

Physical and optical properties of Ni²⁺ ions in borate glass

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Abstract

In this research, the effect of nickel ions (Ni²⁺) on physical and optical properties in borate glasses has been investigated. The glass samples were prepared in composition (40-x)B₂O₃ : 20Al₂O₃ : 20CaO : 20Na₂O : xNiO (where x = 0.00, 0.01, 0.02, 0.03, 0.04, and 0.05 mol%) by the normal melt-quenching technique at 1,200 °C for 3 hours in normal atmosphere. The results show that the density, refractive index and molar volume of glass samples are not dependent on NiO concentration. The optical absorption spectra of glass samples were measured by UV-visible spectrophotometer in the wavelength range 300-1100 nm and color coordinate in CIE L*a*b* system. The absorption peaks were observed and located at 430 nm which are attributed to ³A_{2g}(P) → ³T_{1g}(F) and associated to Ni²⁺ ions that produce the brown color.

Keywords: glasses, Nickel oxide, optical absorption spectra

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1. Introduction

Borate glass is considered as an important amorphous material due to their specific structure and physical properties in the field of effective gamma-ray shielding materials, radioactive waste immobilization, luminescent materials, optical waveguides and optic fiber [1, 2]. The structure of borate glass consists of both triangular (BO₃) and tetrahedral (BO₄) groups. Furthermore, these two fundamental units can be arbitrarily combined to form different B_xO_y structural groups. Borate glasses based on transition metal ions are also interesting as inorganic hosts [3, 4, 5]. Transition metal (TM) ions embedded in glass matrix give rise to optical absorption spectra due to electron transitions between normally degenerate energy levels of d-electron that is the source of the glass coloration. Each 3d-transition metal can exist in more than one oxidation or coordination states and normally gives rise to specific absorption spectra [6, 7]. Among various transition metal oxides, nickel oxide (NiO) is very interesting optical properties. Nickel ion in glass structure is stable in form of Ni²⁺ oxidation stage under normal atmospheric conditions. The various colors of nickel are not caused by a change in the valence electron because nickel is always in divalent state, but depending on the different numbers of surrounding oxygens which mainly coordinate with nickel [8, 9]. Ni²⁺ ion can exist in two different states

of coordination, octahedral (NiO₆) and tetrahedral (NiO₄) coordinations. The introducing NiO₆ group produces the yellow color while the presence of NiO₄ groups generates the pink or violet color. Furthermore, the ratio of both NiO₆ and NiO₄ coordinations depend on the glass composition, polarisability of the oxygen ligands surrounding the nickel ion, quantitative properties of modifiers [10, 11]. To understand these behaviors of nickel in glass, the effect of NiO concentrations on the physical and optical properties in borate glass have been investigated.

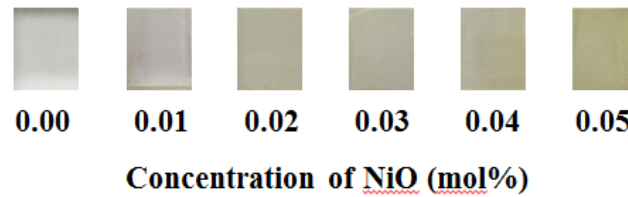
2. Materials and methods

The glass samples were prepared in composition (40-x)B₂O₃ : 20Al₂O₃ : 20CaO : 20Na₂O : xNiO (where x = 0.00, 0.01, 0.02, 0.03, 0.04, and 0.05 mol%) as shown in Table 1. All of chemical composition was mixed together and filled in a high purity alumina crucible. Each batch weighs about 20 g was placed in an electrical furnace and then melted at 1200°C for 3 hours. After complete melting, the melts were quenched in air using a preheated stainless steel mould. The quenched glasses were annealed at 500°C for 3 hour to reduce thermal stress, and cooled down to room temperature. Finally, all glass samples were cut and then finely polished to a dimension of 0.3cm x 0.5cm x 1.0cm for further investigation. The density was measured by the Archimedes method using

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Table 1 Chemical compositions of the glass samples

Concentration of NiO (mol%)	Glass composition (mol%)				
	B ₂ O ₃	Al ₂ O ₃	CaO	Na ₂ O	NiO
0.00	40	20	20	20	-
0.01	39.99	20	20	20	0.01
0.02	39.98	20	20	20	0.02
0.03	39.97	20	20	20	0.03
0.04	39.96	20	20	20	0.04
0.05	39.95	20	20	20	0.05

**Figure 1** Glass samples with different concentration of NiO**Table 2** Density, refractive index and molar volume values of glass samples

Concentration of NiO (mol%)	Parameters		
	ρ , (g/cm ³)	V _m , (cm ³ /mol)	RI
0.00	2.4664	29.1323	1.5416
0.01	2.4687	29.1054	1.5455
0.02	2.4722	29.0646	1.5448
0.03	2.4604	29.2035	1.5446
0.04	2.4650	29.1502	1.5451
0.05	2.4785	28.9911	1.5471

xylene as a immersion fluid. The refractive index (RI) was measured by DR-M2 refractometer. The sodium vapor lamp as the light source (539 nm) was used for measurement and the mono-bromonaphthalene was used as an adhesive liquid. The corresponding molar volume (V_M) was calculated using the relation, $V_M = M_T/\rho$, where M_T is the total molecular weight of the multi-component. The UV-visible spectrophotometer (Cary-50) was used to measure the optical spectra of glass sample and CIE L*a*b* color coordinate calculation.

