

Investigation on Luminescence Properties of P₂O₅-CaO-Na₂O-K₂O: Tm₂O₃ Glasses

T.Satyanarayana¹, P.Krishna Kanth², G. Nagarjuna³, B. Nagamani⁴, and N. Srinivasa Rao⁵

¹Department of Electronics & Instrumentation Engg., Lakireddy Bali Reddy College of Engineering (Autonomous), Mylavaram-521230, Krishna, A.P., India
satyamphysics@gmail.com

²Department of Mechanical Engg., Lakireddy Bali Reddy College of Engineering (Autonomous), Mylavaram-521230, Krishna, A.P., India
pkpamarthi@gmail.com

³Department of Chemistry, S.R.R. & C.V.R. Govt. College, Vijayawada -520004, Krishna, A.P., India
gnrgjcn@gmail.com

⁴Department of Physics, S.R.R. & C.V.R. Govt. College, Vijayawada -520004, Krishna, A.P., India
nagamani1411@gmail.com

⁵Department of Physics, Dharma Appa Rao College, Nuzvid -521201, Krishna, A.P., India
nsrao71@rediffmail.com

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 Tm³⁺ ions that give photoluminescence in the IR region. We have synthesized glasses of the particular composition (50-x) P₂O₅-27 CaO-20 Na₂O-3 K₂O: x Tm₂O₃ (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 Tm₂O₃, 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, Tm³⁺ 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 Tm³⁺ 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., Er³⁺ and Tm³⁺ doped phosphate, silicate, germanate, 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. Tm³⁺ 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 Tm³⁺ ions incorporated into phosphate based glasses.

2. Experimental Methods

For the present study, a particular glass composition (50-x) P₂O₅-27 CaO-20 Na₂O-3 K₂O: x Tm₂O₃ (0.5 ≤ x ≤ 2.0 mol %) is chosen. The details of the composition and corresponding nomenclature are given below.

PTM₅: 49.5 P₂O₅-27 CaO-20 Na₂O- 3 K₂O: 0.5 Tm₂O₃

PTM₁₀: 49.0 P₂O₅-27 CaO-20 Na₂O- 3 K₂O: 1.0 Tm₂O₃

PTM₁₅: 48.5 P₂O₅-27 CaO-20 Na₂O- 3 K₂O: 1.5 Tm₂O₃

Phosphorous pentoxide (P₂O₅) was added in the form of

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Department of Physics, Government College (A), Rajahmundry, Andhra Pradesh, India

ammonium dihydrogen orthophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) whereas sodium, potassium, and calcium were introduced in the form of their respective anhydrous carbonates. But Tm_2O_3 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 transferred to a regulated muffle furnace at 480 °C for annealing. After 1 h, the muffle furnace was left to cool to room temperature at a rate of 30 °C $^{-1}$. 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 CuK_α 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 Tm^{3+} ion concentration N_i , mean Tm^{3+} ion separation r_i , polaron radius r_p using experimental density values and same shown in Table 1.

Table 1 Physical parameters of P_2O_5 - CaO- Na_2O - K_2O :

Glass sample	Conc. of Tm^{3+} ions N_i ($10^{21}/\text{cm}^3$)	Inter ionic distance of Tm^{3+} ions r_i (Å°)	Polaron radius r_p (Å°)
PTM ₅	12.42	0.43	0.17
PTM ₁₀	25.84	0.33	0.14
PTM ₁₅	40.25	0.29	0.11

Tm_2O_3 glass samples.

A slight increase in density 'd' with increase in Tm_2O_3 content has been observed that can be associated to the replacement of P_2O_5 (molecular weight 283.8 g/mol) with

Tm_2O_3 (molecular weight 385.86 g/mol). The increase in density behaviour very indicates that the addition of Tm_2O_3 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 the 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 P_2O_5 - CaO- Na_2O - K_2O : Tm_2O_3 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.

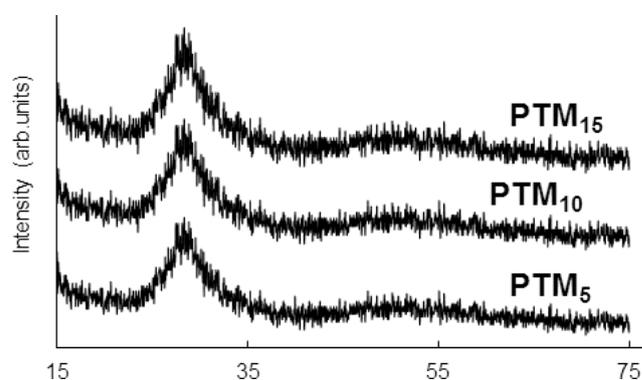


Figure 1: XRD patterns of P_2O_5 - CaO- Na_2O - K_2O : Tm_2O_3 glasses.

