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Sm^{3+} Incorporation Effects On The Microstructure And Optical Performance Of Phosphate Glasses

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Abstract: A series of Sm^{3+}-doped phosphate glasses were synthesized using the melt-quenching technique. The base composition of the glass system was (mol%): $50P_2O_5–5Bi_2O_3–25Li_2O–20Na_2O$, where 1 mol% of Bi_2O_3 was replaced by Sm_2O_3. Although the host matrix melts near 650 °C, all samples were melted at 900 °C to reduce viscosity and eliminate entrapped bubbles. The resulting glasses exhibited excellent optical transparency and structural homogeneity, enabling efficient visible and near-infrared (NIR) luminescence. Structural and optical investigations confirmed the amorphous nature of the samples, strong Sm^{3+} emission in the orange-red region, and potential for use in photonic device applications.

***Index Terms* -** phosphate glass; Sm^{3+} doping; Structural characterization; Absorption; Photoluminescence;

I. Introduction

Phosphate glasses have attracted significant attention for optical and photonic applications due to their wide transmission range, high rare-earth solubility, and relatively low melting temperature [1, 2]. These features make them excellent host matrices for rare-earth ions such as Sm^{3+}, Eu^{3+}, and Nd^{3+}, which exhibit sharp 4f–4f transitions resulting in distinctive emission colors [3–5].

Among these ions, samarium (Sm^{3+}) is particularly important because of its intense orange-red emission, primarily arising from the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition, which makes it highly suitable for display, lighting, and optical marking technologies [6–8].

The inclusion of Bi_2O_3 in phosphate glass matrices significantly improves the refractive index, optical basicity, and radiative transition probabilities [9]. It also enhances glass stability and reduces non-radiative losses by lowering phonon energy, leading to increased luminescence efficiency [10]. However, achieving optical homogeneity and preventing rare-earth clustering remains a challenge when working at moderate melting temperatures [11].

In this study, Sm^{3+}-doped phosphate glasses with the base composition $50P_2O_5–5Bi_2O_3–25Li_2O–20Na_2O$ were prepared using the melt-quenching method. The structural, absorption, and luminescence characteristics were examined using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, UV–Vis absorption, and photoluminescence (PL) spectroscopy. The main objective is to understand how Sm^{3+} ions influence the phosphate network structure and optical performance of the glass.

II. EXPERIMENTAL METHODS

Glass samples were prepared using high-purity reagents: $NH_4H_2PO_4$, Bi_2O_3, Li_2CO_3, Na_2CO_3, and Sm_2O_3. The raw materials were weighed stoichiometrically, thoroughly mixed, and preheated at 350 °C for 1 hour to remove volatile components. The mixture was then melted in a silica crucible at 900 °C for 1 hour and quickly quenched on a preheated stainless-steel plate. The glasses were annealed at 350 °C for 2 hours to relieve internal stress and prevent cracking.

The amorphous nature of the samples was confirmed using X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.5406 Å). FTIR spectra were recorded using a Bruker Vertex 70 spectrometer over the 400–4000 cm^{-1} range. Optical absorption spectra were obtained using a JASCO V-660 spectrophotometer, and photoluminescence measurements were carried out using an Edinburgh Instruments FLS-920 spectrofluorimeter with 405 nm excitation.

III. RESULTS AND DISCUSSION

X-RAY DIFFRACTION (XRD):

The XRD patterns of both undoped and Sm^{3+}-doped phosphate glasses display two broad halos centered around 2θ = 17° and 32°, confirming their amorphous nature. The absence of sharp peaks indicates that Sm^{3+} incorporation does not cause crystallization or devitrification [12].

