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INFLUENCE OF Sm^{3+} ON POLARIZABILITY AND METALLIZATION PROPERTIES ON WILLEMITE GLASS CERAMICS FOUND FROM WASTE MATERIAL

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ABSTRACT

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Sm^{3+} doped willemite was successfully synthesized using melt quenching technique. This study intends to design and identify the effect of the Sm^{3+} ion on zinc silicate. Samarium oxide doped zinc silicate 5 wt% has the highest density. In any case, the most minimal thickness, reflection and refraction list uncovers with samarium oxide 3 wt% doped zinc silicate. The $\text{Zn}_2\text{SiO}_4: \text{Sm}$ 3 wt% has most extreme estimations of energy band crevice, molar volumes, molar refraction, polarizability, and transmittance. This material sample is an improvement to produce optical materials and an optical disc for storing information.

INTRODUCTION

Among the several luminescence host materials, zinc silicate (Zn_2SiO_4) is recognized as a suitable host matrix to integrate with rare earth ions and transition metal ions developing in a first luminescence region in blue, green and red spectra, Eevon *et al.* (2016). In recent technology, rare earth ions are better dopants for light activators in the host matrix materials than transition metals, Syamimi *et al.* (2014). The outermost orbitals of $5s_2$ and $5p_6$ completely sheltered the filled $4f$ shells. The emanation changes supply shrill lines in the optical spectra pleasing phosphors with over the top iridescence productivity. Also, the rare earth (RE) particles have attracted consideration regarding substituting as an effective particle in numerous optical materials because of their huge number of

retention and emanation groups surfacing from the moves inside the vitality levels. Given these factors, many scientists focused their interest on trivalent samarium ions as a luminescence centers in deep red emission arising from conduction band $^4G_{5/2} \rightarrow ^6H_{9/6}$ transition, Deepa *et al.* (2016). Right now, the samarium (Sm^{3+}) particle is a standout amongst the most appealing and significant rare-earth dopants considering Sm^{3+} doped phosphors are normal to be ideal materials for optical enhancers, lasers, and electroluminescent devices Thomas & Sebastian (2009). Different techniques have been developed to get ready $\text{Zn}_2\text{SiO}_4: \text{Sm}^{3+}$, for example, sol-gel combination, sprays pyrolysis, co-precipitation union, solid-state reaction and hydrothermal technique, Sahu *et al.* (2015).

As a complexity, the steady states procedure points a superior lucidity in the modern application than sol-gel technique. Nevertheless, this system routinely utilized extremely expensive SiO₂ source to combine the zinc silicate Lukić et al. (2008). To overwhelm the disadvantage, it requires changing a new silicate sources from waste rice husks silica (WRHS) glasses for expense saving. The husks silicate glass established to be an appropriate optical material with prominent transparency, excellent rare-earth ion solubility, high thermal stability, and low melting point Sánchez-Royo et al. (2014). Hence, this paper will intend to show the synthesis and optical properties of Sm³⁺ doped Zn₂SiO₄ host matrix by adopting an inexpensive solid-state reaction method. Impacts of Sm₂O₃ variety focus in Zn₂SiO₄ (willemite) on the polarizability, metallization and optical properties were investigated, Azlan et al. (2014).

METHODOLOGY

A melt quenching technique was used to produce samarium Zn₂SiO₄ [(70-X) Zn₂XSm₃₀SiO₄] based glass ceramics. The doping extents were 1, 3 and 5wt% of the samarium oxide Reacton 99.9 %(REO). Zinc oxide 20 nm particle size and 99.5% purity was mixed with 63-micron mesh of silica. The silica was obtained from waste rice ash. The mixing process was carried out for 24 hours with low energy ball milling. The mixture was heated in a furnace for 1500 °C for a period of four hours. The liquid blend was extinguished in water and shaped a glass fritz at room temperature. At that point, the glass fritz was pounded and sieved with 63 microns mesh. Polyvinyl alcohol (PVA) was used to act as a binder to the samples powder. The sample powder was turned to pellets, with 3.5 tons of pressure for 5 minutes and sintered at the temperature of 1000 °C for two hours, which, was then calcined at 400 °C for an hour. At room temperature, Shimadzu UV-visible spectroscopy was performed in the range of absorption spectra measurements of 217.49–800 nm wavelengths. The optical band gaps of the material were used to analyze the sample absorption edges.

