

Investigation on the Structural and Dielectric Properties of The $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ Nano-material

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Abstract— the material has been successfully prepared by the most convenient solid state reaction route method. The material has been structurally analyzed using X-ray Diffraction (XRD). The sample has been found to be crystalline, single phase with particle size of the order of 80nm. The sample was found to exhibit the orthorhombic structure with the space group $Pnma$. The so obtained XRD pattern was Rietveld refined which confirmed the purity, single phase and orthorhombic structure. The dielectric measurements have been carried out which indicated that the as prepared sample is a good dielectric material. The loss is low. The dielectric constant decreases initially at low frequency and attains a minimum value which later at higher frequency tends to increase again. The loss initially is found to increase and after attaining a peak value, it decreases smoothly and tends to obtain a lower value of dielectric loss but shows a sign of increase at higher frequency.

Keywords— Nanoparticles; X-ray diffraction; Rietveld Refinement; dielectric

I. INTRODUCTION

Rare earth doped silicate phosphor materials are technologically important due to their electronic and optical features arising from the 4f electrons. Due to the possession of the feature of valence fluctuation i.e. having valence state of both di- and trivalent nature, the Eu^{2+} element is the most efficient element as dopant [1].

From the perspective of technological applications, silicates and their related structures has been a subject of immense interest. Currently, there is a great deal of interest due to the optical and structural properties of nanometre sized semiconductor particles or thin films [2]. As these silicates are often used as the luminescent materials, they are regarded as the next generation solid state lighting materials and have attracted attention of the scientific community due to their potential applications. They are efficient in comparison to the existing traditional lamps in power, reliability and long life time. In addition, they are compact, environment friendly and need low maintenance.

The frequently used approach to modify and improve the properties of the materials is to dope the parent lattice by suitable cations. Also the properties are altered to a great extent by the methods of synthesis. The chemical and

physical properties of inorganic micro/nano structured materials are dependent on their chemical composition, size, morphology, phase and also dimensionality [4,5]. Therefore, in the past decade, extensive research work was devoted to have control over these parameters [6]. More applications and novel functional materials might emerge, if shape-controlled nano/micro-crystals could be achieved with high complexity [7].

Solid-state reaction method is usually used to prepare $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ material. In this method, the reactants are mixed thoroughly and the mixture is then heated or fired under an appropriate atmosphere. To facilitate the reaction and to improve the crystallinity of the material, flux agents or molten salts are often added to provide a more interactive medium for the reaction [8]. In the present study, we report the synthesis of europium and dysprosium doped strontium silicate phosphor by high temperature solid state reaction method. This report describes the structural characterization on the basis of X-Ray diffraction and dielectric studies of $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ material. The objective of the present study aims at the investigation of the effect Eu^{2+} and Dy^{3+} ions on structural, electrical and dielectric nature of rare-earth doped strontium silicate with general formula $\text{Sr}_{1.94}\text{Eu}_{0.02}\text{Dy}_{0.04}\text{SiO}_4$. The ionic radii of Eu^{2+} and Dy^{3+} are 1.09Å and 0.908 Å, respectively; hence they are expected to replace Sr which has ionic radius of the order of

(1.12 Å) without any distortion in the structure of the unit cell and maintain a single phase.

II. RELATED WORK

In this section, the author describes the previous research works in the form of title, problem statement, objectives, not repeat the information discussed in Introduction [3].

III. METHODOLOGY

The pure, crystalline and single phase $\text{Sr}_{1.94}\text{Eu}_{0.02}\text{Dy}_{0.04}\text{SiO}_4$ sample was successfully prepared by conventional solid state reaction method. The starting materials were highly pure SrCO_3 and SiO_2 which were mixed and ground for 2 hours. Then two other oxides namely Eu_2O_3 and Dy_2O_3 were taken in test tubes separately and two to three drops of HNO_3 were added to convert them into nitrates. After that the early weighed and ground mixture of oxides and the later prepared nitrates were mixed. The whole mixture was again ground for two hours. The prepared mixture was calcined at 800°C for four hours to enhance reactivity of the composition. The calcined powder was again ground for four hours and once again annealed at 1150°C for three hours in reducing atmosphere employing charcoal. After making pellet of the prepared sample of the diameter of 10mm with the thickness of about 2.6mm applying the pressure of two tones, it was sintered at 1250°C for 10 hours to make it compact and was later on silver pasted to make it ready for the dielectric measurement [9].