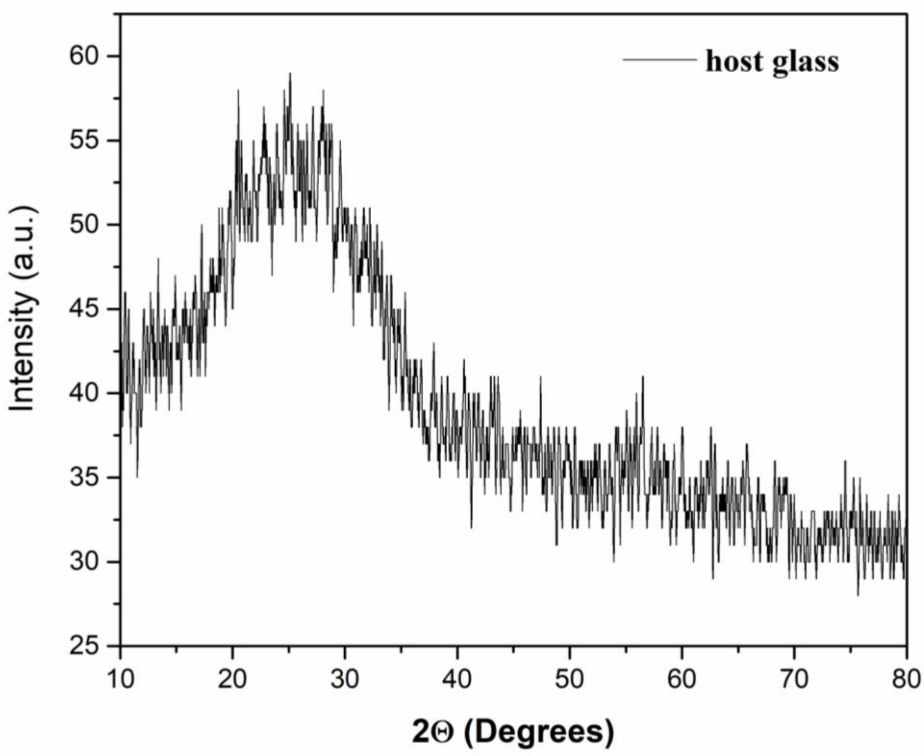

Fig. 1. XRD pattern of phosphate glass matrices for host glass matrix.

3.2. FTIR SPECTROSCOPY:

FTIR spectra exhibit characteristic phosphate network vibrations, including:

- Symmetric and asymmetric P–O–P stretching in the 740–880 cm^{-1} region,
- $(PO_3)^{2-}$ group vibrations around 1050 cm^{-1}, and
- $(PO_2)^{-}$ terminal group modes near 1250 cm^{-1} [13,14].

Changes in the band intensities with Sm^{3+} doping indicate modification of the phosphate network, possibly due to the substitution of Bi^{3+} or Na^{+} ions by Sm^{3+}, forming new Sm–O–P linkages that enhance the glass network's connectivity and stability.

