



Transport and spectroscopic properties of nickel ions in ZnO–B₂O₃–P₂O₅ glass system



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ABSTRACT

Physicoelectrical properties like density, dielectric properties, optical absorption and infrared absorption data are presented for borophosphate glasses doped with nickel ions. Standard samples of ZnO–B₂O₃–P₂O₅ glass system were prepared by the melt quenching technique in the compositional series containing 0.2, 0.4, 0.6, 0.8 and 1.0 mol% of nickel. The dc conductivity for these samples measured in the temperature range 473–623 K. The analysis of dc conductivity, electrical conductivity is affected by the structural change. The electronic conduction seems to be dominant in the higher concentration range. From the optical absorption and IR spectral studies, nickel ions prefer to occupy both tetrahedral and octahedral positions in the glass network; compare to tetrahedral, octahedral positions seems to dominate when the concentration of NiO is raised above 0.6 mol% in the glass matrix.

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1. Introduction

Glasses have the unique property of high durability together with transparency at room temperature. Borate glasses belong to valuable and interesting systems which find extensive applications for optical, thermal, electrical and biological purposes [1–3]. B₂O₃ forms a glass by itself and forms binary borates with many oxides [4]. This is basically because it is more energetically favorable to form BO₄ tetrahedra than to break B–O–B bridges and give non-bridging oxygen [5] and also the addition of modifier oxides to B₂O₃ changes some BO₃ triangles to BO₄ tetrahedron exists in different structural borate groups.

Combination of P₂O₅ with other glass formers has found more applications, since valuable specific effects of P₂O₅ may be retained at better chemical resistivity [6]. With the increasing need for improved higher energy density and higher recharge cycle life, the borophosphate glasses have received attention for their use in various applications for fast ionic conductors and biomedical applications [7,8]. The combination of these two glass formers B₂O₃ and P₂O₅ is an intrinsically interesting subject of study. The properties of the borophosphate glasses are probably due to the mixture of two former oxides as well as distinct networks of borate or

phosphate. The basic units of pure amorphous phosphate and borate glasses are PO₄ trigonal BO₃ groups, respectively [9,10].

The use of glass modifier, zinc oxide (ZnO) is widespread in the glass industry because of its versatile nature and improves the mechanical properties and, also, the chemical resistance of the glasses attracted many scientists [11,12]. In glasses, Zn²⁺ may form ZnO₄ as well as ZnO₆ groups, but the structure of the Zn²⁺ ion cannot be recognized through visible spectroscopy due to colorlessness [13]. The nickel ions mostly exist in divalent state and are extremely stable even at room temperature. Ni²⁺ ions exhibit several strong absorption bands in the visible and near infrared regions where the pumping sources are easily available [14]. The octahedrally positioned Ni²⁺ ions in glass matrix are anticipated to exhibit emission of wavelength at about 1.5 μm due to ³T₂ → ³A₂ under normal atmospheric conditions, this transition is of great significance in telecommunications [15] and also the fluorescence of Ni²⁺ is much stronger in glass ceramics and crystals than in real vitreous substrate.

2. Experimental work

2.1. Preparation of the glasses

The glass samples of the formula (10–X) ZnO–40B₂O₃–50P₂O₅: XNiO, where, X=0–1.0 mol% have been prepared by the conventional melt quenching method. The

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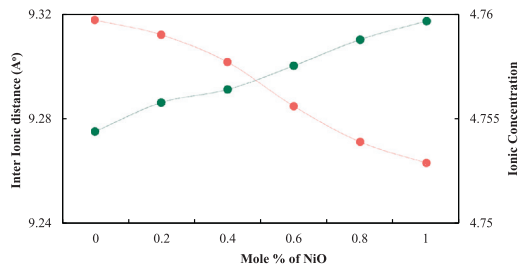


Fig. 1. Variation of ionic concentration, Inter ionic distance with NiO mol%.

chemicals required of analytical grade zinc oxide, boric oxide, phosphate and nickel oxide. The proper compositions were mixed together continuously using an agate mortar and the mixture was melted in platinum crucible at about 1200 K using PID controller furnace at about 1 h to get homogenize the melt. The glass samples were annealed at 500 K for 2 h to avoid the mechanical strains developed during the quenching process. The prepared glass samples were polished and the surfaces are made perfectly plane.

2.2. Density

The density of the glasses was determined to an accuracy of (± 0.0001) by the standard principle of Archimedes' using O-xylene as the buoyant liquid. Ohaus digital balance Model AR2140 was used for the mass of the samples with an accuracy of 0.1 mg for calculating the density.

2.3. Optical absorption spectral measurements

The optical absorption spectra of the samples were recorded at ambient temperature in the spectral wavelength range 300–1800 nm with a resolution of 0.1 nm using JASCO Model V-670 UV – vis – NIR spectrophotometer.

2.4. IR spectral measurements

Infrared transmission spectra were recorded on a Bruker-FTIR-TENSOR 27 spectrophotometer up to a resolution of 0.4 cm^{-1} in the range of $200 - 1800 \text{ cm}^{-1}$ using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg).

