

Article

Spectroscopic Studies of PbO-Al₂O₃-P₂O₅ glass-system by means of Nickel ions

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Abstract

The present study is to investigate various spectroscopic properties viz., optical absorption, and IR spectra of PbO-Al₂O₃-P₂O₅ glasses doped with different concentrations of NiO were reported. These glasses were fabricated using conventional melt quenching technique. The amorphous nature of the glasses was confirmed by X-ray diffraction studies. The optical absorption spectra of these glasses exhibited four clearly resolved absorption bands in the visible and NIR regions around 1272 nm, 794 nm, 590 nm, and 474 nm assigned to transitions ${}^3A_2(F) \rightarrow {}^3T_2(F)$ (octahedral band 1), ${}^3A_2(F) \rightarrow {}^3T_1(F)$ (octahedral band 2), ${}^3A_2(F) \rightarrow {}^3T_1(P)$ (tetrahedral band) and ${}^3A_2(F) \rightarrow {}^1T_2(D)$ (octahedral band 3) respectively. The IR spectral investigations indicate that there is a gradual transformation of nickel ions from octahedral to tetrahedral positions as the concentration of NiO is increased beyond 0.8 mol%. The studies on optical absorption and IR spectra have indicated that there is a higher concentration of nickel ions that occupy tetrahedral positions in the samples containing more than 0.8 mol% of NiO. Finally, from the careful analysis of these results, it is felt that there is a possibility for getting high intense lasing emission (corresponding to ${}^3A_2(F) \rightarrow {}^3T_2(F)$ transition in the NIR region) if these glasses are doped around 0.8 mol% of NiO.

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1.Introduction

The objective of the present investigation is to have a comprehensive understanding of the structural influence of nickel ions in PbO-Al₂O₃-P₂O₅ glass network by studying quantitatively various spectroscopic properties (viz., optical absorption, IR spectra). The divalent nickel ion is an interesting paramagnetic ion to probe in the glass systems. Nickel ions are reported to occupy both tetrahedral and octahedral positions in the glass matrices [1-4]. The octahedral positioned Ni²⁺ ions are expected to exhibit eye safe laser emission of wavelength 1.56 μ m (${}^3T_2 \rightarrow {}^3A_2$) even at room temperature with low threshold energy, which is of great importance in telecommunications [5]. The introduction of Al₂O₃ in to lead phosphate glass

network is expected to enhance the chemical durability of phosphate glass, since Al_2O_3 enters into the glass network with AlO_4 structural units. Incidentally, the vibrational frequency of Al-O stretching in AlO_4 structural units is found to be around 700 cm^{-1} in this region the band due to P-O-P stretching vibrations of PO_4 groups is also present. As a consequence, it is quite likely that tetrahedral Al ions to cross link with the neighbouring phosphor chains by the formation of AlPO_4 species that strengthen the glass network.

2. Experimental Methods

Within the possible glass forming region of $\text{PbO-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glass system, a particular compositions $30\text{PbO-(5-x)Al}_2\text{O}_3\text{-65P}_2\text{O}_5\text{:xNiO}$ with the value of x ranging from 0 to 1.0 mol% is chosen for the present study; the samples are labeled as N_0 (x = 0), N_2 (x = 0.2), N_4 (x = 0.4), N_6 (x = 0.6), N_8 (x = 0.8), N_{10} (x = 1.0). Analytical grade reagents of Al_2O_3 , P_2O_5 , PbO and NiO powders in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range of $900\text{-}1050\text{ }^\circ\text{C}$ in a PID temperature controlled furnace for about 1 h. The resultant bubble free melt was then poured in a brass mould and subsequently annealed at $300\text{ }^\circ\text{C}$. The glass specimens with various concentrations of NiO were heat treated in a furnace at $400\text{ }^\circ\text{C}$ for 6 h. Automatic controlling furnace was used to keep the temperature at the desired level. After the heat treatment in the furnace at specified temperature, the samples were chilled in air to room temperature. The samples prepared were ground and optical polished to the dimensions of $1\text{ cm}\times 1\text{ cm}\times 0.2\text{ cm}$. It may be noted here that as the concentration of NiO is increased, the colour of the glass ceramics is gradually turned from brown to thick brown and beyond 1.0 mol% of NiO, the colour of the samples became thick black and opaque. Hence, the concentration of the dopant is limited to only up to 1.0 mol%.

3. Results

The absence of peaks in the X-ray diffraction pattern (shown in Fig.1), indicate that the samples prepared were of amorphous in nature.

Based on the glass density (d) and calculated average molecular weight (\bar{M}), various physical parameters such as nickel ion concentration (Ni_i), mean nickel ion separation (r_i) are evaluated for understanding the physical properties of these glasses using the conventional formulae [6] and the values obtained are presented in Table 1.

