamics (MHD) waves has been discussed extensively in solar physics for understanding the outstanding problems of solar coronal heating and the solar wind accelerationMechanisms[1]. For derivation of dispersion relation we have to consider following MHD equation

$$\rho \frac{\partial v}{\partial t} + \rho (v \cdot \nabla) v = \frac{1}{\mu} (\nabla \times B) \times B + \rho \upsilon \nabla^2 V \tag{1}$$

$$\frac{\partial B}{\partial t} = \nabla \times \left(v \times B \right) + \eta \nabla^2 B \tag{2}$$

$$\nabla \cdot \boldsymbol{B} = \boldsymbol{0} \tag{3}$$

The equations (1), (2) and (3) are known as momentum equation, Induction equation and Magnetic flux conservation equation respectively. Where v is the velocity, B the magnetic field and ρ , μ , η , V are, respectively, the mass density, Magnetic permeability, magnetic diffusivity and the coefficient of viscosity.

Taking the perturbations from the equilibrium (Priest [2]) and linearize the equations (1) through (3) by neglecting squares and products of the small quantities. After solving above equations we get a dispersion relation as follows

$$\omega^{2} = k^{2} \left[v_{A}^{2} - i\omega(\upsilon + \eta) \right] + \upsilon \eta k^{4}$$
⁽⁴⁾

Where $V_A = B_0/(sqrt\{\mu\rho_0\})$ is the Alfven velocity. The dispersion relation was obtained by Pekunu et al. [3] &Kumthekar [4]. This dispersion relation is applied for the plasma in the North Polar Coronal Hole where assumed the angular frequency ω to be a real quantity and the wave number *k* as a complex quantity.

RESULT AND DISCUSSION:

For a given value of $\omega = 2\pi/\tau$ and the physical parameters discussed in the Kumthekar [3] and solved with the help of a FORTRAN program. I assumed the angular frequency ω to be a real quantity and thewave

number k as a complex quantity so that k = kr + iki. When both the krand kiare positive numbers, they are related to the damping length D and the wavelength λ of the wave as Chandra et al. [5]

$$D = \frac{2\pi}{k_i}$$
 and $\lambda = \frac{2\pi}{k_r}$

Equation (4) is a simple quadratic equation it can be solved for getting roots of equation. This equation can be studied for three cases (i) Magnetic diffusivity only (ii) viscosity only and (iii) when both are present.

Case I: Magnetic diffusivity:

Let us consider the case of magnetic diffusivity only. That is, there is no viscosity (v = 0). For this case, equation (4) gives *kr* and *ki*values. Then we can apply a condition $\omega r < v_A^2$, we get

$$k_r = rac{\omega}{v_A}$$
 and $k_i = rac{\omega^2 \eta}{2v_A^3}$

Thus, we have two roots; one with positive values of kr and ki, and the other with the negative values. For the positive values, the damping length D and wavelength λ are calculate as a function of R, for $\tau = 10^{-2}$ s, 10^{-3} s and 10^{-4} s and are given in Fig.1 (a). As from the expressions, here the damping length is much larger than the wavelength. While D shows a large variation, with a maximum around $1.2R_{\odot}$, the λ remains nearly constant. Fig.1 (a) shows that the wavelength is proportional to τ whereas the damping length is proportional to τ^2 .

Case II: Viscosity only:

Let us consider the case of viscosity only. That is, there is no magnetic diffusivity ($\eta = 0$). For this case, equation (4) gives *kr* and *ki*values. Then we can apply a condition $\omega \upsilon \gg v_A^2$, we get

$$k_r = \frac{\sqrt{\omega}}{\sqrt{2v}} and k_i = \frac{\sqrt{\omega}}{\sqrt{2v}}$$

Again, we have two roots; one with positive values of kr and ki, and the other with the negative values. For the positive values, the damping length D and wavelength λ are calculate as a function of R, for $\tau = 10^{-2}$ s, 10^{-3} s and 10^{-4} s and are given in Fig.1 (b).

As from the expressions, as long as $\omega v \gg v_A^2$, the damping length and the wavelength are equal to each other. There is a maximum around $1.2R \bigcirc$. It is the case for $\tau = 10^{-3}$ s and 10^{-4} s. But, for $\tau = 10^{-2}$ s, the D and λ differ slightly from each other, showing that the condition $\omega v \gg v_A^2$ is not satisfied here. There is a maximum around $1.2R \bigcirc$.

Case III: Both are Present $v \neq 0$ and $\eta \neq 0$.

Equation (4) is a quadratic equation in k2 and therefore, its roots are of the form of two pairs: \pm (kr1 +iki1) and \pm (kr2 +iki2). These two pairs for the roots correspond to the fast-mode and slow-mode waves. The damping length D and wavelength λ for the two modes as a function of R for $\tau = 10^{-2}$ s, 10^{-3} s and 10^{-4} s are shown in Fig. 2. It is interesting to note that the variation D and λ for the fast-mode wave is similar to that for the case of $\eta = 0$. Theslow-mode wave shows an opposite behaviour for the variation of D as well as λ . There is a minimum around *1.2R*. Here, also, D is nearly equal to λ for $\tau = 10^{-3}$ s and 10^{-4} s. But, for $\tau = 10^{-2}$ s, the D and λ differ slightly fromeach other. Comparison of the fast and slow modes explicitly shows that the damping length as well as the wavelength for the fast-mode waves is much larger than those for the slow-mode wave. Thus, the slow-mode waves cannot propagate through the corona.

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Fig. 1:Variation of damping length D and the wavelength λ as function of R for $\tau = 10^{-2}$ s, 10^{-3} s and 10^{-4} s for two cases v=0 and $\eta = 0$.



Fig. 2:Variation of damping length D and the wavelength λ for fast mode and slow mode waves as function of R for $\tau = 10^{-2}$ s, 10^{-3} s and 10^{-4} s for two cases $\nu \neq 0$ and $\eta \neq 0$.

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SYNTHESIS AND DOSIMETER PROPERTIES OF Ce³⁺ACTIVATED LiCaPO₄ PHOSPHOR FOR RADIATION DOSIMETRY

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ABSTRACT :

The goal of this work was to investigate the relevant dosimetric and luminescent properties of $LiCaPO_4:Ce^{3+}$ phosphor for radiation dosimentry. The structural property was studied through X-ray diffraction and surface morphology was studied through scanning electronic microscope. Additionally, the photoluminescence (PL), thermoluminescence (TL) and optically stimulated luminescence (OSL) behaviors of $LiCaPO_4:Ce^{3+}$ phosphor was studied. The XRD pattern of $LiCaPO_4:Ce^{3+}$ phosphor fully matched with the International Center for Diffraction Data (ICDD) file with card no 01-079-1396. The PL spectra of asprepared $LiCaPO_4:Ce^{3+}$ phosphor showed characteristic emission in near-UV region, when excited by 314 nm under UV excitation. The TL glow curve of $LiCaPO_4:Ce^{3+}$ phosphors were consist overlapping peaks in temperature 50–450°C. Also $LiCaPO_4:Ce^{3+}$ phosphors show excellent CW-OSL response under β irradiation.

KEYWORDS: Luminescence properties, Radiation dosimetry, X-ray diffraction, Optically Stimulated Luminescence.

1. INTRODUCTION

Thermoluminescence / Optically Stimulated Luminescence dosimetry (TLD/ OSLD) is generally known as a multipurpose technique for the quantitative measurement of ionizing radiations i.e., x-rays, γ -rays and β -rays, particularly in personnel monitoring [1]. Currently, many commercial TLD phosphors are available and used in radiation dosimetric fields. These TLD compounds work as key players in the field of radiation dosimetry. As compared to the TL technique, the OSL technique is becoming more popular in radiation dosimetry [2]. The use of OSL for personal dosimetry was first suggested s by Antonov-Romanovskii et al. [3]. Optically Stimulated Luminescence (OSL) technique is becoming a widespread method for personal and medical dosimetry after development of Al₂O₃:C [4].

Many researcher groups have already developed new OSLD/TLD dosimetry phosphors such as α -Al₂O₃:C, LiMgPO₄:Tb³⁺,B [5], SrSO₄:Eu²⁺[6], Li₂B₄O₇:Cu-Ag[7], KMgPO₄:Tb³⁺[8], KCaPO₄:Ce [9], Li₃PO₄:Cu [10], SrB₄O₇:Eu²⁺[11], LiCaAlF₆:[12] and LiBaPO₄:Tb³⁺[13] which plays a vital role in radiation dosimetry. The main applications of thesephosphors are in radiation dosimetry for personnel and environmentalmonitoring.

In the present paper, LiCaPO₄: Ce^{3+} phosphor was developed by using Sol-Gel method and its TL/OSL properties under β irradiation studied.

2. Experimental and Characterizations

The stearic acid Sol-Gel method was employed for the synthesis of LiCaPO₄:Ce³⁺ phosphors [14].Phase purity of LiCaPO₄:Ce³⁺ phosphorwas checked by means of X-ray diffraction (XRD) using a Rigaku miniflex II diffractometer with Cu K α (λ = 1.5405 Å) operated at 5 kV. The morphological

characteristic was studied by using scanning electron microscope (SEM). Irradiations of all the samples were performed at room temperature using a calibrated ⁹⁰Sr/⁹⁰Y beta source in-housed in RISO TL/OSL Reader (DA-15 Model). The activity of the source was 40mCi and the dose rate was 20mGy/sec. The PL and PL excitation (PLE) spectra were measured on (Hitachi F-7000) fluorescence spectrophotometer with a 450W Xenon lamp, in the range 200–500 nm, with spectral slit width of 1 nm and PMT voltage at 700V at room temperature.

3. Results and discussion

3.1 X-Ray diffraction Patterns and canning electronic microscope

The X-ray diffraction pattern of LiCaPO₄:Ce³⁺ phosphor was prepared by using SG method as shown in Fig. 1 (a). The XRD patterns were well match with ICDD (International center for diffraction data) file with card No. 01-079-1396 and found to be in agreement confirming the formation of the materials.The SEM micro images of LiCaPO₄:Ce³⁺ phosphor was synthesized via SG method as shown in Fig. 1 (b). It was observed that microstructure of the phosphor consist of irregular grains with heavy agglomeration.The average sizes of as-prepared particles were found to be in the range 2-10µm.



Fig.1(a). XRD diffraction patterns of LiCaPO₄:Ce³⁺ phosphor with ICDD file and Fig. 1 (b) Surface morphology of LiCaPO₄:Ce³⁺ phosphor

3.2 Photoluminescence Properties (PL)

The combined excitation and emission spectra of $LiCaPO_4:Ce^{3+}$ phosphor was synthesized via SG method as shown in Fig. 2. The excitation and emission spectra were observed under 369 and 314 nm respectively.



Fig 2. Excitation and Emission spectra of LiCaPO₄:Ce³⁺ phosphor

The excitation spectra of LiCaPO₄:Ce³⁺phosphor was consist broad band in the range 200-340 nm and maximum intensity was observed at 314 nm and emission spectra consist of broad band in range from 340-500 nm and maximum intensity was observed at 369 nm. The Ce³⁺ luminescence in LiCaPO₄ was caused by the transitions from the lowest energy level of the Ce³⁺ 5d configuration to the spin-orbit split ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ levels [15].

3.3 Thermoluminescence (TL) Properties of LiCaPO₄: Ce³⁺ Phosphor

Fig. 3 represents the TL glow curve of LiCaPO₄:Ce³⁺ phosphor prepared by using Sol-Gel method under 100mGy of β irradiation.From Fig. 3 observed that the TL glow curve consist overlapping peaks in temperature rang 50-450°C and the TL glow curve of LiCaPO₄:Ce³⁺ phosphor consist two peaks and first peak (P₁) was appeared at 190°C and second peak (P2) at 303°C.



Fig. 3. TL glow curve of LiCaPO₄:Ce³⁺ phosphor under beta irradiation

3.4 Optically stimulated luminescence (OSL) Properties

The CW-OSL response of LiCaPO₄:Ce³⁺ phosphor synthesized via Sol-Gel method was as shown in Fig.4. The CW-OSL response of LiCaPO₄:Ce³⁺ phosphor was measured under 20mGy of β irradiation for 60 sec stimulation of blue LED.The CW-OSL decay pattern of LiCaPO₄:Cephosphor was same than CW-OSL decay pattern of commercial available α -Al₂O₃:C phosphor. The MDD was found out to be 18 µGy for SG method (dose corresponding to 3 σ of the background).



Fig.4. CW-OSL responses of LiCaPO₄:Ce³⁺phosphor under β irradiation

4. CONCLUSIONS

In this reports LiCaPO₄:Ce³⁺ phosphor was synthesized via Sol-Gel method. The XRD pattern of prepared LiCaPO₄:Ce³⁺ phosphor was perfectly matched with ICDD file. The surfacemorphology of prepared phosphor was found to in submicron range and phopshor showed excellent TL property. The TL glow curve consist overlapping peaks in temperature 50-450°C range and one peaks was observed at 190°C, another prominent peak was observed at 303°C. The emission spectra of prepared phosphor was observed in 340-500nm range. The CW-OSL decay pattern of prepared LiCaPO₄:Cephosphor was found out to be 18µGy (dose corresponding to 3 σ of the background).The effective atomic number of prepared LiCaPO₄:Ce³⁺ is not a material equivalent to tissue but, due to its high TL and OSL sensitivities, this phosphor can be proposed as a suitable candidate for radiation dosimetry, of course, after further progress in the studies.

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DC CONDUCTIVITY OF H+, Cd++ AND Zn++ MODIFIED ZSM-5 AND ZEOLITE Y USING FROM COAL FLY ASH

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ABSTRACT:

Zeolites synthesized from coal fly ash were attracting huge attention in current era of research because of their uncomplicated, unhazardous synthesis way. The eco-friendly properties have opened a wide field of applications of using these materials in different technologically important fields such as catalysis, adsorption and gas separation. Hence, the commercial zeolite ZSM-5 and zeolite Y with their modified forms which were synthesized from coal fly ash is used to test their applications as adsorbents and ion conducting materials

Zeolites are ion conducting and dielectric materials. The complex electrical properties such as of zeolite have been the subject of intense studies for more than three decades. These properties of the zeolites are mainly related to the chemical composition, Si/Al ratio, the type of exchangeable cations, degree of exchangeable cations, the state of hydration and temperature.

Compared with other ionic crystalline solids, zeolites have a high electric conductivity. This conductivity results from the great mobility of exchangeable cations. Thus zeolites can be regarded as weak electrolytes. Their conductivity is of the cations between close sites. Dc conductivity of modified form of ZSM-5 and Y were studied.

KEYWORDS: CFA, Si/Al ratio, DC Conductivity, modified form of ZSM-5 and Y.

INTRODUCTION:

The study of variation of DC conductivity with 1000/T over fly ash prepared HZSM-5, HY and their modified form with Cd++ and Zn++. The circuit diagram is as shown in Figure -1 It contains ionic conductivity cell, muffle furnace, DC source, DC voltmeter, DC micrometer. Its melting point is 1500 0C and low coefficient of thermal expansion. The pellet of sample under study can be sandwiched between two brass electrodes, B1 and B2, which internally make good contacts with the central rod F and one supporting rod G of the frame through the base plate respectively. The maximum height of the sample which could be sandwiched between two electrodes is about 1mm. The marble tiles are used to support the entire frame, also serve as electrical and thermal insulators. The muffle type furnace is used to give temperature up to 1000 0C. For measurement of ionic conductivity in micro porous materials, water must be removed from the pores, as the presence of any water has been observed to significantly affect the conductivity.

All the samples of the modified forms of zeolite were pelletized under an appropriate amount of pressure of 5 tons. The diameter (d = 13mm) and thickness (t = 1mm) of sample pellet is measured. The pellet is placed between two brass electrodes of the conducting cell. The central rod is tightened to make good contact between brass electrodes and pellet surface. The conducting cell is placed inside the muffle furnace, such that marble foil M1, has got the same size as that of the muffle furnace, covers the mouth of the furnace. The connections are made as shown in Figure -1. The temperature of the furnace increased gradually from ambient to 900 OC. To make good electrical contacts, tighten the rod F further. The temperature of the furnace is measured by a thermocouple calibrated directly to give the temperature in

centigrade. The current is noted at a constant known voltage at different temperature when substance is allowed to cool

The type of zeolite used is called Mobil Synthetic Zeolite ZSM-5, which was developed by Argauer and Landolt in 1972. Since its inception, ZSM-5 has been widely used for hydrocarbon inter conversion in the petroleum industry. ZSM-5 zeolites in protonic type (HZSM-5) have been extensively used in this research¹. The topology of the zeolite framework is given by a unique three-letter code, which is not related to the composition of the material. Generally, based on the pore openings zeolite ZSM-5 is a medium pore zeolite material with Mobil Five (MFI) topology.

The MFI structure is built up by ²⁻⁵ secondary building units (SBU); the smallest number of TO4 units, where T is Si or Al, from which zeolite topology is built which are linked together to form a chain and the interconnection of these chains leads to the formation of the channel system in the structure Faujasite Y is according to the International Zeolite Association, the structure is a FAU type⁶⁻⁹ which crystallizes in the cubic space group Fd₃ m with a lattice constant ranging from about 24.2-25.1Å, depending on the framework aluminum concentration, cations, and state of hydration. This zeolite is most conveniently visualized as being formed from 24- tetrahedra cubic octahedral units (sodalite cages), joined through hexagonal prisms (also known as double 6-rings), The structure can be viewed as the diamond structure, with the sodalite cages playing the role of carbon atoms, and the double 6-rings the role of C-C bonds

Zeolite Y is the most important catalytic zeolite, and is generally synthesized in the Na form. Most of the catalysis of interest is acid catalysis, which requires replacing the Na cations by protons, converting the sieve into the H-form. This cannot be done by direct ion exchange, since most H-faujasite are not acid stable. An indirect strategy is therefore used. An ammonium exchange is carried out, followed by a calcination to decompose the NH4 + cations into ammonia and protons. Solid ion conducting materials have grown interest due to their potential applications in various electrochemical devices such as fuel cells, batteries, sensors and electro chromic display devices¹⁰. Although, a vast number of various solid electrolytes have already been identified but the development of chemically and thermally stable super ionic conductors still remains one of the prime goals of research in solid state electrochemistry and material science. Currently considerable efforts are being devoted to the synthesis and characterization of inorganic materials, which form a new class of solids with properties, combining the high chemical and thermal stability.

The electrical properties of zeolites solid ion conducting materials and related pore or channel structures have been the object of intense studies for more than three decades. Most of the experiments on these micro porous solids have been done by Freeman and Stamires and by Schoonheydt and Uytterhoeven¹¹⁻¹⁴ focusing on the mobility of the exchangeable cations in zeolites by means of dielectric spectroscopy. Zeolite contains mobile cations which are located in sites, in cavities, on the channel walls and free within the channels co-ordinate with water molecule¹⁵. These cations compensate the negative charge of the zeolite framework. Since cations are free, they can move to new positions under the influence of an external electric field, which causes the electric charge transport. It is conductivity and dielectric relaxation. Compared with other ionic crystalline solids, zeolites have a high electric conductivity¹⁶⁻¹⁸. This conductivity results from the great mobility of exchangeable cations. Thus zeolites can be regarded as weak electrolytes. Their conductivity is of the cations between close sites. The mobility of exchangeable cations in zeolites has been investigated by electrical conductivity measurement¹⁹⁻²². Beattie and Dyer have shown that electrical conduction of zeolites occurs by the migration of cations41. At room temperature the conductivity increases sharply on adsorption of water in the zeolites. Freeman and Stamires served a strong dependence of activation energy on the type of cation in ZSM-5 and Y type zeolite and proposed the existence of at least two types of cation sites $^{23-25}$.

EXPERIMENTAL:



Figure -1: Circuit diagram to measure DC conductivity

RESULTS AND DISCUSSION:

D. C. Conductivity of HZSM-5 and modified forms of HZSM-5 with Cd++ and Zn++:

Figure -2 represent the plot of variation of dc conductivity with 1000/T of HZSM-5. From the conductivity plot of HZSM-5 sample it is observed that as temperature increases the conductivity increases linearly. With pure ZSM-5, in which less number of mobile free carrier are available hence the density of mobile ions for conductions leads to the less conductivity. It could be expected that exchange with high mobility protons H+ would create an increase of the conductivity. In case of modified HZSM-5 samples with divalent Cd++ and Zn++ the conductivity is also high for high temperature. But the conductivity for H+ forms was sharper than divalent metal forms of ZSM-5 which is illustrating in the Figure 3.8 and Figure 3.9. This may be due to increased ionic radii of zinc and cadmium with respective to protons, which has been suggested as a potential reason for the increased activation energy and decreased conductivity of the metal modified zeolite.

Another reason may affect that, in zeolites, the anionic framework sites are created by framework aluminum and are univalent 49. During the ion exchange two of these univalent sites must be in an appropriate arrangement to electro statically charge balance a divalent ion, from the geometry of the framework and distribution of aluminum among the T site, could lead to a reduced number of mobile cations and a reduced number of accessible hopping sites (increasing the distance between available sites, decreasing the conductivity), thereby decreasing the conductivity and increasing the hopping activation energy in zeolite. The specific conductivity in H.T. region is depends on the number of ions per unit cell, on the nature of the exchangeable ion. As the ZSM-5 samples modified with increasing in Zn++ and Cd++ metal ion percent in exchange solutions during ion exchange, the dc conductivity of the modified samples were gradually decreases as the ion percent increases in the exchange solution, this may be due to reducing the number of accessible hopping sites. Fig. 3 and 4 comparative illustration of the variation of conductivity with respect to the 1000/T for H+ and post modified forms of zeolites(Cd++ and Zn++) with increasing of metal ions percent. From the conductivity plots it was observed that conductivity not only a function of exchangeable metal ions but also the percent of the metal ions present in the zeolite In case of all the pre and post modified forms the linearity predicted by

Arrhenius law is almost perfect in the region of the higher temperature (H.T.). At low temperature (L.T.) important deviations of linear behavior were observed. This may be indicating that other mechanism occur at that temperature. The deviation from straight line behavior in the low temperature region is further dependent on the relative importance of two phenomenons: lonic conductivity and dipole absorption



Cd ZSM-5 (2wt %), Cd ZSM-5 (4wt %) and Cd ZSM-5 (6 wt %) Zeolites





From the above observations the conductivity is greater in H-ZSM-5 sample than Zn (2wt%, 4wt% and 6wt %) ZSM-5 and Cd (2wt%, 4wt% and 6wt %) ZSM-5. The variation of the conductivity as a function of nature of exchangeable cations follows the order H+>Zn++ >Cd++ for ZSM-5 zeolite. From the plot it is learnt that at higher temperature the conductivity is high and it linearly reduces with temperature. It is observed that the as the metal percent of divalent cations increases the activation energy increases which leads to decrease in conductivity

D.C. Conductivity of HY and modified forms of HY with Cd++ and Zn++:

Zeolite Y have received the greatest attention in literature on the conducting properties of zeolites, perhaps due to early reports revealing a high frequency relaxation in these materials, or because of the wealth of crystallographic knowledge pertaining to the FAU structure, i.e., aluminum framework sites, cation positions, etc. Fig. 4 represent the plot of dc conductivity verses temperature (1000/T) of HY. It is seen that in all the modified forms of Y samples with Zn++ and Cd++, the conductivity is high for high temperature. It observed that conductivity increases with increasing temperature. For each sample the linearity predicted by Arrhenius law is almost perfect in the region of the higher temperature (H.T.). At low temperature (L.T.) important deviations of linear behavior are observed. The specific conductivity is greater in HY sample than Zinc and Cadmium modified forms with the different metal ion percents.

This is because protonic forms mobility values are much greater when compare to the Zinc and Cadmium ions due to its structural features. In zeolite Y, activation energy for cation transport was observed to monotonically increase with increasing cation percent; this was attributed to decreased electrostatic interaction between the charge balancing cation and the anionic framework site. As the metal ion percent of zinc and cadmium increases (in the exchange solution) the same trend was observed as that was observed for zeolite ZSM-5 samples. Cd (6wt %) Y sample given lowest conductivity when compared with the other 2wt% and 4wt% of CdY forms. The variation of the conductivity as a function of nature of exchangeable cations follows the order H + > Zn++ > Cd++ for Y zeolite.



Fig. 4 : D.C. conductivity of fly ash synthesized HY Zeolites

Dielectric study of H+, Zn++ and Cd++ modified Zeolite ZSM-5 and Zeolite Y synthesized from fly ash:

The dielectrical studies have been performed on pre and post modified forms of zeolites ZSM-5 and Y. These studies deal with the influence of absorbed molecules or cation exchanges on electrical properties of the sample. Electrical conductivity and dielectric properties have been experimentally studied for many synthetic and natural zeolites, with various cationic compositions (di-valent cations with increasing cation concentration) in the presence of different adsorbents or in dehydrated form. At low frequencies (up to 10 MHz) dielectric properties are dominated by cation jumps between sites located at the same or different zeolites cavities. Thus they are very important to understand ion exchange, molecular sieve effects or high temperature catalysis and also to evaluate zeolites as a solid electrolyte. Local (intra sites) motions are expected to contribute at higher frequencies.

SUMMERY AND CONCLUSION:

The dc.conductivity, dielectric properties of HY, HZSM-5 zeolites prepared from coal fly ash and their modified forms were measured. In our observations Conductivity as a function of nature of exchangeable cations follows the order HY > ZnY > CdY zeolite and H ZSM-5 > Zn ZSM-5 > Cd ZSM-5 zeolite. In both the type

of the samples as the metal percent increases the Al frame work content decreases and the conductivity decreases. In ZSM-5 samples, the conductivity is high for high temperature. In the case of zeolite Y samples as the temperature increases sudden drop in the conductivity was observed in the case of H+, it may appear due sudden decrease in framework aluminum content. Further for each sample the linearity predicted by Arrhenius law is almost perfect in the region of the higher temperature (H.T.). At low temperature (L.T.) important deviations of linear behavior are observed in both type of sample. The deviation from straight line behavior at high temperature region is dependent on the relative importance of lonic conductivity and dipole absorption.