Crystal structure and phase formation of the sample were examined using an X-ray powder diffraction technique at room temperature, using Bruker D8-Advance X-ray diffractometer with $\text{CuK}\alpha 1(1.5406 \text{ \AA})$ radiation. The diffraction data is collected with a step size of 0.02 over the angular range $20 < 2\theta > 60^\circ$, generating X-ray by 40 kV and 40 mA power settings. The sample was coated with a thin layer silver and then frequency dependent dielectric behavior of the prepared sample was carried out by Wayne Kerr, Model 6500B, Precision Impedance Analyzer.

IV. RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis was used to characterize the synthesized sample. The analysis of XRD data of Sr_2SiO_4 phase is usually qualitative, based on relative peak intensities. Strontium silicate exists in monoclinic (β - Sr_2SiO_4) phase at low temperatures and in orthorhombic (α' - Sr_2SiO_4) phase at high temperatures with a transition temperature of $\sim 85^\circ\text{C}$. It has been reported that the crystal structure of α' - Sr_2SiO_4 (orthorhombic) and β - Sr_2SiO_4 (monoclinic) are similar [10]. The typical X-ray diffraction pattern of the resultant $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ is shown in Figure 1. The XRD pattern for the $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$ is given for

comparison as Figure 2: where identified peaks are marked with asterisks. The XRD data were indexed an orthorhombic system with space group $Pnma$ having cell parameters.

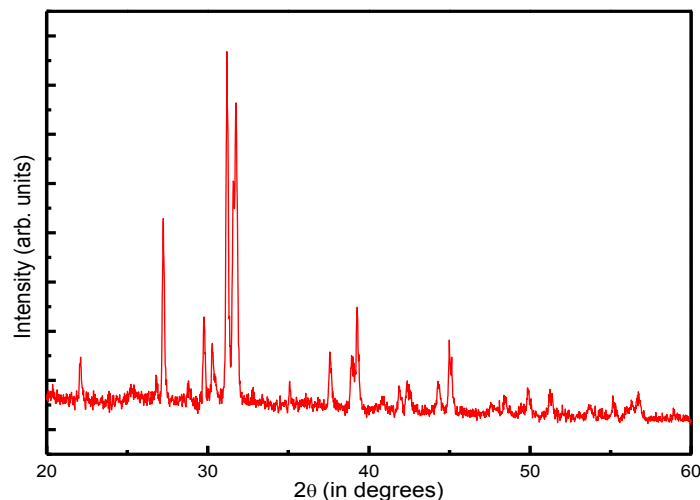


Fig.1: XRD pattern of the $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ sample

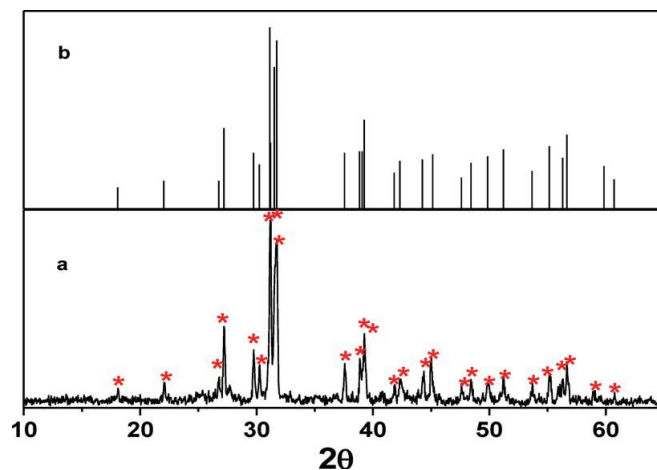


Figure 2: (a) XRD pattern of $\text{Sr}_{1.99}\text{Eu}_{0.01}\text{SiO}_4$, (b) The standard ICDD stick patterns with file no-39-1256[11].