Theory and calculations

At room temperature Archimedes standard and refined water as a drenching fluid was utilized to quantify the thickness of glass ceramic samples. The computerized measuring machine with a precision of ±0.0001g was utilized to weigh the glass ceramic tests noticeable all around and refined water individually. Using the formula:

$$V_m = \frac{M}{\rho} \tag{1}$$

the equivalent molar volumes (V_m) were computed. Where ρ is the density and M is the atomic weight of the glass-ceramic specimen. By using EL X-02C, high precision ellipsometer the refractive index (n) was calculated as one of the optical properties. In addition, Dimitrov and Sakka (1996) proposed the relation:

$$\sqrt{\frac{E_g}{20}} \tag{2}$$

$$\frac{n^2-1}{n^2+2} = 1 -$$

where E_g is the energy band gap. The computed energy band gaps (E_g) were extrapolated from the straight district which met hν pivot at (αhν)^{1/2} = 0. Thus, the connection decided molar refraction (R_m) as

$$R_m = \frac{(n_0^2 - 1)}{(n_0^2 + 2)} V_m \tag{3}$$

where n is the refractive record, ρ is the thickness The Lorentz–Lorentz relation estimated the polarizability of glass ceramic samples to be

$$\alpha_m = \frac{3}{4\pi N_A} R_m \tag{4}$$

As per Eraiah and Bhat (2007) the α_m in Equation 4 was converted to.

$$\alpha_m = \frac{R_m}{2.52} \tag{5}$$

This implies N_A is representing the Avogadro number, V_m is the molar volume of sample and α_m is the polarizability. From Equation 6 Metallization criterion (M) of oxides, glass demonstrates the relationship with other parameters.

$$M = 1 - \frac{R_m}{V_m} \tag{6}$$

where all the parameters retain to their usual meanings above.

RESULTS AND DISCUSSION

Table 1 shows that increase in the Sm_2O_3 content leads to the decrease in $Zn_2SiO_4:Sm$ 3wt%, as per Wagh et al. (2015). This scenario indicates the restricting of the compound by substituting the zinc ion by samarium ion leading to increase in the chemical bonds, which leads to the increase in the entire volume of the sample. Hence, increase in volume leads to the decrease in density. Further, addition of the dopant concentration leads to the increase in density and decrease in volume. In the event the crystal size of the sample increases the porosity decreases the entire volume decreases Dou et al. (2012).

Table 1: Density, mass in air and molar volume of bismuth doped zinc silicate

| Samples (wt%) | Mass in air (g) | Molar volume (V_m)(cm^3) | Density (ρ) (g/cm^3) |
|-----------------------|-----------------|----------------------------------|---------------------------------|
| Zn_2SiO_4 (70 - 30) | 28.0 | 8.3 | 3.336 |
| $Zn_2SiO_4:Sm$ 1 | 29.0 | 9.0 | 3.238 |
| $Zn_2SiO_4:Sm$ 3 | 30.0 | 9.7 | 3.092 |
| $Zn_2SiO_4:Sm$ 5 | 29.0 | 8.3 | 3.442 |

Optical band figure is among the optical properties of any semiconductor materials, which has no clear shape. The pure zinc silicate crystal is anticipated to have the optical band gap of 5.5 electron volt (eV). The samarium doped zinc silicate shows the increasing of optical band gap up to 3.47 eV with $Zn_2SiO_4:Sm$ 3wt% due to the restructuring which converts non-bridging oxygen to bridging oxygen that leads to the increasing in size and volume of the compound Qazvini et al. (2012). While for further doping of samarium, the band gap decreases to 3.21 eV, which reveals the generation of more non-bridging oxygen as indicated in Fig. 1, Sreedhar et al. (2014). In same vein, a sudden increase in density is experienced when the dopant concentration reaches up to 5wt% of samarium. As shows the density increase from 3.092 to 3.442 g/cm^3 .