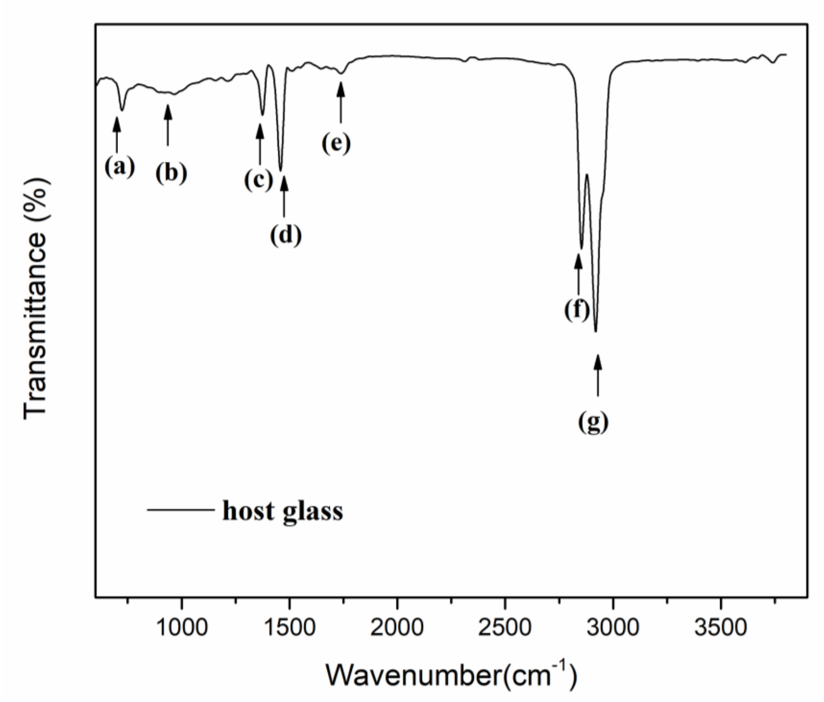

Fig. 2. FTIR spectra of phosphate glasses for host glass matrix.

UV–VIS ABSORPTION SPECTRA

The UV–Vis absorption spectra (Fig. 3) display several narrow peaks corresponding to intra-configurational 4f–4f transitions of Sm^{3+} ions:

$^6H_{5/2} \rightarrow {}^6P_{3/2}$ (404 nm), $^6H_{5/2} \rightarrow {}^6P_{5/2}$ (416 nm), $^6H_{5/2} \rightarrow {}^4G_{7/2}$ (450 nm), and $^6H_{5/2} \rightarrow {}^4G_{5/2}$ (478 nm) [15–17]. These peaks are sharp, confirming that Sm^{3+} ions occupy well-defined local environments with minimal phonon coupling, which is beneficial for radiative transitions. The most of the transitions in the spectra originated from induced electric dipole interactions with selection rule $\Delta J \leqslant 6$. . 6H5/2 → 6F1/2 and 6H5/2 → 6F3/2 transitions are hypersensitive transitions in nature, which obeys the selection rules $|\Delta S|=0$, $|\Delta J| \leqslant 2$ and $|\Delta L| \leqslant 2$. The position, shape and intensity of these transitions are found to be very sensitive to the ligand coordination. The transitions in the NIR region are spin allowed ($\Delta S=0$) and hence they show the high intensity.