The orthorhombic phase diffraction peaks of the pure $\text{Sr}_2\text{SiO}_4:\text{Eu}$ material were clearly observed in the XRD pattern of the prepared sample under investigation. The position and intensity of diffraction peaks of the XRD pattern of the prepared sample can be matched with the reference parent sample XRD pattern and could be indexed to the orthorhombic phase of α' - Sr_2SiO_4 . These results revealed that the crystal structure of the prepared sample has been retained. This behavior can be attributed to the nearly same ionic radii of $\text{Sr}^{2+}(1.12 \text{ \AA})$, $\text{Eu}^{2+}(1.09 \text{ \AA})$ and $\text{Dy}^{3+}(0.908 \text{ \AA})$ as a result of which the Sr^{2+} site in the parent matrix is easily occupied by the Eu^{2+} and Dy^{3+} ions. Powder-XRD pattern

shown by Figure 1: indicates that the material so synthesized is crystalline and single phased. All the reflections were indexed according to the standard pattern of orthorhombic α -Sr₂SiO₄ available in JCPDS No 39-1256. The lattice constants found were nearly, a= 7.0708 Å, b= 5.6588 Å and c= 9.7325 Å which are consistent with the report [11].

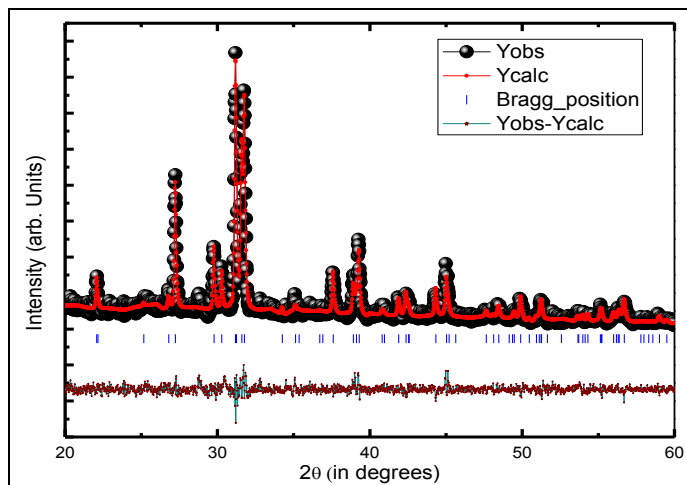


Figure 3: Retveld Refined XRD pattern of Sr₂SiO₄: Eu²⁺, Dy³⁺ sample.

Table 1: Details of Rietveld refined XRD pattern of the Sr₂(Si)₄:Eu, Dy

Parameters	Obtained Values
Space group	<i>P n m a</i>
<i>a</i> (Å)	7.0708
<i>b</i> (Å)	5.6588
<i>c</i> (Å)	9.7325
<i>V</i> (Å ³)	389.421
Density	9.922 g/cm ³
<i>R_F</i>	6.59
<i>R_{Bragg}</i>	7.81
<i>R_{wp}</i>	31.5
<i>R_{exp}</i>	26.00
<i>R_p</i>	33.40
χ^2	1.471
GOF	1.2

An estimation of average crystalline size for the sample was done using Debye Scherrer’s formula [12]

$$t=0.94\lambda/\beta\cos\theta$$

Where ‘t’ is the crystalline size, λ is the wavelength (for Cu K α 1, $\lambda=1.5406$ Å), β is the full width at half maximum (FWHM) and ‘ θ ’ is the Bragg’s angle. As shown in Figure 1: the principal diffraction peaks are at $2\theta = 30.6, 31.2, 31.8$. The crystal size of Sr₂SiO₄:Eu²⁺, Dy³⁺ calculated using Debye Scherrer’s formula was found to be about 78 nm

which was expected from the sharpness and narrowness of FWHM of the characteristic peak in the obtained spectrum.

The XRD spectrum was Retveld refined using FullProf software [13]. The Retveld refinement of the spectrum is give in Figure 3: which confirms the orthorhombic structure of the prepared sample with the space group *Pnma*.

Also it is clear that the sample is pure and single phase crystalline which is also indicated by the sharpness of the characteristic peak. The various parameters obtained from the Retveld Refinement are given in Table-1

The value of real part of dielectric constant (ϵ') is calculated by using $\epsilon = ct/A \epsilon_0$ where ‘ ϵ_0 ’ is the permittivity of free space, ‘t’ is the thickness of pellet, ‘A’ is the cross sectional area and ‘C’ is the capacitance of pellet. Figs. 4 and Fig.5: shows room temperature variations in dielectric constant (ϵ') and dielectric loss factor ($\tan\delta$) with increasing frequency in the logarithmic scale from 20 Hz to 1 MHz.

