

## Improved absorbance of holmium activated magnesium-zinc-sulfophosphate glass

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### Abstract

Constant efforts are dedicated to overcome the limitations of phosphate based glass system, where sulfophosphate glasses (SPGs) played a key role. Rare earth ions (REIs) doped magnesium zinc SPG (MZSPG) systems are technologically prospective due to their several unique attributes. Construction of integrated light amplifier and solid state laser needs the maximum gain within small component dimensions. Thus, Ho<sup>3+</sup> ions doped SPGs are believed to meet this demand. Ho<sup>3+</sup> ions having sharp optical absorption peaks in the spectral range of 200–900 nm is useful for diversified applications. Conversely, SPGs comprising of oxides of sulphur, phosphorous and at least one other component with SO<sub>4</sub><sup>2-</sup> ions contents lower than PO<sub>4</sub><sup>3-</sup> with low melting temperature makes them a distinctive class of technologically potential disordered system. In this view, modification of Ho<sup>3+</sup> ions absorbance inside SPGs network is challenging. To achieve this goal, following melt-quenching route we prepared a series of Ho<sup>3+</sup>-doped MZSPG system of composition (60-x)P<sub>2</sub>O<sub>5</sub>-(20)ZnSO<sub>4</sub>-(20)MgO-(x)Ho<sub>2</sub>O<sub>3</sub>, where x = 0.0, 0.5, 1.0, 1.5 2.0, and 2.5 mol%. The influence of Ho<sub>2</sub>O<sub>3</sub> concentration on the density, refractive index, and optical absorption properties of the synthesized glass system is examined. The density and refractive index is found to increase with increasing Ho<sub>2</sub>O<sub>3</sub> concentration. The absorption spectra obtained using Shimadzu UV-3101PC spectrometer revealed nine prominent peaks centered at 387, 418, 450, 484, 538, 642, 1148 and 1945 nm. The glass absorbance is enhanced with increasing Ho<sup>3+</sup> contents. Optical band gap energy is found to range from 3.847 to 3.901 eV. The Urbach energy reduced from 0.257 to 0.191 eV with increasing Ho<sup>3+</sup> contents. In-depth investigations on the structural and optical properties of MZSPG system are underway to achieve the milestones set for photonic devices.

**Keywords:** Holmium, absorption, band gap, Urbach energy

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## INTRODUCTION

Unquestionably, REIs doped oxide glass systems are prospective for the applications of sensor, color display, laser, and optical storage (Seshadri et al. 2010). In depth understanding of the optical and structural properties of REIs doped glass is prerequisite for the improvement of optical performance. Absorption and luminescence properties are strongly depend on the glass composition. Phosphate as host glass is promising due to its interesting features such as low melting point, high thermal expansion coefficient, high refractive index and high ultraviolet (UV) transmission (Dousti et al., 2013; Seshadri et al., 2010; Vijayakumar et al., 2015). However, pure phosphate glass possesses low chemical durability with high hygroscopicity that restricts its potential application (Vijayakumar et al. 2015). It is established that the incorporation of metal oxide ions such as Mg<sup>2+</sup> and Zn<sup>2+</sup> improve the structural properties and chemical durability by the formation of P-O-M bond (where M is metal cation). In this situation, glass system becomes stable toward atmospheric hydrolysis or moisture attack (Omran et al., 2015).