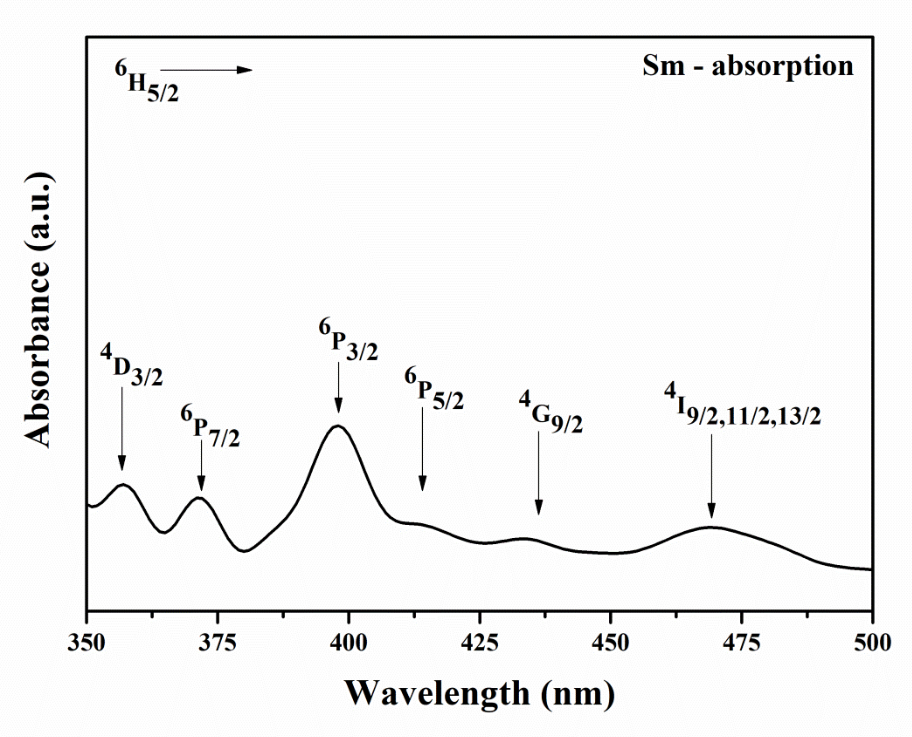

Fig. 3. Optical absorption spectra of phosphate glasses for 1mol% Sm2O3

PHOTOLUMINESCENCE (PL) SPECTRA

Under 405 nm excitation, the photoluminescence spectra (Fig. 4) reveal four emission bands at:

- 563 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$),
- 597 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$),
- 644 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$), and
- 705 nm ($^4G_{5/2} \rightarrow {}^6H_{11/2}$).

The intense orange-red band at 597 nm, corresponding to the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition, dominates the spectrum. This transition is hypersensitive, making it strongly dependent on the local symmetry and bond covalency around Sm^{3+} ions [18,19].The ratio $R = I(^6H_{7/2}) / I(^6H_{5/2})$, known as the asymmetry ratio, increases with Sm^{3+} incorporation, indicating a non-centrosymmetric local environment.

The measured radiative lifetime of the $^4G_{5/2}$ excited level is approximately 2.5 ms, implying efficient radiative decay and minimal non-radiative relaxation. These results suggest a uniform distribution of Sm^{3+} ions in the glass matrix without clustering, making the material suitable for photonic and display devices [20].

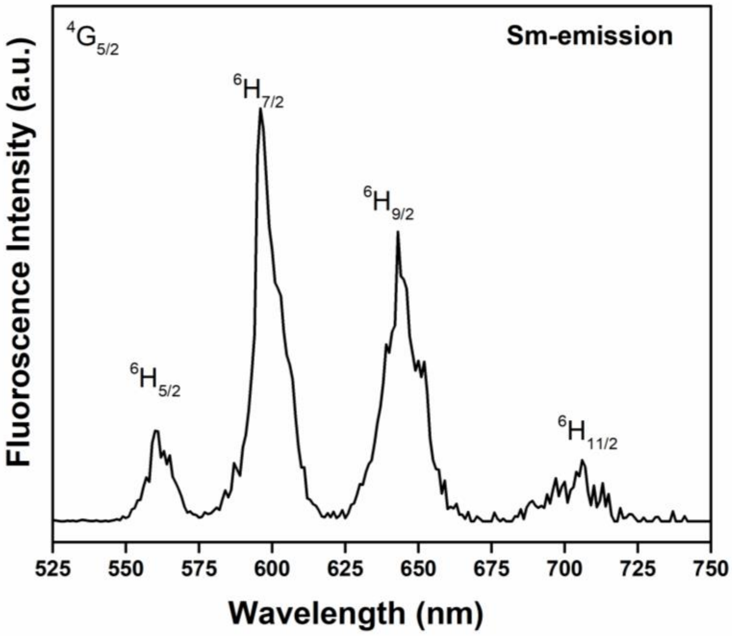

Fig. 4. Emission spectra of Phosphate glasses for 1mol% Sm2O3

IV. CONCLUSIONS

Sm^{3+}-doped phosphate glasses with composition $50P_2O_5$–$5Bi_2O_3$–$25Li_2O$–$20Na_2O$ were successfully synthesized by the melt-quenching method. The samples are amorphous, transparent, and structurally homogeneous.

FTIR and XRD analyses confirmed that Sm^{3+} ions form Sm–O–P bonds, which strengthen the phosphate network. Optical absorption spectra exhibited well-defined 4f–4f transitions, while PL spectra showed intense orange-red luminescence dominated by the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition.

The excellent luminescence efficiency and spectral stability demonstrate that these materials are promising candidates for solid-state lighting, photonic amplifiers, and optical marking applications.

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