From the observations it is learnt that at higher temperature the conductivity is high and it linearly reduces with temperature. In the study of dielectric constant as a function of frequency the dielectric constant continually increases as frequency decreases, all metal loaded zeolite samples shows the same pattern. The dielectric relaxation in zeolites is assumed to be due to a change of dipole moment vector, formed between the cations in the cavities and framework anions, when the cations migrate. The adsorbed polar water affects the relaxation phenomenon. In our observations metal loaded zeolites capacitance, dielectric constant (ϵ ') decreases as the frequency increases this was verified by the literature that due to the decrease in the dipole distance the freedom of the lattice decreases which in turn changes the electrical properties of the zeolites.

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POST SYNTHESIS MODIFICATION OF RICE HUSK ASH RHA-SBA-16 BY ALUMINUM AND TITANIUM METAL IONS

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ABSTRACT :

Spherical particles of mesoporous silica SBA-16 with cubic Im3m structure were synthesized at low pH using Pluronic F127 as template and RHA as silica source. The diameter of the spherical particles can be controlled in the range of 0.5–8 µm by varying Spherical particles of mesoporous silica SBA-16 with cubic Im3m structure were synthesized at low pH using Pluronic F127 as template and RHA as silica source. It is suggested that this morphology transition is due to a change in hydrolysis and condensation rate of the silica source and as a result the assembly of F127 micelles will differ. The SBA-16 samples were characterized using powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Nitrogen adsorption techniques.

KEYWORDS: SBA-16; Spherical particles; Synthesis temperature; Morphology; Pluronic F127.

INTRODUCTION:

Spherical particles of mesoporous silica SBA-16 with cubic Im3m structure were synthesized at low pH using Pluronic F127 as template and RHA as silica source. The diameter of the spherical particles can be controlled in the range of $0.5-8 \mu$ m by varying¹. The synthesis of mesoporous materials by a liquid-crystal template mechanism was reported The properties of these materials make them attractive for adsorption, catalysis, separation, chemical sensing, optical coating, drug delivery and electronic applications. For practical purposes, the overall morphology of a mesoporous material is a necessary requirement in combination with their internal structure. SBA-16 is a mesoporous material with 3D cubic pore arrangement corresponding to Im3m space group In this body-centred-cubic structure each mesoporous is connected with its eight nearest neighbours to form a multidirectional system of mesoporous network²⁻⁴Due to its large cage, high surface area and high thermal stability. This material appears to be one of the best candidates for catalytic support and packing materials for separation. Using F127 as a surfactant is the common way of synthesizing SBA-16.However, there are also reports on alternative surfactants such as F108,a blend of P123 and F127⁵⁻⁸.

Micro porous zeolite are widely used as solid acid catalysts, but their applications are intrinsically limited by drawback of zeolite is that the small size of the channels (less than 0.8 nm) and cavities (<1.5 nm) imposes diffusion limitations on reactions that can cause high back pressure on flow systems. The dimensions of the zeolite micro pores (< 2 nm), mesoporous (2-50nm) and macro pores (> 50 nm) permit faster migration of guest molecules in the host frameworks. Since fast mass transfer of the reactants and products to and from the active sites is required for catalysts⁹⁻¹¹, the concept of infusing mesoporous into zeolite particles has attracted much attention. Recent progress involving this issued to ordered mesoporous materials such as MCM-41, SBA-16 and SBA-15¹²⁻¹⁶. These mesoporous materials have pore diameters of 3.0 nm– 8.0nm and exhibit catalytic properties for the catalytic conversion of bulky reactants, but unfortunately, when compared with micro porous zeolite¹⁷⁻¹⁸, the catalytic activity and hydrothermal stability are relatively low, which can be attributed to the amorphous nature of the mesoporous walls. To overcome this problem, some recent research efforts have been concentrated on introducing mesoporous or macro pores linked to the zeolite micro pores.

These materials called Hierarchical zeolite materials with combinations of micro/meso/macro pores would further extend the application of zeolite as solid acid¹⁹.

POST MODIFICATION OF RHA-SBA-16 BY AI⁺⁺⁺ and Ti⁺⁺:

So as to impart the catalytic and adsorptive activity to the chemically inert mesoporous silicate framework, substitution of Si⁴⁺ ions by other heteroatom in the prepared materials has been endeavored. This part describes the synthesis procedures used for post modification of RHA-SBA-16 by introducing heteroatoms such as Aluminum and Titanium into their meso-structures to improve their catalytic activity of reactions of bulky molecules and the adsorption activity significantly²⁰⁻²². The post modification synthesis of RHA-SBA-16 can be possible by various methodologies; among them we have followed the ion exchange method. In this method, the presence of Aluminum in the silica alumina mesoporous framework gives rise to anion, which attracts cations in the framework as they are loosely bounded. The replacement of cation held in the framework structure is possible by the ion present in the external solution. Hence ion exchange is possible²³. Initially RHA-SBA-16 was converted in to their protonic forms. The 100% crystalline RHA-SBA-16 sample in its protonic form was selected and was further modified by using batch ion exchange method with metal ions like Al⁺⁺⁺ and Ti⁺⁺ with different metal ion concentrations. Introduction of metal ions such as Al, and Ti, creates new Lewis acid sites and Bronsted basic sites respectively within the RHA-SBA-16 host.

EXPERIMENTAL:

Post Synthesis Modification of RHA-SBA-16 with H⁺:

Exchange of RHA-SBA-16 in to its protonic form was done by batch ion exchange method using subsequent acidic salt solutions. Ammonium nitrate 2.5wt % (2g) was taken in a 150 ml single neck round bottomed flask and 25 ml methanol was added into it as a solvent.

10g of the dried RHA-SBA-16 powder was also added and the blend was stirred under reflux condition for 3h at 80° C. Then this mixture was allowed to cool to room temperature by natural convection followed by filtration. Further the filtrate was washed repeatedly with deionized water. The residue is NH₄-RHA-SBA-16. It is dried for overnight by heating at 100° C in an oven. Later on, NH₄-RHA-SBA-16 is heated at 500° C in automated muffle furnace for 3h, to exile ammonia and is converted in H⁺ form i.e.H-RHA-SBA-16.

Post Synthesis Modification of H-RHA-SBA-16 by Al⁺⁺⁺ metal ions:

To tune and enhance the acidic behavior of RHA-SBA-16, we have exchanged its protonic form into modified Al-RHA-SBA-16 using corresponding metal salt solutions of different molarities by ion exchange method as described earlier. The calculated quantity of concentrated salt solution of Al⁺⁺⁺ [Al2(SO4)3.18 H2O] i.e.10.28g for 1M, 8.23g for 0.8M and 5.15g for 0.5M in 30g of methanol were taken in three different single neck round bottom flask (RBF) of 150 ml. Then 5g of the dried H-RHA-SBA-16 powder was added to it and was stirred under reflux condition for 6h at 100^oC. Later the mixture was brought to room temperature naturally and then the solvent was evaporated. The residue was dried in the oven at 100^oC, and calcined at 450° C to 500° C for 4h.To ensure the ion exchange of the Al⁺⁺⁺ in RHA-SBA-16 we have examined the elemental composition of the calcined samples by EDAX and came to know that their Si/Al ratio varies from 4-9. These modified forms were named as Al-RHA-SBA-16 (Si/Al = 4, 7 and 9).

Post Synthesis Modification of H-RHA-SBA-16 by Ti⁺⁺ metal ions:

To tune and enhance the basic behavior of RHA-SBA-16, we have exchanged its protonic form into modified Ti-RHA-SBA-16 using corresponding metal salt solutions of different molarities by ion exchange method as described earlier. The calculated quantity of concentrated salt solution of TiO_2 i.e.0.8g for 2wt%, 1.3g for 4wt% and 1.9g for 6wt% in 30g of methanol were taken in three different single neck round bottom flask (RBF) of 150 ml. Then 5g of the dried H-RHA-SBA-16 powder was added to it and was stirred under reflux condition for 6h at 90^oC. Later the mixture was brought to room temperature naturally and later the solvent was evaporated. The residue was dried in the oven at 100^oC, and calcined at 450^oC to500^oC for 4h.To ensure the ion exchange of the Ti⁺⁺in RHA-SBA-16 we have examined the elemental composition of the

calcined samples by EDAX. These modified forms were named as Ti-RHA-SBA-16 (2wt%, 4wt% and 6wt%).

RESULTS AND DISCUSSION:

Energy Dispersive Analysis of X-ray (EDAX):

 Table 1 Elemental Composition of the Samples Analyzed by EDAX

Sample name	Si	Al	Si/Al ratio	Ti Metal ion wt%
Al-RHA-SBA- 16 (Si/Al=4)	56.81	14.68	$\approx^{1.31}_{4}$	_
Al-RHA-SBA- 16 (Si/Al=7)	64.62	9.42	3i/Al=6.86 ≈ 7	_
Al-RHA-SBA- 16 (Si/Al=9)	69.30	7.83	3i/Al=8.85 ≈ 9	_
Ti-RHA-SBA- 16 (2wt %)	68.47	1.74	_	$\stackrel{\text{Ti}=1.91}{\thickapprox}_2$
Ti-RHA-SBA- 16 (4wt %)	63.71	1.78	_	Ti = 3.83 ≈ 4
Ti-RHA-SBA- 16 (6wt %)	64.11	1.81	_	$\overrightarrow{\text{Ti}} = 5.76$ ≈ 6



Fig.1. (A) EDAX IMAGES OF (a) Al-RHA-SBA-16(Si/Al=5), (b) Al-RHA-SBA-16(Si/Al=9) and (c) Al-RHA-SBA-16(Si/Al=11).

(B) EDAX IMAGES OF (a)Ti-RHA-SBA-16 (2wt %), (b) Ti-RHA-SBA-16 (4wt %) and (c) Ti-RHA-SBA-16 (6wt %).

The observed EDAX spectra for all the modified samples analyzed are shown in Fig. 1.(A, B). In EDAX, X-ray photons emitted from the sample are dispersed by a crystal and plotted as a function of energy. The X-rays being analyzed came from the area being imaged, so elemental composition is determined as a function of location on the sample. Outstandingly it is observed that the atomic percentage of Si, Al, Ti and O in modified forms of the RHA-SBA-16 are almost uniform. Even the Si/Al ratio is observed to be within the range in case of modified RHA-SBA-16 which shows that, the elementary compositions in the modified samples are uniform. The observations made by using SEM-EDAX correlate well with the XRD data for all the analyzed samples. The amount of Ti- metal ions weight percentage in all the samples is found to be around 1.93–5.71wt%. The metal compositions after the modification with the RHA-SBA-16 samples are given in Table 1.

X-ray diffraction (H-RHA-SBA-16, Al-RHA-SBA-16, TI-RHA-SBA-16)

This section gives detailed information on characterization data of the H-RHA-SBA-16, Al-RHA-SBA-16 and Ti-RHA-SBA-16 samples with different Si/Al ratios and with different wt.% of Ti- exchanged respectively. The XRD patterns of the calcined parent H-RHA-SBA-16 Al-RHA-SBA-16 and Ti-RHA-SBA-16 samples with different Si/Al ratios (4, 7 and 9) and with different wt.% of Ti (2wt.%, 4wt.% and 6wt.%) respectively are presented in Fig. 2 (A, B, C) respectively. The spectra showed XRD patterns identical to that reported for standard SBA-16 materials. Beck*et al.* indexed these peaks for a hexagonal unit cell, the parameter of which was calculated from the equation $a_0 = \sqrt{2}d_{110}$.

On calcination of samples, the peak is shifted to lower d_{110} spacing value probably due to condensation of internal Si-OH groups giving rise to a contraction of the unit cell. The unit cell parameter and d-spacing of the Al-RHA-SBA-16, Ti-RHA-SBA-16 samples and H-RHA-SBA-16 are given in Table 2. The slight increase in d-spacing and unit cell parameters of both Al-RHA-SBA-16 and Ti-RHA-SBA-16 compared to H-RHA-SBA-16 suggests the presence of Aluminum and Titanium in the framework respectively. The increase in unit cell parameter on Al or Ti incorporation is probably due to the replacement of shorter Si-O bonds by longer Al-O and Ti-O bonds in the structure respectively. It is also observed that along with an increase in the unit cell parameter, the (110) diffraction peak becomes broader and less intense with increasing Aluminum or Titanium content, probably because of the change of the Al-O-Al and Ti-O-Ti bond angle, causing a distortion in the long range ordering of the hexagonal mesoporous structure.



Si/Al=4, 7, 9)



Fig. 2. (B, C) illustrate that in all the modified forms of H-RHA-SBA-16 sample, there are marginal changes in the crystallinity but almost no changes in the phase purity and structural morphology are being observed after modification with different amounts of Al^{+++} and Ti^{++} percentage. This indicates the structural stability of the parent sample and presence of metal ions in the intra-crystalline voids of the H-RHA-SBA-16. The percent crystallinity of the samples is drawn with the amount of metal ion percent in them. From the Table 2.as the metal ions percent increases in modification, an increase in the crystallinity of the samples was observed up to Si/Al=4 and 6wt% of Ti. But when Si/Al > 4 and Ti incorporation is more than 6wt% i.e. when the metal ion concentration increases then the sample declines from good crystallinity to amorphous nature. This is because of the fact that, Al itself is having an amorphous nature and Ti being strong earth metal it produces other amalgamations in the structure influencing the crystallinity, hence the modification was stopped after Si/Al=4 and more than 6wt% of Ti incorporation to retain the crystallinity of the sample. The crystallinity of the sample was 100% for H-RHA-SBA-16.If the 'Al' metal ion concentration in H-RHA-SBA-16 was 6i/Al = 4 crystallinity was 98.5% and then gradually decreased for Si/Al=7, 9 as 91.3% and 86.5% respectively. However, if the 'Ti' metal ion concentration in H-RHA-SBA-16 was 6wt%, it was 96.5% and then gradually decreased for 4wt% and 2wt% as 84.3% and 80.4% respectively.

Fig. 3.depicts the co-relation between % crystallinity and concentration of Al and Ti metal ions.



Fig.3 Effect of the metal concentration on Percent CrystallinityofH-RHA-SBA-16

Furthermore, XRD patterns recorded at higher angles up to 80° showed no peaks. Therefore, the presence of any crystalline Al or Ti containing species can be excluded.

Table 2 Thysicoencinear properties of M-MIM-5DM-10 and TI-MIM-5DM-10 samples							
Sample	d ₁₁₀	Surface Area(m ² /g)	Pore Volume (ml/g)	Pore diameter(A ⁰)	% Crysta llanity	Acidity (mmole/g)	
H-RHA-SBA-16	33.16	954.22	0.65	27.3	100	0.014	
Al-RHA-SBA-16 (Si/Al=4)	33.32	852.00	0.76	28.6	98.5	0.192	
Al-RHA-SBA-16 (Si/Al=7)	34.62	826.46	0.71	31.2	91.3	0.086	
Al-RHA-SBA-16 (Si/Al=9)	35.75	938.61	0.69	26.8	86.5	0.044	
Ti-RHA-SBA-16 (2wt%)	45.56	789.36	0.62	30.9	80.4	0.017	
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Ti-RHA-SBA-16 (4wt%)	45.85	809.58	0.68	30.4	84.3	0.019	
Ti-RHA-SBA-16 (6wt%)	45.58	926.25	0.72	29.8	96.5	0.024	

Sorption studies:

The BET surface areas, average pore diameters and pore volumes calculated from N₂-sorption isotherms of Al-RHA-SBA-16 (Si /Al = 4, 7, 9) and Ti-RHA-SBA-16 (2wt%, 4wt%, 6wt%) presented in Table 2. According to IUPAC classification, the isotherms are of type IV⁶⁸ presented for Al-RHA-SBA-16 (Si /Al = 4, 7, 9) and Ti-RHA-SBA-16 (2wt%, 4wt%, 6wt%) in Fig. 4. (A, B) and 5.(A, B) respectively.



Fig. 4.A) N₂-adsorption-desorption isotherms and (B) Pore size distribution of Al-RHA-SBA-16(Si /Al = 4, 7, 9)



Fig. 5.A) N₂-adsorption-desorption isotherms and (B) Pore size distribution of Ti-RHA-SBA-16(2wt%, 4wt%, 6wt%)

The position of p/p_0 at which inflection starts is related to the diameter of the mesopores. The sharpness in this step indicates the uniformity of the pore size distribution. In the case of both M-RHA-SBA-16 (M = Al or Ti), this step of isotherm shifts slightly towards higher relative pressure p/p_0 with increase in

metal content of the sample indicating increase in the pore size. However, broadening of the hysteresis loop increases with increase in the metal content. This may be due to changes in the contour of the mesopores. The hysteresis loop in the range of $p/p_0 > 0.8$ due to capillary condensation in the inter-particle mesopores is observed in case of M-RHA-SBA-16. A comparison of the hysteresis loops of these two sets of samples at higher relative pressure region indicates difference in their textural mesoporosity. The pore diameters increase with increasing metal (Al or Ti) content of the samples.

Temperature Programmed Desorption of Ammonia



Fig.6. Temperature Programmed Desorption of Ammonia of Ti-RHA-SBA-16

The acidities of the H-Al-SBA-16 samples were characterized by the TPD of Ammonia. The acid strengths appear to be rather moderate as nearly all the Ammonia desorbed below 250° C.The acidities (mmol/g) based on the Ammonia desorbed by the samples beyond 90° C are presented in Table 2.

As the Aluminum content increases, the total acidity increases in the samples (Al-RHA-SBA-16(Si/Al=9) <Al-RHA-SBA-16(Si/Al=7) <Al-RHA-SBA-16 (Si/Al=4). However as the Titanium content increases, the total acidity decreases in the samples (Ti-RHA-SBA-16 (2wt%)< Ti-RHA-SBA-16 (4wt%) < Ti-RHA-SBA-16 (6wt%)).

SEM



(Si/Al=4) (Si/Al=7) (Si/Al=9) Fig. 7.Scanning electron micrograph of Al-RHA-SBA-16.



Fig. 8. Scanning electron micrograph of Ti-RHA-SBA-16.

Scanning electron micrographs of all the modified Al-RHA-SBA-16 (Si/Al=4, 7, 9) and Ti-RHA-SBA-16 (2, 4, 6wt %) samples is presented in Fig. 7.and Fig. 8.respectively. The micrographs reveal two morphologies, such as hexagonal and spherical habit and majority of them are hexagonal shaped agglomerates of small particles of the size between 3.10–10.60A⁰. It is seen that the morphology of the crystals gets affected as the metal ion percent gradually increased. The SEM photograph of H-RHA-SBA-16 sample shows bigger crystal size while the modified forms the metal ions have decreased crystal size which may affect the surface properties of the H-RHA-SBA-16 which tend to use it for different applications.

FTIR



Fig.9.FTIR spectra of calcinedH-RHA-SBA-16 and its modified forms with Al⁺⁺⁺ and Ti⁺⁺ ions.

The IR spectra of lattice vibration of calcined H-RHA-SBA-16 Al-RHA-SBA-16 and Ti-RHA-SBA-16 are presented in (Fig. 9.(A, B)). The spectra shows four main absorption bands between the regions 1210-1230, 1045-1080, 790-815 and 440-470 cm⁻¹. The T-O-T lattice vibrations are found to shift to lower wave numbers for Al-RHA-SBA-16 probably due to the incorporation of Al into the channel walls, as Al-O bond is longer than Si-O bond.

The band in the region 1210 to 1230 cm⁻¹ is due to external asymmetric stretching vibrations of five member Si-O rings, which is an evidence for the presence of 8 member rings in the walls of SBA-16 structure. This band becomes less intense in the calcined samples indicating probably a rearrangement of the wall structure due to high temperature treatment.

The band in the region 1045-1090 cm⁻¹due to internal asymmetric stretching mode of $SiO_4(TO_4)$ skeleton appears to be the strongest band in the spectra of all silicates. The broadening of this band on calcination may be due to superimposition of many bands ascribable to TO_4 arising from different T-O-T angles, this band is significantly shifted to a lower wave number (1066cm⁻¹). This may be due to the stretching

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of Si-O bond by long chain surfactant molecules forming micelles around which the SiO4 species are wound during formation of the mesoporous molecular sieves. Interestingly, this band at~ 1066 cm⁻¹ of mesoporous molecular sieves is found to be shifted to the higher wave number i.e.~1085 cm⁻¹ on removal of the surfactant molecules during calcination. This suggests that contraction of Si-O bond takes place during calcination, which has also been confirmed by XRD characterization.All IR spectra exhibit one common feature, a band at ~970 cm⁻¹. The correct interpretation of this vibrational band has been a matter of extensive studies. Fig.9. shows that within corporation of metal ions, the intensity of this band marginally increases. This band is generally considered as a proof for the incorporation of the heteroatom into the framework.

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SINGLE STEP SYNTHESIS AND CHARACTERIZATION OF SODIUM SUPEROXIDE

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ABSTRACT :

The electron/ionic conductivity and crystal structure are the intrinsic properties of sodium superoxide. These are greatly affecting the kinetics in the cells that results in various electrochemical behaviours at the oxygen-evolution-reaction(OER) process. In the presentresearch work, sodium super oxide was synthesized by single step method using sodium nitrate and hydrogen peroxide in oxygen rich environment. The average crystallitesize was estimated from X-ray diffractometer (XRD). It was found to be 15.75 nm. The peaks were observed in the XRD spectrum very well matched with the standard data. The band gap was found to be 3.62 eV estimated from UV-Vis spectroscopy. The peaks obtained in FTIR may be due to Oxygen bonding.

KEYWORDS: Sodium superoxide, average crystallite size, single step method.

INTRODUCTION:

Superoxide is a compound that is having a chemical formula O^{2-} containing superoxide anion. The standardized name of anion is dioxide (1⁻). The reactive oxygen anion superoxide is same as the product of one-electron reduction of dioxygen O₂. The superoxide is formed by leaving a charged ionic species with a single unpaired electron and the addition of an electron which fills one of the two degenerate molecular orbits and a net negative charge -1. Sodium superoxide The desirable formation of sodium superoxide (NaO₂) through the electrolyte-filled cathode structure at the oxygen side is due to the transport limitation of gaseous oxygen[1]. The sodium superoxide (NaO₂) can be formed as a stable and solid compound. The discharge product in a NaO₂ cell with a diglyme based electrolyte is Sodium superoxide (NaO₂). The discharge products are more easily noticeable due to the stronger interaction of sodium with spectroscopic probes than LiO₂ batteries so the NaO₂ offers easier access to the analysis of the cell chemistry [2].

Bi et al [4] have reported the sodium superoxide batteries. Their research is highlighted the importance of the cell design and emphasize the critical environment of the formation of discharge products of NaO₂batteries.Lutz et al [5] have studied the performance of Na–O₂ batteries under the impact of the sodium salt anion. On the choice of sodium salt, it is found that there is strong need of the solid electrolyte interphase (SEI) stability.Dilimon et al [6] have reported the Lewis basicity of solvent moleculesaswell asanions of sodium salts represents by donor numbers (DNs) quantitatively, that shows the reversibility of sodium-oxygen batteries and the superoxide stability.

In this work, sodium super oxide is synthesized by single step method using sodium nitrate and hydrogen peroxide in oxygen rich environment. The material is characterized by XRD, UV Visible spectroscopy and FTIR analysis.

Experimental *Materials*

Sodium Nitrate (NaNO₂) (98% purity, SD fine), Hydrogen peroxide (H_2O_2) (30% purity, Merck specialities PVT Ltd.) are used as precursors. The de-ionised water was used in the experiment. *Method*

For synthesis of sodium superoxide, a single step method is used. It consists of heating of sodium nitrate in oxygen rich environment [3]. Initially 1 M (6.9 g) of sodium nitrate NaNO₃ is dissolved in 10 ml of distilled water and 10 ml of hydrogen peroxide was added to the solvent. The molar ratio of sodium nitrate to hydrogen peroxide was 1:4. The reaction mixture was heated for 10 hours at some temperature on magnetic stirrer. Synthesised material then subjected to open heat at 50°C for 2 hours. The schematic diagram of the reaction is as shown in figure 1.



Fig. 1.Schematic diagram of the reaction of synthesis of NaO₂

Characterization

The as-synthesized material was characterised by XRD, UV-Visible and FTIR analysis. The average crystallite size of NaO₂ were estimated by XRD using a Rigaku (Tokyo, Japan) Miniflex X-ray diffractometer with Cu-K α radiations ($\lambda = 0.15406$ nm) in the 2 θ range from 20° to 70°. The UV-VIS spectrums presented is recorded using a Perkin Elmer spectrophotometer (Lambda-25). The FTIR analysis is done by using Infra-red Spectrophotometer, Brucker.

RESULTS AND DISCUSSION

The X-ray diffraction patternprovides the variety of information about structural idea. The peak position in the XRD pattern containsthe information about unit cell dimension, qualitative phase identification, crystal system, space group symmetry and translation symmetry. Similar, the scrutiny of peak shape and width (full width at half maximum) of the Braggs peaks of the X-ray diffraction pattern is provide the information on the crystallite size. From the resulting diffraction pattern the crystallite size (D) was estimated using the Scherrer equation (1).

$$D = K\lambda /\beta \cos\theta \tag{1}$$

where, K is the Scherrer constant, quite arbitrary value that falls in the range 0.87-1.0, λ is the X-ray wavelength (1.54 A°), θ is the Bragg angle of the peak, β is the full width at half maximum(in radians) at 2 θ . The XRD spectrum is as shown in fig 2.



Fig. 2.XRD spectrum of Sodium superoxide (NaO₂)

The crystalline phase of sodium superoxide was confirmed by XRD pattern as shown in the fig. 2. It can be seen that the prior peaks were obtained at (2 0 0), (2 2 0), (3 1 1) and (2 2 2). The result shows that all peaksoftheNaO₂were very well match with the JCPDS reference card No. 01-077-0207[7]. The average crystallite size estimated by eq. 1 for NaO₂ and it was found to be 15.75nm.