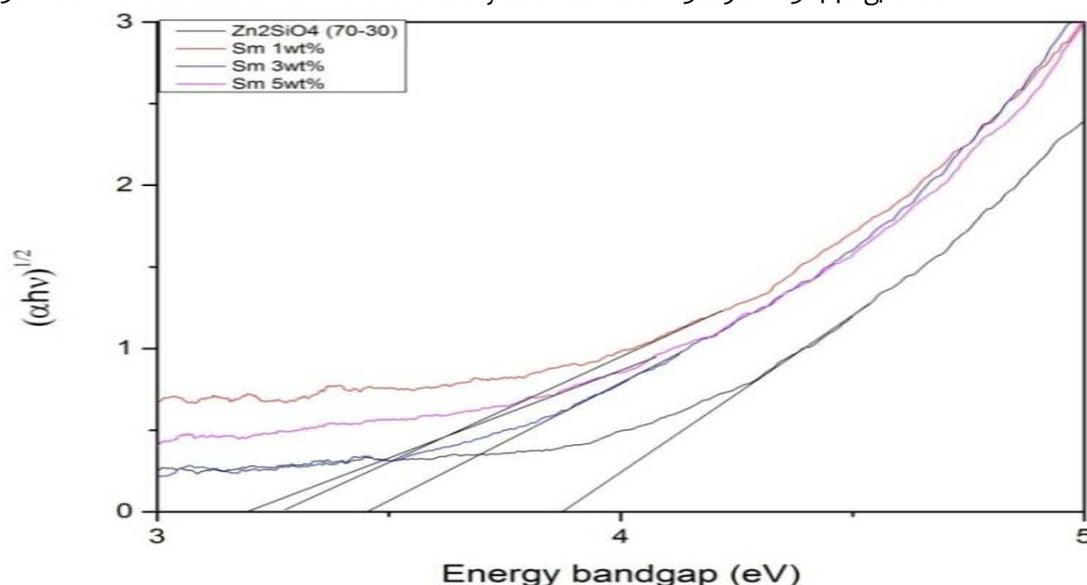


Figure. 1 Optical bandgap of (70-X) $Zn_2XSm_{30}SiO_4$ with X= 0, 1, 3 and 5 wt%

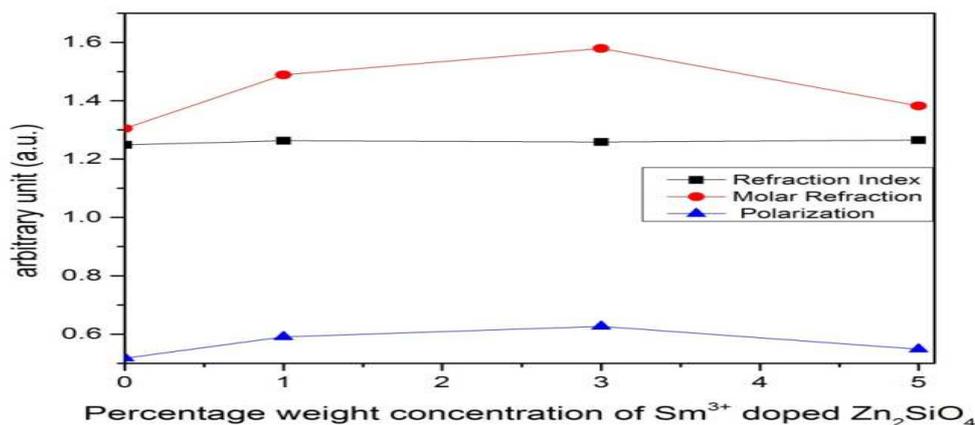


Figure. 2 Refractive index, molar refraction, and polarizability of samarium doped zinc silicate
Absorption is a physical or chemical mechanism in which molecules, atoms or ions permit into the material medium and convert the radiation. As the energy is transient through the samples three different activities are taking place absorption, reflection, and transmission.

$$1 - R - T = A \tag{7}$$

Absorption is written as:

$$2 - \log_{10} \%T = A \tag{8}$$

Where T is transmission R is the reflection, and A is absorption. Radiation above ingestion point demonstrates T and R are at their least. This shows that there is neither transmission nor reflections. Only retention dominates the process. Toward the starting, the specimens mirror some piece of radiations in the retention and transmission spectra. This fact leads to understanding the simple relationship between refractive indices and reflectance of the samples.

$$R = \left(\frac{n - 1}{n + 1}\right)^2 \tag{9}$$

Where n is refractive index. The act of radiation via material medium is identified as transmission. The transmission is mostly or entirely obligated to the material medium El Ghoul *et al.* (2012). Conversely, in this event, some part of the radiations are reflected, absorbed, and transmitted as revealed in Fig. 3. However, transmission is likewise related to the refractive index as:

$$T = \frac{2n}{n^2 + 1} \tag{10}$$

Zn₂SiO₄:Sm 3 wt% transmits the most elevated radiation of 2.589372 joules contrast and remaining specimens. In like manner, a similar specimen absorbs and reflects slightest values as 1.5868 and 0.013088 joules separately. This shows the wavelength of the radiations is so small compared remaining samples. This fact is evident in Fig. 3.