In order to improve REIs optical performance, SO<sub>4</sub><sup>2-</sup> ions are added to the glass, which are largely dissolved in the phosphate glass. The existence of weak interaction between SO<sub>4</sub><sup>2-</sup> ions and metaphosphate ions (Ganguli et al., 1999) are thought to be responsible for such improvements. The interaction between the two ions create appropriate

environment for incorporation of REIs (Ahmadi et al., 2016). Consequently, the glass reveals high luminescence efficiencies with minimal non-radiative losses. Trivalent lanthanides are characterized by their luminescence properties in the presence of sharp band emission and relatively long luminescence lifetime (Babu et al., 2015). Among various REIs, Ho<sup>3+</sup> ion is attractive for its several electronic transitions with prominent emission bands in the ultraviolet, visible and infra-red regions (Mahamuda et al., 2013; Malinowski et al., 2004; Venkateswarlu et al., 2015). Moreover, Ho<sup>3+</sup> ion also possesses well separated energy levels that undergo radiative transitions suitable for several up and down conversion emission mediated applications (Babu et al., 2015). Literature survey revealed that the information on Ho<sup>3+</sup> ions doped MZSPG systems are lacking despite their applied interests.

This communication reports the synthesis of Ho<sup>3+</sup> doped MZSPG system using melt-quenching technique and Ho<sup>3+</sup> ions concentration dependent physical (density, molar volume, refractive index, molar refractivity, electronic polarizability, optical band gap and Urbach energy) and absorption properties at room temperature. Results are analyzed, compared and discussed.

## EXPERIMENTAL PROCEDURES

Series of MZSPG systems were prepared via melt-quenching technique with different Ho<sub>2</sub>O<sub>3</sub> concentration. Analytical grade

chemical reagents of P<sub>2</sub>O<sub>5</sub>, ZnSO<sub>4</sub>, MgO and Ho<sub>2</sub>O<sub>3</sub> (Sigma Aldrich, 99% purity) in powder (as raw materials) form were taken as glass constituents. A batch of homogeneously ground mixture of 22 g were placed in an alumina crucible and then preheated for 30 minutes before being melted in an electrical furnace at 1100°C for 1.5 hour. The mixture is then annealed at 300°C for 3 hour and gradually cooled down to room temperature. The frozen solid was cut and polished for optical measurement. Table 1 enlists the compositional designations (MZSPGHx) of the prepared glass system for varying Ho<sub>2</sub>O<sub>3</sub> contents of x = 0.0, 0.5, 1.0, 1.5 2.0, and 2.5 mol%.

The glass density was determined using Archimedes method with toluene as immersion liquid. The glass density ( $\rho$ ) was calculated via:

$$\rho = \frac{W_a}{W_a - W_l}(\rho_l - \rho_a) \tag{1}$$

where  $W_a$  and  $W_l$  are the weights of the sample in air and in toluene having density  $\rho_l$ , and  $\rho_a$  is the air density.

The molar volume ( $V_m$ ) in terms of molecular weight yields:

$$V_M = \frac{M}{\rho} \tag{2}$$

The value of refractive glass index ( $n$ ) in terms of optical band gap ( $E_g$ ) was evaluated using (Mahraz et al., 2014):

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{\frac{E_g}{20}} \tag{3}$$

The molar refractivity ( $R_m$ ) and electronic polarizability ( $\chi$ ) was calculated from (Zhao et al., 2007):

$$R_m = \left( \frac{n^2 - 1}{n^2 + 2} \right) V_M \tag{4}$$

$$\chi = \left( \frac{3}{4\pi N} \right) R_m \tag{5}$$

where  $N$  is the Avogadro's number.

The room temperature UV-Vis-IR absorption spectra of all prepared samples were recorded using Shimadzu UV-3101PC

spectrometer in the wavelength range of 300–1000 nm with a resolution of  $\pm 1$  nm. The UV edge data of the absorption spectrum was used to evaluate the optical transition and band gap energy. Davis and Mott (Davis and Mott, 1970) formula was exploited to evaluate the optical band gap for the direct and indirect allowed transitions. The optical absorption coefficient,  $\alpha(\nu)$  was calculated via (Mahraz et al., 2014):

$$\alpha(\nu) = \frac{2.303A}{d} \tag{6}$$

where  $A$  is the absorption intensity and  $d$  is the sample thickness.