2.5. Dielectric measurements

The dc conductivity of the sample was measured by using a Keithley Digital Multimeter (Model 2000) in the temperature range 300 – 600 K. The frequency (75 kHz – 30 MHz) dependence of dielectric constant was computed by Hewlett Packard (Agilent) 4285 A precision LCR meter at room temperature.

3. Results

Fig. 1 shows, increasing the mol% of NiO at the cost of ZnO by keeping the formers at constant, the inter ionic distance increasing, while the ionic concentration decreases, which suggests the increased free space within the glass structure [16,17]; it means that the glass structure becomes loosely packed [18].

Fig. 2 represents the optical absorption spectra of the ZnO–B₂O₃–P₂O₅: NiO glasses it consist of five absorption bands, the spectrum of the glass (N₄) exhibited five clearly resolved intense absorption bands at around 420, 620, 792, 1050 and 1280 nm and a sixth weak band at 472 nm. We categorize the absorption bands around 420, 792 and 1280 nm as octahedral (O) bands and the absorption bands around 620 and 1050 nm as

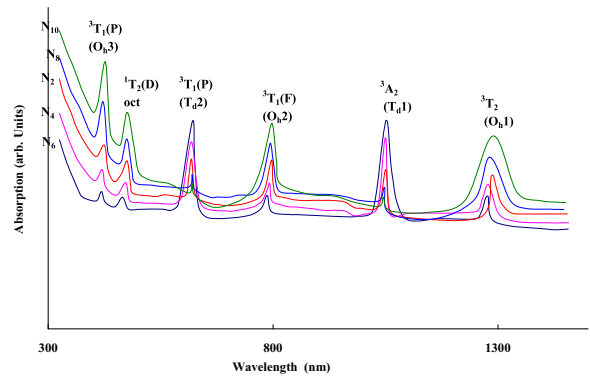


Fig. 2. Optical absorption spectra of ZnO–B₂O₃–P₂O₅: NiO glasses.

Table 1

Summary of the data on optical absorption spectra of NiO doped ZnO–B₂O₃–P₂O₅ glasses.

Transitions of nickel ions	Band positions (cm ⁻¹)				
	N ₂	N ₄	N ₆	N ₈	N ₁₀
Octahedral transitions					
³ A ₂ (F) → ³ T ₂ (F)	1285	1280	1276	1282	1289
³ A ₂ (F) → ³ T ₁ (F)	796	792	786	794	798
³ A ₂ (F) → ¹ T ₂ (D)	425	420	418	422	427
³ A ₂ (F) → ³ T ₁ (P)	475	472	465	475	475
Tetrahedral transitions					
³ A ₂ (F) → ³ A ₂ (F)	620	620	620	620	620
³ A ₂ (F) → ³ T ₁ (F)	1050	1050	1050	1050	1050

tetrahedral (T) bands hereafter. The absorption bands of the cast glass were similar to trigonal bipyramidal arrangement of Ni²⁺ ions in borophosphate glasses. The O bands at about 420, 792 and 1280 nm could be tentatively assigned to the transitions of trigonal bipyramidal arrangement of Ni²⁺ ions. It is thought that most of the Ni²⁺ ions in the cast glass occupy trigonal bipyramid fivefold sites.

The T bands around 620 and 1050 nm could be assigned to the spin-allowed broadband transitions of Ni²⁺ ions occupying tetrahedral sites. The absorption measurement results indicate that Ni²⁺ ions in the present glass system would have been changed their sites from trigonal bipyramid fivefolded in the cast glass change to octahedral sixfolded sites. As the concentration of NiO is varied, the following changes have been noticed in the absorption spectra:

(i) The positions of the bands O_{h1}, O_{h2} and O_{h3} are shifted toward slightly lower wavelength, with decreasing intensity, whereas the meta centers of T_{d1} and T_{d2} absorption bands remain unchanged; however, a gradual increase in the intensity has been observed with the increase in the concentration of NiO from 0.2 to 0.6 mol%.

(ii) In the range 0.8 – 1.0 mol% of NiO the positions of the O_{h1}, O_{h2} and O_{h3} bands are shifted toward slightly higher wavelength with increasing intensity at the expense of T_{d1} and T_{d2} bands and no detectable changes are observed on the position. The summary of the data on the positions of various absorption bands is furnished in Table 1.

The infrared spectra of ZnO–B₂O₃–P₂O₅:NiO glasses (Fig. 3) exhibited conventional vibrational bands due to phosphate groups in the regions 1260 – 1300 cm⁻¹ (due to asymmetrical vibrations of PO₄³⁻ groups/P=O stretching vibrations), 1020– 1100 cm⁻¹ (a normal vibrational mode of PO₄³⁻ groups/BO₄ units arising due to symmetric stretching), 1100 – 1150 cm⁻¹ (due to P–O–P asymmetric bending vibrations/this region may also consist of bands due to pyrophosphate groups P₂O₇⁴⁻) and another band in the region of 750 – 800 cm⁻¹ due to P–O–P symmetric stretching vibrations [19] (Table 2).

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