3.3 SEM Pictures

Scanning electron microscopy (SEM) pictures for some of the P_2O_5 -CaO- Na_2O - K_2O : Tm_2O_3 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.

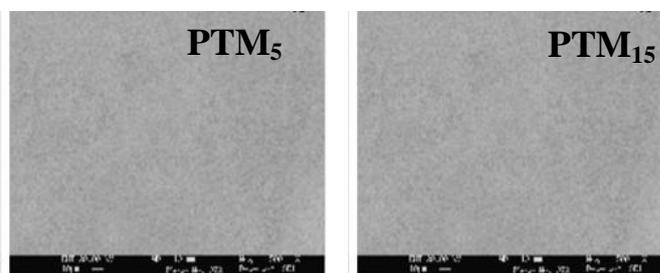


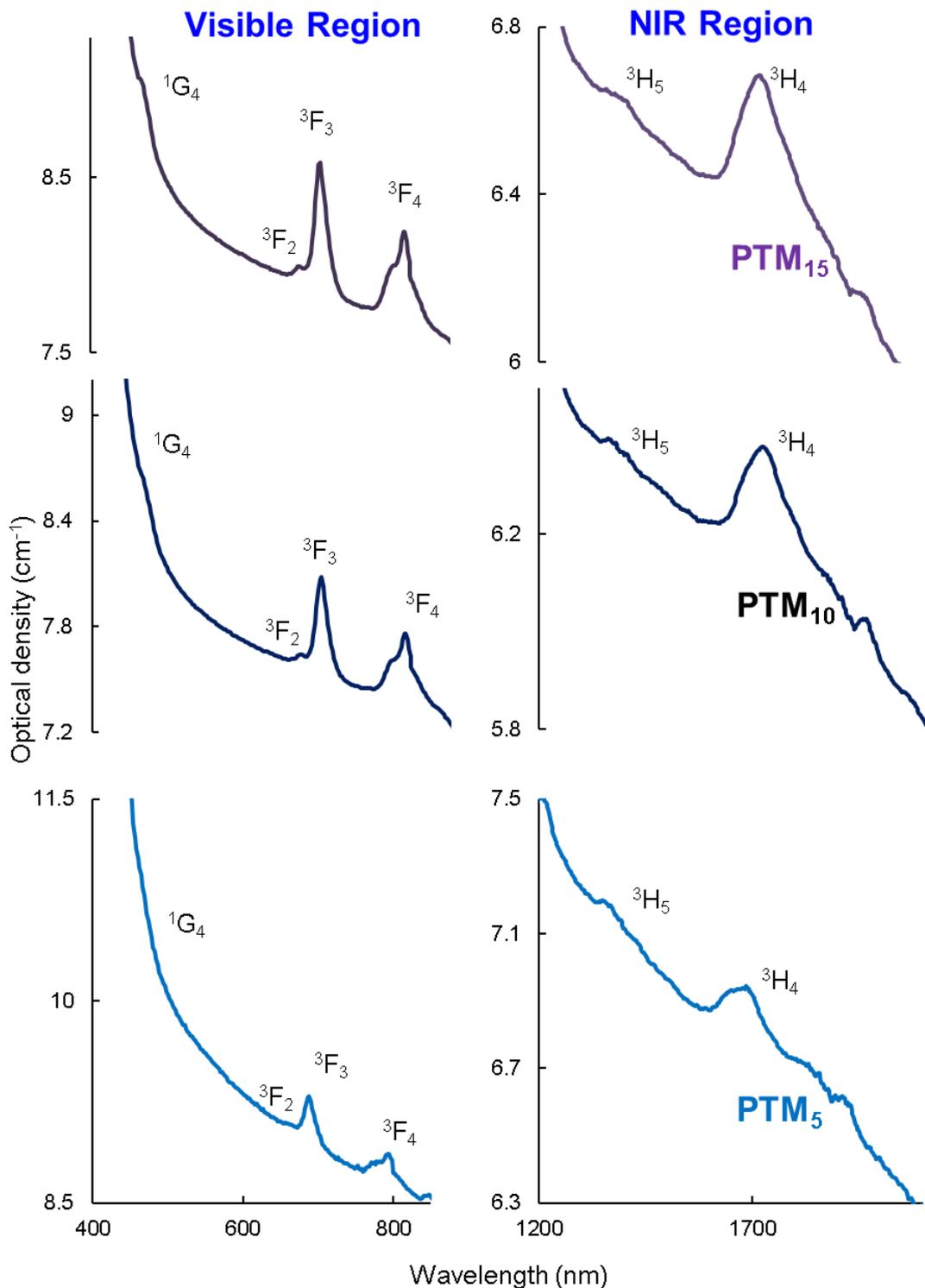
Figure 2: SEM pictures for some of P_2O_5 -CaO- Na_2O - K_2O : Tm_2O_3 glasses.

