Investigation on Luminescence Properties of $P_2O_5$-CaO-Na$_2$O-K$_2$O: Tm$_2$O$_3$ Glasses

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Abstract: The research on rare earth (RE) ions doped phosphate glass ceramics has gained momentum due to their prominent applications such as lasers, sensors and optical amplifiers. Phosphate glasses are being considered as suitable hosts for rare earth ions like Tm$^{3+}$ ions that give photoluminescence in the IR region. We have synthesized glasses of the particular composition (50-x) $P_2O_5$-27 CaO-20 Na$_2$O-3 K$_2$O: x Tm$_2$O$_3$ (0.5 ≤ x ≤ 1.5) using conventional melt quenching. Later samples were characterized by X-ray diffraction (XRD) and SEM techniques. Optical absorption spectra of samples recorded at room temperature in visible and NIR regions. The luminescence properties were investigated by excitation and emission spectra. With increase in the concentration of Tm$_2$O$_3$, the intensity of the peaks found to be slightly increased. The infrared radiation about 1800 nm has been observed in all samples when pumped at 686 nm.

Keywords: Phosphate glass, Tm$^{3+}$ ions, absorption, fluorescence.

1. Introduction

Glasses playing a very crucial role in the progress of society by finding the applications in various fields viz., lasers, telecommunication, optical fibers, architecture, medicine, automation etc. Glass materials are very cheap, easy to prepare over a wide range of compositions. They have good mechanical, electrical and thermal properties, high chemical durability and low coefficient of thermal expansion. These materials act as gain media for ultra-broadband optical fibre amplifiers, tuneable lasers and ultra-short pulse lasers. Now a days, modern optoelectronics has chosen glasses doped with laser acting materials as key elements to build all optical network and also for the constructions of fibre lasers. Generally, phosphate glasses are being considered as suitable hosts for rare earth ions like Tm$^{3+}$ ions that give photoluminescence in the IR region. These glasses are being used as potential candidates for many applications such as solid state electrolytes, sealing materials and medical use due to their superior physical properties viz., low melting temperature, high thermal expansion coefficient, low softening temperature, low glass transition temperature and high ultraviolet transmission compared with conventional borosilicate glasses.

Lot of research being carried out on trivalent rare earth ions viz., Er$^{3+}$ and Tm$^{3+}$doped phosphate, silicate, germinate, bismuth and tellurite glasses that have been developed for infrared active optical devices [1-3]. Recently, research focus on rare earth doped glasses is not limited to infrared optical devices but there is a growing interest in visible optical devices. Tm$^{3+}$ ions got the capability of infrared emission around 2 μm and up-conversion of infrared to visible light [2, 3, 4-7]. The present work is aimed to investigate the optical features of Tm$^{3+}$ions incorporated into phosphate based glasses.

2. Experimental Methods

For the present study, a particular glass composition (50-x) $P_2O_5$-27 CaO-20 Na$_2$O-3 K$_2$O: x Tm$_2$O$_3$ (0.5 ≤ x ≤ 2.0 mol %) is chosen. The details of the composition and corresponding nomenclature are given below.

PTM$^{15}$: 49.5 $P_2O_5$: 27 CaO-20 Na$_2$O- 3 K$_2$O: 0.5 Tm$_2$O$_3$
PTM$^{15}$: 49.0 $P_2O_5$: 27 CaO-20 Na$_2$O- 3 K$_2$O: 1.0 Tm$_2$O$_3$
PTM$^{15}$: 48.5 $P_2O_5$: 27 CaO-20 Na$_2$O- 3 K$_2$O: 1.5 Tm$_2$O$_3$
Phosphorous pentoxide ($P_2O_5$) was added in the form of
ammonium dihydrogen orthophosphate (NH₄H₂PO₄) whereas sodium, potassium, and calcium were introduced in the form of their respective anhydrous carbonates. But Tm₂O₃ was added directly as available. All the raw materials of chemicals were of analytical grade and were used without further purification. All reagents were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range of 1300 to 1500 °C in a PID temperature controlled furnace for about half an hour. The resultant melts were rotated several times 30 min apart to achieve homogeneity. The homogeneous resultant bubble free melts were cast into preheated stainless steel moulds of the required dimensions. The prepared samples were directly annealed. After 1 h, the muffle furnace was left to cool to room temperature at a rate of 30 °C/h. The samples prepared were ground and optical polished to the dimensions of 2 cm × 2 cm × 0.2 cm. The amorphous nature of samples was identified using Rigaku D/Max ULTIMA III X-ray diffractometer with CuKα radiation, radiation. Scanning electron microscopy studies were also carried out on these samples to observe the crystallinity using HITACHI S-3400N Scanning Electron Microscope. The density d of the bulk samples was determined to an accuracy of (± 0.0001) by the standard principle of Archimedes’ using o-xylene (99.99% pure) as the buoyant liquid. Ultraviolet, visible and NIR absorption spectra were recorded for perfectly polished glass samples with a spectral resolution of 0.1 at room temperature in the spectral wavelength range covering 300–1100 nm using JASCO Model V-670 UV–vis-NIR spectrophotometer. The luminescence spectra of the glass samples were recorded at room temperature on a Photon Technology International (PTI) fluorescence spectrophotometer.