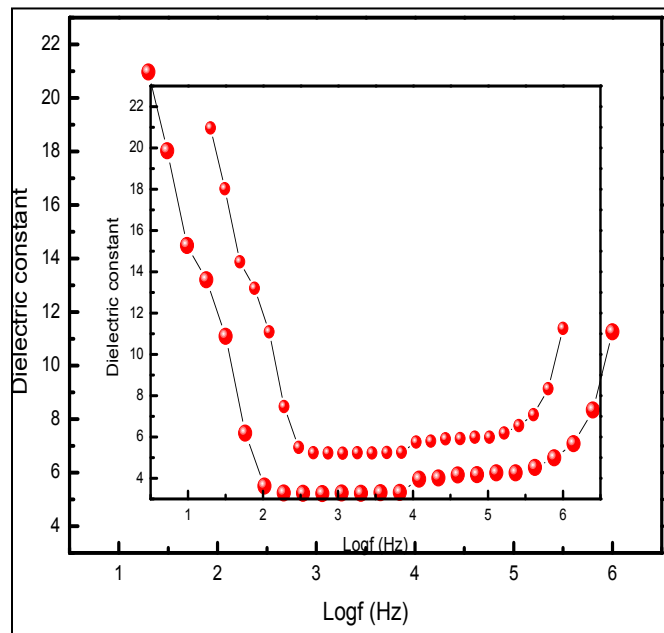


Figure.4: Dielectric constant as a function of Frequency

The dipolar and interfacial polarizations are said to be the strongly affecting factors on the dielectric constant. Fig.4: clearly indicates the decrease in dielectric constant with the increase in frequency attaining constant minimum value at higher frequencies which can be explained by Maxwell-Wagner model [14].

The dielectric constant of the nanoparticles change very lightly at higher values of frequency due to the reason that the applied field is not obeyed by the electronic exchange between the metal ions beyond a certain critical frequency.

Generally, it can be considered that the exchange of electrons between Sr^{2+} ions in the presence of varying valence state dopant ions results in local displacement of electrons in the direction of the electric field which is responsible for the observed change in dielectric loss factor or dissipation factor i.e. ratio of the power loss in a dielectric material to the total power transmitted through the dielectric material with frequency in Fig.5:

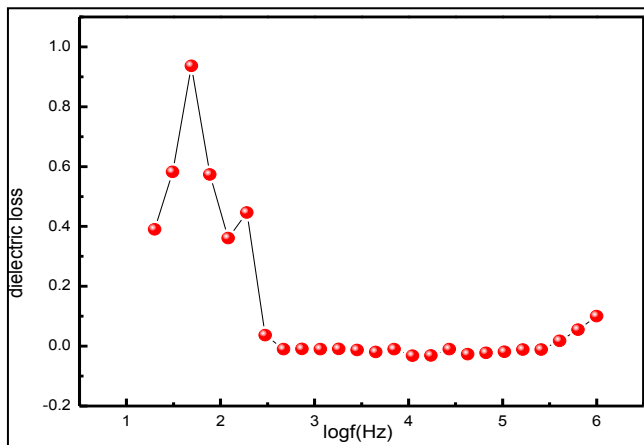


Figure.5: Dielectric loss as a function of Frequency

The shielding effect is more prominent at higher values of frequency as a result of which dielectric loss decreases. The samples synthesized show similar trends for ϵ and $\tan\delta$. The value of dielectric constant and the dielectric loss are high at lower frequencies. The dielectric loss is found to be maximum at lower frequencies due to nearly equal hopping frequency between different ionic sites and frequency of the applied field [15,16].

V. CONCLUSION AND FUTURE SCOPE

In summary, we have synthesized $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$, Dy^{3+} nanocrystalline samples using solid state reaction method. X-ray diffraction (XRD) confirmed the single-phase cubic structure with $Pnma$ space group for the prepared sample. The XRD spectrum was refined and the parameters were satisfying. Also the structure and purity of the sample was confirmed. The dielectric measurements confirmed the polarization behavior of the sample where the dielectric constant is found to be moderate and the loss is small making a promise to be studied and improved in the said field.

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