3. Results and discussion

The glass samples with different NiO concentrations of 0.00 to 0.05 mol% are illustrated in Figure 1. The undoped glass shows colorless whereas the glasses with 0.01 to 0.05 mol% of NiO are light brown color and the intensity of color increase with increasing NiO content.

The obtained values of density, refractive index and molar volume are shown in Table 2. The obtained values of density are within the range of 2.4604-2.4785 g/cm³, the refractive index values are within the range of 1.5416-1.5471 and the molar volume

values are in the range of 28.9911-29.2035 cm³/mol. It has been observed that there is no effect of NiO concentration on these parameters. Actually, when high density component are added in glass composition, the density and refractive index should be increased. In the present work, the density and refractive index were not dependent on NiO concentration because of the glass ratio is not the same glass formula and also due to the volatilization of Na₂O which low melting point component [12].

The optical absorption spectra of glass samples were recorded in the range of 300-1100 nm at room temperature, as shown in Figure 2. The absorption bands were observed in all spectra with the peaks around 430 nm are attributed to the transitions $^3A_{2g}(P) \rightarrow ^3T_{1g}(F)$ transitions of Ni²⁺ and the absorption intensity increased with increasing NiO concentration [13]. Moreover, the absorption spectra also confirmed and corresponded with brown color coordinate in CIE L*a*b* system, as shown in Figure 3. Both absorption spectra and color coordinate of glass samples indicate that Ni²⁺ ions occur in octahedral coordination. These similar results were reported in the previous literature of Terczyn ska-Madej [3].

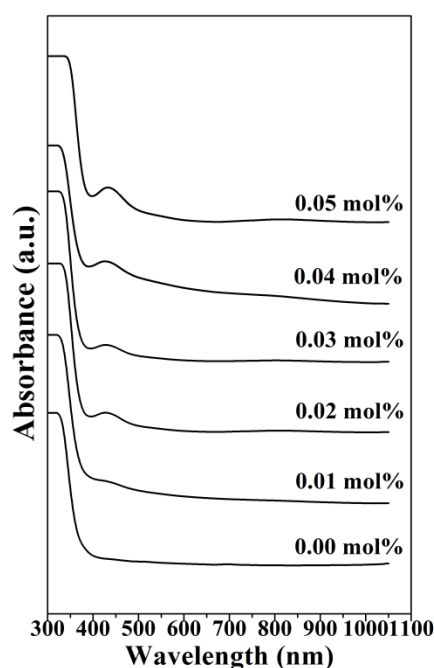


Figure 2 Optical absorption spectra of glass samples

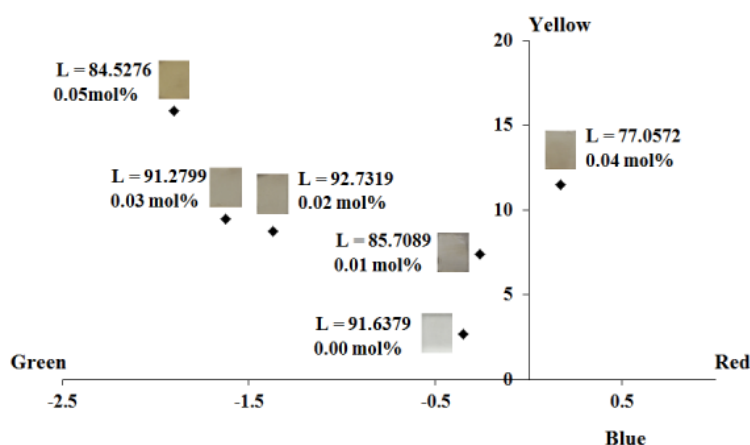


Figure 3 CIE L*a*b* color scale of glass samples

4. Conclusions

In this research, the borate glass containing nickel oxide with composition $(40-x)\text{B}_2\text{O}_3 : 20\text{Al}_2\text{O}_3 : 20\text{CaO} : 20\text{Na}_2\text{O} : x\text{NiO}$ (where $x = 0.00, 0.01, 0.02, 0.03, 0.04$, and 0.05 mol%) were prepared by melt quenching technique. The physical and optical properties were characterized on density, refractive index, molar volume, optical absorption spectra and color coordinate in CIE L*a*b* calculation. The results show that the density, refractive index and molar volume of glass samples did not depend on the concentration of NiO. The absorption peak was observed around 430 nm corresponding to the transitions $^3\text{A}_2(\text{P}) \rightarrow ^3\text{T}_{1\text{g}}(\text{F})$ transitions of Ni^{2+} . The color coordinate in CIE L*a*b* system confirmed the brown color in glasses.

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