3. Results & Discussion

3.1 Physical Parameters

First and foremost we calculated physical parameters viz., such as Tm³⁺ ion concentration Nᵢ, mean Tm³⁺ ion separation rᵢ, polaron radius rᵢ using experimental density values and same shown in Table 1.

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>Conc. of Tm³⁺ ions Nᵢ(10²¹/cm³)</th>
<th>Inter ionic distance of Tm³⁺ ions rᵢ(Aᵢ)</th>
<th>Polaron radius rᵢ(Aᵢ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTM₅</td>
<td>12.42</td>
<td>0.43</td>
<td>0.17</td>
</tr>
<tr>
<td>PTM₁₀</td>
<td>25.84</td>
<td>0.33</td>
<td>0.14</td>
</tr>
<tr>
<td>PTM₁₅</td>
<td>40.25</td>
<td>0.29</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Tm₂O₃ glass samples.

A slight increase in density ‘d’ with increase in Tm₂O₃ content has been observed that can be associated to the replacement of P₂O₅ (molecular weight 283.8 g/mol) with Tm₂O₃ (molecular weight 385.86 g/mol). The increase in density behaviour very indicates that the addition of Tm₂O₃ extended the structure of loose glass network. In general, the degrees of structural compactness, the modification of the geometrical configuration of the glassy network, change in the coordination of the glass forming ions and the fluctuations in the dimensions of the interstitial holes are some of the factors that influence the density of the glass material [8].

3.2 XRD Patterns

Fig. 1 shows X-ray diffraction spectra of P₂O₅-CaO-Na₂O-K₂O: Tm₂O₃ glasses. The spectra clearly indicated the absence of peaks which confirm prepared glasses were of amorphous. It is also an indication for the absence of sign of crystallinity that might be possible during the heating procedure.

![Figure 1: XRD patterns of P₂O₅-CaO-Na₂O-K₂O: Tm₂O₃ glasses.](image)

3.3 SEM Pictures

Scanning electron microscopy (SEM) pictures for some of the P₂O₅-CaO-Na₂O-K₂O: Tm₂O₃ glasses are presented in Fig. 2. These pictures clearly indicate that prepared glasses do not contain any crystal grains that confirming amorphous nature to them. These pictures support the XRD spectra results.

![Figure 2: SEM pictures for some of P₂O₅-CaO-Na₂O-K₂O: Tm₂O₃ glasses.](image)

3.4 Optical Absorption Spectra

Fig. 3 represents the optical absorption spectra of P₂O₅-CaO-Na₂O-K₂O: Tm₂O₃ glasses recorded at room temperature in the wavelength range 300–2100 nm. The spectra have exhibited nine (9) absorption bands: ³H₆ (the ground state of
Tm$^{3+}$ ion) $\rightarrow$ $^1$G$_4$, $^3$F$_5$, $^3$F$_4$, $^3$H$_6$ and $^3$H$_4$. Among these, transitions $^3$H$_6$ $\rightarrow$ $^1$G$_4$ lies in the blue region where as $^3$H$_6$ $\rightarrow$ $^3$F$_2$, $^3$F$_3$, $^3$F$_4$ are lying in orange and red spectral regions. Another two transitions $^3$H$_6$ $\rightarrow$ $^3$H$_5$, $^3$H$_4$ are found to be in the infrared region. From the spectra, it is clear that the increasing concentration of thulium ions in the glass matrix does not alter the spectral positions of the absorption bands [3].

Fig. 5 represents the emission spectrum of P$_2$O$_5$-CaO-Na$_2$O-K$_2$O: 0.5 Tm$_2$O$_3$ glass excited with 460 nm ($^3$H$_6$ $\rightarrow$ $^1$G$_4$) have exhibited. Figure 3: Optical absorption spectra of P$_2$O$_5$-CaO-Na$_2$O-K$_2$O: Tm$_2$O$_3$ glasses (all the transitions from ground state $^3$H$_6$).

When pumped by 686 nm, two well resolved bands viz., $^3$F$_4$ $\rightarrow$ $^3$H$_4$, $^3$H$_4$ $\rightarrow$ $^3$H$_6$ in the NIR region have been obtained (Fig. 5). The emission spectra of remaining samples also produce the same with minor intensity changes.
4. Conclusion

P$_2$O$_5$-CaO-Na$_2$O-K$_2$O: Tm$_2$O$_3$ glasses have been synthesized by melt quenching and further samples were characterized by XRD, SEM, and spectral Studies viz., optical absorption and fluorescence. XRD and SEM studies indicated that prepared glasses have pure amorphous structure. The optical absorption spectra have exhibited nine (09) absorption bands all from $^3$H$_6$. With increase of Tm$_2$O$_3$, no significant increase/shift in peaks has been observed. Emission spectra also recorded with two excitation wavelengths corresponding to visible and NIR regions. The infrared radiation is found in all samples at about 1800 nm that would be more useful in modern optoelectronic devices.

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