Following standard procedure (Davis and Mott 1970), Tauc plots of all samples were generated to estimate the value of  $E_g$  via:

$$\alpha(\nu) = \frac{B(h\nu - E_g)^{1/r}}{h\nu} \tag{7}$$

where  $B$  is a constant called band tailing parameter,  $n$  is the index number depending on the type of transition and  $E_g$  values.

Tauc plot of  $(\alpha h\nu)^{1/r}$  versus photon energy ( $h\nu$ ) were drawn by substituting the value of  $r = 1/2$  in equation (7) for direct allowed transition and  $r = 2$  for indirect allowed transition. Values of direct and indirect  $E_g$  were obtained by extrapolating the linear part of  $(\alpha h\nu)^2 = 0$  and  $(\alpha h\nu)^{1/2}$  curve, respectively

Generally, the band tailing (a measure of defect states or materials disorder) in the forbidden optical energy band gap that exist in the glass and amorphous materials are characterized in terms of Urbach energy (Jlassi et al., 2016). The Urbach energy ( $\Delta E$ ) of all glass samples was estimated through (Urbach, 1953):

$$\alpha(\nu) = C \exp\left(\frac{h\nu}{\Delta E}\right) \tag{8}$$

where  $C$  is a constant.

## RESULTS AND DISCUSSION

### Physical Properties

Table 1 enlists the values of the density ( $\rho$ ), molar volume ( $V_m$ ), refractive index ( $n$ ), molar refractivity ( $R_m$ ) and electronic polarizability ( $\chi$ ) of all the synthesized glass samples.

**Table 1** Physical properties of the prepared glass systems.

	MZSPH 0.0	MZSPH 0.5	MZSPH 1.0	MZSPH 1.5	MZSPH 2.0	MZSPH 2.5
$\rho$ (g/cm <sup>3</sup> )	2.633	2.675	2.703	2.725	2.754	2.777
$V_m$ (cm <sup>3</sup> /mol)	57.259	56.793	56.638	56.621	56.445	56.396
$n$	2.200	2.197	2.196	2.194	2.190	2.189
$R_m$ (cm <sup>3</sup> )	32.147	31.843	31.736	31.698	31.535	31.489
$\chi$ ( $\times 10^{-23}$ cm <sup>3</sup> )	1.274	1.262	1.258	1.257	1.250	1.248

Figure 1 shows the Ho<sub>2</sub>O<sub>3</sub> concentration dependent variation in the glass density and molar volume. Density being an effective parameter to comprehend the changes in the structure and coordination of glasses (Wu et al., 2016) was evaluated. Glass density was increased with increasing Ho<sub>2</sub>O<sub>3</sub> contents which was attributed to the replacement of phosphorous having low molecular weight (141.94 g/mol) by higher molecular weight holmium (377.86 g/mol). Moreover, the larger ionic radii of Ho<sup>3+</sup> (1.015 Å) that replaced the phosphate (0.17 Å) played a significant role (Shannon, 1976) to make the the glass structure more

compact and hence dense. Conversely, the molar volume was reduced from 57.259 to 56.396 cm<sup>3</sup>/mol with the addition of Ho<sub>2</sub>O<sub>3</sub> which was ascribed to the shrinkage of bond length and inter-atomic distance in the glass network. The glass structure being rich with bridging oxygen (BO) in turn enhanced the network rigidity (Azmi et al., 2015). The declining molar volume is often credited to the improved compactness of the glass network structure (Mhareb et al., 2016).

According to Jlassi (2016), glasses with higher density is most likely to have larger value of refractive index because more ionic

dipoles can be activated in the presence of electric field. However, the refractive index of the current glass system was decreased from 2.200 to 2.189 with increasing Ho<sub>2</sub>O<sub>3</sub> contents from 0-2.5 mol%. This reduction in the refractive index values was attributed to the formation of BO because BO are weakly ionic in nature with higher bond energies than non-bridging oxygen (NBO). This resulted a lowering in the electronic polarizability of the studied glass system (El-Mallawany et al., 2013; Singh & Singh, 2014).