The NaO₂is formed by oxygen reduction reaction(ORR) attached to the formation of sodium superoxide. The reaction is takes place by dissolving oxygen molecule (O_2) after one electron transfer to it and producing the superoxide ion (O2⁻). The product of sodium superoxide is crystallizes as a solid that obtained due to sodium cations $(Na^+)[2]$.

The UV-Visible absorption spectrum of NaO₂nanoparticles is represented in Figure 3. The NaO₂ nanoparticlesshows an intense peak around 258 nm. The band gap is found to be near about 3.62 eV.Theligand-to-metalcharge transfer is in the ultraviolet region from 200 to 400 nm (in term of chargetransfer-direct transition). In the existing case, Na⁺ion field transition is observed. The pair excitation processes is assigned to the visible region contributed by ligand field transitions[7].



Fig. 3. UV-Visible spectroscopy of NaO₂ particles.

The Figure 4 shows the FTIR Spectroscopy of NaO₂ particles. The two characteristics peaks are observed at 831.44 cm⁻¹ and 1339.14 cm⁻¹ respectively[8]. The peaks obtained in FTIR graph may be shows the bonding of O^{2-} ion and Na-O bonding.



Fig. 3. FTIR spectroscopy of NaO₂ particles.

CONCLUSIONS

The single step method is a simple and easy method to synthesised sodium superoxide (NaO₂). The XRD analysis shows the crystalline phase of the NaO₂ particle. The result shows that all peaks are very well match with the JCPDS reference card No. 01-077-0207. The average crystallite size estimated from XRD datais found to be 15.75nm. The UV-Vis spectra shows the intense absorption peak at 258 nm. The charge transfer - direct transition in the 200-400 nm UV region is seen. The FTIR analysis shows the NaO₂ bonding from the peaks observed. The resultant sodium superoxide is crystallizes as a solid that produced due to sodium cations (Na⁺). The sodium superoxide (NaO₂) is used as battery and supercapacitorapplications.

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Compliance with ethical standards

Conflict of Interest: The authors declare that they have no conflict of interest.

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SYNTHESIS AND FLUORESCENCE PROPERTIES OF Eu(III) DOPED Y₂(MoO₄)₃ BY USING RE-CRYSTALLIZATION SYNTHESIS TECHNIQUE

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ABSTRACT :

In the present work we report the preparation of $Eu^{3+} Y_2(MoO_4)_3$. The crystalline fine powder $Y_2(MoO_4)_3$ sample has been prepared by a novel re-crystallization method. The formation of samples was confirmed by powder XRD technique and particle size was calculated from Debye-Scherrer formula. The photoluminescence study shows that the emission of $Y_2(MoO_4)_3$: Eu^{3+} phosphor is in red color.

KEYWORDS: *Yttrium molybdates, re-crystallization method, x-ray diffraction.*

1. INTRODUCTION

The properties of doping with trivalent lanthanides is desired, two possibilities exist for using molybdates with the respective M^{3+} cations [1-3]. Molybdates are known as rather good host lattices, especially because scheelite-type compounds [4, 5]. The scheelite structure type naturally contains divalent cations, but the number of divalent lanthanides series for doping is limited. However, yttrium and molybdates phosphors are widely used in many applications originated in the basis of luminescence phenomenon such as field emission displays (FEDs), cathode ray tubes (CRTs) and a new generation of fluorescent lamp phosphor [6,7]. All over the decades, the above said phosphors attracted researchers only because of its physical and chemical properties suitable for luminescence application. There are various types of yttrium based molybdates, related to the location of cations groups [-MoO₄] in the lattice structure are studied and reported till date. Mostly the compounds were synthesized at high temperatures using oxide precursors (in corresponding to their molar ratio). Therefore, well-crystallized Eu³⁺ doped -MoO₄ microcrystal's have possibility of improvement and always considerably in terms of their luminescence properties.

In present report, the preparation and structural studies are reported. The processing route selected on the basis of low cost, low temperature preparation of homogeneous sized ceramics. There are many reports for on synthesis of various structure types of yttrium out of all, re-crystallization synthesis provides the necessary conditions. In light of discussion, it has been decided to synthesis of $Y_2(MoO_4)_3$ by using re-crystallization method and studied for the structural fluorescence properties.

2. EXPERIMENTAL METHOD

The $Y_2(MoO_4)_3$ crystalline material prepared by using the re-crystallization technique. This sample was prepared by dissolving Y_2O_3 (1.12405 gm) and Eu_2O_3 in distilled water. Finally, HNO₃ (5 ml) was added to this solution and heated to form the $2Y(NO_3)_3$: $Eu_{0.005}$. The $(NH_4)_6Mo_7O_{24}$ 4H₂O (2.648 gm) which dispersed in 20 ml hot distilled water. The $(NH_4)_6Mo_7O_{24}$ 4H₂O totally soluble in double distilled water this $(NH_4)_6Mo_7O_{24}$ 4H₂O was added drop by drop in the beaker solution of $2Y(NO_3)_3$: $Eu_{0.005}$ and ammonia (3 ml) was added drop by drop in beaker under the vigorous stirring by a magnetic stirrer. This mixed solution was

stirred and the heating at 90°C upto get dry precipitate. The dry precipitate was calcined at 1000°C for 4h in furnace and cooled at room temperature [8].

3. RESULTS AND DISCUSSION

The phase purities of $Y_2(MoO_4)_3$ sample were studied using Rigaku miniflex II X-ray Diffractometer with scan speed of 4.000°/min and Cu K α ($\lambda = 1.5406$ Å) radiation in the range 10° to 70°.

3.1. XRD patterns of $Y_2(MoO_4)_3$

The formation of the crystalline phase of as-prepared products was confirmed by X-ray diffraction patterns of $Y_2(MoO_4)_3$ as shown in Figure 1 to verify the phase purity and crystal structure. The X-ray pattern of re-crystallization synthesized sample at 1000°C indicated a dominant phase of the standard $Y_2(MoO_4)_3$ and all the peaks are in good agreement with the (ICDD, 00-028-1451). The XRD pattern for $Y_2(MoO_4)_3$ agrees well with the standard data from ICDD file (00-028-1451). The high intensity peaks i.e., 18.0517, 20.9341, 21.4982, 23.8357, 25.2806, 31.3385 and 31.8425 forms ICDD file shows exact matching with the XRD pattern of phosphor prepared by re-crystallization method. This agreement indicates that the phosphor $Y_2(MoO_4)_3$ has been successfully prepared by using the re-crystallization method. Also the XRD shows that the formed material is completely crystalline and is in single phase.



Figure 1: XRD patterns of the Y₂(MoO₄)₃ phosphor synthesized by re-crystallization method.

Fig. 1 shows XRD Pattern of $Y_2 (MoO_4)_3$ material. It is observed that XRD pattern contains most of peaks between position $2\theta = 20^{\circ}-40^{\circ}$. The average crystallite size, determined from XRD pattern using Scherrer formula. The average crystallite size of $Y_2(MoO_4)_3$ phosphor by using Scherer's formula estimated 256 nm.

$$D = \frac{K \lambda}{\beta \cos \theta}$$
(1)

Where, θ is the Bragg angle of diffraction lines, K is a shape, λ is the wavelength of incident X-rays (λ =0.154056 nm), and β is the full-width at half maximum (FWHM).

3.2 Photoluminescence study

Fig.2. shows combine emission and excitation spectra of $Y_2(MoO_4)_3$:Eu³⁺ phosphor prepared by Recrystallization method. The excitation spectrum consist of a broad band widening from 200 to 300 nm region with maximum at 270 nm of UV radiation due to the charge transfer band (CTB) of Eu³⁺–O²⁻ bond and the energy of charge transfer depends upon O²⁻ ion in the crystal field. The emission spectra consist of peaks at 613 nm corresponding to ${}^{5}D_0 \rightarrow {}^{7}F_2$ transition of Eu³⁺ [9].



Re-crystallization method.

CONCLUSIONS

The polycrystalline sample of $Y_2(MoO_4)_3$ was successfully prepared by re-crystallization method. The XRD pattern completely agrees with ICDD (International centre of diffraction) file. $Y_2(MoO_4)_3$ has potential to make a very good luminescence phosphor.

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PHOTOLUMINESCENCE (PL) PROPERTIES OF NaLi₂PO₄:Eu³⁺ PHOSPHORFOR SOLID STATE LIGHTING APPLICATION

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ABSTRACT :

The polycrystalline $NaLi_2PO_4$: $_xEu$ (x=0.005) phosphor was successfully synthesized via modified solid state diffusion method. The structural of prepared phosphor was confirmed by using XRD (X-ray diffraction)technique. Additionally, the photoluminescence (PL) behaviors of $NaLi_2PO_4$: $_xEu$ phosphor was studied. The XRD pattern of prepared phosphor is well matched with JCPDS file with card no. (JCPDS # 80-2110). The PL excitation of prepared phosphor was monitored at 618nm while emission was monitored at 393 nm. The CIE co-ordinates were calculated and obtained in orange- red region.

KEYWORDS: NaLi₂PO₄:Eu; Photoluminescence; JCPDS and CIE co-ordinates

1.INTRODUCTION

Since 1962, orthophosphates with the general formula $ABPO_4$ (where A and B are monovalent cation and divalent cation) compose a large family of mono-phosphates with different structure types depending on the relative size of the A and B ions [1]. The compounds $ABPO_4$ show excellent thermal and hydrolytic stability and are considered to be efficient luminescent hosts [2,3]. The Eu²⁺activated $ABPO_4$ phosphors have been reported as blue-emitting phosphors excited by near UV- LEDs [4].

Phosphate compounds are usually referred as orthophosphates, have extensive utilization these days precisely in the field of lighting[5,6]. Being low-phonon energy materials[7,8]they could be important host materials for producing efficient luminescence. They possess excellent optical and ferroelectric properties along with many intriguing features such as good thermal, chemical and mechanical stability that make them unique for almost any display.

The NaLi₂PO₄ phosphor is belonging in ABPO₄ family. Shinde*et al.* reported luminescence properties of NaLi₂PO₄:Eu phosphor in 2011 and this phosphor was developed by using solid state reaction and time require was more than 24h [9].Sahare*et al.*also reported photoluminescence properties of Eu doped NaLi₂PO₄ phosphor and compared its color purity with commercial red emitting Y_2O_3 :Eu phosphor [10]. Sahare*et al.* reported TL and OSL properties of NaLi₂PO₄:Ce phosphor [11,12]. In 2016 Singh *et al.* reported radiation induced abnormal reduction of Eu³⁺ in NaLi₂PO₄ phosphor [13].

In the present paper, we have reported the preparation and characterization of $NaLi_2PO_4:Eu^{3+}$ phosphor synthesized via modified solid state reaction. The structural phase purity of prepared sample was obtained low temperature as compared to reported ones. Also color purity of phosphors was checked by Commission International de l'Eclairage (CIE) co-ordinates witnessing the pre-pared phosphor as prime candidate for SSL and LED based applications.

2. SYNTHESIS METHOD

The Eu³⁺ activated NaLi₂PO₄ phosphor was successfully synthesized by using Modified Solid State Diffusion method [14-19]. During synthesis, the stoichiometric amounts of high purity starting materialswere

used. The detail of molar ratio of constituent used for phosphor synthesis was given in **Table 1**. The starting materials were taken in a proper stoichiometric ratio together in china basin and adding small amount of acetone and clear solution was obtained. This mixture was heated on hot plate at 50°C for 30 min and then sample was placed in muffal furnace with the instalment of heating and heating profiles is given in **Table 2**. The sample was suddenly quenched at room temperature and between two intermediate regrinding.

Table 1: Molar ratio of ingredients used for material preparation and corresponding chemical reaction

S.N.	Products	Corresponding reaction with balanced molar ratios		
		of precursors		
1	$Na_{(1-x)}Li_2PO_4$: _x Eu(x=	$Na_{(1-x)}NO_3+2 x LiNO_3 + NH_4H_2PO_4 + _x(Eu_2 O_3 + HNO_3) $ {In stock		
	0.005).	solution form $1\text{gm}=100\text{ml}$ $\longrightarrow \text{Na}_{(1-x)}$ Li ₂ PO ₄ : _x Eu+Gaseous products (H ₂ O, NH ₃ and NO ₂) (x=0.005). Δ (Heating) = 100°C for 30min,200°C for 2h, 400°C for 2h, 800°C for 3h. Then sample was grounded in agate mortar and heated at 1000°C for next 5h in the presence of airatmosphere.The sample was suddenly quenched at room temperature and sample was grounded in agate mortar.		

The phase purity of prepared phopshors were checked by means of X-ray powder diffraction (PXRD) using a Rigaku miniflex II diffractometer with Cu K α ($\lambda = 1.5405$ Å) operated at 5 kV. The structural and morphological characteristics i.e., particle size and shape of powdered samples were studied using a Scanning Electronic Microscope (SEM). In this study, samples in powder form (100-150µm) were placed directly into a SEM for imaging. The measurements were performed using a ZEISS EVO/18 Research at Department of Physics RTM University Nagpur. The PL and PL excitation (PLE) spectra were measured on (Hitachi F-7000) fluorescence spectrophotometer with a 450W Xenon lamp.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction (XRD) pattern

The XRD pattern of prepared NaLi₂PO₄:Eu phosphor is shown in Fig. 1.



Fig.1. X-ray diffraction pattern of NaLi₂PO₄: Euphosphor matched with JCPDF file

The peak positions in the diffraction pattern of the synthesized material is compared them with the standard data available in the literature (JCPDS # 80-2110) [20]. No separate peaks corresponding to any impurity phase are observed at concentration (0.005mole) showing that the impurity has a good solubility in the matrix.

3.2 Surface Morphology

The SEM micro images of Eu^{3+} doped NaLi₂PO₄ phosphor is as display in Fig. 2. It was observed that microstructure of the phosphor consist of irregular grains with heavy agglomeration. The average size of asprepared particles was found to be in the range 1-5µm.



Fig. 2 Surface morphology of prepared NaLi₂PO₄:Eu phosphor

3.3 Photoluminescence properties

The combined excitation and emission spectra of NaLi₂PO₄:Eu phosphor is shown in **Fig. 3**. The excitation was monitored at 618 nm and emission was monitored at 393 nm. The excitation spectra consists of sharp lines at 310, 363, 377 and 394 nm correspond to the ${}^{7}F_{0} \rightarrow {}^{5}H_{3}$, ${}^{7}F_{0} \rightarrow {}^{5}D_{4}$, ${}^{7}F_{0} \rightarrow {}^{5}L_{7}$ and ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ transitions respectively. Out of all these peaks, the excitation at 394 nm is the strongest, as shown in **Fig. 2**. On the other hand emission spectra consist of two sharp peaks 595nm and 618nm with one weak peak at 653nm. The emission at 595 nm corresponds to the ${}^{5}F_{0} \rightarrow {}^{7}D_{1}$ (magnetic dipole), the emission at 618 nm corresponds to the ${}^{5}F_{0} \rightarrow {}^{7}D_{2}$ (electric dipole) and weak emission at 653nm corresponds to the ${}^{5}F_{0} \rightarrow {}^{7}D_{3}$ transition of Eu³⁺ ions [21].



Fig.3. Combine excitation and emission spectra of NaLi1.995PO4:0.005Eu phosphor

3.4 CIE chromaticity diagram

The CIE chromaticity coordinates were plotted using Radiant Imaging software. The calculated CIE parameters were plotted on a CIE 1931 x–y chromaticity diagram [22-24]. Figure 4 represents the CIE 1931 x–y chromaticity diagram of the NaLi₂PO₄:Eu³⁺ phosphor. The CIE chromaticity coordinates were found to be

at (0.6747, 0.3250) at dominant wavelength point of 618 nm and this point corresponds to red color emission. The as prepared phosphors were found to be suitable candidates for red LEDs



Fig. 4 CIE colour coordinates for NaLi₂PO₄:Eu³⁺ phosphor

4. CONCLUSIONS

The polycrystalline NaLi₂PO₄:Eu³⁺phosphor was successfully synthesized by modified solid state diffusion method. The XRD pattern of prepared NaLi₂PO₄:Eu³⁺phosphor was in good agreement with the JCPDS file with card no. 80-2110. The excitation was monitored at 618 nm and emission was monitored at 393 nm. The excitation spectra consists of series of sharp lines at 310, 363, 377 and 394 nm correspond to the ${}^{7}F_{0} \rightarrow {}^{5}H_{3}$, ${}^{7}F_{0} \rightarrow {}^{5}D_{4}$, ${}^{7}F_{0} \rightarrow {}^{5}L_{7}$ and ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ transitions respectively. On the other hand emission spectra consist of two sharp peaks 595nm and 618nm with one weak peak at 653nm. The emission at 595 nm corresponds to the ${}^{5}F_{0} \rightarrow {}^{7}D_{1}$, the emission at 618 nm corresponds to the ${}^{5}F_{0} \rightarrow {}^{7}D_{2}$ and weak emission at 653nm corresponds to the ${}^{5}F_{0} \rightarrow {}^{7}D_{3}$ transition of Eu³⁺ ions. The CIE chromaticity coordinates of the as-prepared phosphorswere determined to be (0.6747, 0.3250). The results indicate that NaLi₂PO₄:Eu³⁺phosphor is a potential candidate for Solid State Lighting.

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A REVIEW ON CURRENT TRENDS IN SYNTHESIS OF MIX METAL OXIDES: SPECIAL REFERENCE TO BIOMEDICAL APPLICATION

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ABSTRACT :

The synthesis part of Nano particle is always of curiosity because of its scope of modification and scope of improvement. Till date many reported given lots of fascinating reports regarding modification in synthesis of Nano materials and their functional properties related to physical and medical science. Current article focus on the synthesis of mix metal oxides and their biomedical application. An exhaustive literature review was carried out on the synthesis approaches used till date for the synthesis of metal oxides and their concluding remarks were drwn on the basis of result interpreted in article.

1. NANO TECHNOLOGY PAST AND PRESENT

Nanotechnology or nano bio materials applications have not been promoted long enough for entitlements to be substantiated about dangers to human health or the environment. Still, small nanoparticles can enter the human body through pores and may gather in cells. Nevertheless, the health effects of such nanoparticles are unknown. It is needed to reveal the effects and potential applications of nanomaterials. Also, it is a need of the society to get new, modified and simple way of remedies over the complex technology available in the market that too on affordable cost and easy to access process.

It can be argued that whilst nanoparticles (NPs) have existed naturally for millions of years, the 'notion' of nanotechnology was first introduced in 1959 by Richard Feynman in his talk "There's Plenty of Room at the Bottom", where he described the potential to develop a system of manipulating individual atoms and molecules.

The nano-materials such a thought-provoking area of research. However, it is not simply the shrinking of particles. It means alteration in physical and chemical properties as compared to bulk product. This only be possible due to the quantum size effect phenomenon.

Besides, the enhancement in properties are frequently seen for significantly lower weight loadings of nanoscale material as compared to the bulk scale equivalent. In other words this can be interpreted that there is a need of less materials as compared to bulk when considered for its physical application in market place. This means, there is need of less production which automatically reduce the cost of production and sales too. Additionally, for some selected fields, such as electronics, devices can be made smaller without compromising on performance.

In this journey many researches were giving their inputs for making this idea as a successful product. And hence, Private and public research efforts worldwide are thinking on developing nano products aimed toimprovisation physical and chemical properties those can be utilized in physical and medical research. This is evidenced that most of the assumptions made prior are now entered in the marketplace, more are on the verge of doing so, and others remain more a vision that a reality. Few of them are

(i) Sensors for medical and environmental monitoring and for preparing pure chemicals and pharmaceuticals.

- (ii) Light and strong materials for defense, aerospace, automotive, and medical applications.
- (iii) Lab-on-a-chip diagnostic techniques.
- (iv) Sunscreens with ultraviolet-light absorbing nanoparticles. Moreover few reports also said the following applications are expected in the next decade:
- (v) Longer-lasting medical implants.
- (vi) The capability to map an individual's entire genetic code almost instantaneously.
- (vii) The ability to extend life by 50% from present expectations

The potential for these innovations is enormous, but questions remain about their long term safety and the risk–benefit characteristics of their usage. Thus modifications in the field are required and have lots of scope for work with a prime motivation for welfare of society [Bhushan, B.]

2. LITERATURE

In 2009, Tsuzuki given the graphical representation (Figure 1) of broad application of nano particles and makes the field more elaborative and simple[Tsuzuki, T.]. However for nano materials, now a days biomedical applications has been more underlined. As, most of the building blocks of biological systems, i.e. DNA and proteins, have their constituents in nano scale range. As explained Alberts *et al.*, 2002 haemoglobin has a 5.5 nm diameter while insulin measures 3 nm in width and a DNA double helix has intra-strand spacing of 2 nm [Alberts, B., et.al.]. Liu and Webster described that that cause of many biochemical disorders, becomes feasible as pharmaceutical research has begun to focus on developing drugs at a nanoscale level using their ability to directly target erroneous proteins [Liu, H. et. al.,]. Geinguenaud *et al.*, 2012, revels that due to small size many nano particles have potential to penetrate cell membranes[Geinguenaud, F. et. al.,]. Followed to this in 2013, Krol *et al.*, has given the report on penetration of the blood brain barrier by the nano scale materials [Krol, S., et.al.,]. These kind of research have explored as an opportunity to treat genetic mutations or abnormalities, this also gives rise to the thought that nanomaterials could pose a massive health and safety risk.





3. FOCUS TOWARDS INORGANIC MATERIALS

Presently, inorganic nanomaterials, like metal oxide nanoparticles, have emerged as promising candidates in the field of bio medical application due to greater durability, lower toxicity and higher stability and selectivity when compared to organic materials. Literature supports that nanostructured metal oxides have already been extensively studied for their promising use in technology. This has resulted in development of numerous reproducible procedures for the synthesis of nanoparticles with desired characteristics—like size,

shape, morphology, defects in the crystal structure, monodispersity—providing a rich background for research relevant to antibacterial applications. Following table summarize the possible applications of nano particles in the field of medical and pharmaceutical science.

SN	Class of Particle	Reported Application
1	Natural Materials or its derivatives	Drug Delivery or Gene Delivery
2	Dendrimers fullerenes	Drug Delivery
		Photo Dynamic Drug Delivery
3	Polymer Carriers	Drug Delivery or Gene Delivery
4	Ferrofluids	Imaging (MRI)
5	Quantum Dots	Imaging
		In Vitro Diagnosis
6	Metal or non Metal Nano Particles	Gene Delivery

Recent achievements in nanotechnology of metal oxides include elaboration of nanostructured oxides consisting of two or more metallic components. Their potential applications are immense due to their unique electronic, optical, magnetic and other physicochemical properties. Multi-metal oxide nanoparticles, like $Zn_xMg_{1-x}O$, Ta-doped ZnO, Ag/Fe₃O₄ nanocomposites, are being studied extensively as potential antimicrobial agents owing to the beneficial synergistic effects of their components. These nanoparticles have shown promising solutions to problems seen in pure metal oxide nanoparticles, like high cytotoxicity or agglomeration.