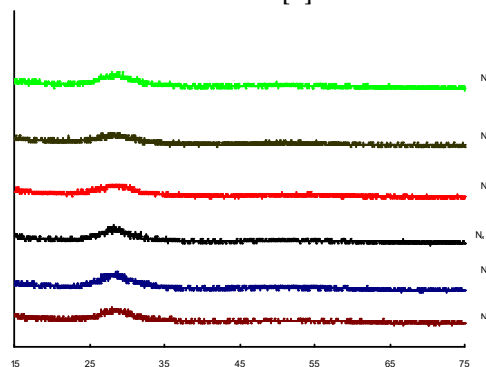


Fig. 1 X-Ray diffraction pattern of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_5$ glasses with NiO

Table 1

Various physical parameters of PbO-Al₂O₃-P₂O₅ glasses doped with NiO

Glass	Density d (g/cm ³)	Avg. mol. wt. (\bar{M})	Total nickel ion concentration Ni (10 ²¹ ions/ cm ³)	Inter-ionic distance of Ni ions R _i (Å)
N0	4.610	256.52	-	-
N2	4.615	256.47	2.17	7.73
N4	4.621	256.45	4.34	6.13
N6	4.626	256.42	6.52	5.35
N8	4.632	256.31	8.71	4.86
N10	4.637	256.25	10.91	4.51

The optical absorption spectra of NiO doped PbO-Al₂O₃-P₂O₅ glasses were recorded at room temperature in the wavelength range 350-1400 nm are shown in Fig.2. The spectrum of NiO free glasses does not exhibit any absorption bands. The spectrum of the glass (N₂) has exhibited, six clearly resolved intense absorption bands in the visible and NIR regions at 1272 nm, ³A₂ (F) → ³T₂ (F) (octahedral band1), 794 nm, ³A₂ (F) → ³T₁ (F) (octahedral band 2), 590 nm, ³A₂ (F) → ³T₁ (P) (tetrahedral band), and 474 nm, ³A₂ (F) → ¹T₂ (D) (octahedral band 3) respectively.

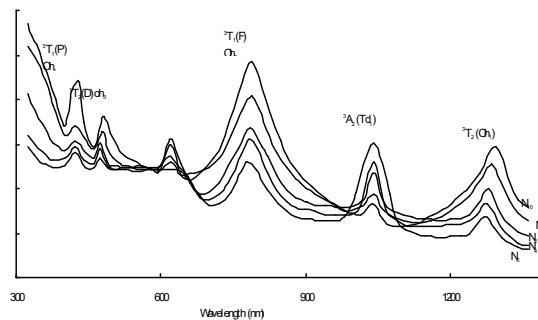


Fig2. Optical absorption spectra of PbO-Al₂O₃-P₂O₅ glasses. All the transitions are from the ground state ³A₂.

As the concentration of NiO is increased up to 0.8 mol % the intensity of the octahedral bands (oh bands) is observed to decrease with a shift towards slightly lower wavelength; in this concentration range the intensity of the two tetrahedral bands (Td bands) is observed to increase with no considerable shift in the band positions. With the increase in the concentration of NiO from 0.8 to 1 mol % the positions of the octahedral bands are shifted towards slightly higher wavelength with increasing intensity at the expense of T_{a1} and T_{a2} bands. The summary of the data on the positions of various absorption bands is furnished in Table 2.

Table 2

Summary of the data on optical absorption of BaO-Al₂O₃-P₂O₅:NiO glasses.

Glass	N ₂	N ₄	N ₆	N ₈	N ₁₀
Ni²⁺ transitions (cm⁻¹)					
Octahedral transitions					
³ A ₂ (F) → ³ T ₂ (F)	7825	7863	7906	7911	7759
³ A ₂ (F) → ³ T ₁ (F)	12736	12822	12834	12836	12667
³ A ₂ (F) → ¹ T ₂ (D)	21052	21186	21256	21268	20952
Tetrahedral transitions					
³ T ₁ (F) → ³ T ₁ (P)	16393	16393	16393	16393	16393

The infrared transmission spectrum of NiO free PbO-Al₂O₃-P₂O₅ glasses (Fig.3) exhibit vibrational bands at 1290 cm⁻¹ (identified due to P=O stretching vibrations, this region may also consists of bands due to anti symmetrical vibrations of PO₂⁻ groups), 1020 cm⁻¹ (a normal vibrational mode in PO₄³⁻ arising out of \otimes_3 - symmetric stretching), 905 cm⁻¹ (due to P-O-P asymmetric bending vibrations) and at 806 cm⁻¹ (due to P-O-P symmetric stretching vibrations) [7,8]. Additionally a feeble band at about 785 cm⁻¹ (presumably due to Al-O stretching in AlO₄ groups) is also located in the spectrum of these glasses.