The molar refractivity and electronic polarizability was decreased from 32.147 to 31.489 cm<sup>3</sup> and 1.274×10<sup>-23</sup> to 1.248×10<sup>-23</sup> cm<sup>3</sup>, respectively with increasing Ho<sub>2</sub>O<sub>3</sub> concentration. Molar refractivity being a measure of the bonding condition in the glass provided the information about the total drop of the contribution of cationic refraction and oxygen ionic refraction (Mahamuda et al., 2013). The incorporation of Ho<sub>2</sub>O<sub>3</sub> indeed led to the structural polymerization and increased the cross-linking in the glass system. Furthermore, low molar refractivity suggested the highly solubility of Ho<sub>2</sub>O<sub>3</sub> in the MZSPG system that is required for high lasing transition probabilities, enhanced absorption and stimulated emission cross-section. Electronic polarization together with optical nonlinearity emerges whenever an intense light beam is incident upon a material (Zhao et al., 2007). In the present case, the observed considerable reduction in the electronic polarizability with increasing Ho<sub>2</sub>O<sub>3</sub> contents suggested that the cationic charges (Ho<sup>3+</sup>) seem to hold the cationic electrons (Honma et al., 2000). Moreover, the usual condition where the polarization is directly proportional to field strength is also depends on glass composition (Yusoff & Sahar, 2015). In this regard Ho<sup>3+</sup> ions probably participated in the glass structure formation, leading towards lowering of the electronic polarizability.

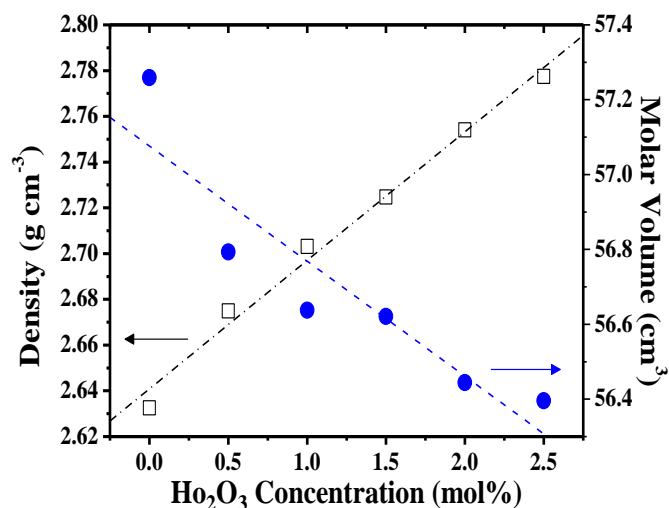


Fig. 1 Ho<sup>3+</sup> ions content dependent variation in the glass density and molar volume.

**Absorption Properties**

Figure 2 displays the room temperature UV-Vis absorption spectra of as-synthesized Ho<sup>3+</sup> doped MZSPG system. It was comprised of nine peaks assigned to the transitions of <sup>5</sup>I<sub>8</sub> → <sup>3</sup>H<sub>6</sub> (362 nm), <sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>4</sub> (387 nm), <sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>5</sub> (418 nm), <sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>6</sub> (450 nm), <sup>5</sup>I<sub>8</sub> → <sup>5</sup>F<sub>3</sub> (484 nm), <sup>5</sup>I<sub>8</sub> → <sup>5</sup>F<sub>4</sub> + <sup>5</sup>S<sub>2</sub> (538 nm), <sup>5</sup>I<sub>8</sub> → <sup>5</sup>F<sub>5</sub> (642 nm), <sup>5</sup>I<sub>8</sub> → <sup>5</sup>I<sub>6</sub> (1148 nm) and <sup>5</sup>I<sub>8</sub> → <sup>5</sup>I<sub>7</sub> (1945 nm). Occurrences of these absorption bands were attributed to the 4f-4f electronic transitions of Ho<sup>3+</sup> ions from the ground state (<sup>5</sup>I<sub>8</sub>) to different excited states as indicated. The measured peak positions are consistent with the earlier studies on Ho<sup>3+</sup> doped barium phosphate (Satyanarayana et al., 2010), fluoro-phosphate (Babu et al. 2015), lead-zinc-borate (Hussain et al., 2006) and tellurite (Seshadri et al., 2014) glass systems. The identification and assignment of the energy levels are in accordance to the existing report (Carnall et al., 1968). Furthermore, the absorption peak appeared sharper and more intense as the Ho<sub>2</sub>O<sub>3</sub> concentration was increased. Transition of <sup>5</sup>I<sub>8</sub> → <sup>3</sup>H<sub>6</sub> and <sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>6</sub> was identified as hypersensitive because they obeyed the selection rules of ΔJ≤2, ΔL≤2 and ΔS=0 (Prasad et al., 2003; Seshadri et al., 2014). The pale yellow (~550 nm) color absorption of