4. EFFECT OF SYNTHESIS APPROACH

The synthesis part of nano particle is always of curiosity because of its scope of modification and scope of improvement. Till date many reported given lots of fascinating reports regarding modification in synthesis of nano materials and their functional properties related to physical and medical science. The field of medical science attracted the researchers most, Because, Many of the building blocks of biological systems, namely DNA and proteins, are sized in the nanometre range and can be repaired or replaced by the artificial made materials. The synthesis methods were explored and few of the reports related to this are listed below

SN	Name of method	Reported	Name of Author	Concluded Remarks
		Materials		
1	Sonochemical	TiO ₂	Yu JC, et.al.	The advantages
	method	ZnO	Jung S-H, et. al	associated with
		CeO ₂	Zhang D, et.al.	sonochemical methods
		MoO ₃	Krishnan CV, et.al.	include uniform size
		V_2O_5	Mao CJ, et.al.	distribution, a higher
		In_2O_3 and	Dutta DP, et.al.	surface area, faster
		Eu/Dy-doped		reaction time and
		In_2O_3		improved phase purity of
		ZnFe ₂ O ₄	Sivakumar M, et.al.	the metal oxide
		PbWO ₄	Geng J, et.al.	nanoparticles
		BiPO ₄	Geng J, et.al.	
		$ZnAl_2O_4$ and	Dutta DP, et.al.	
		ZnGa ₂ O ₄ —		
		pure and		
		doped with		
		varying		
		combinations		
		of Dy^{+3} , Tb^{+3} ,		
		Eu ⁺³ and Mn ⁺²		

