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Spectral and Structural Analysis of Neodymium-Doped Phosphate Glass Systems

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Abstract:

A series of Nd^{3+}-doped phosphate glasses were synthesized using the melt-quenching technique.The base composition was (mol%): $50P_2O_5$–$5Bi_2O_3$–$25Li_2O$–$20Na_2O$, where 1 mol% of Bi_2O_3 was replaced by Nd_2O_3. Although the host matrix melts near 650 °C, all samples were prepared at 900 °C to reduce viscosity and eliminate entrapped bubbles. The resultant glasses exhibited excellent optical transparency and structural homogeneity, enabling efficient luminescence across the visible and near-infrared regions.

Keywords — **Phosphate Glass; Nd^{3+} Dopant; Structural Characterization; Absorption, Photoluminescence; Visible and NIR emission.**

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1 INTRODUCTION

Phosphate glasses are widely regarded as versatile optical materials because of their broad optical transparency, low refractive index, and relatively low melting temperature [1, 2]. These properties make them excellent host matrices for rare-earth (RE) dopants, which impart strong luminescent features. Their favorable glass-forming ability and high solubility for RE ions enhance their suitability for photonic, optoelectronic, and laser applications [3–5].

The luminescent behavior of RE ions arises from intra-4f electronic transitions, which are weakly influenced by the host matrix due to the shielding effect of outer $5s^25p^6$ orbitals. Consequently, RE ions display sharp and element-specific emission lines with minimal spectral broadening [6]. Compared with silicate, borate, and germanate glasses, phosphate glasses possess lower phonon energies (~900 cm^{-1}), resulting in reduced non-radiative relaxation and improved luminescence quantum efficiency [7].

Among various RE ions, neodymium (Nd^{3+}) is particularly important due to its efficient near-infrared (NIR) emission around 1.06 µm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$), which is crucial for solid-state lasers, fiber amplifiers, and optical communication systems [8, 9]. However, one major challenge in RE-doped phosphate glass fabrication lies in maintaining optical homogeneity and preventing phase segregation or micro-crystallization. Undissolved RE oxides can lead to scattering centers that reduce transparency and luminescence efficiency [10, 11].

In this study, we report the synthesis and characterization of Nd^{3+}-doped phosphate glasses with the nominal composition $50P_2O_5$–$5Bi_2O_3$–

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$25Li_2O–20Na_2O$. The inclusion of Bi_2O_3 is expected to improve refractive index and radiative probability, while maintaining good glass-forming ability [12]. The structural and optical properties were investigated using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, UV–Vis–NIR absorption, and photoluminescence (PL) spectroscopy. The results demonstrate that these Nd^{3+}-doped phosphate glasses possess excellent transparency, strong emission, and high potential for laser and photonic applications.

2 Experimental Methods

2.1 Glass Preparation

Phosphate glasses with the base composition $50P_2O_5–5Bi_2O_3–25Li_2O–20Na_2O$ were prepared by the melt-quenching technique. Analytical-grade reagents $NH_4H_2PO_4$, Bi_2O_3, Li_2CO_3, Na_2CO_3, and Nd_2O_3 were used. The raw materials were precisely weighed, thoroughly mixed, and preheated at 350 °C for 1 h in a silica crucible to remove moisture and volatile residues.

The preheated batch was melted at 900 °C for 1 h to achieve complete homogenization. The melt was then quenched in air and pressed onto a preheated stainless-steel plate to form transparent glass samples. The glasses were annealed at 350 °C for 2 h to remove residual thermal stresses and then slowly cooled to room temperature.

2.2 Structural and Optical Characterization

The **amorphous nature** of the glasses was confirmed using **X-ray diffraction (XRD)** with Cu Kα radiation (λ = 1.5406 Å).

Fourier-transform infrared (FTIR) spectra were recorded on a **Bruker Vertex 70** spectrometer in the 400–4000 cm^{-1} range to study structural bonding and phosphate network units.

Optical absorption measurements in the UV–Vis–NIR range (300–1100 nm) were carried out using a **JASCO V-660 spectrophotometer**.

Photoluminescence (PL) spectra were recorded using an **Edinburgh Instruments FLS-920 spectrofluorimeter** at room temperature, with excitation provided by an **808 nm diode laser**.

3. Results and Discussion

3.1. X-ray diffraction (XRD):

The XRD patterns (Fig. 1) for both undoped and Nd^{3+}-doped phosphate glasses exhibit two broad diffuse halos centered at approximately 2θ = 17° and 32°, confirming the amorphous nature of all samples. The absence of sharp diffraction peaks indicates that Nd^{3+} incorporation does not induce crystallization or devitrification within the host network [13].