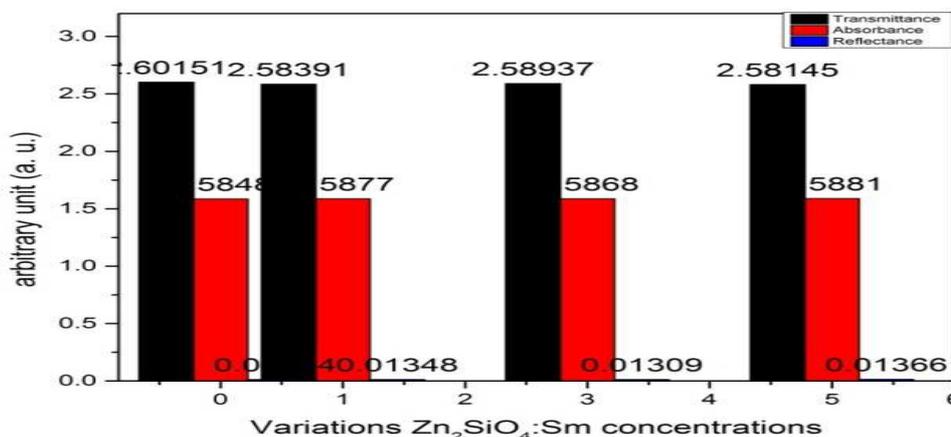


Figure 3: Variation of Sm₂O₃ against Reflection, Transmission and Absorption

The transformation of nonmetallic substance to metallic via the closing of a band gap at high pressure or transition of allotrope is known to be metallization as according to Patra *et al.*, (2005). The incubation of air in porous site allows low temperature to seal of ceramics and glass to metals. The metallization values of $(70-X) \text{Zn}_2\text{XSm}_3\text{SiO}_4$ with $X= 0, 1, 3$ and 5 wt% fall within the range of 0.833478 to 0.837178. The range displays that samarium oxide doped zinc silicate is nonmetallic. Since the values fall below one with highest metallization value at $\text{Zn}_2\text{SiO}_4:\text{Sm}$ 3 wt% and least value at $\text{Zn}_2\text{SiO}_4:\text{Sm}$ 5 wt%. This is similarity with the optical behavior of the energy band crevice of these samples.

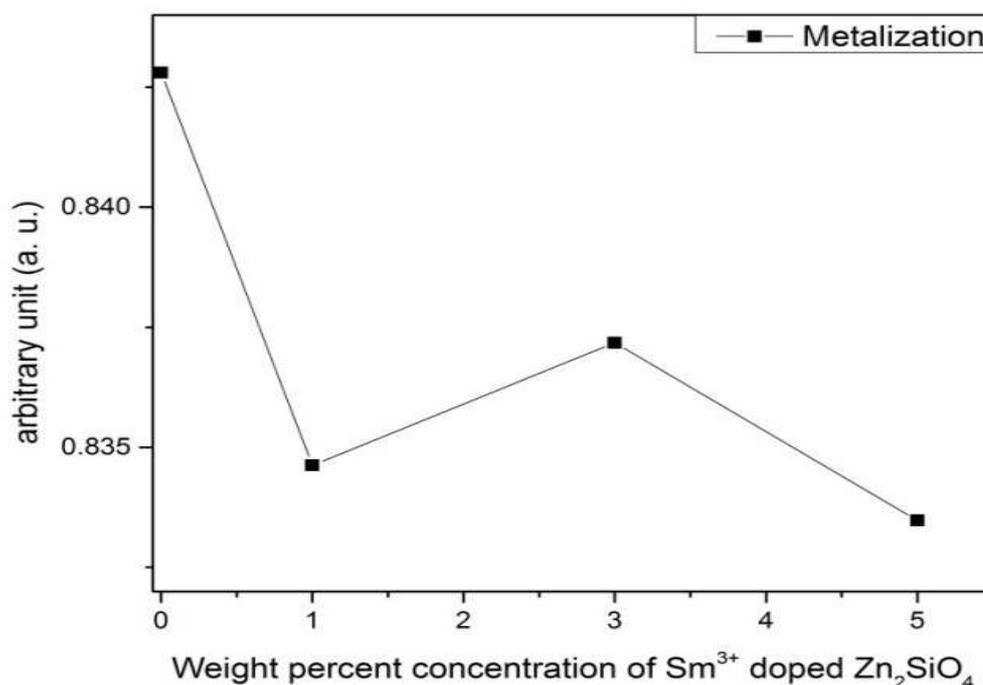


Figure 4: Variation of Sm^{3+} concentration against metallization

Fig.4 is narrating the summary of the entire work, when zinc silicate is not doped the optical bandgap is higher. However, when doped with Sm^{3+} 1wt% it drops to 0.835 eV as the doping increases to Sm^{3+} 3wt% the energy bandgap increases but decreases with Sm^{3+} 5wt% as shown in Fig.4.

CONCLUSION

Conventional melt quenching technique was successfully used to synthesize Sm^{3+} doped Zn_2SiO_4 with different weight concentrations. The molar refraction, polarizability, and metallization of these samples are directly proportional. This is because the refractive index depends on the electron density of ions or polarizability. Furthermore, the ions and

electrons are generated from oxygen in the glass ceramics lattice. Our results may contribute towards the improvement of optical discs.

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