		E O		
		Fe_3O_4	Vijaya Kumar R, et.al.	
		$BaFe_{12}O_{19}$	Shafi KVPM, et.al.	
		Mn-doped γ -	Lai J, et.al.	
		Fe_2O_3		
		1ron-ox1de	Bang JH, et.al.	
-	a	nanoparticles		
2	Co-precipitation	ZnO	Farahmandjou M, et.al.	The advantages of this
	method	MnO ₂	Kumar H, et.al.	method are low cost, mild
		BiVO ₄	Zhanga X, et.al.	reaction conditions like
		MgO	Ganapathi Rao K, et.al.	low
		Ni _{1-x} Zn _x Fe ₂ O ₄	Velmurugan K, et.al.	synthesis temperature, the
		SnO ₂	Tazikeh S, et.al.	possibility to perform
		Cu-doped	Mukhtar M, et.al.	direct
		ZnO		synthesis in water,
		MgFe ₂ O ₄	Balavijayalakshmi J,	simplicity of processing,
			et.al.	the ease of
		Ni–CeZrO ₂	Roh HS, et.al.	scale-up, flexibility in
		$Y_2O_3:Eu^{+3}$	Jadhav AP, et.al.	surface properties
3	Solvothermal	Nb ₂ O ₅	Feldmann C, et.al.	use of suitable surfactants
_	method	MgO	Kim DH. et.al.	that can tune the particle
		TiO	Subramania A et al	Characteristics and limit
		$(M)Fe_2O_4$	Wang WW et al	their agglomeration.
		[M=Mn, Co]		
		Fe ₂ Q ₄	Wan L et al	
		shape-tuned	Zhai Y et al	
		Ag cores and a		
		Fe_3O_4 shell		
		Graphene-	Gopalakrishnan K. et.al.	
		TiO ₂		
		CoFe ₂ O ₄ @Ba	Raidongia K. et.al.	
		TiO ₃	,	
		Fe ₃ O ₄ @NiO	Liu Z. et.al.	
		and	. ,	
		Fe ₃ O ₄ @Co ₃ O ₄		
		TiO ₂	Ren Y. et.al.	
		WO _x	Soultanidis N. et.al.	
4	Sol-gel method	TiO ₂	Antonelli DM, et.al.	leads to the production of
-	~~~ g	ZnO	Alwan RM, et.al.	ultrafine porous oxides in
		MgQ	Wahab R. et.al.	the desired crystal phase
		CuO	Armelao L. et.al.	
		$\frac{2}{2}r\Omega_{2}$	Suh DI et al	
		andNb ₂ O ₅		
		$LiCoO_2$ thin	Li G. et.al.	
		film	-,	
		Cu doped ZnO	Liang X, et.al.	
		nanoparticles		
		CuO/Cu ₂ O	Mallick P.	
		composites		
		Ce-doped	Gionco C, et.al.	
		ZrO_2		

		oxides of Hf,	Buha J, et.al.	
		Ta and Nb		
5	Microwaveassiste	CaO	Roy A, et.al.	relatively low energy and
	d method	Fe_3O_4 , Mn_2O_3	Bilecka I, et.al.	time consuming
		Cr ₂ O ₃ BaTiO ₃		
		CeO ₂	Goharshadi EK, et.al.	
		MO [M=Mn,	Polshettiwar V, et.al.	
		Zn, Co, Mg]		
6	Micro emulsion	CeO ₂	Sanchez-Dominguez M,	The ability to control the
	method		et.al.	formation of different
		NiO	Solans C, et.al.	kinds of core–shell
		iron oxide	Wu W, et.al.	structures with sub-
		nanoparticles		nanometric resolution
		TiO ₂	Zhang RB, et.al.	
		ZnO	Bumajdad A, et.al.	
		CuO	Kumar A, et.al.	
		BaAlO ₂ ,	Zarur AJ, et.al.	
		iron-oxide	Tartaj P, et.al.	
		doped alumina		
		nanoparticles		

The as conveyed by the literature nano particles have several applications because nanoparticles with varying physicochemical characteristics exhibit different antibacterial mechanisms and effects, nanoparticles with a combination of two or more metals can be developed for efficient elimination of various bacterial strains including those highly resistant to existing treatments. Also many times metal oxides doped with the high valence metal impurity increases electrostatic attractions between metal oxide nanoparticles and the bacterial surface which also facilitated the bactericidal action. The differences in bactericidal efficiencies observed with various strains may originate from different structure and composition of the bacteria.

5. CONCLUSION

The synthesis method employed for the preparation of functional materials always affects the chemical and physical behavior of these materials. Also the condition and surrounding of the laboratory also render a difficulty. Though the many researchers are trying their best to overcome the difficulties but still effective and innovative cost cutting methods need to be developed. However size and structure of material also change with change in process of working and that tooaffects the physicochemical properties of the materials. So it is always a part of curiosity to maintain the structure of the synthesized materials. That's because the cost effective techniques need to be developed and additionally the improvement in structural behavior is achieved then it will very much helpful to overcome said problems.

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QUALITATIVE STUDY OF DYNAMIC DEFORMATION USING ELECTRONIC SPECKLE PATTERN INTERFEROMETER (ESPI)

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ABSTRACT :

In the present work, we have used Electronic Speckle Pattern Interferometry (ESPI) technique for qualitative study of dynamic acoustic deformation. For these we have used a vibrating and reflecting thin aluminum foil as diaphragm which is placed in front of loudspeaker is used as an object. Thus by applying frequency to an object the deformation is created. Using charge couple device (CCD) camera the entire deformation on the diaphragm can be record in a computer and analyzed qualitatively.

KEYWORDS: Speckle, Speckle Interferometry, ESPI, Acoustic deformation.

1. INTRODUCTION

In 1969, Archbold developed the speckle interferometry [1]. He has designed Speckle interferometer to observed surface deformation using a telescope. He discovered that when surface deform speckle pattern is produced. These patterns are recorded with the help of telescope. Later on Speckle interferometry was developed by Leendertz [2], Butter and Leendertz [3], Jones and Leendertz [4]. Leendertz modify Michelson interferometer replacing mirror by optically rough surface to measure out-of-plane displacement and inplane displacement.

Electronic Speckle pattern Interferometry was first developed by Butter and Leendertz [5] & Macovski *et al* [6] simultaneously. This is widely used technique to measure full-field deformation on surfaces of many kinds of objects. It has been invented in 1970s by J. N. Butters and J. A. Leendertz [3]. Butter and Leendertz developed Electronic Speckle Pattern interferometer using two beams. In this both beam illuminate the test object at equal angle from opposite side of the normal. The resultant fringe called correlation fringe can be obtained by subtraction of two recorded speckle patterns corresponding to two different object positions with help of CCD (charge coupled device) camera. This system is used to measure the vibration ofdisc. Dynamic study requires an optical set-up which is complicated and expensive. For simple calculation we require two dimensional Fourier transform which also very difficult to apply. But there are many methods available for dynamic study of ESPI [7].

An electronic speckle pattern interferometry (ESPI) technique makes it possible to observe dynamic phenomena. This technique is used primarily to measure the displacement of the rough surface of a test object. Interference is a consequence of wave property of light. When two light waves are superposed, the resultant intensity at any point depends on whether they reinforce or cancel each other. This is the well-known phenomenon of interference. Light waves that are in phase with each other undergo constructive interference. Light waves that are exactly out of phase with each other undergo destructive interference and their displacements (electric fields) cancel. In the intermediate cases, the total displacement is given by the vector resultant, and the intensity is proportional to the square of resultant displacement amplitude.

2. EXPERIMENTAL SETUP:

The most interesting dynamic deformation for study is the deformation created by acoustic wave on the thin reflecting surface. For this, a vibrating and reflecting thin aluminum foil as diaphragm is placed in front of a loudspeaker is used as an object. Thus by applying frequency to an object the deformation is created which emitting a mixture of audible frequencies. Using CCD camera the entire deformation can be recorded in the form of video and analyzed.

Figure1 shows experimental setup used to measure the dynamic deformation using electronic speckle pattern interferometer. In this setup we have used a vibration isolation optical breadboard (200mm x 900mm size). Vibrating and reflecting thin aluminum foil of thickness 0.008 mm is used as diaphragm placed in front of loudspeaker is used as an object. Frequency generator is used to apply input frequency (sine wave) to an object (vibrating and reflecting diaphragm). Object is deformed when frequency is applied on it. A linearly polarized 6328 A⁰ U i.e. 632.8 nmHe-Ne laser with 5 mW output power is used as the light source. A beam splitter (50/50) splits the laser beam into two beams. The transmitted beam illuminates the test object (vibrating and reflecting thin aluminum foil) uniformly via spatial filter assembly while the reflected beam falls on the CCD camera as reference beam. The image of the illuminated test object is captured by zoom lens (18-55 mm focal length) and CCD (1280 x 1024 resolution). Thus there is superposition of two beams i.e. transmitted beam and reference beam takes placed produces a speckle pattern. In order to get the interference, the reference beam path length should be exactly ame as the object beam path length. The path length can be matched by adjusting the position of few plane mirrors in the reference path. A diffuser plate is used in the reference path to get the speckled reference beam and the size of speckles can be adjusted by changing its position from the CCD. Also a linear polarizer rotator is used in the reference path to control the intensity of the reference beam. The resultant speckle pattern video has been recorded using Holmarc camera application software and analyzing the images.



Figure 1. Schematic diagram of ESPI for measurement of acoustic deformation

3. RESULTS AND DISCUSSION:

In this experiment we have recorded the speckle pattern video for 30.400 sec using charged coupled device (CCD) camera. The recorded video can be converted into frames using virtualDub-1.10.4 software; therefore there are total 228 frames for 30.400 sec. The time required for completing one cycle is found to be 1 sec using Digital Storage Oscilloscope (DSO) is as shown in **Figure 2.** Therefore for one sec there are total 8 frames. Thus the difference of two subsequent frames can be taken out for 8 frames (i.e. for one cycle). That's why there are total 7 resultant correlation frames for one cycle. The resultant

experimental correlation fringes of dynamic deformation using electronic speckle pattern interferometry are as shown in the **Figure 3.**



Figure 3. The resultant experimental correlation fringes of dynamic deformation using electronic speckle pattern interferometry

From **Figure 3.**it can be conclude that if the subsequent difference between frames is zero then the fringe patterns with constant amplitude displacement will result in zero or not detectable while if the subsequent difference between frames is non zero then the fringes with constant amplitude displacement will be detectable.

3.1. Graph

Graphical representation of dynamic deformation using ESPI is shown in **Figure 4**. The ac signal i.e. input frequency applied to the object for three cycles is as shown in **Figure 4(a)**. Whereas the deformation output i.e. resultant correlation fringes for three cycles is as shown in **Figure 4(b)**. From these it can be conclude that the deformation output is same for each input cycle. That means the deformation is a continuous function of time.



Figure 4. Graphical representation of dynamic deformation

4. CONCLUSIONS

Qualitatively the acoustic dynamic deformation has been successfully studied using electronic speckle pattern interferometry. We have used a novel thin vibrating and reflecting aluminum foil as a test object to study acoustic dynamic deformation using Electronic Speckle Pattern Interferometry. Qualitatively dynamic deformation has been calculated for three cycles.From the experimental result it can be seen that the cycle is repeated after a specific interval of time. From this it can be conclude that the deformation is same for each cycle.

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ZERO MASS SCALAR FIELD WITH HOMOGENEOUS HYPERSURFACE SPACE TIME IN f(R,T) THEORY OF GRAVITATION

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ABSTRACT :

Homogeneous-Hypersurface space time in presence of bulk viscosity and zero mass scalar field cosmological models in the f(R,T) theory of gravitation have been considered. The solutions of field equations are obtained. The universe is expanding, shearing and accelerating. The universe is found to be anisotropic throughout its evolution. Some physical parameters of the obtained models are discussed in detail.

KEYWORDS: Homogeneous-Hypersurface, Bulk Viscousity, Zero mass scalar field, f(R,T) theory.

1. INTRODUCTION

Theoretical postulates of General Relativity such as bending of light, perihelion of Mercury, gravitational waves and many other are now confirmed by observations. However, cosmic speed is today's challenge which is never explained in General Relativity. Modification of Einstein-Hilbert action is one interesting possibility invoked by cosmologist in order to explain the accelerated expansion of the universe. The process of modification gives rise to new theories which we known as modified theories of gravitation. Among the various modified theories, f(R), f(T), f(G), f(R,G), etc. f(R,T) is the earliest coined by Harko et al. [1]. The f(R,T) gravity theory have been attracted a lot of attention of the researcher in this field to develop cosmological models. The f(R,T) theory is consist of an arbitrary function of the Ricci scalar R and trace of the energy momentum tensor T. Recently Katore et al. [2-4] have explored various cosmological models by considering different sources of matter in the context of f(R,T) theory of gravitation.

Bulk viscosity is important in the early stages of evolution of the universe. When neutrino decoupling occurs, the matter in the universe behaves like a viscous fluid which is responsible for accelerated expansion of the universe [5]. Misner [6, 7] have suggested that viscosity may reduce the anisotropy of the blackbody radiation. When the universe expands, the coefficient of the viscosity is decreases. Murphy [8] in his model consisting of pressure and bulk viscosity have obtained that the Big-Bang type singularity appear in the infinite past. Recently, Singh et al.[9] have reviewed cosmological implications of the bulk viscosity. Singh [10] has studied the effect of bulk viscosity for Friedmann-Robertson-Walker model in General Relativity. Belinskii and Khalatnikov [11] have obtained that the bulk viscosity would not remove the cosmological singularity. Katore et al.[12] have studied effect of bulk viscosity in the reference of f(G) theory of gravitation. Pradhan et al. [13] have investigated Bianchi type VI0 cosmological models with bulk viscosity and string in General Relativity.

2. METRIC AND FIELD EQUATIONS

We consider the Homogeneous Hypersurface space time in the form $ds^2 = -dt^2 + A^2 dx^2 + B^2 (dy^2 + \sum_{i=1}^{2} (y,k) dz^2),$ 1 where *A*, *B* are functions of t and $\sum_{i=1}^{2} (y,k) = \sin y, y$, sinh *y* respectively when k = 1, 0, -1. The evolution

where A, B are functions of t and $\sum_{i=1}^{n} (0, iii)^{-1}$ stars, y, y, stars y respectively when k = 1, 0, -1. The evolution of the universe is complicated process. To tackle the problem of the early universe, one should consider the different types of matter. Bulk viscosity is required to restore equilibrium to a compressed form of expanding theory. Moreover, the entropy of the universe can be studied only by considering bulk viscosity. When a fluid expands rapidly, there is occurrence of viscosity and it cease in the thermodynamic equilibrium. It is here assumed that addition of bulk viscosity in energy momentum tensor does not change the dynamics of the cosmic evolution. The scenario of bulk viscosity and zero mass scalar field is considered in the following form of energy momentum tensor:

$$T_{ij} = \left(\overline{P} + \rho\right) u_i u_j - \overline{P} g_{ij} + \left(\Psi_{,i} \Psi_{,j} - \frac{1}{2} \Psi_{,m} \Psi^{,m}\right), \qquad 2$$

together with $u_i u^i = 1$, $\overline{P} = P - 3\eta H$ and here u^i is the four velocity vector of the distribution, ρ is the energy density, p is the barotropic pressure, η is the coefficient of bulk viscosity, Ψ is the zero mass scalar field and (;) denotes covariant differentiation. Weinberg [14] has been studied role of viscous fluid.

The action of f(R,T) gravity is of the form

$$S = \frac{1}{16\pi} \int f(R,T) \sqrt{-g} d^4 x + \int L_m \sqrt{-g} d^4 x , \qquad 3$$

where f(R,T) is an arbitrary function of the Ricci scalar R and the trace T of the energy momentum tensor $T_{\mu\nu}$. The L_m corresponds to the matter Lagrangian density and g is the determinant of metric tensor $g_{\mu\nu}$. The energy momentum tensor $T_{\mu\nu}$ is given by

$$T_{\mu\nu} = -\frac{2}{\sqrt{-g}} \frac{\partial(\sqrt{-g}L_m)}{\partial g_{\mu\nu}}.$$
4

By assuming that the Lagrangian density L_m of matter depends only on the metric tensor components $g_{\mu\nu}$ and not on its derivatives we obtain

$$T_{\mu\nu} = g_{\mu\nu} L_m - 2 \frac{\partial L_m}{\partial g_{\mu\nu}}.$$
5

There is no conventional theory to answer all the questions about the universe. This inspired us to investigate bulk viscosity in the context of f(R,T) theory. The field equations of f(R,T) gravity models are

$$f_{R}(R,T)R_{\mu\nu} - \frac{1}{2}f(R,T)g_{\mu\nu} + \left(g_{\mu\nu}\nabla^{\mu}\nabla_{\nu} - \nabla^{\mu}\nabla_{\nu}\right)f_{R}(R,T) = 8\pi T_{\mu\nu} - f_{T}(R,T)T_{\mu\nu} - f_{T}(R,T)\Theta_{\mu\nu}.$$

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where
$$f_R = \frac{\partial f(R,T)}{\partial R}$$
, $f(R,T) = \frac{\partial f(R,T)}{\partial T}$, ∇_{μ} is the operator for covariant derivative and
 $\Theta_{\mu\nu} = -2T_{\mu\nu} + g_{\mu\nu}L_m - 2g^{\alpha\beta}\frac{\partial^2 L_m}{\partial g^{\mu\nu}\partial g^{\alpha\beta}}$.

Now assuming the function f(R,T) in the following form

$$f(R) = R + \mu f_1(T). \tag{7}$$

where μ is arbitrary constant. Recently, many authors [15-18] have been studied this conventional form of the function in the f(R,T) modified theory of gravitation.

The zero mass scalar field $\Psi_{;j}^i = 0$ leads to

$$\Psi_{44} - \left(\frac{A_4}{A} + 2\frac{B_4}{B}\right)\Psi_4 = 0$$

where '4' here and elsewhere denotes differentiation with respect to time t. The field equations for the line element (1), using equations (3), (6) and (7) takes the form

$$2\frac{B_{44}}{B} + \frac{B_4^2}{B^2} + \frac{k}{B^2} = -(8\pi + 5\mu)\overline{P} + 2P\mu + \mu\rho - 2(2\pi + \mu)\Psi_4^2.$$

$$\frac{A_{44}}{A} + \frac{B_{44}}{B} + \frac{A_4B_4}{AB} = -(8\pi + 5\mu)\overline{P} + 2P\mu + \mu\rho - 2(2\pi + \mu)\Psi_4^2.$$
10

$$2\frac{A_4B_4}{AB} + \frac{B^2}{B^2} + \frac{k}{B^2} = (8\pi + 3\mu)\rho - 4\mu\overline{P} + 2\mu P + 4\pi\Psi_4^2.$$
 11

Using equations (9) and (10), we get

$$\frac{B_{44}}{B} - \frac{A_{44}}{A} - \frac{A_4B_4}{AB} + \frac{B_4^2}{B^2} + \frac{k}{B^2} = 0$$
12

Using the transformation $d\tau = Adt$ equation (12) reduces to the following equation

$$\frac{\ddot{B}}{B} - \frac{\ddot{A}}{A} - \frac{\dot{A}^2}{A} + \frac{\dot{B}^2}{B^2} + \frac{k}{A^2 B^2} = 0,$$
13

where the overdot denotes differentiation with respect to τ . In order to solve the equation (13) we put $a = A^2$, $b = B^2$. Thus, the equation (13) further reduces to

$$\frac{\ddot{b}}{b} - \frac{\ddot{a}}{a} + \frac{2k}{ab} = 0$$
 14

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Equation (14) is in two variables, to solve it, we assume the following adhoc relation.

$$\frac{\ddot{a}}{a} = 0$$
. 15

Equation (15) gives us

$$a = c_1 \tau + c_2. \tag{16}$$

For simplicity we take $c_2 = 0$, so that using (15) in (14), by simple mathematical manipulation we arrive at

$$b = -\frac{2k}{c_1} \left(\tau \log \tau - \tau\right).$$
17

Using equations (16) and (17), we get

$$\Psi = -\frac{c \ k \ \tau^2}{c_1} \left(\log \ \tau - \frac{3}{2} \right)$$
18

From equation (18), it is clear that for k=-1, Ψ is positive and for k=1, it is negative whereas for k=0, $\Psi=0$. Also, equation (18) reveals that the zero mass scalar fields not only depends on but also on space time,

The Volume of the universe is obtained as

$$V = AB^{2} = (c_{1}\tau)^{\frac{1}{2}} \left(-\frac{2k}{c_{1}} (\tau \log \tau - \tau) \right),$$
19

One can see that for k=-1, the volume V is decreasing and negative whereas for k=1, it is increasing and positive (figure 1).

The expansion scalar (θ), mean anisotropic parameter (Δ), shear scalar (σ) and deceleration parameter (q) of the model are found to be

$$\theta = 3H = (c_1 \tau)^{\frac{1}{2}} \left(\frac{1}{2\tau} + \frac{\log \tau}{\tau \log \tau - \tau} \right),$$
20

Expansion scalar

The mean anisotropic parameter $\Delta = \frac{1}{3} \sum_{i=1}^{3} \left(\frac{H_i - H}{H}\right)^2 = \left(\frac{1}{1 - 3\log \tau}\right)^2$, 21

Shear scalar
$$\sigma = \frac{3}{2}\Delta H^2 = \frac{(c_1\tau)^{\frac{1}{2}}}{\sqrt{3}} \left(\frac{1}{2\tau} - \frac{\log \tau}{2(\tau\log \tau - \tau)} \right),$$
 22

Deceleration parameter

$$q = \frac{d}{dt} \left(\frac{1}{H}\right) - 1 = -\frac{(c_1 \tau)^{\frac{1}{2}}}{H^2} \left\{ \frac{c_1^{\frac{1}{2}}}{6\tau^{\frac{1}{2}}} \left(\frac{1}{2\tau} + \frac{\log \tau}{\tau \log \tau - \tau}\right) + \frac{(c_1 \tau)^{\frac{1}{2}}}{3} \left(-\frac{1}{2\tau^2} + \frac{\log \tau - 1 - (\log \tau)^2}{(\tau \log \tau - \tau)^2}\right) \right\} - 1$$
 23

The sign of deceleration parameter q indicate whether the model inflates or not. The negative sign of q describes the accelerated model positive one describes the decelerating expansion of the universe. The zero value of the deceleration parameter indicate that the universe is accelerating with constant rate. In this model, we can see that deceleration parameter is zero throughout the evolution of the universe. Thus, the universe is accelerating with constant rate (figure 2). The expansion scalar is decreasing function of τ . It is maximum near $\tau = 0$ and gradually decreases with increasing τ (figure 3). The mean anisotropic parameter is constant. Thus the universe is anisotropic and shearing.



Figure 2.Deceleration parameter with time



Figure 3. Expansion scalar with time

The bulk viscous pressure, energy density and coefficient of bulk viscosity are found to be

$$\overline{P} = -c_1 \tau \begin{cases} l_1 (\tau \log \tau - \tau)^2 + \frac{l_2 \log \tau}{\tau (\tau \log \tau - \tau)} + \\ \frac{l_2 (\log \tau)^2}{(\tau \log \tau - \tau)^2} + \frac{l_4}{\tau (\tau \log \tau - \tau)} \end{cases}$$

Bulk viscous pressure

$$\rho = -\frac{c_{1}\tau}{k_{1}} \begin{cases} l_{5}(\tau \log \tau - \tau)^{2} - \frac{(4\pi + \mu)\log \tau}{\tau(\tau \log \tau - \tau)} - \\ \frac{2k_{3}(\log \tau)^{2}}{(\tau \log \tau - \tau)^{2}} + \frac{4k_{3}}{\tau(\tau \log \tau - \tau)} \end{cases} \end{cases}$$
(25)

Energy density

Coefficient of bulk viscosity

$$\eta = \frac{c_{1}\tau}{9\mu H} \begin{cases} k_{5}(\tau \log \tau - \tau)^{2} + \frac{k_{6}\log \tau}{\tau(\tau \log \tau - \tau)} + \\ \frac{k_{7}(\log \tau)^{2}}{(\tau \log \tau - \tau)^{2}} + \frac{k_{8}}{\tau(\tau \log \tau - \tau)} \end{cases} \end{cases}, \qquad 26$$

where

$$\begin{split} l_{1} &= \frac{(\gamma - 1)k_{2}k^{2}c^{2}}{c_{1}^{2}} + \frac{k_{5}}{3\mu}, l_{2} = \frac{k_{6}}{3\mu} - \frac{(\gamma - 1)(4\pi + \mu)}{k_{1}}, l_{3} = \frac{k_{7}}{3\mu} - \frac{2k_{3}(\gamma - 1)}{k_{1}}, l_{4} = \frac{k_{8}}{3\mu} - \frac{4k_{3}(\gamma - 1)}{k_{1}} \\ l_{5} &= \frac{k_{2}k^{2}c^{2}}{c_{1}^{2}}, k_{1} = 64\pi^{2} + 48\pi\mu + 8\mu^{2} + 16\pi\mu\gamma + 4\mu^{2}\gamma, k_{3} = \pi + \mu, \\ k_{2} &= 128\pi^{2} + 128\pi\mu + 24\mu^{2}, k_{4} = \frac{8\pi + 4\mu - \mu\gamma}{k_{1}}, k_{5} = \frac{(k_{4} + k_{2})k^{2}c^{2}}{c_{1}^{2}}, k_{6} = \frac{1}{2} - (4\pi - \mu)k_{4}, \\ k_{7} &= \frac{1}{4} - 2k_{3}k_{4}, k_{8} = 4k_{3}k_{4} - \frac{1}{2}. \end{split}$$

The energy density is negative near $\tau = 0$ and gradually increases to positive and attains its maximum and eventually tends to constant positive value at large time. In the figure (4) and (5), we can find that for

 $\mu = 0.1$ and $\mu = 10$, there is a variation of the energy density near $\tau = 0$. Thus, it is clear that the matter function play an important role in the evolution of the universe.

Figure (6) and (7) reveals that coefficient of bulk viscosity is positive in the early stages of the evolution of the universe. At some stage it is suddenly increases and falls to negative which eventually stable to negative at large value of τ . There is no variation found in η due to variation in values of μ . One can observe that at the sudden rise of η , the energy density is seem to attain its maximum.

The behavior of ρ , η in our model is different as compared to that of ρ , η obtained in General Relativity [18] and modified gravity [19].





Figure 7. Coefficient of bulk viscosity with time

3. CONCLUSION

We have investigated Homogeneous Hypersurface space time with zero mass scalar field and bulk viscosity in the context of f(R,T) modified theory of gravitation. We have solved the field equation by using simple mathematical techniques. It is found that

- Ψ is positive for k = -1 and negative for k = 1. It is zero for k = 0. 1.
- 2. The energy density is positive with increasing time. In the early stages of evolution of the universe, the effect of matter clearly observed in the variation of energy density.
- 3. The coefficient of bulk viscosity is positive near $\tau = 0$ and eventually tends to negative at large τ .
- 4. The expansion rate is maximum in the early stages of the universe and gradually decreases with increasing time.
- The universe is accelerating, shearing and anisotropic. 5.

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PHOTOLUMINESCENCE STUDY OF NARROWBAND UVB EMITTING KSrPO4:Gd³⁺ PHOSPHORS

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ABSTRACT :

 Gd^{3+} doped KSrPO₄ phosphor was synthesized by modified solid state diffusion method. The phase purity and crystallinity of phosphors confirmed by X-ray diffraction (XRD) analysis while surface morphology studied by scanning electron microscopy (SEM). The PL excitation spectra of KSrPO₄: Gd^{3+} phosphor exhibit peak at 272-280 nm due to the ${}^{8}S_{7/2} \rightarrow {}^{6}I_{J}$ transition of Gd^{3+} ions. The emission spectra of synthesized phosphor show sharp NB-UVB emission at 312 nm under the excitation of 274 nm. The result shows that as prepared phosphor could be good candidate as phototherapy lamp phosphor.

KEYWORDS: XRD, Photoluminescence, Phototherapy, SEM.

1. INTRODUCTION

Host lattices which are easily synthesizable and structurally viable for doping at multiple cationic sites present in the lattice are of recent interest. From available literature, it has been observed that most of the UV emitting phosphors are based on Silicates, Fluorides, Aluminates or Phosphate. Phosphate-based compounds are considered to be an important group of luminescent materials owing to their excellent thermal stability and tetrahedral rigid three-dimensional matrix, which is expected to be ideal for charge stabilization.

Phosphates with general formula ABPO₄, where A is a monovalent cation (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺) and B is a divalent cation (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺), (A = alkaline metals, B = alkaline earth metals) are of interest for their optical and ferroelectric properties.

The phosphate family has paying much attention as luminescent host material because of its exceptional thermal and charge stabilization. For example LiBaPO₄ [1], KSrPO₄ [2], NaCaPO₄ [3] have been reported to act as new phosphor materials for applications of radiation dosimetry and w-LEDs. Furthermore KSrPO₄:Eu²⁺phosphor are a promising candidate for NUV-LEDs and possess excellent thermal stability [4]. It is also found that LiSrPO₄doped $Eu^{2+}/Mn^{2+}/Tb^{3+}$ and $Eu^{2+}-Pr^{3+}$ co-doped phosphors show tunable luminescence as well as act as solar spectral convertor respectively [5, 6]. Many researchers prepared phosphate phosphors such as LaPO₄:Eu³⁺ [7], Sr₃Bi(PO₄)₃:Eu²⁺/Mn²⁺ [8], GdPO₄:Tb³⁺ [9]. NaBaPO₄:Eu²⁺/Tb³⁺ [10] and YPO₄:Eu³⁺ [11] by different methods.

The main emission peak of Gd^{3+} ion is in narrow band UVB region, which is efficiently useful for the application of phototherapy. In our previous work we have reported some UV emitting phosphor materials such as NaSr₄(BO₃)₃ [12], LaPO4:Gd³⁺ [13], LiSr₄(BO₃)₃:Gd³⁺, Pr³⁺ [14], LiSrPO₄:Gd³⁺, Pb²⁺ [15], LaBaB₉O₁₆:Ce³⁺ [16] and Sr₂Mg(BO₃)₂:Pr³⁺, Gd³⁺ [17].

However, to the best of our knowledge there is no report on Gd^{3+} doped LiSrPO₄ host. In this report we studied the photoluminescence properties as well as the concentration quenching mechanism of Gd^{3+} ion doped KSrPO₄ phosphors.

2. EXPERIMENTAL

2.1 Synthesis Technique

The phosphor KSrPO₄doped with various concentration of Gd^{3+} were prepared by modified solid state diffusion method. During synthesis, the stoichiometric amounts of high purity starting materials, KNO₃ (A.R.), Sr(NO₃)₂(A.R), NH₄H₂PO₄(A.R.) and Gd₂O₃ were used for phosphors preparation. The molar ratio of constituent materials used during phosphor synthesis is (x=0.005, 0.01, 0.02, 0.03) mole of the Gd³⁺. Ingredients were mixed thoroughly with acetone so that the paste was formed. Prepared pastes were kept on hot plate at 80°C up to the removal of acetone completely. The obtained solid material then transferred directly to the pre-heated muffle furnace maintained at 700°C for 1hr. After that the material was crushed by using agate mortars. The resulting fine powders were annealed for 2½ hr at temperature 950°C and then suddenly quenched to room temperature and taken for characterization. The complete process involved in the reaction was represented as a flow chart in Fig. 1.



Fig. 1 Flow chart of synthesis method

2.2 Characterizations of materials

The confirmation of as prepared materials was done by XRD method by using Rigaku miniflex II Xray diffractometer with scan speed of 2.000°/min and Cu K_a ($\lambda = 0.15406$ nm) radiation in the range 10° to 80°.The structural and morphological characteristics i.e., particle size and shape of particle sample was studied using a SEM analysis. The measurement was performed using a ZEISS EVO/18 Research. In this study, sample in powder form (100-150 µm) was placed directly on sample holder of SEM for imaging. The PL emission and PL excitation spectra were recorded at room temperature on (Hitachi F-7000) fluorescence spectrometer associated with 450W Xenon discharge lamp in wavelength range 200 - 400 nm. The measuring parameter such as width of monochromatic slit (1.0 nm), photomultiplier tube (PMT) detector voltage, scan speed (240 nm/min), spectral resolution were kept constant throughout the analysis of materials.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction Pattern

The crystal structure and the phase purity of KSrPO₄ phosphor doped with 0.02 moles of Gd³⁺ ion was confirmed by XRD pattern as shown in **Fig. 2.** The XRD pattern of KSrPO₄ phosphor shows well agreement with the standard data from ICDD (International Centre for Diffraction Data) having PDF file number (**00-033-1045**). Also the XRD pattern show that the synthesized material was completely crystalline and in single phase, where a = 7.3507, b = 9.6340 Å and c = 5.5621 Å. The prepared materials crystallize in orthorhombic

phase.



Fig. 2. (A) XRD pattern of KSr_{0.98}PO₄:_{0.02}Gd³⁺ phosphor with standard ICDD file.

3.2. Scanning Electron Microscopy (SEM)

Fig. 3. shows the SEM image of $KSr_{0.98}PO_4$:_{0.02}Gd³⁺ powder prepared by using MSSD method. It was observed that the microstructure of the phosphor consist of irregular grains with heavy agglomeration. The heavy agglomeration is because of high temperature synthesis method. Also the micrograph shows that synthesized sample consists of irregular shape particles. The average sizes of as prepared particles were found to be in the range 2 μ m.



Fig. 3. SEM image of prepared KSr_{0.98}PO₄:_{0.02}Gd³⁺ phosphor

3.3. Photoluminescence study

Generally it is well known that the ultraviolet radiations are useful for phototherapy, mainly those in the UVB (280 - 320 nm) region. Phosphor materials that give sharp emissions in the UVB region are used in phototherapy lamps. The emission of Gd^{3+} ion doped phosphors is in the narrow UVB region (280 - 320 nm), therefore it is usually useful for the treatment of many skin diseases such as psoriasis, vitiligo, atomic dermatitis, etc.

Fig. 4. shows the photoluminescence excitation and emission spectra of KSrPO₄ prepared with various concentrations of Gd^{3+} ions. The excitation and emission spectra were monitored at 274 nm and 312 nm respectively. The Gd^{3+} ion gave the sharp and intense emission spectra in NB-UVB region around 312 nm when excited by radiation of wavelength 274 nm corresponding to ${}^8S_{7/2} \rightarrow {}^6I_J$ transition. Moreover the emission spectra consists of a weak line at 305 nm followed by the strong one at 312 nm. These lines correspond to the

 ${}^{6}P_{5/2} \rightarrow {}^{8}S_{7/2}$ and ${}^{6}P_{7/2} \rightarrow {}^{8}S_{7/2}$ transitions of the Gd³⁺ ion, respectively. It is also observed that the photoluminescence emission and excitation spectra of KSrPO₄:Gd³⁺ phosphor linearly increases with increase in concentrations of Gd³⁺ ion and reaches a maximum at 0.02 mol. And after that intensity of emission and excitation decreases suddenly due to the well known phenomena concentration quenching. No shifting was observed in emission because of high concentration of Gd³⁺ ion.



Fig. 3.4: Photoluminescence excitation and emission spectrum of $KSr_{(1-x)}PO_4:xGd^{3+}$ (x=0.002, 0.005, 0.01, 0.02 and 0.03)

According to Blasse [18], the concentration quenching of the luminescence is due to the energy transfer from one activator to another until all the energy is consumed. The concentration quenching phenomena is observed because of non-radiative energy transfer among the identical Gd^{3+} ions. It is well recognized that the concentration quenching phenomena will not take place if the average distance between the identical Gd^{3+} ions is so large that the energy migration is in a weak position. The critical distance is an essential parameter to understand the phenomenon, as the probability of energy transfer between two activators is inversely proportional to the nth power of the distance of the activator ions. The critical distance R_0 can be estimated using the following formula