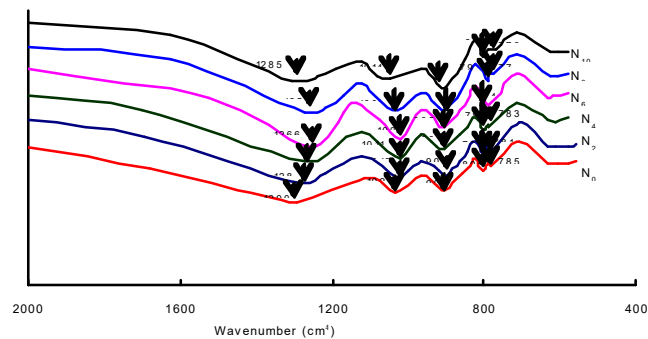


Fig.3. IR Spectra of PbO-Al₂O₃-P₂O₅:NiO glasses.

With the introduction of NiO into the glass network up to 0.8 mol %, the intensity of the bands due to P=O stretching vibrations and \otimes_3 - symmetric stretching vibrations of PO₄³⁻ units is observed to increase; the bands due to P-O-P bending vibrations .

AlO₄ groups have gradually come closer and finally merged with exhibiting a common meta center in the spectrum of the glass N₈. For further increase in the concentration of NiO (> 0.8 mol %) this common band is observed to resolve. The intensity of the other two (viz., P=O stretching vibrations and ν₃ - symmetric stretching vibrations of PO₄³⁻ units) bands is observed to decrease gradually with the increase in the concentration of NiO beyond 0.8 mol %.

A summary of the data on the positions of various bands in the IR spectra of PbO–Al₂O₃- P₂O₅ glasses doped with different concentrations of NiO are presented in the Table 3

4. Discussion

The Ni²⁺ ions seem to exist in both four fold and in six-fold coordination in the present glass networks. Tetragonally positioned Ni²⁺ ions do not induce the formation of any non bridging oxygen ions but octahedrally positioned ions may act as modifiers [9]. The bands O_{h1}, O_{h2} and O_{h3} are assigned to the transitions from the ³A₂ ground state of octahedrally positioned Ni²⁺ ions to ³T₂(F), ³T₁(F) and ³T₁(P) excited states respectively. Thus, the measurements indicate that Ni²⁺ ions exist both in octahedral and tetrahedral sites in the glass network. Further, the way the intensity of these bands varies with the concentration of NiO suggests that at smaller concentrations (≤ 0.8 mol %), Ni²⁺ ions prefer to occupy tetrahedral positions whereas at larger concentrations, these ions prefer mostly octahedral sites in the glass network.

Table 3.

Data on IR band positions (cm⁻¹) of PbO-Al₂O₃-P₂O₅: NiO glasses

Vibrational groups	Glass N ₀	Glass N ₂	Glass N ₄	Glass N ₆	Glass N ₈	Glass N ₁₀
P=O stretching	1290	1286	1274	1266	1255	1285
PO ₄ ³⁻ groups	1020	1018	1011	1008	1004	1014
P-O-P asymmetric bending	905	905	905	905	905	905
P-O-P symmetric stretching	806	794	788	794	796	803
AlO ₄ Units	785	781	783	781	776	770

These observations also reveal that the ratio Ni²⁺ (oct) /Ni²⁺ (tet) increases with increase in the concentration of NiO beyond 0.8 mol%; Further, the d-d transitions of the tetrahedral complexes are electric dipole allowed whereas those of octahedral complexes are electric dipole forbidden and are mainly due to the static or dynamic distortions from the regular octahedral geometry of the glass network and they can also be magnetic dipole allowed.

Further support for the conclusion that the Ni²⁺ ions occupy tetrahedral sites in the networks of glasses N₂ to N₈ can also be obtained from the analysis of the IR spectral data of these glasses. If NiO takes octahedral positions and act as modifier, the σ -bond of P=O may be ruptured with the creation of new non-bridging oxygens; as a result, we expect the decrease in the intensity of the band due to P=O (band at about 1290 cm⁻¹) vibrations in the IR spectra. Instead, the intensity of this band is observed to increase with the increase in the concentration of NiO. Similar is the case with the vibrational band of PO₄³⁻ units, P-O-P symmetric stretching. With increase in the concentration of NiO from 0.2 to 0.8 mol % a gradual merging of bands due to P-O-P bending vibrations and AlO₄ groups has been observed the merger of bands indicates the formation of P-O-Al linkages. The highest intensity of this band observed in the spectrum of the glass N₈ supports the view point that the nickel ions occupy mostly tetrahedral positions in this concentration range (≤ 0.8 mol %) and increase the rigidity of the glass network.

Finally, the analysis of the results of various studies viz. optical absorption, IR spectra PbO-Al₂O₃-P₂O₅: NiO glasses indicate that the nickel ions occupy both tetrahedral and octahedral positions in the glass network.

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