3.4 Optical Absorption Spectra

Fig. 3 represents the optical absorption spectra of P_2O_5 -CaO- Na_2O - K_2O : Tm_2O_3 glasses recorded at room temperature in the wavelength range 300-2100 nm. The spectra have exhibited nine (09) absorption bands: $^3\text{H}_6$ (the ground state of

Tm³⁺ ion) → ¹G₄, ³F₂, ³F₃, ³F₄, ³H₅ and ³H₄. Among these, transitions ³H₆ → ¹G₄ lies in the blue region where as ³H₆ → ³F₂, ³F₃, ³F₄ are lying in orange and red spectral regions. Another two transitions ³H₆ → ³H₅, ³H₄ 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 P₂O₅-CaO-Na₂O-K₂O: 0.5 Tm₂O₃ glass excited with 460 nm (³H₆ → ¹G₄) have exhibited ³H₅ → ³H₄ and ¹G₄ → ³H₆. When the concentration of Tm³⁺ ions in the glass matrix is increased from 5 to 15 mol%, the intensity of the ³H₅ → ³H₄ and ¹G₄ → ³H₆ transitions in the NIR region have been obtained (Fig. 5). The emission spectra of remaining samples also produce the same with minor intensity changes.



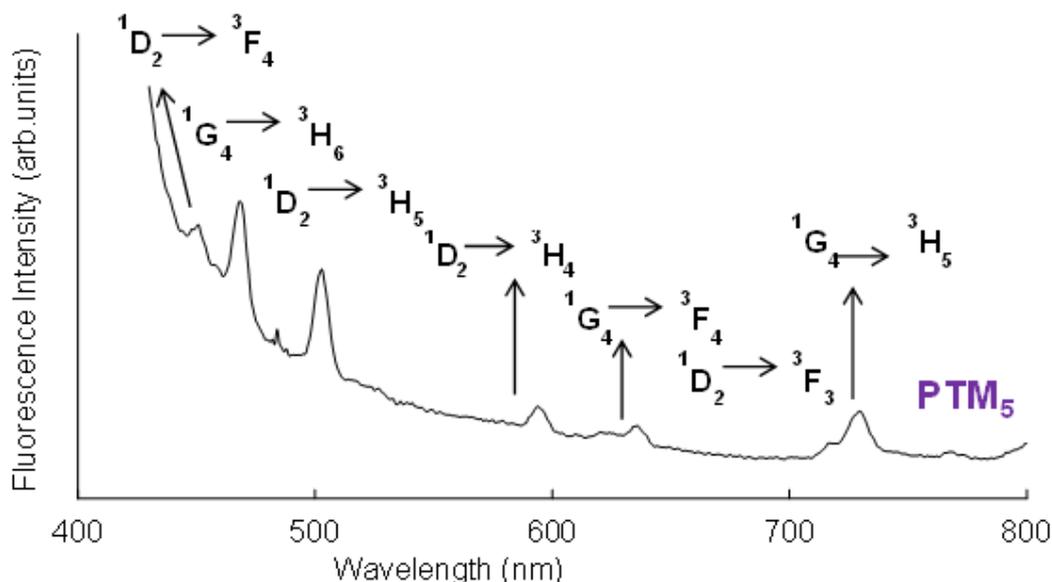


Figure 4: Emission spectra for P_2O_5 -CaO- Na_2O - K_2O : $0.5Tm_2O_3$ glass ($\lambda_{exc} = 460$ nm).

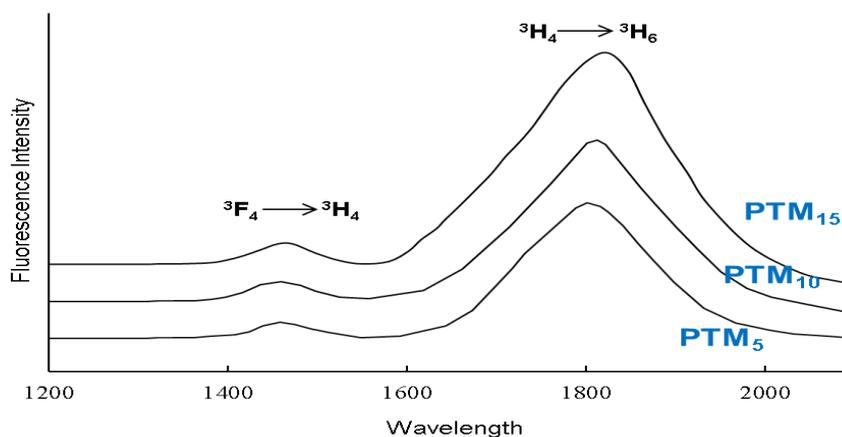


Figure 5: Emission spectra of P_2O_5 -CaO- Na_2O - K_2O : Tm_2O_3 glasses in NIR region ($\lambda_{exc} = 686$ nm).

4. Conclusion

P_2O_5 -CaO- Na_2O - K_2O : Tm_2O_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 3H_6 . With increase of Tm_2O_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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