$$R_0 = 2 \times \left(\frac{3V}{4\Pi \chi_c N}\right)^{1/3}$$

Where, V is the volume of the unit cell (in Å), X*c* is the atom fraction of activator at which the quenching occurs, the so called optimum concentration, and N is the number of cations in the unit cell. According to the above experimental results and the crystal structure of the compound KSrPO₄, the value of Xc=0.02, N=4 and V= 393.889, the critical distance R₀ of Gd³⁺ in KSrPO₄ phosphor is calculated to be about 21.11 Å.

Since the critical distance R_0 is greater than 5Å, only a multipole - multipole interaction is important where the exchange interaction becomes ineffective. If the distance is shorter than 5Å then the exchange interaction becomes effective.

CONCLUSIONS

Phosphors KSrPO₄ doped with Gd^{3+} ions was successfully synthesized by the modified solid state diffusion method. XRD pattern shows good matching with the ICDD file No. (**00-033-1045**)

- ➤ The excitation spectra shows peak in the range 272 280 nm corresponding to ${}^{8}S_{7/2} \rightarrow {}^{6}I_{J}$ transition of Gd³⁺ ion.
- The emission spectra of KSrPO₄:Gd³⁺ show sharp NB-UVB emission at 312 nm under the excitation of 274 nm.
- > The concentration of Gd^{3+} for which maximum intensity of emission is obtained was found to be 0.02 mol.
- \blacktriangleright The critical distance was found to be 21.11 Å.

Obtained result shows that KSrPO₄:Gd³⁺phosphor could be a potential candidate for Phototherapy Lamp Applications.

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COMPARISON OF OPTICAL PROPERTIES OF poly(vinyl acetate)/polyindole COMPOSITE FILM PREPARED USING DIFFERENT OXIDANT

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ABSTRACT:

In present research paper, comparison of optical properties of poly(vinyl acetate)/polyindolecomposite film prepared using different oxidants via chemical oxidative polymerization method. The developed composites films were characterized via ultraviolet-visible (UV-Vis) and X-ray diffraction (XRD) technique. The XRD pattern of composite represents the semi crystalline nature of the prepared materials. The PVAc/PIN composite films developed through oxidant ferric chloride has higher optical energy band gap as compared to via chromium chloride. The optical band gap energy represents the application potential in optical devices.

KEYWORDS : *Poly(vinyl acetate)/polyindole; composite; optical; band gap.*

1. INTRODUCTION

The polymers are generally known as insulator. The worldwide use of polymers as insulating material is at large scale. Recently, the new trend is emerged to prepare the conducting polymers rather than the traditional polymers (insulating materials). The conducting polymers like polyaniline, polypyrrole, polythiopene, polyindole are synthesized and modified in last few decades. Moreover, the derivatives, co–polymers, composites and nanocomposites of conducting polymers are developed through different synthesis methods in recent years. Also, there various properties are widely studied like, electrical properties, optical properties, thermal properties and sensing properties on the basis of their application point of view. The polyindole is a newest and least investigated conducting polymer as compared to other. Therefore, polyindole got more research interest than other in last few years.Polyindole is prepared via various synthesizing techniques and represents the remarkable application potential in various fields [1–16].

Some researchers were reported the their work on synthesis and application of PIN, Its copolymers and composites with various polymerization technique like, Giribabu et al. synthesized polyindole nanowires by oxidative polymerization and studied electrochemical properties [17].Bhagat et al. reports the UV–VIS spectroscopic studies of novel one pot synthesized polyindole/poly(vinyl acetate) (PIN/PVAc) composite films chemically using an oxidant nickel nitrate [18].Gupta et al. reported interfacial synthesis as well as miscible solvents aqueous phase synthesis of polyindole moreover development of polyindole microspheres and nanorods [19].Sari et al. synthesized polyindole (PIN) and polyindole/polyethylene (PIN/PE) conducting composites, having different amounts of PIN by chemical polymerization using FeCl₃ as an oxidant and taking the ratio of salt:monomer.Moreover, studied conductivities, sedimentation stabilities, ER properties as well as creep–recovery response of the prepared materials [20].Bhagat et al. investigated optical parameters and thermal analysis of Cu doped poly(vinyl acetate)/polyindole composites using cupric chloride as an oxidant [21]. An et al. reported a comparative study of the microemulsionas well as interfacial polymerization for polyindole [22].

The aim of the present work is to developed the composite material where indole is polymerized in presence of polymer matrix by a simple, inexpensive and environment friendly chemical oxidative polymerization technique to prepare poly(vinyl acetate)/polyindole composite film.

This paper presents the comparison of optical properties of poly(vinyl acetate)/polyindole(PVAc/PIN) composite film prepared using different oxidants like ferric chloride and chromium chloride. The synthesized composites films were characterized by ultraviolet–vis (UV–Vis) and X–ray diffraction (XRD) technique.

2. EXPERIMENTAL

All chemicals were analytical grade (AR). Moreover, indole as monomer, ferric chloride (FeCl₃), and chromium chloride (CrCl₃) used as oxidants, methanol used as organic media and all were procured from SD Fine Chemicals, India. The poly(vinyl acetate) (PVAc) used as polymer procured from Himedia Chemicals, India.

The poly(vinyl acetate)/polyindole (PVAc/PIN) composite films were synthesized at room temperature by chemical oxidative polymerization technique. The ferric chloride (FeCl₃), and chromium chloride (CrCl₃) were used as oxidant. Mixed solutions of PVAc and methanol were developed by suspendingpolyvinyl acetate (1 g) in methanol (9 ml) and mixed about 1 h and kept it for 24 h to create homogenous solution. Subsequently, indole (0.5 g) (monomer)was added into poly(vinyl acetate) solutions and constantly stirred for 60 Min. The monomer indole was chemically polymerized by adding oxidants FeCl₃ and CrCl₃(each 0.08823 g) (15 wt%), respectively, and constantly stirred about 120 Minute to complete reaction of chemical oxidative polymerization.PVAc/PIN composite solutions were kept for 60 Minute to obtain settled solutions. Then, these mixed solutions of PVAc/PIN were poured on optically plane and chemically cleaned glass plates to developed films.

The composite films were dried out by an isothermal evaporation of organic solvent. Consequently, complete assembly was located in a dust-free chamber retained at steady temperature. After evaporation of organic solvent isothermally, films were rinsedby hot distilled water and take out from glass plates. Then, PVAc/PIN films were once moredried out for 6 h at room temperature. In that manner, PVAc/PIN composites with different oxidants were prepared.

The Ultraviolet–Visible (UV–Vis) spectroscopy was carried on Agilent Technologies, Cary 60 UV– Vis, toestimate optical band gap and studied the %absorption of material. The X–ray diffraction patterns were deliberateviaCuK α ($\lambda = 1.5406$ Å) radiation. The intensity was considered as a purpose of 2θ ranges over 10– 70° at room temperature.

3. RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis

The figure 1. reflects XRD patterns of PVAc/PIN composite films. The broad hollow and noisy peaks presents in XRD patterns are attributed to presence of polyindole, demonstrating its amorphous nature. The polymer chain separation has been estimated using the relation given in equation [21],

$$R = \frac{5\lambda}{8\sin\theta} \tag{1}$$

Where, $\lambda =$ Wavelength of X–ray source used for XRD pattern analysis and θ is diffraction position. The values of polymer chain separation of PVAc/PIN composite films were estimated viathe peak value of the broad hollow. The 2 θ position ranges over 16.45–26.61° and the average polymer chain separation was in the range 5.3954 and 4.6178 Å respectively.



The 2θ position of broad hollow and value of average polymer chain separation of synthesized PVAc/PIN composite films are listed in table 1.

Fable 1: Broad hump at 2 the	ta position, average p	olymer chain se	paration.
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Sample	Broad hump at 2 theta position	Average polymer chain separation R (Å)
FeCl ₃	16.45-25.69	5.3954
CrCl ₃	17.84-26.61	4.6178

UV–Vis Analysis

The UV–Vis spectrum of PVAc/PIN composite filmsranges over190–450 nm reflects in figure 2. Moreover, it is observed that the higher wavelength has lower percentage absorption and lower wavelength side has higher percentage absorption. It was undoubtedly observed that the strongest peak of the absorption for chromium chloride ferric chloride emerges at wavelength 225 nm and owing to the optical transition to the conduction band from valence band [23–25].



Optical Band Gap

The optical band gaps of PVAc/PIN composite films has been calculated from figure 3as well as following equation [26, 27],

$$\alpha = \frac{A(h\nu - Eg)^n}{h\nu} \tag{2}$$

where, hv is the incident photon energy, α is the absorption coefficient, E_g is the optical band gap of material, and A is the constant. The figure directly shows that PVAc/PIN composite films prepared through oxidizing agent chromium chloride have lower optical energy band gap value than ferric chloride. The values of optical band gap energy of the developed composites were determined as 3.31 and 2.459 eV for oxidants ferric chloride and chromium chloride, respectively. These composite materials have application potential in the polymeric optical devices, photo catalytic activities, as well as polymeric solar cells that is observed from optical energy band gap values of both materials.



The optical energy band gap of PVAc/PIN composite filmsshows the little difference in values, it may due to structural change in synthesized materials due to different oxidants used for synthesis. Moreover, it is cleared that, PVAc/PIN composite films synthesized using oxidant chromium chloride has lower optical energy band gap as compared to using ferric chloride.

4. CONCLUSION

The successful developments of PVAc/PIN composite films were done by chemical polymerization technique through two different oxidants. The values of optical band gap energy of the prepared composites were estimated to be 3.31 and 2.459 eV for oxidants ferric chloride and chromium chloride, respectively. The optical band gap energy has represents the potential for photovoltaic activities. Therefore, it concludes that PVAc/PIN composite film potential of application in the polymeric solar cells and optical devices.

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CONVENTIONAL SYNTHESIS OF 1,5-BENZODIAZEPINES USING 2-METHOXYETHANOL AS AN ALTERNATIVE REACTION SOLVENT

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ABSTRACT:

An improved condensation reaction between substituted halohydroxychalcones and ophenylenediamine using piperidine in 2-methoxyetahnol as an efficient and alternative reaction medium. The clean reaction conditions, easy work up, time saving and higher yields are notable advantages of present method.

KEYWORDS: *Halohydroxychalcones;* 2-*methoxyethanol; green chemistry.*

INTRODUCTION

Benzodiazepines have attracted attention as an important class of heterocyclic chemistry [1]. They are finding numerous new applications and widely used as anticonvulsant, anti-inflammatory, analgesic, hypnotic, sedative and antidepressive agents [2]. Moreover 1,5-benzodiazepines are also useful precursor for the preparation of other fused ring compounds such as triazolo-, oxadiazolo-, oxazino- or furano benzodiazepines [3].

A classical synthesis of these compounds involves condensation reaction between *o*-phenlyenediamine with α , β -unsaturated carbonyl compounds, β -diketones. Recently some well known modified method have reported for synthesis of 1,5-benzodiazepines such as BF3-etherate [4], NaBH4 [5], SiO2 [6], Amberlyst [7], Yb(Otf)3 [8], MgO/POC13 [9], Al2O3/P2O5 [10], TiCl4/THF [11], ionic liquid [12], silica gel [13], CeCl3/silica gel [14].

However, many of these reported procedures have one or more disadvantages such as use of expensive catalyst, low selectivity, harsh reaction time, low yield, relatively long reaction time and environmental concern. In recent years replacement of hazardous-solvent with environmentally benign solvents is one of the major focus areas of green chemistry. The utility of alternative reaction solvents such as water [15], Ionic liquid [16], flourous [17], supercritical media [18] and polyethylene glycol [19] (PEG) is rapidly growing.

Green chemistry focuses on research that attempts to reduce or eliminate negative environmental impacts. Green chemistry aims to prevent waste and generate substances with little or no toxicity to humans and the environment, There by maximizing atom economy [1]. This is achieved by assuring that the final product contains the greatest possible proportion of the starting materials and avoiding the use of harmful solvents. Due to the wide range of pharmacological activity, promoted towards the synthesis of 1,5-benzodiazepines using piperidine in 2-methoxyethanol as an alternative reaction solvent.

MATERIAL AND METHODS

Melting points were uncorrected and determined in an open capillary tube. IR spectra were recorded on FTIR Shimadzu spectrometer. 1H NMR spectra were recorded in CDCl3 on Avance 300 MHZ spectrometer using TMS as an internal standard. The mass spectra were recorded on EI-Shimadzu-GC-MS spectrometer. Elemental analyses were performed on a Carlo Erba 106 Perkin-Elmer model 240 analyzer.

Typical procedure for synthesis of 1,5-benzodiazepines 2(a-l)

A mixture of substituted halohydroxychalcones 1 (0.01mol), O-phenylenediamine (0.012mol) and piperidine (3-4 drops) in 2-methoxyethanol (15mL) was refluxed for 15 minutes. Then reaction mixture was cooled to room temperature. Solid separated was isolated by simple Buchner filtration; final purification was achieved by crystallization from ethanol.

Scheme:



Scheme 1 : Synthesis of 1,5-benzodiazepines

						Ar =
No. of	R		R ₂	R ₃	Ar	
comp		1				
61	OH		Н	Cl	А	
		r				
62	OH		CH ₃	C1	A	
63	OH		CH ₃	Cl	A	
		r				
64	OH		Н	Cl	А	
65	Н		OH	Br	А	B→
		H ₃				
66	Н		OH	Ι	А	OMe
		H ₃				
67	Н	Cl	OH	Cl	А	
68	OH	Cl	OH	Cl	А	
69	OH		CH ₃	Cl	В	Oivie
		r	5			
70	OH		Н	Cl	В	
		r				
71	OH		Н	Cl	C	
		r				
72	OH		CH ₃	Cl	C	
		r]

2-Bromo-4-chloro-6-(4-naphthalen-1-yl-4,5-dihydro-3H-benzo[b][1,4]diazepin-2-yl)-phenol(61): IR v max cm-1: 3350 (N-H), 1592 (C=N), 1512, 1450 (C=C). ¹H NMR (CDCl3): δ 3.09 (dd, 1H, H_A), δ 3.46 (dd, 1H, H_B), δ 5.74 (dd, 1H, H_x), δ 6.90 (s, 1H, N-H), δ 7.55-8.22 (m, 13H, Ar-H), 11.2(s, 1H, OH). MS (m/z): 476 (M+).

4-Chloro-2-iodo-3-methyl-6-(4-naphthalen-1-yl-4,5-dihydro-3H-benzo[b][1,4]diazepin-2-yl)-phenol(62) :

IR v max cm-1: 3353 (N-H), 1590 (C=N), 1512, 1455, 1420 (C=C). ¹H NMR (CDCl3): δ 3.32 (s, 3H, CH₃), δ 3.10 (dd, 1H, H_A), δ 3.45 (dd, 1H, H_B), δ 5.73 (dd, 1H, H_X), δ 6.90 (s, 1H, N-H), δ 7.52-8.32 (m, 12H, Ar-H), 11.2(s, 1H, OH). MS (m/z): 537 (M+).

2-Bromo-4-chloro-3-methyl-6-(4-naphthalen-1-yl-4,5-dihydro-3H-benzo[b][1,4]diazepin-2-yl)-phenol(63):

IR v max cm-1: 3350 (N-H), 1592 (C=N), 1512, 1450 (C=C). ¹H NMR (CDCl3): δ 3.32 (s, 3H, CH3), δ 3.08 (dd, 1H, H_A), δ 3.48 (dd, 1H, H_B), δ 5.75 (dd, 1H, H_X), δ 6.92 (s, 1H, N-H), δ 7.52-8.32 (m, 12H, Ar-H), 11.2(s, 1H, OH). MS (m/z): 490 (M+).

CONCLUSION:

In summary, the present work describe a simple condensation reaction between substituted halohydroxychalcones with *o*-phenylenediamine using piperidine in 2-methoxyethanol as an efficient and green reaction solvent. The advantages of present protocol are simplicity of operation, time saving, high yields of products and avoidance of expensive catalyst and usage of volatile organic solvent.

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DC HUMIDITY SENSING PROPERTIES OF NANOSTRUCTURE SnO₂ SYNTHESIS WITH CO-PRECIPITATION METHOD

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ABSTRACT:

In this paper Stanninc oxide (SnO_2) nanoparticles was synthesized by a chemical precipitation method. The synthesized samples were characterized using X-ray powder diffraction (XRD). Sensing material was made as in the form of thick film by using screen printing method. Surface mor- phologies of the samples were analyzed using Field emission Scanning electron microscopy (FE-SEM). The XRD pattern indicates that SnO_2 has a tetragonal phase structure having minimum crystallite size 23.19 nm. Further, humidity sensing investigations of these sensing materials were done. The SnO₂ sample shows good sensitivity towards the relative humidity. Our result indicate that pure SnO_2 resistance decreases from $10^{11} \Omega$ to $10^8 \Omega$. in form of thick film was most sensitive. The activation energy measured from Arrhenius plot of conductivity at different RH and found to be 4.6010^{-4} eV respectively. The results were re- producible up to $\pm 77\%$ after 2 months of observations.

1. INTRODUCTION

Recently, humidity sensors are of great significance in many fields, including environmental monitoring, industrial production, agricultural planting, aviation, and medical and chemical monitoring, etc. [1,2]. There are various kinds of nanostructure materials have been extensively studied. Semiconducting materials, such as SnO_2 , WO_3 , and ZnO for the humidity sensor are also applied in variety of different areas [3-6]. The band gap SnO2 wide (~3.7 eV) has distinctive electrical properties and high physical/chemical stability [7, 8]. The 3D hierarchical SnO_2 dodecahedral nanocrystals based nanosensor, exhibited superior humidity-sensing properties. These nanostructures SnO_2 provides a regular porosity and a large specific surface area, allow high accessibility for the water molecules and providing more active site for the surface physical/chemical interaction between water molecules and the nanostructure SnO_2 materials [9]. Thus due to effective approach toward an understanding, and the design, of nanostructure SnO_2 based humidity sensing materials.

2. EXPERIMENTAL

Synthesis of tin oxide (SnO_2) : All the chemicals used in this study were of GR grade purchase from Sd-fine, India (purity 99.99%). The chemicals are used without any further purification. Stannous chloride dehydrates (SnCl₂.2H₂O), Ammonia solution and deionized water were used during reaction. The conducting silver paint (Sigma Aldrich Chemical, USA) is used to form electrodes. In preparation of SnO₂ nanoparticle the Stannous chloride dehydrates (SnCl₂.2H₂O), Ammonia solution and deionized water were used as starting materials. Initially, 2 g (0.1 M) of stannous chloride dehydrate (SnCl₂.2H₂O) is dissolved in 100 ml water. After complete dissolution, about 4 ml ammonia solution is added to above aqueous solution with magnetic stirring. Stirring is continued for 20 minutes. White gel precipitate is immediately formed. It is allowed to settle for 12 hrs. Then it is filtered and washed with water 2-3 times by using deionized water.

precipitate were mixed with 0.27 g carbon black powder (charcoal activated). The obtained mixer is kept in vacuum oven at 70 °C for 24 hours so that the mixer gets completely in to dried powder. Then this dry product was crushed into a find powder by grinder. Now obtained product of fine nanopowder of SnO_2 was calcinated at 700°C up to 6 hours in the auto controlled muffle furnace (*Gayatri Scientific, Mumbai, India.*) so that the impurities from product will be completely removed.

glass substrate. Initially, for the screen printing the thixotropic paste was formulated by mixing the sintered fine powder of pure nano powder of SnO_2 in different molecular weight ratios, a with a solution of ethyl cellulose as (10% temporary binder) in a mixture of organic solvent such as butyl cellulose, butyl carbitol acetate and turpineol. The ratio of inorganic to organic part was kept as 75:25 in formulating the paste. The paste of pure materials of SnO_2 was screen printed on a glass substrate in the form of thick films and it was dried at 80-110°C in oven for 1hrs. The dried films is fired at 500°C for 25 min in muffle furnace (Kumar make Mumbai), to remove organic impurities form the sensor material. For the surface conductance measurement the electrodes of silver paint were formed on adjacent sides of the films.

3. CHARACTERIZATION

Figure 1 shows the XRD pattern of pristine stannic oxide (SnO_2) nanostructure synthesized by liquid phase via co-precipitation method calcinated at 400°C it is clearly observed that the highest intensity peak is obtained at (110) crystal planes and other peaks lying at (101), (200), (211), (220) and (002) of SnO₂. All the peaks match well with the standard tetragonal structure of SnO₂ with lattice constant a = 4.723 nm and c = 3.238 nm and its unit cell volume (V=72.24A^{o3}) with JCPDS card no. 71-0652. All the peaks are perfectly match with pure SnO₂ nanostructure, which indicates the high purity of obtained SnO₂ nanoparticles. The average



crystalline size was found to be 23.19 nm calculated by using Deby Figure 1: XRD pattern of SnO₂

TEM

Figure 2 shows the TEM image of pristine Stannic oxide (SnO_2) which shows the formation of highly crystalline stannic oxide (SnO_2) nanoparticle by using liquid phase method via coprecipitation method. The shape of SnO_2 nanoparticles are like tetragonal pattern of sports and their average crystalline size is found to be 29.15 nm [11,12].



Figure 2: TEM images of SnO₂



Figure 3: Fe-SEM images of SnO₂

FE-SEM

Figure 3 decipts the FE-SEM micrograph of pristine Stannic oxide (SnO_2) nanostructure thick films. In this the particles are found to in the tetragonal shape within the particle size in the range of about 15nm to 31.2 nm. The average particle size observed in both FE-SEM and TEM measurement where found to be nearly equal [13].

Result and Discursion Hysterias Plot





Figure 4 shows hysteresis plot of Stannic oxide (SnO_2) at different constant temperature 30° C, 40°C, 50°C and so on. Hysteresis plot shows the variation between resistances of sample with respect to the relative humidity in increasing and decreasing order (30 to 90 % RH and 90 to 30 % RH) in steps of 5 % RH. Particularly, figure 4 is corresponds to resistance measurement by Keithley voltage source meter (2400) at constant temperature 30°C and so on. Overall in all the samples hysteresis plot measurement carried by Keithley voltage source meter (2400) at different constant temperature from 30 °C to 90 °C in steps of 10 °C and relative humidity varies from 30 to 90 % RH in steps of 10 % RH and vice versa also.

In these the resistance of sensors decreases by increasing the relative humidity from 30 to 90% RH and the resistance of sensors increases by decreasing the relative humidity from 90 to 30% RH at respective constant temperature varying from 30 to 90°C and vice versa. The presences of hysteresis shows the processes of adsorption and de-adsorption are not so faster at particular humidity. In this processes the adsorption would not be efficient which cause a small change in the resistance. The physisorbed water molecules is converted into chemisorbed by donating the surface electron at the constant temperature [14] and for the deadsorption it requires large activation energy [15]. On the other hand a sample shows comparable decrease in resistance with an increase in % RH which indicates that the conduction occurred at the grain surface by release of electron from the water molecule. However, the sample pure Stannic oxide (SnO₂) shows the remarkable change in the resistance values in between the humidity range 30-90 % RH and possessed a high sensitivity factor due to large surface area and porosity in the form of thick films.

A very small hysteresis present during forward and reverse cycle of relative humidity, where as a very significant average change observed in the value of resistance of sample, in the range of $10^{11}\Omega$ to $10^8 \Omega$ in all the samples from 30 to 90% RH.

Sensitivity





The pure Stannic oxide (SnO₂) nanoparticles thick film exhibits significantly higher sensitivity due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapuors [16]. The fall in resistance is mainly due to the increased amount of conduction electron or charge carrier upon adsorption of water vapours by the surface layer of the thick films. The fall in resistance is mainly due to the increased amount of conduction electron or charge carrier upon adsorption of water vapours by the surface layer of the thick films. Initially, at low humidity levels the adsorbed water molecules get ionized on the surface and the hydronium ions are produced by the assistance of high electric charge density in the neighbourhood of the hydroxyl (OH-) sites resulting in the protonic conduction to the adjacent sites [17]. For pure Stannic oxide (SnO₂) nanoparticles thick film the sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant as shown in figure 6.

Activation Energy

The Arrhenius plot for all the samples found to be linear and by using Arrhenius equation;

The activation energy ΔE for nanostructured stannic oxide (SnO₂) samples is found to be quite reasonable for the electrical conduction the values of activation energy is much more smaller at constant different RH. This shows that the smaller amount of energy is required for the conduction of electrons due to absorption of water molecules there by increasing the number of donor electron [18]. The activation energy was found to be 4.6010⁻⁴ eV.

CONCLUSION.

Nanostructured SnO₂ was successfully synthesized by liquid phase via co-precipitation method. Minimum crystallite size was found to be for SnO₂ it is found to be 23.19 nm . Surface morphology of Nanostructured stannic oxide (SnO₂) shows that most particles are spherical in shape leaving more space as pores and hence it was most sensitive. The purity of sample was also conform with Transmission electron microscopy. The Hysteresis plot shows very significant average change in the value of the resistance from $10^{11} \Omega$ to $10^8 \Omega$ during forward and reversed cycles. The sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant and shows that it more sensitive. This nanocomposites carries a good scope for the development of moisture sensor in the range of relative humidity 30% to 90% RH. Activation energy measured and found to be 4.6010^{-4} eV respectively. This nanocomposites carries a good scope for the development of moisture sensor in the range of relative humidity 30% to 90% RH.

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TIME DOMAIN REFLECTOMETRY TECHNIQUES TO STUDY SIMULATION DIELECTRIC SPECTRA OF POLAR LIQUIDS

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ABSTRACT :

Laplace Transform (LT), Discrete Fourier Transform (DFT) and Fast Fourier Transform (FFT) are few powerful techniques mostly employed in the determination of dielectric properties of polar liquids using Time Domain Reflectometry (TDR) waveforms. In the present paper, Fourier Transform algorithms can be used to study complex permittivity spectra of some polar liquids. Electrical permittivity, conductivity and relaxation time are important parameters to explain dielectric dispersion properties in the microwave region. Comparison of simulated spectra using standard Debye model or using the complex permittivity spectrum with static dielectric constant ε_{0} , dielectric constant at optical frequency (ε_{∞}) and relaxation time (τ) can be estimated by using Havriliak-Negami like expression and actual recorded data can be fitted and dielectric properties of unknown samples can be estimated with good reliability. The pico-second Time domain pulse reflected from sample contains high frequency dispersion/relaxation data, usually in microwave region, may contain resonant/ anti-resonant peaks which masks true dispersion behaviour. For corrections generally bilinear calibrating samples are considered.

KEYWORDS: Electrical permittivity, Havriliak-Negami model, Fourier Transform (FT), simulated spectra.

INTRODUCTION

Time domain spectroscopy (TDS) has been extensively used to determine dielectric parameters of polar as well as non-polar liquids in the GHz. region [1-4]. In the present TDR technique a step voltage pulse of rise time about 40 pico-second generated by a tunnel diode is driven along a precision transmission line connected to the SMA cell having 50 Ohms characteristic impedance. In the open load condition, the transient reflected pulse response-waveforms from air and loaded with the liquid under consideration, are digitized and stored in the memory of the broad band sampling oscilloscope. These waveforms are suitably used to obtain the complex reflection coefficient ρ^* over the broad range of frequencies by using Fourier transforms. Also, the dispersion curves for complex permittivity data (real and imaginary parts) can be obtained [3,4]. The complex dispersion spectra can be simulated by using Havriliak Negami expression. Further Cole-Cole plot helps us to check the quality of data measurement over large frequency range.

EXPERIMENTAL

HP-54750A digitizing oscilloscope along with HP-54754A differential TDR module has been used in the present experimental setup. The matching 50 Ohms SMA cell has been properly connected to the matching microwave transmission line. An incident step pulse of 200 mV magnitude and rise time about 40 ps is coupled to the cell. The reflected step pulse is observed from the open end of the SMA cell. The reflected pulses (step)without sample $R_1(t)$ in air and with sample $R_x(t)$, were digitized in to 1024 points in the memory of the oscilloscope and transferred to a PC for further analysis. Several polar liquids have been tested without disturbing the electrical connection of the line.

DATA ANALYSIS

The Fourier Transformation

The time domain data is converted in to frequency domain data using Fourier transform. While performing Fourier transform, one should be careful about the nature of the curve of which transform is to be obtained. Since nature of curves of p(t) and q(t) is different, different methods of Fourier transforms are to be used. The Fourier transform of p(t) (closed waveform) is obtained by the summation method [5,6], defined by the equation,

$$p(\omega) = T \sum_{n=0}^{N} \exp(-j\omega nT) p(nT)$$
(1)

The Fourier transformation using summation method has some limitations that for all the sampling intervals. The nature of pulse form must be known. Furthermore the transform p(t) is simply the area under the curve p(t) which has an initial peak followed by a decay to zero or a finite limiting value strictly to infinite time.

The pulse form of q(t) is not known exactly. The q(t) rises monotonically to a long time limit. Therefore summation method of Fourier transforms can not be used for q(t) curve. The Fourier transform of such type of open curves can be obtained by the Samulon method [7] defined by the expression as follows.

$$q(\omega) = \frac{T}{1 - \exp(-j\omega T)} \left[\sum_{n=0}^{N} (q(nT) - q(n-1)T) \exp(-j\omega nT) \right]$$
(2)

In equation (1) and (2) ω is angular frequency, T is the sampling interval or time difference between two adjacent points and N is number of points. In our experiment N is 1024 points and T depends on time window and number of points per waveform (N). For example if time window is 5 ns then T is 4.88 ps for 1024 points per waveform. Thus the time domain data is converted into frequency domain data in the selected frequency range of 10 MHz to 20 GHz [8,9].

Simulated spectra for water using Havriliak-Negami model.

Using the complex permittivity spectrum static dielectric constant (ε_0), dielectric constant at infinite frequency (ε_{∞}) and relaxation time (τ) can be calculated by using Havriliak-Negami expression [10,12].

$$\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_{o} - \varepsilon_{\infty}}{\left[1 + (j\omega\tau)^{1-\alpha}\right]^{\beta}}$$
(3)

Where α and β are fitting parameter of the relaxation process. For α =0 and β =1 above equation reduces to famous Debye's relaxation formula. The permittivity $\epsilon^{*}(\omega)$ is given by-

$$\varepsilon^{*}_{(\omega)} = \frac{c}{i\omega d} \frac{\ell(\mathbf{r}_{o} - \mathbf{r}_{x})}{\ell(\mathbf{r}_{o} + \mathbf{r}_{x})} z \cot z$$
(4)

where r_o is value of incident step pulse and $\ell()$ represents Laplace/Fourier transforms of reflected pulses with air and sample liquid. The relative complex reflection coefficient for a system with respect to air can be obtained as:

$$\frac{c}{i\omega d} \frac{p_{(\omega)}}{q_{(\omega)}} = \frac{z_1 \cot z_1 \varepsilon^* - z_2 \cot z_2 \varepsilon^*}{z_1 z_2 \cot z_1 \cot z_2 + \left(\frac{\omega d}{c}\right)^2 \varepsilon^* \varepsilon^*} \varepsilon^*}{z_1 z_2 \cot z_1 \varepsilon^* - z_2 \cot z_2 \varepsilon^*}$$

$$\rho^*_{(\omega)} = \frac{z_1 \cot z_1 \varepsilon^* - z_2 \cot z_2 \varepsilon^*}{z_1 z_2 \cot z_1 \cot z_2 + \left(\frac{\omega d}{c}\right)^2 \varepsilon^*} \varepsilon^*} \varepsilon^*$$
where $p_{(\omega)} = \ell[r_1(t) - r_x(t)]$
 $q_{(\omega)} = \ell[r_1(t) + r_x(t)]$
 $\varepsilon^*_1, \varepsilon^*_2$ are the permittivity for the air and a liquid under consideration
 $z_1 = \frac{\omega d}{c} \sqrt{\varepsilon^*}$
 $u = 2\pi f;$

d is effective pin length; c is velocity of light in air.

$\rho^{*}(\omega)$, can be obtained experimentally to get permittivity spectra.

The permittivity spectra is obtained as :

,

$$\varepsilon^*(\omega) = \frac{\mathbf{A}^* \boldsymbol{\rho}^*}{1 - \mathbf{B}^* \boldsymbol{\rho}^*} \tag{5}$$

where $A^{*}B^{*}$ are coefficients with the theoretical values as

$$A^{*}=B^{*}=\left(\frac{\omega d}{c}\right)^{2}$$