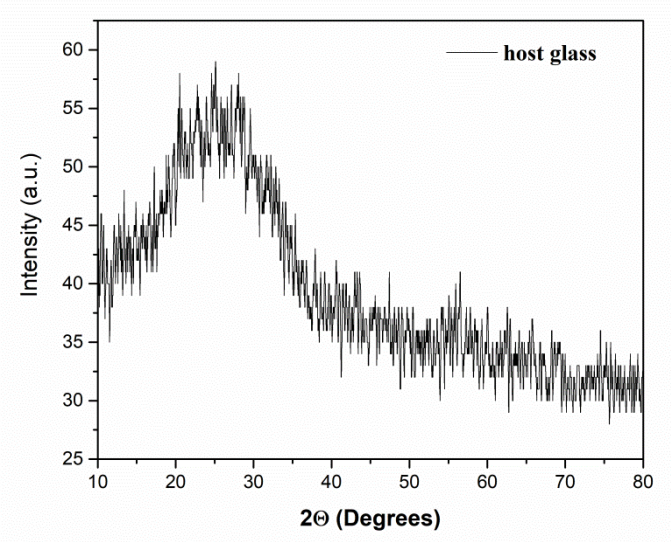

Fig. 1. XRD pattern of phosphate glass matrices for host glass matrix.

3.2. FTIR Spectroscopy:

FTIR spectra (Fig. 2) reveal several prominent vibrational bands typical of phosphate glass networks:

- 730–780 cm^{-1}: symmetric P–O–P stretching vibrations
- 890 cm^{-1}: asymmetric P–O–P stretching
- 1030–1050 cm^{-1}: symmetric $(PO_3)^{2-}$ stretching in Q^2 units
- 1350–1500 cm^{-1}: asymmetric $(PO_3)^{2-}$ and $(PO_2)^-$ terminal group vibrations
- 2750–3000 cm^{-1}: hydroxyl (O–H) groups indicating residual water content

The intensity variation of the P–O–P and $(PO_3)^{2-}$ bands with Nd^{3+} doping suggests modification of

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the phosphate network, likely due to partial substitution of Bi^{3+} and Na^{+} by Nd^{3+} ions, leading to the formation of stronger Nd–O–P linkages [14]. This structural reinforcement contributes to improved luminescence and thermal stability.

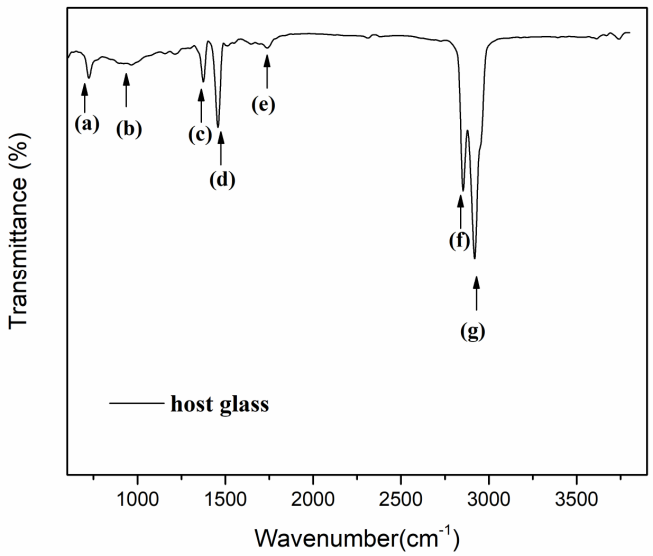

Fig. 2. FTIR spectra of phosphate glasses for host glass matrix.

3.3. Optical and Luminescent Properties

Optical Absorption

The room-temperature absorption spectrum (Fig. 3) of 1 mol% Nd^{3+}-doped glass in the 300–900 nm range exhibits several sharp peaks corresponding to transitions from the ground state $^4I_{9/2}$ to higher excited states of Nd^{3+}: $^4F_{3/2}$ (873 nm), $^4F_{5/2}$ + $^2H_{9/2}$ (802 nm), $^4F_{7/2}$ + $^4S_{3/2}$ (746 nm), $^4F_{9/2}$ (682 nm), $^2H_{11/2}$ (625 nm), $^4G_{5/2}$ + $^2G_{7/2}$ (583 nm), $^4G_{7/2}$ (524 nm), $^4G_{9/2}$ + $^2K_{13/2}$ (511 nm), $^2D_{3/2}$ + $^2K_{15/2}$ (475 nm), $^2P_{1/2}$ + $^2D_{5/2}$ (429 nm), and $^4D_{3/2}$ + $^4D_{1/2}$ (353 nm) [15–17].