Ho<sup>3+</sup> doped glass was overmasked by the strong absorption in the blue violet region (450 nm) (Rai & Fanai 2016).

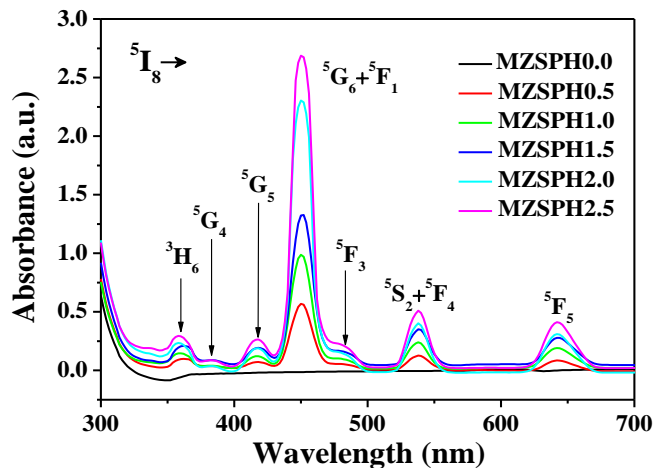


Fig. 2 Absorption spectra of Ho<sup>3+</sup>-doped MZSPH system.

Further in-depth analysis of the absorption spectra provides useful information about the glass structure and ligand bondings. Full width half maximum (FWHM) of the most intense absorption peak (<sup>5</sup>I<sub>8</sub> → <sup>5</sup>G<sub>6</sub> at 450 nm) was calculated. Figure 3 illustrates variation of FWHM for the specified peak as a function of Ho<sub>2</sub>O<sub>3</sub> contents. The spectral line width of optical transition in REIs doped materials are governed by two major factors. First, the temperature dependent lattice vibration which contributes to the homogeneous line broadening and is common for both amorphous and crystalline materials. Second is the inhomogeneous broadening which is more prominent in non-crystalline material. Inhomogeneous broadening increases the spectral line width and is caused by the site-to-site variation of the ligand field surrounding of REIs (Lee et al., 2008; Mahamuda et al., 2013).

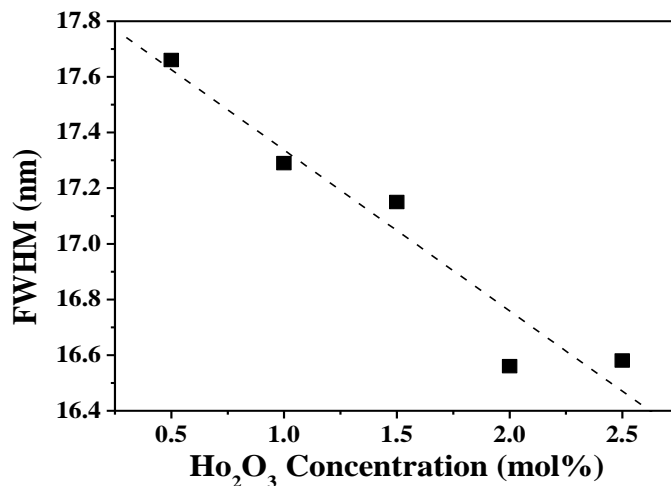


Fig. 3 Ho<sub>2</sub>O<sub>3</sub> concentration dependent variation of FWHM for the intense peak appeared at 450 nm.