$$\varepsilon^{*}(\omega) = \frac{Z_{1} \cot Z_{1}\varepsilon^{*}_{2} - Z_{2} \cot Z_{2}\varepsilon^{*}_{1}}{Z_{1}Z_{2} \cot Z_{1} \cot Z_{2} + \left(\frac{\omega d}{c}\right)^{2}\varepsilon^{*}_{1}\varepsilon^{*}_{2}}$$
(6)

The values of A^{*},B^{*} can be determined experimentally by using two calibrating systems of known spectra. These coefficients are used to investigate unknown system.

But, when |z| is not negligible as compared to unity, zcotz $\neq 1$; especially when $z = \frac{\pi}{2}$; zcotz =

0, which corresponds to a sample one quarter wavelength long. The value of zcotz changes rapidly near this region which hinders the true values of permittivity. This quarter wave resonance effect is more dominant for liquids having high permittivity and high frequency. Therefore the bilinear calibration method may not provide correct results with the same kind of accuracy for all the liquid systems and numerical iterative methods such as Newton-Raphson or similar methods to find roots found valuable tools.



Fig.3. Typical dispersion spectra low permittivity such as chlorobenzene (ε =10) in extended giga-hertz region, showing resonant/anti-resonant /quarter-wave resonance.

 $2 \cdot \pi$

CONCLUSIONS:

Time Domain studies are effectively used to obtain static permittivity and relaxation values. The simulation spectra for water like polar liquids shows resonant and anti-resonant behavior at higher range in giga hertz frequency region. These resonant unwanted signals need for corrections, generally bilinear calibration methods or Newton Raphson numerical methods may found useful. By changing the values of α and β fitting parameters one can study relaxation processes in the polar molecules.

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A REVIEW ON NANOTECHNOLOGY AND ITS NOVEL APPLICATIONS IN DAIRY & FOOD INDUSTRY

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ABSTRACT :

Nano science and nanotechnology are the study & application of extremely small things which can be used across all the field of science. Wide range of applications of nanotechnology observed in the field of dairy & food industry for development in sensory attributes of productslike taste, color, flavor & texture etc. There is important role of nanotechnology in creating fortified or enriched products with improved digestibility and higher quality from the nutritional, sensory and functional standpoint. This review presents the potential application of nanomaterial in Delivery system, food fortification, novel food packaging, safety and security of dairy & food products. It also highlighted the risk assessment of nanomaterial and toxicological impact of it in dairy & food products along with some safety issues and regulatory concerns on Nano-processed food products.

KEYWORDS: Electrical permittivity, Havriliak-Negami model, Fourier Transform (FT), simulated spectra.

INTRODUCTION

The concept nanotechnology comprise a range of technologies, processes, materials and application that involve manipulation of substances at sizes in nano scale range(23). The concept 'Nanotechnology'was introduced to the world by Richard Feynman 1959. The term 'Nano' is a Greek word, which means dwarf and one nanometer(nm) is equal to one billionth of a meter i.e. 10^{-9} m(4). Recent developments in nanotechnology have revolutionized the food industry with its various applications in processing, safety and security, as well as its strides in enhancing nutraceutical value, extending shelf life and reducing packaging waste(18).Nanotechnology are a rapidly evolving area with potential current and future application for the dairy & food industry. By the study of Kaiser, H.(2009), it is claimed that the nanofood market is expected to surge from 2.6 billion USD to 7.0 billion USD in 2015 & to 20.4 billion USD in 2020. By 2020 Asia with more than 30% of world population will be the biggest market for nanofood (23).

Numerous application of nanotechnology in food systems and processing have been developed in many countries. Some of which include Nano-based food additives, Nano sensors, Nano capsules, Nano based smart delivery systems, Nanopackagings, detection of food borne pathogens, toxins and other contaminants which can cause serious treats to human health. The conventional methods for the detection of pathogen and their toxins are labor intensive and time consuming. Advances in nanotechnology have expedited the addressing of food safety issues in microbial contaminants and have improved toxin detection, shelf-life and packaging strategies.

NANOTECHNOLOGY IN FOOD ADDITIVES

There has been a significant interest in exploring the potential of nanotechnology in encapsulation and delivery of biologically active substances into targeted tissue. A number of novel nanotechnology derived procedures have been found to bear the potential providing solutions to dairy & food processing industries. Functional ingredients like drugs, vitamins, antimicrobials, antioxidants, flavoring, colorants and preservatives etc. and their required concentration of desired site can ready to utilize directly in their pure

form .They are often incorporated into some form of delivery system like Association colloids, Bio polymeric Nanoparticles, Nano-emulsion, Nanofiber, Nanotube, Nano capsules etc.(14).

1.Association colloids

Association colloids are smallest kinetic units (molecules or ions which do not have colloidal dimensions (15) and its particles made up of the dimensions of many association colloids ranges from 5-100nm and hence considered as nanoparticles(1).Surfactant micelles vesicles, reverse micelles and liquid crystals are some examples of association colloids, which have been used to encapsulate & deliver polar, nonpolar & amphiphilic functional ingredients dairy & food products(16).

2. Nano-emulsion

Nano emulsion is the nanoform of emulsion produced by high–pressure value homogenizers or micro fluidizers with a droplet diameter less than 100-500nm(17). The functional food components can be incorporated within such droplets, the interfacial region or the continuous phase. The small droplet size gives homoemulsion unique rheological and textural properties which renderthen transparent and pleasant to the touch(2). This facilitate the use of less fat without compromise in creaminess for calorie concern people. Such concept is utilized in nanosize emulsion based ice-cream with lower fat content by Nestle & Unilever(4). Other products of this type include low fat nanostructured mayomaise, spreads etc.

3.Biopolymeric Nanoparticles.

Food grade biopolymers could be used for the production of nanometer ranges particle. Such nanoparticles are mostly produced by proteins or polysaccharides through self association or aggregation or by inducing phase separation in mixed biopolymer systems.PLA is a commonbiodegradable nanoparticles which is often used to encapsulate & deliver the micronutrients like iron, vitamin, protein etc. in dairy & food products(1).

4.Nanotubes

Nanotubes are essentially buckyballs that have been on two sides with additional atom groups added in the characteristic hexagon shape to form a hallow carbon tube. The properties of nanotubes, thermal resistance, strong &flexible structure could be used in industrial food processing equipment. The partial hydrolysis of milk protein a- lactalbumin by a protease from *B.licheniformis* can be made to self-assemble into similar nanotubes under appropriate environmental conditions which can be used in food with important nutritional value(1). The desirable properties of nanotubes include, high ability to withstand pasteurization temperature, encapsulating agent (3), Being basically milk proteins it is easy to apply in other dairy products. Its hydrolysis increase digestibility & nutritive value of food(4).

5.Nano capsules

Casein micelle (CM) is found to play a role as natural Nano-capsular vehicle for nutraceuticals(R2). It act as a natural Nano capsules for calcium & phosphates. It covers these components & supply to neonates. Apart from these it has significant nutritive value.C.M. has high biological activity, good disparity retain their basic structural identity trough processing. A novel approach is using casein micelle for capsulation of hydrophobic molecules and for enrichment of high fat or low fat food products. They have no influence on a sensory attributes of final product.Nano capsulation is helpful to increase absorption and control bioavailability of vitamin, phytochemicals, nutrients & minerals(4).

6. Nano fibers

It is not from food grade biopolymer, its use is limited in food industry(4). Nano fibers are manufactured by utilizing electro spinning technology capable of producing thin, solid, polymer strand from solution by applying a strong electric field to a spinneret with a small capillary orifice(1). These Nano fibers of diameter from 10 to 1000 nm, which makes them ideal for serving as a platform for bacterial cultures as well as structural matrix for artificial foods.

Nanotechnology in food fortification 1. Nanoceuticals

These are the Nano version of neutraceuticals which are manufactured by nanoparticles using nanotechnology (7). This substances having nutritional quality, exhibit health promoting benefits same like nutraceutical. These are the compounds like biological proteins which can used in functional foods to imparts health benefits to consumer in addition to the nutrition that the food itself offers. (5,7). The concept of 'nanoceuticals' is gaining popularity and commercial dairy & food supplements containing nanoparticles are available (8,9) like carotenoids minerals, omega-3 fatty acids, certain probiotic bacterial species, lycopene& vit.D₂. (10,11), chitosan, isoflavone, mistletoe, C.L.A, *innota obliquus* and peanut sprout extract also used. Marine fish oil and peanut sprout extract are the two substances that have been used to develop nanoceuticals yogurt(12). While Ivanov & Rashevskaya(2011) developed functional butter with Nano sized herbal supplements like polysaccharides, pectin, insulin, cryopowders of red beets, carrots, black currents buds with surface active properties(2). One another examples of nanoceutical is carotenoids nanoparticles which can added in fruit drinks to improved bioavailability(4).

2. Nano encapsulation

Currently it is second largest area of application of nanotech in dairy & food sector(6). Nano encapsulation is the incorporated of ingredients in small vesicles or walled materials with Nano (submicron)sizes (2). These nanomaterials offer several advantages such as delivery vehicle for lipid soluble ingredients, protection from degradation during processing or in gastrointestinal tract, controlled site specific release, compatibility with other food constituents, grater residence time & greater absorption(8). The protection of bioactive compounds, like vitamin, antioxidants, proteins & lipids & carbohydrates may be achieved by using encapsulation for production of functional foods with enhanced functionality and stability (2). A good example are liposome encapsulated enzymes in dairy products. Flavor enzyme in cocktail etc. Neutral bacterial protease, acid fungal protease & lipase could be incorporated into cheese milk for a balanced ripening(12). Nano encapsulation can make significant savings for formulators, as it can be reduce the amount of active ingredients needed(2).

Nanotechnology in Food Packaging

Food packaging is considered to be one of the earliest commercial application of nanotechnology in the food sector (2). The packaging of food is one of the most critical step in terms of safety. In recent years it has been great interest of using these nanoparticles in antimicrobial food packaging (20). Recent trends in food packaging are encouraging the use of biodegradable polymers reinforced with nanofillers, which are eco-friendly. The significant purpose of Nano-packaging is to set longer shelf life of food by improving the barrier properties packaging materials. Nano-packaging can also be designed to release antimicrobials antioxidants, enzymes, flavors and nutraceuticals etc. Antimicrobial properties can be developed by impregnating natural antimicrobial agents to Nano composite matrix. For example silver with extremely small sized of nanoparticles increases the antimicrobial efficiency. Packaging material incorporating silver nanoparticles are reported to be commercially available. Nanosilver, nanomagnesium oxide, nanocopper oxide, nano titanium dioxide and carbon nanotubes are also predicted for future use in antimicrobial food packaging. The application of nanoparticles in nanocomposite and nanolaminates have been actively used in food packaging to provide a barrier from extreme thermal & mechanical shock extending food shelf-life (20).

1.Nanocoating

Recently, nanotechnology has enabled the development of nanoscale edible coating as thin as 5nm wide which are invisible to the human eye.Edible coating and films are currently used on a wide variety of foods including fruits, vegetables, meats, chocolates, cheese, candies, bakery products and French fries(19).An edible antibacterial nanocoating was developed in the United States which can be applied directly to bakery goods.

2.Nanolaminates

Nanotechnology offer food scientists with a number of ways to create novel laminate films suitable for use in the food & dairy industry. A nano laminate consists of two or more layers of materials with nanometer dimensions that are physically or chemically bonded to each other. Weiss et.al (2006) reported that nano laminates have some advantages for the preparation of edible coating and films over conventional technologies and may thus have a number of important application within the food & dairy industry. Different absorbing substances likenatural polyelectrolytes (Protein polysaccharides) and colloidal particles(micelles, vesicles, droplets)could be used to create the different layers. It would be possible to incorporate active functional agents such as antimicrobials, anti-browningagents, antioxidants, enzymes, flavours and colours into the film. These functional agents would increase the shelf life and quality of foods(2). Use of inert nanoscale fillers such as clay and silicate nanoplatelets silica(SiO₂), nanoparticles, chitin or chitosan gives better thermal properties (20).

3. Biodegradable packaging materials

Biodegradable polymers include polymers that are directly extracted or removed from biomass such as polysaccharides, proteins, polypeptides and polynucleotides. But these natural polymer have the poor barrier properties and weak mechanical properties. The application of nanocomposites promises to expand the use of biodegradable as well as edible films. The application of nanotechnology to these polymers may open new possibilities for improving not only the properties but also the cost price efficiency. So far, the most studied biodegradable nano composites suitable for packaging applications are starch & derivatives, polylactide, polyhydroxyl butyrate and aliphatic polyesters as poly carpolactone. Biodegradable starch based polymers have poor moisture barrier properties due to their hydrophilic nature and inferior mechanical properties compared to plastic film. The incorporation of clay nanoparticles in starch polymers has been reported to improve moisture barrier & mechanical properties(2).

Nanotechnology in food safety

Globally, food safety is a growing public health concern. The primary goal of food safety is to ensure that food will not cause any harm to the consumer during preparation and consumption. Food must be protected from any types of physical, chemical and biological contamination during processing, handling and distribution. Nanotechnology can assist in the safety of dairy & food products. In this view various types of biosensors have been developed to detect food borne pathogen, food spoiling materials(18), gases and toxins, gases and toxins(3).

Nano sensor

Nano sensor or Nano biosensors are used for the detection of pathogen in processing plants or in food material. Nanosensor is a device consisting of an electronic data processing parts & a sensing part which can translate a signal such as light or presence of organic substance or gas into an electronic signal. These sensors can be integrated into food processing equipment or refrigerator or into the food itself and will help to improve food safety by enabling faster quality control & testing up to the consumer level. Biosensor based on carbon nanotubes also gained much attention due to their rapid detection , simplicity and cost effectiveness and have also been successfully applied for the detection of microorganisms , toxins and other degraded products in food & beverages (20). To ensure food safety, packaging materials incorporated with nano structured biosensors or DNA-based biochips are being developed(2). The Nano sensor worksas an indicator that respond to change in environmental conditions such as humidity or temperature in storage rooms, microbial contamination or product degradation(20). The embedded sensors a packaging film will be able to detect pesticides, allergens toxins, food borne pathogens and food- spoilage organisms & trigger a color change to alert the consumer about these facts. The quartz crystal microbalance(QCM) based Electric Nose & Electric Tongue widely used in food & dairy industry. Nanomaterial's for the construction of biosensors offers the high level of sensitivity and other novel attributes.

- **I.Electric Nose:**Electric nose is a device which is applied for identifying different types of odors (3), the interaction between various odorants & chemicals can be detected with the help of this (20).Gas sensors are the main components in an Enose and composed of nanoparticles.E.g.Zinc oxide nanowires.
- **II.Electric Tongue:** It consist of an array of nano sensors which are extremely sensitive to gases released by food as it spoils, causing a sensor strip to change color which gives a clear visible signal whether food is fresh or not(2).Kodak is using nanotechnology to develop antimicrobial packaging as well as active packaging that absorb oxygen to keep food fresh that will be commercially available in near future.The Netherlands researcher are developing intelligent packaging that will release a preservatives if the food within begins to spoil. This 'release on command' preservative packaging is operated by means of a bio switch development through nanotechnology (2).

Nanomaterials, including metal nanoparticles carbon nanotubes, quantum dots and other active nanomaterials can be used to develop biosensors for the quantification of microbes& other tests for food safety application (18).

1.Nanoparticles for the detection of food borne pathogens.

Recent years various new nanoparticle- based detection platforms have been developed.Surface enhanced. Raman Scattering (SERS) is employed as a nanobiosensing tool to rapidly and accurately detect microbial pathogens. Lateral–flow immune test strips with palladium nanoparticles allowed for the specific binding and visualized detection of specific bacteria.Detection of single *E.coli* bacterial cell using a reduced grapheme nanoparticle based, field effect transistor device is takes place.Research graph developed on electrochemical sensing platform based on graphene oxide gold nanoparticles to detect *cronobacter sakazakii* which is bacterium that is hazardous to infants in infant formula powders with a detection limit of $2.0X10^1$ cfu/ml(20).

2.Nanoparticles for protection from allergens

Nanotechnology has been employed as basic tool to control and manage food allergens. Zhang et.al reported a magnetic nanoparticle assisted optamer based fluorescence assay to detect allergens in food material. Brotons-conta et.al evaluated the positive effect of poly(anhydride)nanoparticles as an oval vehicles for immune therapy against experimental peanut allergies. Several other studies demonstrated the promising application of nanotechnologies in vaccinology & allergen immunotherapy (18)

3.Nanoparticles for preventing heavy metal reduction

Cationic surfactant coated silica modified magnetic nanoparticles act as adsorbents for the micro extraction and have ability to determine trace amount of Cu,Ni, Co, Cd, Pb, and Mn from food samples.Many nanomaterial have tremendous potential for the remediation of contaminates and inexpensive substrate for the recovery of heavy metals from various sources.Animated magnetic iron oxide nanoparticles especially Cu²⁺, Ni²⁺, Pb²⁺ and Zn⁺ act as adsorbent to remove aqueous heavy metal ions.

4.Nanoparticles for the inhibition of biofilm formation

Biofilms are tightly packed bunch of bacterial cells that adhere to many substrate and produce a polymeric extracellular matrix that is extremely difficult to penetrate. The biofilm formation begins with the attachment of free floating microorganisms to the surface by employing van der Waals forces that create problems such as biocorrosion, biofauling and accumulation in the food processing industries. Glycerol monolaurate(GML) has been shown to inhibit the biofilm formation of three different strains of *s.aureus* and of MRSA. The use of antimicrobials throughout the nano-fibers of filter membranes is employed to prevent biofilm formation. Nanosilver particles at low concentration (0.2 ppm) enhanced bacterial metabolism Nickel oxide nanoparticles(NiO NPS) have been proposed as prospective antibacterial and anti-tumor agents. The bio applicability of zinc oxide nanoparticles for hindering fungal biofilm like *p.chrysogenum* and *aspergillus niger* etc. Two types of super magnetic iron oxide (IONs) like naked ION and IONs coated with 3-amino propyltriehoxy silane against β . *subtilis* in terms of their ability to inhibit its biofilm formation, bacterial

growth and cell viability. In this way nanoparticles could be applied in several industries to combat the growth of bacterial biofilm(18).

Nanotechnology in food Processing

The use of nanomaterials provide superior quality in food matrices(3) like Nanocapsules for improving bioavailability of neutraceuticals in standard ingredients such as cooking oils.Nanocapsulated flavor enhancers, Nanotubes and nanoparticles as gelation & viscosifying agents, Nanocapsules infusions of plant-based steroids as a replacement for meat cholesterols(6). In Nano frying new Nano ceramic products has been marketed by US based oil fresh corporation , in which reduced amount of oil is use in restaurants & fast food shops by half because its large surface area.Nano-silicon dioxide particles effectively hydrolyzed olive oil with modified stability, adaptability & reusability(3).Kraft foods & Nanoteck consortium have plans to incorporate the electronic tongue (which is chemical change biosensor) into novel food to release accurately controlled amount of the suitable molecules for the customized tailor foods.NF separating materials of less than 0.001 μ in size and rejects divalent & multivalent ions.It has application in desalination, milk, and whey and juice filtration.Demineralization, color removal, conc. Of products, waste water treatment and water purification (21).

Safety Issues with reference of nanomaterials.

Besides a lot of advantages of nanotechnology to the food industry, safety issues associated with the nanomaterialwhich cannot be neglected. For the examples, silica nanoparticles which are used as anticaking agents can be cytotoxic in human lung cells when subjected to exposure. Migration of silver and copper from nano composites & observed that the percentage of nanofiller in the nanocomposites. Determination of solubility of nanoparticles & their biological fate & effects on the health are very important. Risk assessment of nanoparticles and nanostructures showed that the potential routes of human exposure to nanoparticles are skin, lungs and gastrointestinal tract. Now a days, there are no special regulations for using nanotechnology in food. British government agreed to this suggestion that nanoparticles ingredients be subjected to a full safety assessment before using them in food products. FAO and WHO have recently started preparations to hold an expert consultation in 2008 that identify the application of nanotechnology in the food sector at present or in the future and the potential food safety issues as well as exploring areas for future research and international guidance. Regulatory authorities ensure product quality, health & safety and environmental regulations(21).

CONCLUSION

Nanotechnology is a very promising area in food & Dairy industry. It is expected to offer technological advantages in production, processing, storage, transportation, traceability and safety of food. Nanomaterials offer excellent vehicle systems to deliver bioactive compound to the target tissues. Potential reduction in the amount of fat, Salt and other additives, enhancements in the absorption, bioavailability of nutrients and supplements can possible. Nanomaterials will serve as moisture, lipid & gas barriers as well as carriers of agents like color, flavor, antioxidants, nutrients and antimicrobials and could increase the shelf life of manufactured foods, even after the packaging is opened. Commercial application of nanotechnology derived products can be done only after the safety issues are resolved so further research studies are required to investigate the hazards of nanomaterials. There is also an immediate need for regulation of nanomaterials before their incorporation into food & dairy Processing including packaging. Nanotechnology enables to change the existing food systems by ensuring products safety, creating a healthy food culture and giving the nutritional quality to food.

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LaPO₄:Tb³⁺ NANOPHOSPHOR: LOW TEMPERATURE SOLUTION COMBUSTION ROUTE AND PHOTOLUMINESCENCE PROPERTIES

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ABSTRACT:

Terbium III doped LaPO₄ has been prepared using low temperature solution combustion route with metal nitrates as precursors and urea as a fuel. The X-ray diffraction (XRD) revealed the single phase monoclinic structure of LaPO₄. The crystallite size by Scherrer formula is found to be 42 nm. The nanorod structure was confirmed by transmission electron microscopy (TEM). The phosphor exhibited bright green emission upon excitation of 278 nm ultra violet (UV) light. The characteristics photoluminescence peaks between 425 nm to 650 nm are attributed to ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 6, 5, 4, 3) transitions of Tb³⁺ ions respectively. Thus the present phosphor can be used as a green emitting phosphor in tricolor lamps and display devices.

KEYWORDS: Nanophosphor, Lanthanum Orthophosphate; green emission; Nanorods.

1. INTRODUCTION

Particles at nanoscale have been intensively studied over the last two decades because they reveal interesting and useful properties like luminescence, biocompatibility, targeted drug delivery and other optoelectronic properties [1-6]. The luminescent nanomaterials form a group of special interest wherein inorganic host materials like aluminate, borate, phosphate, silicate and vanadate are doped with lanthanides [7, 8]. They have high temperature resistance and they can form a stable colloidal solution which is the desired feature for biocompatible materials. They have less possibility of degradation over a long period of time [9].

Tb³⁺ doped inorganic phosphors have been widely used as green color emitting phosphors because of their intense ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ emission in green spectral region [10-13]. LaPO₄:Ln³⁺ have attracted lots of attraction due to their unique photoluminescence properties [14, 15] which is prerequisite for lighting and display applications. LaPO₄:Tb³⁺ has been synthesized by various methods like co-precipitation [16], hydrothermal [17-19], Microwave assisted method [20]. In this work, solution combustion method is used for synthesizing LaPO₄:Tb³⁺ nanophosphor, which is a promising material for optical devices like tricolor lamps, displays like plasma panel displays, white light emitting diodes (WLED) etc. The morphology and photoluminescence properties of the prepared samples are studied.

2. EXPERIMENTAL

Solution combustion synthesis is a self-propagating, effective and low cost method for the production of very fine agglomerated multi component oxide ceramic powders without intermediate decomposition and/or calcinations steps [21-24]. It has been reported in our previous work that nanophosphors or metal-oxide nanoparticles can be produced by combustion synthesis technique [7, 8, 15]. The advantages of combustion synthesis method such as inexpensive sources, easy to set-up equipment and a facile process to produce the nanoscale materials led to use this method for reported work.

The aqueous solutions of corresponding metal nitrates (oxidizers) and the organic fuel urea (reducer), predetermined in stoichiometric ratio, were heated slowly in a preheated furnace maintained at $500 \pm 10^{\circ}$ C to evaporate water until rapid combustion occurs. The mixture ignited and a self-sustaining fast combustion

reaction produced fine crystalline oxide powders. The formation of nanoparticles with no subsequent particle growth was the result of the explosive nature of the combustion reaction. Ultimately, by adjusting the fuel-to-oxidizer ratio, the reaction temperature is maintained and thus, the particle size is controlled [25]. In this work the nanophosphor LaPO₄:Tb³⁺ is synthesized as per the following chemical reaction

(1-x) La $(NO_3)_3.6H_2O + NH_4H_2PO_4 + 5(NH_2)_2CO + xTb (NO_3)_3.5H_2O \rightarrow (1-x)$ LaPO₄:xTb³⁺ (x= 0.01, 0.03, 0.05).

The prepared samples were subjected to the X-Ray Diffraction (XRD) analysis on Rigaku Miniflex X-ray Diffractometer operating at 40 kV, 30 mA with scan speed of 2.000 deg./min and with Cu K α radiation ($\lambda = 1.5405$ Å). The photoluminescence properties of the phosphor (excitation and emission) were measured using Hitachi F-7000 fluorescence spectrophotometer at room temperature. The morphology and particle size of the sample was determined for Transmission Electron Microscopy (TEM) on Philips CM 200 TEM machine operated at a voltage of 200 kV and having resolution of 0.23nm.

3. RESULTS AND DISCUSSION

3.1 Structural and Morphological properties

3.1.1 X-Ray Diffraction analysis

The XRD patterns are well matched with standard International Centre for Diffraction Data (ICDD) file no. 01-084-0600 of LaPO₄ as shown in Figure 1(Inset).



Figure 1: X-Ray Diffraction pattern for LaPO₄[Inset-ICDD file of LaPO₄]

LaPO₄ has a single pure phase with a monoclinic monazite crystal structure, whose lattice constants are a = 6.84 A°, b = 7.07 A° and c = 6.45 A°, and inter planar angles are $\alpha = \gamma = 90^{\circ}$ and $\beta = 103.85^{\circ}$. As the Tb³⁺ ionic radius (r=1.12Å, CN=9) is closest to that of La³⁺ (r=1.17Å, CN=6), it is believed that the La³⁺ sites are replaced by Tb³⁺ in this lattice. The crystallite size calculated by Scherrer formula was found to be nearly equal to 42 nm [26-28].

3.1.2 TEM analysis

TEM micrograph revealed the shape of the particles as nanorods [Figure 2(a) (b) (c)] with average width in the range 30-50 nm. The Selected Area Electron Diffraction (SAED) pattern [Figure 2(d)] showed the concentric rings of the crystalline planes corresponding to diffraction peaks shown in XRD pattern.



Figure 2: (a) (b) (c) TEM images and (d) SAED pattern of LaPO₄: Tb³⁺

3.2 Photoluminescence properties

The photoluminescence excitation (PLE) spectra [Figure 3 (a)] showed a broad band peaking at 220 nm and 278 nm that is attributed to the charge-transfer band (CTB) which is the result of transferring the electrons in the neighboring anions to a 4*f* orbital, leading to $f \rightarrow f$ emissions [29]. The excitation lines between 300 nm – 400 nm correspond to the direct excitation from the terbium ground state to the higher excited states of the terbium f-electrons. This is attributed to the fact that the 4f electrons in RE³⁺ ions are effectively shielded from surrounding crystal fields because of the filled outer shells of $5s^2$ and $5p^6$ electrons. Two types of electronic states with different characteristics are shown by the rare earth ions. They are the 4fn-5d¹ states and the charge transfer states. In the first case one of the 4*f* electrons is transferred to a 5d orbital and in second case electrons in the neighboring anions are transferred to a 4*f* orbital. Both cases show strong optical absorption [30, 31].



Figure 3: Photoluminescence (a) excitation (PLE), (b) emission (PL) spectra, (c) color chromaticity graph and (d) Spectral power distribution graph of LaPO₄: Tb³⁺ (5 mol %)

The emission spectra [Figure 3(b)] consist of the typical sharp line emissions ranging from 425 to 650 nm originated from the ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 6, 5, 4, 3) transitions of Tb³⁺ ions. The intensity of 543 nm peak which is attributed to ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ is remarkably high. The optimum concentration was found to be 5 mol % of Tb³⁺ions. The transitions attributed to ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ corresponding to blue light emission (488 nm) has less intensity than the transition attributed to ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (543 nm). The other two transitions corresponding to ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$ (622 nm) have weak emission. The color chromaticity values calculated using Radiant imaging color calculator 2.0 software [32] for reported phosphor were found to be (0.2577, 0.7276) that are close to Commission Internationale de'Eclairage (CIE) color coordinates of green color [Figure 3(c)]. This indicates the feasibility of the reported phosphor as a green light emitting phosphor for 278 nm excited tricolor lamps and display devices. Figure 3(d) showed spectral power distribution graph of reported phosphor can be excited at 395 nm, the spectral distribution graph is plotted by considering narrow emission peak of Full Width at Half Maximum (FWHM) 15 nm at 543 nm. It is slightly shifted from the ideal peak of 556 nm green color emitting LED.