These absorption features correspond to well-known intra-configurational 4f–4f transitions of Nd^{3+} and confirm that the ions occupy optically active sites within the glass. The broadening of the bands is due to inhomogeneous effects from the amorphous matrix.

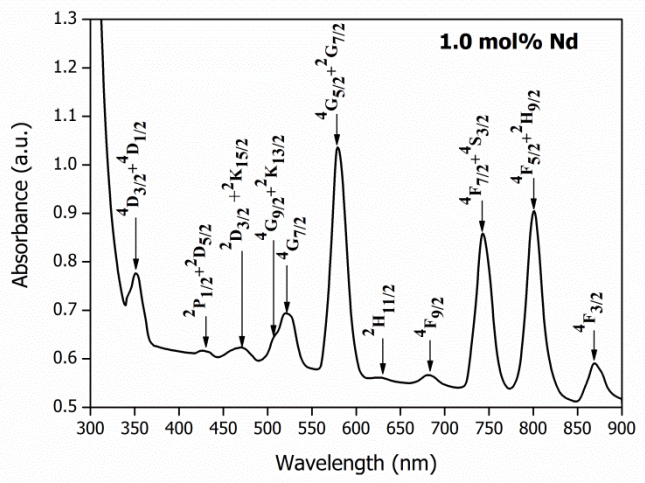

Fig. 3. Optical absorption spectra of phosphate glasses for 1mol% Nd_2O_3

Photoluminescence (PL)

The PL spectra (Fig. 4) recorded under 808 nm excitation show three prominent emission bands centered at 0.9 µm, 1.05 µm, and 1.33 µm, corresponding to $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$, and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions, respectively. Among these, the 1.05 µm band is the most intense and sharp, representing the main lasing transition of Nd^{3+} ions [18].

A slight red-shift in emission peaks with Bi_2O_3 incorporation is observed, attributed to the nephelauxetic effect, where Bi^{3+} increases covalency in the Nd–O bond network [19]. The partially resolved structure near 1.05 µm indicates Stark splitting of the $^4I_{11/2}$ manifold, enhanced by increased Bi_2O_3 content.

These results confirm efficient population of the $^4F_{3/2}$ metastable level, followed by radiative transitions that yield bright NIR emission. The observed spectral sharpness and intensity demonstrate minimal concentration quenching and confirm the suitability of Nd^{3+}-doped phosphate

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glasses for laser amplifier and optical sensor applications [20, 21].

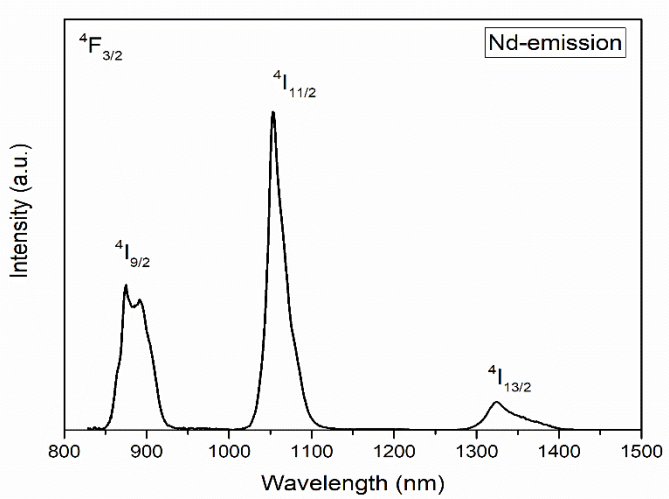

Fig. 4. Emission spectra of Phosphate glasses for 1mol% Nd_2O_3

4. Conclusions

Nd^{3+}-doped phosphate glasses with composition $50P_2O_5–5Bi_2O_3–25Li_2O–20Na_2O$ were successfully synthesized by the melt-quenching technique. The glasses are amorphous, transparent, and structurally homogeneous. Structural analyses (XRD and FTIR) confirmed that Nd^{3+} ions integrate into the phosphate network by forming Nd–O–P linkages, enhancing rigidity and luminescence efficiency.

Optical studies revealed multiple absorption transitions characteristic of Nd^{3+} ions and strong emission bands at 0.9, 1.05, and 1.33 µm, corresponding to the $^4F_{3/2} \rightarrow {}^4I_j$ transitions. The incorporation of Bi_2O_3 increased the local field strength, inducing slight Stark splitting and spectral red-shift. These glasses exhibit excellent potential for NIR laser, amplifier, and photonic device applications.

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