The observed decrease in the FWHM value from 17.66 to 16.58 nm with the increase of Ho<sub>2</sub>O<sub>3</sub> concentration from 0 to 2.5 mol% was attributed to the narrowing of the inhomogeneous broadening (Lee et al., 2008). Actually, the incorporation of Ho<sub>2</sub>O<sub>3</sub> might have suppressed the site-to-site interaction in the glass system where the vibronic transitions remains unresolved and hence merged into a broad absorption feature (Alivisatos et al., 1988). Hence, the narrower absorption feature was correlated to the highly well-defined vibronic transitions. The increment of Ho<sub>2</sub>O<sub>3</sub> concentration in the glass had shifted the ground and excited electronic potential surface in the vibrational coordinate and led to enhanced line broadening. Table 3 presents the calculated optical band gap and Urbach energy of the synthesized MZSPG system.

**Table 3:** Optical band gap and Urbach energy of Ho<sup>3+</sup>-doped MZSPG system

	MZSPH 0.0	MZSPH 0.5	MZSPH 1.0	MZSPH 1.5	MZSPH 2.0	MZSPH 2.5
E <sub>g</sub> (eV)	3.847	3.860	3.866	3.875	3.895	3.901
ΔE (eV)	0.257	0.221	0.217	0.271	0.197	0.191

Increase in the optical band gap energy from 3.846 – 3.901 eV with increasing Ho<sub>2</sub>O<sub>3</sub> concentration from 0 to 2.5 mol% was attributed to the generation of more BO via the formation of P-O-Ho-O-P chains. The chains linked the phosphate tetrahedral within the glass matrix and enhanced the bond strength. Therefore, BO could bound an electron more tightly than NBO (Khor et al., 2012). In this situation, higher energy was required to excite the electron thereby widening of optical band gap energy of the glass system was observed with increasing Ho<sub>2</sub>O<sub>3</sub> concentration. Conversely, the achievement of the low Urbach energy (0.257 to 0.191 eV) of the present glass system with increasing REIs contents indicated the existence of less number of defects/disorder and high compactness of the glass network (Nurhafizah et al., 2016; Yusoff et al., 2015). Reduction of the Urbach energy can be interpreted in terms the generation of local long range order structure in the glass in which increasing concentration of Ho<sub>2</sub>O<sub>3</sub> led to the formation of large number of BO and hence enhanced orderness in the structure. This result complemented the enhancement in the optical band gap wherein according to Davis and Mott prediction the presence of high density of localized state in the band structure is responsible for the narrowing of the optical energy band gap (Davis and Mott 1970; Khor et al. 2012).

## CONCLUSION

We determined the physical and absorbance characteristics of MZSPH as a function of Ho<sup>3+</sup> dopding contents. Glass system was prepared via conventional melt-quenching method. Density, molar volume and refractive index were found to vary in the range of 2.633 to 2.777 g/cm<sup>3</sup>, 57.259 to 56.396 cm<sup>3</sup>/mol and 2.200 to 2.189, respectively. Both molar refractivity and electronic polarizability were reduced with increasing Ho<sub>2</sub>O<sub>3</sub> contents. The optical band gap energy (3.847 to 3.901 eV) as well as the Urbach energy (0.257 to 0.191 eV) was strongly influenced by the variation of Eu<sub>2</sub>O<sub>3</sub> concentration. The formation of more number of BO was responsible for the alteration of glass network structures. The proposed glass compositions be potential for up/down-converted lasing system.

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