4. CONCLUSIONS

LaPO₄:Tb³⁺ nanophosphor powder was successfully prepared by low temperature facile combustion synthesis method. The prepared LaPO₄ powder crystallizes in a single-phase monoclinic structure with a rod shape particle approximately 30 nm - 50 nm in width. The maximum intensity was found for 5 mol % of Tb³⁺. The photoluminescence emission spectrum shows bright green color showing maximum peak at 543 nm which is characteristics transition ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ of Tb³⁺. The color chromaticity co-ordinates for this phosphor are calculated as (0.2577, 0.7276). Thus, reported phosphor can be used as a green color emitting phosphor in optical devices like 254 nm excited tricolor lamps and 395 nm excited white light emitting diodes (WLED) lamps.

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DIELECTRIC RELAXATION STUDY OF N, N-DIMETHYLACETAMIDE in 1, 4-DIOXANE SOLVENT USING TIME DOMAIN REFLECTOMETRY TECHNIQUE UP TO 30GHz

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ABSTRACT :

Complex dielectric permittivity measurements in the frequency range 10MHz-30GHz has been carried out for N, N-Dimethylacetamide (DMA) – 1, 4 -dioxane (Dx) mixtures over the entire concentration range using a time domain reflectometry (TDR) method at room temperatures. The hydrogen bonded model has been applied to understand the dielectric behavior of amides solution in terms of molecular interaction. Luzar proposed a more realistic hydrogen bonding model. The Luzar theory is applied to compute the Kirkwood correlation factors for the mixtures. It adequately reproduces the experimental value of static dielectric constants.

KEYWORDS : Dielectric permittivity; Relaxation time; Time domain reflectometry (TDR); Dielectric Relaxation.

1. INTRODUCTION

Amides are the simplest molecules having a peptide linkage. Due to high polarity, strong solvating power and large liquid state range, amides are the important class of organic solvents. Amides posses the donor-acceptor –CO-NH- peptide bond and most of them form the self association through H-bond[1-3].

Dielectric relaxation of liquid mixtures gives information about molecular interactions. Dielectric relaxation phenomena of binary polar mixture of amides dissolved in non polar solvent are of special interest to research workers [4-8] since long. The dielectric studies on binary mixtures are useful to investigate molecular and intermolecular interactions, it also yield the Kirkwood correlation factor, which is strongly correlated with the solute–solvent interaction [9]. Dielectric relaxation spectroscopy, for instance, is a powerful tool for examining the underlying physics of solvent systems and for exploring the molecular dynamics of liquids, which is characterized by inter- and intramolecular structures that vary rapidly with time.

The main trusts of these studies were to understand the structure of N, N-Dimethylacetamide (DMA) in terms of hydrogen bonding and modification of hydrogen bonding due to the presence of 1, 4-dioxane (Dx) molecule. The aim of present study is to investigate the dielectric properties of DMA - Dx mixtures of various concentrations at 25°C employing Time Domain Reflectometry (TDR) in the frequency range of 10 MHz to 30 GHz.

2. EXPERIMENTAL

2.1 Materials:

N, N-Dimethylacetamide was obtained commercially of s d fine-chem limited company (AR Grade 99%). The different volume percentage of amides and 1, 4-dioxane was prepared at 16 concentrations over the composition range at room temperature.

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2.2 Measurements:

The dielectric spectra were obtained by the time domain reflectometry (TDR) technique [10, 11]. The Tektronix model no. DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 has been used for the time domain reflectometer (TDR). A repetitive fast rising voltage pulse with 18ps incident pulse rise time and 20ps reflected pulse rise time was fed through coaxial line system of impedance 50 ohm. Sampling oscilloscope monitors changes in step pulse after reflection from the end of line. Reflected pulse without sample R1(t) and with sample Rx(t) were recorded in time window of 2ns and digitized in 2000 points. The Fourier transformation of the pulses and data analysis were done earlier to determine complex permittivity spectra $\varepsilon^*(\omega)$ using non linear least squares fit method [11, 12].

3. RESULTS AND DISCUSSION

Figure 1 (a, b) shows frequency dependent complex permittivity spectra for DMA – 1, 4-dioxane mixtures at 25° C. The complex permittivity spectra measured using TDR is fitted by the non-linear least squares fit method to the Havriliak - Negami expression [13, 14]

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{\left[1 + (j\omega\tau)^{1-\alpha}\right]^{\beta}}$$
(2)

where ε_0 is the static dielectric constant, ε_{∞} is the permittivity at high frequency, τ is relaxation time and $\alpha \& \beta$ is the Cole-Cole and Davidson-Cole distribution parameters respectively. Equation (2) includes the Debye ($\alpha = 0, \beta = 1$) [15] Cole-Cole ($0 \le \alpha \le 1$ and $\beta = 1$)[16] and Davidson – Cole ($\alpha = 0$ and $0 \le \beta \le 1$) [17]. The static dielectric constant and relaxation time for DMA + 1, 4-dioxane mixture decreases with concentration of 1, 4-dioxane in DMA. The experimental values of static dielectric constant and relaxation time are quit agree with the literature. The non linear behaviour of the static dielectric constant against X_{DX} of the investigated binary mixtures suggests the formation of hydrogen bond complexes between DMA and 1, 4dioxane molecule.

3.1. Kirkwood correlation factor

The dipolar correlation factor, introduced originally by Kirkwood has been used in the literature for extracting information related to the internal structure of fluids whose molecules experience strong directional forces. The interpretation of correlation factor in mixtures is less straight forward, especially in systems where the solvent and solute molecules can H-bond with each other, since it contains combined information related to dipolar correlations between various types of molecules presents in the system. Luzar [18] proposed a simplified model to calculate hydrogen bond in systems using the Kirkwood Frohlich equation [19]:

$$\frac{(\varepsilon_{0i} - \varepsilon_{\infty i})(2\varepsilon_{0i} + \varepsilon_{\infty i})}{9\varepsilon_{0i}} = \frac{4\pi}{9kT} \sum_{i=1}^{2} g_i \rho_i \mu_i^2 \qquad (3)$$

where *i*=1 and 2 represent DMA and DX, respectively. Here μ_i is the corresponding dipole moment in the gas phase, ρ_i is the density, k is Boltzmann constant, T is the temperature and g_i is the Kirkwood correlation factor for the *i*th liquid component. The interpretation of dielectric phenomena in terms of Kirkwood correlation factor is very difficult for a mixture of associated compounds. It is impossible to separate the average correlation factor g_1 and g_2 from single value of the static dielectric constant without any assumptions. Luzar suggested theoretical model based on mean field approximation for hydrogen bonded mixture [18].The correlation factor g_1 and g_2 are calculated by following equations:

$$g_1 = 1 + Z_{11} \cos \varphi_{11} + Z_{12} \cos \varphi_{12}(\mu_2/\mu_1)$$
(4)

$$g_2 = 1 + Z_{21} \cos \varphi_{21} \left(\mu_1 / \mu_2 \right) \tag{5}$$

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where $Z_{11} = 2\langle n^{11}_{HB} \rangle$, $Z_{12} = \langle n^{12}_{HB} \rangle$ and $Z_{21} = \langle n^{12}_{HB} \rangle X_{DX} / (1-X_{DX})$ are the average number of hydrogen bond with DMA - DMA, DMA -DX pairs respectively. φ_{11} and φ_{21} are the average angles between neighboring dipoles of DMA and 1, 4-dioxane molecule. The values of g_1 and g_2 for DMA -DX mixtures are computed and shown in Figure 2. The value of g_1 and g_2 is depends on the concentration of DX in DMA-DX mixtures. Since 'g' is measure of the molecular association between a reference molecule and its nearest neighbors, the departure of 'g' from unity can be indicative of molecular association.

The average number of hydrogen bonds $\langle n^{11}_{HB} \rangle$, $\langle n^{12}_{HB} \rangle$ and $\langle n^{21}_{HB} \rangle$ per DX molecule for 1*i* pairs (*i* =1, 2) has been determined using following relation [18]:

$$\left\langle n_{\text{HB}}^{\text{li}} \right\rangle = n_{1i} \omega^{\text{li}} / n_1 \tag{6}$$

where $\omega^{1i} = 1/[1 + \alpha^{1i} \exp(\beta^{E1i})]$ is the probability of bond formation between DMA and DX. n_1 is the number density of DMA molecules, $\beta = 1/kT$, and α^{1i} are the statistical volume ratios of the two sub volumes of the phase space related to the non hydrogen-bonded and hydrogen bonded pairs. These hydrogen bonded pairs have only two energy levels, E^{11} and E^{12} , for 11 and 12 pair formed bonds, respectively. The values of $\langle n^{11}_{HB} \rangle$ and $\langle n^{12}_{HB} \rangle$ depend on the number densities of the hydrogen-bonded pairs between DMA - DMA and DMA -DX molecules respectively. These can be calculated, during which DMA – DMA (11 pairs) and DMA – DX (12 pairs) are formed [18] and shown in Figure 3.

The concentration dependence of the dielectric permittivity is calculated using equations 3-6 and is compared with experimental data. The model gives a good qualitative account of the dielectric permittivity of the DMA- 1, 4-dioxane mixtures. The theoretical values of static dielectric constants determined from hydrogen bonding model are found in good agreement with the experimental values obtained from TDR technique as shown in Figure 4.

4. CONCLUSIONS

The concentration dependence of the dielectric relaxation parameters of DMA-DX mixtures was investigated using time domain reflectometry technique in the frequency range 10MHz to 30MHz. The experimental dielectric relaxation data contains valuable information regarding solute-solvent interactions in the mixture. The static dielectric constant for the mixtures can be explained using hydrogen bonded model by assuming the formation of hydrogen bond between DMA-DMA and DMA-DX pairs. The number of hydrogen bonds of DMA – DX molecules increases with increasing DX concentration.



Figure 1. Frequency dependent dielectric permittivity (ϵ') and loss (ϵ'') for DMA - Dx mixtures at various concentrations at 25^oC.



Figure 2. Plots of the correlation factor $(g_1 \& g_2)$ Vs mole fraction of 1, 4-dioxane (X_{DX}) at 25^oC.



Figure 3. Plots of the average number of hydrogen bonds between DMA - DMA (n_{11} pair) and DMA - DX (n_{12} pair) Vs mole fraction of 1, 4-dioxane (X_{DX}) at 25^oC.



Figure 5. Theoretical and experimental static dielectric constant for DMA-DX mixtures as a function of mole fraction of 1, 4-dioxane (X_{DX}).

■ – experimental at 25[°]C ▲ – experimental at 30[°]C (Ref.8) ○ – theoretical.

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STUDIES ON STRUCTURAL PROPERTIES OF ZINC OXIDE THIN FILM DEPOSITED BY PULSED LASER DEPOSITION TECHNIQUE

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ABSTRACT:

Zinc oxide thin films (ZnO) have been deposited by Pulsed Laser Deposition (PLD) technique. The ZnO films are polycrystalline in nature and its phase is mainly oriented along (002) orientations. This belongs to the hexagonal phase. Other structural studies, like Scanning Electron Microscopy (SEM) reveals uniform deposition throughout the surface. The Atomic Force Microscopy (AFM) image are also in well agreement with other structural studies.

KEYWORDS : Zinc Oxide thin film (ZnO), Pulsed Laser Deposition (PLD)Technique, Structural Properties.

INTRODUCTION:

Zinc oxide (ZnO) is one of the most important semiconductor amongst various II-VI group semiconductor due to its large band gap (Eg = 3.2 eV), strong binding energy of 60 meV, higher transparency and low electron affinity. Due to these properties, ZnO is attracting the attention of the scientific community. Furthermore, amongst various semiconducting materials, ZnO thin film is attracting the attention of the scientific community due to their wide range of applications such as light emitting diodes [1], thin film transistors[2], gas sensors[3] etc due to its wide band gap (3.2-3.4 eV), large Exciton binding energy (~ 60 meV).

There are a number of methods have been developed to fabricate various types nanostructured ZnO thin films like wise vapour-liquid-solid epitaxial (VLS) method [4], chemical vapour deposition [5] etc. For this study purpose, we have fabricate the ZnO thin films by pulsed laser deposition (PLD) technique. Because, PLD is a versatile technique with a high instantaneous deposition rate, which allows for the formation of thin films with controllable thickness as well as optical and electrical properties [6-7].

EXPERIMENTAL DETAILS:

For this study purpose, pure ZnO thin films were deposited onto the glass substrate by pulsed laser deposition. Prior to the deposition, substrate was ultrasonically cleaned with acetone and methanol. Pure ZnO were used as the target materials. KrF eximer laser (λ =248nm) with the repetition rate of 10 Hz and laser pulse energy of 220 mJ was focused on highly compressed targets. During deposition, oxygen partial pressure was maintained at 1 mTorr and the substrate temperature was maintained at 450°C.A zinc target was laser irradiated in a vacuum chamber under an oxygen flow with a dynamic pressure of 20 Pa. Prior to deposition, the chamber was evacuated to a base pressure of 10-5 mbar.

The thickness of thin films as calculated by Stylus profilometer came out to be ~ 125 nm. X-ray diffraction (XRD) measurements were performed by Bruker D8 Advance diffract meter using Cu Ka radiation. The morphological images of films were obtained by using scanning electron microscopy (SEM, JEOL), Atomic Force Microscopy (AFM), done by using nanoscope III a provided by vecco digital instruments.

RESULT AND DISCUSSION: X-ray diffraction (XRD) studies:



Figure 1

Figure.1 represents the XRD pattern of the as grown ZnO thin films grown by the PLD technique. The crystal structure of the ZnO thin film was found to be hexagonal (JCPDS card no- 80-0075). From the spectrum it was clear that the thin films of ZnO are highly oriented along (200) at 2θ =31.7540 for as grown thin films. Other peaks were observed along (002), (101), (110) etc for the as grown and annealed thin films. The grain size was calculated using the Scherrer's formula,

$$D = \frac{K\lambda}{\beta Cos\theta}$$

Where,

'D' is crystallite size, ' λ ' is the X-ray wavelength used, ' β ' is the angular line width of half maximum intensity, ' θ ' is Bragg's diffraction angle and 'K' is some constant, which is 0.9. From this calculation the grain size was found to be 42 nm.

Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM):



Figure 2

Figure.2.a shows the Scanning Electron Microscope (SEM) image of the ZnO thin film grown by Pulsed Laser deposition technique. This figure represents the uniform deposition throughout the sample. The surface morphology was again confirmed by the AFM image (Figure 2.b) of the PLD deposited ZnO thin

films. This image exhibits the compact, void free granular morphology throughout the substrate which is in well agreement with the SEM image of the above mentioned sample.

CONCLUSION:

From this study, the nanostructured good quality ZnO thin film was fabricated by Pulsed laser Deposition technique which was employed for the formation of thin ZnO films and coverage of their surface with uniform ZnO nanoparticles in the form of thin film was confirmed from the surface morphological studies. The structural study (XRD) reveals that the ZnO films are polycrystalline, crystallizing mainly at the (002) orientations of the hexagonal wurtzite phase.

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COMBUSTION SYNTHESIS AND CHARACTERIZATIONS OF SrB₆O₁₀: Cu PHOSPHOR

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ABSTRACT :

The polycrystalline sample of $Sr_{(1-x)}B_6O_{10}$: x Cu was prepared by using combustion synthesis method with some modifications in it. Our sample was confirmed by X-ray diffraction (XRD) technique. The Scanning Electron Microscope (SEM) shows the particles in 0.1 µm to 2 µm range. By exposing with gamma-rays its thermoluminescence properties were recorded. Thermoluminescence (TL) glow curve of $Sr_{0.3}B_6O_{10}$: Cu_{0.7} phosphor following irradiation with ⁶⁰Co gamma-ray source shows a single peak at 229 °C with 5 °C/sec heating rate. The phosphor is found to be about 90 % sensitive toLiF: Mg, Cu, P (TLD-100H) phosphor which is commercially available in market. The effect of dose variation on SrB_6O_{10} : Cu was establish to be undeviating up to 25 Gy dose with fading of about 33 % in 25 days.

KEYWORDS : Thermoluminescence; Combustion Synthesis; Strontium Hexaborate.

1. INTRODUCTIONS

The strontium borate polycrystalline compound SrB_4O_7 : Dy exhibit thermoluminescence which acts as perspective material for solid state dosimetry [1]. The mechanism of incorporation of divalent rare-earth ions into SrB_6O_{10} obtained by solid state synthesis in the air was discussed for Eu [2]. Hydrous red phosphor for the same host SrB_6O_{10} was found in literature for its nano structure [3]. Some other activator like Tb was also tried by the researcher in SrB_6O_{10} with co-dopant like Ce and Li for its thermoluminescence properties with gamma irradiations. [4] Thermoluminescence of borates containing various dopants, such as $Li_2B_4O_7$: Cu [5], CaB_4O_7 : Cu [6] and $K_2B_4O_7$: Cu [7] has been extensively investigated by the researcher in last decade. The copper containing materials are among the most sensitive known thermoluminescence (TL) phosphors [8]. These phosphors are suggested to be used for dosimetry applications [9, 10]. We have already synthesized phosphors in this category [11-15]. In this paper we have thoroughly studies the thermoluminescence properties of cupper doped SrB_6O_{10} phosphor.

2. EXPERIMENTAL

Polycrystalline Sr _(1-x) B_6O_{10} : x Cu[x =0.001, 0.002, 0.005, 0.01 and 0.02] phosphor is prepared by combustion technique with some modifications [16]. At the time of reaction, the all precursor including strontium nitrate, urea, NH₄B₅O₈and CuCl₂ are taken in stoichiometric amounts of ingredientswhich are calculated on the basis of molar ratio. These are well mixed with somr amount of double distilled water. Thus formed aqueous homogeneous solution was then transferred into a china basin. The china bowl was then kept into muffle furnace which is already maintained at (500 ± 10) °C. The entire combustion takes around 5 minutes. Resulting powder is heated in air at 650°C for 2 hours and wait for its cooling till room temperature. Now the prepared sample is ready for the different characterizations.

Table-1: Balance reaction for the phosphor	
Product	Corresponding reaction with balance molar ratios of precursors
Sr _(1-x) B ₆ O ₁₀ :xCu	$ Sr(NO_3)_2 + 1.2 \text{ NH}_4B_5O_8 + 10.2 \text{ CO}(NH_2)_2 + 10.2 \text{ NH}_4NO_3 + x \text{ CuCl}_2 $ $ Sr_{(1-x)}B_6O_{10}:xCu + \text{Gaseous} (H_2O, \text{NH}_4 \text{ and } NO_2 \text{ etc}) $

3. RESULTS AND DISCUSSION

3.1 XRD Analysis and Crystal Structure of SrB₆O₁₀: Cu

Fig. 1 shows the powder XRD pattern of SrB_6O_{10} : Cuour sample which is confirm on Rigaku Miniflex X-ray diffractometer with scan speed of 2.00 deg / min by Cu K α radiations. International Centre for Diffraction Data (ICDD) file (00-020-1190) bargainpeak to peak matching. The formed sample is Centrosymmetric structure and its space group: P21/n.



3.2 SEM Analysis

SEM images of our phosphor SrB_6O_{10} : Cu was taken from SASMIRA, Mumbai (Fig. 2). This material shows irregular spherical as well cylindrical shape particles with canal like structure. Our sample shows size in 0.1 µm to 2 µm range. The synthesis method is somewhat responsible for this irregularity in masses.



Fig. 2 SEM image of SrB₆O₁₀

3.3 FTIR Analysis

Fig. 3 represents the Fourier transformed infrared spectroscopy (FTIR) spectra for SrB_6O_{10} : CuMaterial. The FTIR revealed prominent absorption with peaks for SrB_6O_{10} : Cuare at 1357, 1253, 1112, 1011, 881, 682, 662, 601, 576, 563, 533, 521 and 511 cm⁻¹ as shown in figure. The IR peak at about 1357 is due to presence of orthoborates groups containing BO_3^- while asymmetric stretching vibrations of B-O bonds from orthoborates groups identifies by 1253 cm⁻¹. The peak at 1011 cm⁻¹ is for Pentaborate group used for the preparation of SrB_6O_{10} :Cu. 881 cm⁻¹ is representative for stretching vibrations of tetrahedral BO_4^- units. Lattice dynamic modes are responsible for absorption of IR at wave numbers smaller than 500 cm⁻¹. No clearly distinguished peak at 630 cm⁻¹ from the OH hydroxyapatite group is visible in spectrum. The absence of peaks from 1550 cm⁻¹ to 2500 cm⁻¹ supports the complete elimination of nitrate and organic matter. (19, 20)Both trigonally and tetrahedrally coordinated boron atoms coexist simultaneously.



3.4 Thermoluminescence Studies

Our prepared sample SrB_6O_{10} : Cuphosphor exposed to ⁶⁰Co gamma-ray radiation. The said gamma source is available at RTM Nagpur University and its dose rate is 0.3712 kGy / hr. This newly formed $Sr_{0.3}B_6O_{10}$: Cu_{0.7}for a test dose of 15 Gy is shown in the Fig.4 attain at heating rate of 5°C /sec and compared with commercially available phosphor TLD-100 (Harshaw) available in our laboratory with all similar parameters including weight and dose as that of prepared phosphor. We found our sample about 90 % sensitive to that of commercial LiF: Mg, Cu, P (TLD-100 H) phosphoras shown in Fig. 5. Glow curve for $Sr_{0.3}B_6O_{10}$: Cu_{0.7}has the chief TL peak at around229°C which is good sign for this phosphor to be used as good TLD material. [21-24]



3.5 Dose Response for SrB₆O₁₀: Cuunder gamma rays

Those sample are said to be good material for TL which has absorbed dose is linear over the extensiveseries. Earlierthe sample powder was sintered in air at 500 °C in an alumina crucible for 1 hourbefore characterization. Then the powder got rapidly quenched at room temperature on the thick aluminum block. Five samples were irradiated at a time for each said dose. Each data value resembles to the mean of the five readings. We decide 5Gy to 25Gy dose for irradiations because of availabilities are the source center. After about five hours, TL reading was taken with TL readout heating rate of 5 °C/sec on TL 1009I reader designed by Nucleonix system at SGB Amravati University with the temperature range of integration of the TL signal from 40 °C to 400 °C. The linearity was observed for the first peak in the range from 5Gy to 25Gy. The relationship between the TL response of the first high intensity peak and the absorbed dose for SrB₆O₁₀: Cuphosphor was shown in Fig. 6 and it was found to be linear. The fading of 25 Gy dose sample was found to be about 33 % in 25 days as shown in Fig. 7.



4. CONCLUSIONS

In current report X-ray diffraction result support the complete crystalline formation of SrB_6O_{10} : Cuby combustion synthesis. The thermoluminescence (TL) intensity of SrB_6O_{10} : Cuphosphor was found to be about 90 % of the commercially available LiF: Mg,Cu,P (TLD-100H) phosphor available at our laboratory. The particle sizes in phosphor SrB_6O_{10} : Cu was in scale range from 0.1 µm to 2 µm. The phosphor shows linear dose response from 5 Gy to 25Gy dose. The fading of this sample material is about 33 % in 25 days. From these thermoluminescence studies this phosphor SrB_6O_{10} : Cu is said to be a good candidature for TLD phosphor.

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THERMAL BEHAVIOR OF Na-EXCHANGED HEULANDITE

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ABSTRACT:

Crystals collected from Ajanta, Aurangabad Maharashtra, India have been characterized as heulanditeby x-ray diffraction, IR spectroscopy and chemical analysis.

Three sample of (Na-Heu) was prepared by ion exchange and was fully characterized. Thermal behavior of (Na-Heu) was studied using thermo gravimetric and differential thermal analysis (TGA/DTA)

KEYWORDS : Heulandite, thermal behavior.

1 INTRODUCTION

Heulandite is commonly occurring platy natural zeolite, that belong VII group of zeolites.¹ It occurs in cavities of basalts and in igneous rocks. Heulandite is a zeolite mineral series having the distinctive framework topology and the ratio of Si/Al <4. The structural topology oftetrahedral Heu framework² is well understood topology and Possesses C2/msymmetry. Many researchers have studied the thermal stability of heulandite^{3,4,5,6}

2 EXPERIMENTAL

The crystal were collected from Ajanta ranges and area surrounding Aurangabad city. The collected samples were cleared, crushed and sieved to gel 106μ m sized crystals. The powdered samples were washed repeatedly. The tree verities of samples of as grown heulanditesamples were treated three times at 95° c fortwo hours in o.1M solution of Nacl which a solid solution ratio 1:10 with stirring. After washing with distilled water, filtering and drying at 80° cfor several hours theion exchanged samples were obtained.

Thetree different varities of heulandite were exchanged with Na⁺and were designated as A,B,C. All the samples were characterized my x-ray diffraction, infrared spectroscopy and thermal analysis (DTA/TGA).

2.1 X-ray diffraction :-

The x-ray diffractogram was recorded between 2θ values ranging from 5° to 50° with a chartspeed of 1°/min. onPhillips x-ray diffractometer(modelpw1730) and Ni filtered CuK α radiation γ =1.5406A°). The relative intensities and dvalues compared withstandard d values.

2.2 Thermal analysis :-

The TG/DTG/DTA curves were recorded on Setaram 92-12 thermal analyzerin air using precalcinated α –alumina as reference material. The TG/DTG/DTA curves of sample AB&C are as shown fig 1



Fig1. (TG/DTG/DTA) Curves of sample A,B,C

3 RESULT AND DISCUSSION :-

3.1 XPD Pattern :-

XRD Pattern of heulandite sample have found to be highly crystalline and relative intensities and d values are found to be in close agreement with the standard values.

3.2 TG/DTG/DTA

Incase of sample A two endothermic peaks are observedat around 451 K and 583K. In the temperature range 360Kto 573K, 8% of weight loss is noted. In thetemperature range 573k to 673K another 2.87% of weight loss is noted. The total weight loss is found to be 12.887%.

In case of sample B onebroad endotherm is observedat 402Kand another at 580K. The weightloss at 402K is found to be about 2.7%. The total weight loss at 559K is around 8.7%. The total weight loss is found to be 12.75%.

In case of sample C twocharactersticsendotherms are observed at 393 K and 583K. The weight loss in the temperature range 325 K ro473K is found to be 5.7% and the range 573K to 773K is 2.5%. The total loss is found to be 10.9%. The total weight loss on Sample A > Sample B>Sample C.

CONCLUSION :-

Samples ofheulandite from marathwada region of India maintain highdegree ofcrystallinity .Thermal behavior ofthree varieties of Na-exchanged heulandite is studied and confirmed

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PREPARATION AND SPECTRAL CHARACTERISTICS OF Ce³⁺ ACTIVATED ALUMINO-BORATE BaAl₂B₂O₇

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ABSTRACT :

 Ce^{3+} activated alumino-borate $BaAl_2B_2O_7$ was prepared via the solution combustion technique. The phosphor's phase purity and its emission properties were studied using powder X-ray diffraction pattern and photoluminescence spectroscopy. The photoluminescence properties of borate phosphors have been investigated on fluorescence spectrometer (F-7000). The $Ba_{(0.95)}Al_2B_2O_7$: $_{0.05}Ce^{3+}$ phosphor shows an intense blue emission peaking at about 420 nm upon 336 nm excitation. The CIE chromaticity coordinates for $Ba_{(0.95)}Al_2B_2O_7$: $_{0.05}Ce^{3+}$ were calculated from the PL spectra under 336 nm excitation in the CIE 1931 chromaticity diagram.

KEYWORDS: Alumino-Borates, Combustion Synthesis, XRD, Photoluminescence, LED.

1. INTRODUCTION

Alkaline-earth aluminum borates have been taken interest in by scientists during the past decade because of their potential applications as luminescence hosts [¹-³]. The phase of BaAl₂B₂O₇, is an example of alkaline-earth aluminum borates, was first described by Hu⁻bner [⁴] following a study of the ternary system BaO–Al₂O₃–B₂O₃. It is characterized by having an association of BO₃ triangles, BaO₆ octahedra, and AlO₄ tetrahedra. The crystal structure of BaAl₂B₂O₇ has been reported in detail elsewhere [⁵]. Although the mechanical and electrical properties of BaAl₂B₂O₇ have been studied in detail by Macdowell [⁶].Inorganic Borate host compounds doped with rare earth ions are the important classes of phosphors useful for LED based solid state light. Considering Ce³⁺ as a highly efficient activator, the Ce³⁺ emission spectrum usually consists of a broad band due to transition between the 4f¹ ground state and the 5d excited state configuration, and can occur from the ultraviolet to the red region of the electro-magnetic spectrum, depending on the different host lattices [⁷,⁸]. Doped rare-earth ions such as borates have great potential in LED application due to their advantages of a low synthesizing temperature and good chemical and physical stability. Examples of these known Ce³⁺ doped borate phosphors are, Ca₃La₃(BO₃)₅:Ce³⁺ [⁹], NaBaBO₃:Ce³⁺ [¹⁰], NaSrBO₃:Ce³⁺ [¹¹], NaCaBO₃:Ce³⁺ [¹²].

In the present work, we report synthesis and photoluminescence properties of $BaAl_2B_2O_7$:Ce³⁺. Their photoluminescence properties under the near-UV excitation were evaluated in detail.

2. EXPERIMENTAL

The Powder samples of $Ba_{(0.95)}Al_2B_2O_7$: $_{0.05}Ce^{3+}$ have been prepared by a solution combustion technique followed by heating combustion ash at 800 $^{\circ}C$ in air. The method is based on the exothermic reaction between the fuel (urea) and oxidizer (Aluminum Nitrate). The detailed description of the method was reported in our earlier work [13 - 20]. The stoichiometric amounts of Al(NO₃)₃.9H₂O, Ba(NO₃)₂, H₃BO₃, Ce₂O₃

and $CO(NH_2)_2$ used were of AR grade and the rare earth Ce_2O_3 (99.99% purity) used were from the Indian Rare earth. The stoichiometric amounts of the ingredients were thoroughly mixed in an Agate Mortar, adding little amount of double distilled water to obtain aqueous solution. The aqueous solution was slowly heated at lower temperature of 90°C to remove the excess water. The solution was then introduced into a preheated muffle furnace maintained at (550 ± 10) °C. The solution boils foams and ignites to burn with flame, a voluminous, foamy powder was obtained. The entire combustion process was over in about 5 min. The resulting fine powders were annealed in a slightly reducing atmosphere provided by burning charcoal at temperature 750°C for about 90 min. and suddenly cooled to room temperature. The samples are subjected to XRD analysis. PL measurements were performed on Fluorescence Spectrometer (Hitachi F-7000).

3. RESULTS AND DISCUSSION

The XRD pattern of the polycrystalline powder samples of the phosphor $Ba_{(0.95)}Al_2B_2O_7$; $a_{0.05}Ce^{3+}$ have been analyzed for the structure confirmation. The powder XRD pattern of the phosphor was compared with the standard JCPDS data files and found to be in good agreement with the ICDD File No. 01-086-2168 (Fig. 1).

Fig. 2 shows the typical PL excitation and emission spectra of $BaAl_2B_2O_7$: Ce^{3+} (5 mol.%). The excitation and emission spectra found in Fig. 2 are corresponding to the electronic transitions between 4f¹ ground state and 5d-multiplets of Ce³⁺. The ground state configuration 4f¹ of Ce³⁺ is split into ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ levels by spin-orbit interaction [21]. The phosphor is excited at 336 nm is attributed to electronic excitation from 4f¹ ground state to 5d-multiplets of Ce³⁺. By the excitation of 336 nm wavelength, the phosphor has emission center at 420 nm. The emission peak at 420 nm in the (blue) visible region is attributed to the transition $5d \rightarrow {}^{2}F_{7/2}$ of Ce³⁺. The excitation and emission peaks are characteristic spectra of 5d-4f transition of Ce³⁺. The CIE chromaticity coordinates for $Ba_{(0.95)}Al_2B_2O_7$:_{0.05}Ce³⁺ were calculated from the PL spectra under 336 nm excitation and marked with a star in the CIE 1931 chromaticity diagram in Fig. 3. The chromaticity coordinates (x,y) of this phosphor are calculated to be (0.1714,0.0051), respectively, which indicates that the emission color of the as prepared phosphors is located in the deep blue region.



Fig. 1. XRD pattern of Ba_(0.95)Al₂B₂O₇:0.05</sub>Ce³⁺ phosphor (ICDD Card No. 01-086-2168).



Fig. 2. Excitation & Emission Spectra of Ba_(0.95)Al₂B₂O₇:0.05</sub>Ce³⁺ phosphor.



Fig. 3. Chromaticity coordinates of Ba_(0.95)Al₂B₂O₇:_{0.05}Ce³⁺ phosphor in the CIE 1931 chromaticity diagram.

4. CONCLUSIONS

The inorganic borate host phosphor $Ba_{(0.95)}Al_2B_2O_7:_{0.05}Ce^{3+}$ was prepared by a low cost, simple and time saving solution combustion technique. The powder XRD pattern confirms the structure of prepared $Ba_{(0.95)}Al_2B_2O_7:_{0.05}Ce^{3+}$ phosphor. The phosphor yielded the highest PL intensity at 5 mol% of Ce³⁺ concentration. The PLE spectrum of $Ba_{(0.95)}Al_2B_2O_7:_{0.05}Ce^{3+}$ consists the strongest absorption peak is centered at about 336 nm. The phosphor exhibits a blue emitting band peaking at 420 nm upon 336 nm n-UV excitation. The optimal doping concentration of Ce³⁺ is 5 mol%. The relatively high activation energy results in a good thermal stability for this phosphor. The chromaticity coordinates (x,y) of this phosphor are calculated to be (0.1714,0.0051), respectively, which indicates that the emission color of the as prepared phosphors is located in the deep blue region. The BaAl_2B_2O_7:Ce³⁺ phosphors may be potential blue-emitting components for UV excited w-LEDs.

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Review of Research

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