



Effect of Cr₂O₃ concentration on physical and optical properties of sodium barium bismuth silicate glasses

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Abstract

Cr₂O₃ doped sodium barium bismuth silicate glasses have chemical composition (30-x)SiO₂ : 30Na₂O : 10 Bi₂O₃ : 30BaO : xCr₂O₃ where x is 0.0, 0.1, 0.3, 0.5, 0.7 and 1.0 mol% and characterized physical and optical properties. The densities of Cr₂O₃ doped glasses were increase due to the result of molecular weight of glasses. On the hand, the molar volumes of glasses were decreased. The refractive indexes also increased which vary by densities. The absorption result, the spectra of Cr₂O₃ doped glasses appear broadband around 630 and 690 nm in an octahedral site due to Cr³⁺ ions which corresponding to ⁴A₂ → ⁴T₂ and ⁴A₂ → ²T₁ transition, respectively by Tanabe-Sukano diagram. Nevertheless, the absorbance decreased with Cr₂O₃ concentration since Cr³⁺ may be transfer electron. The optical band gaps were studied with Urbach plot. It found that Cr₂O₃ concentration at 1.0 mol% shows the maximum optical band gap value.

Keywords: absorption, chromium ion, physical, silicate glass

1. Introduction

Glasses are interesting material since it is transparent in the visible region. Glass materials do not show optical anisotropy that is characteristic of some crystals. The structure of glasses is explained in terms of dimensional infinite cross-linking of units forming short-range order [1]. However, glasses have some properties above crystals such as less expensive, easy to manufacture flexible size and shape and can added high concentration as crystals may loss some properties [2]. All of glass, the silicate glass can be useful of photonics advices such as optical fiber, laser, etc., thanks to their excellent compatibility with commonly used optical fibers [3]. Furthermore, the silicate glass is a glass former which has good physical and chemical durability. While, the melting silicate glass need to high temperature, so modifier is added for breaking the bond and reducing melting temperature such as alkali and alkali earth oxide. Moreover, the heavy metal oxide is a play an important role for improving high density, high refractive index, high optical basicity and large optical susceptibility values [4]. Currently, glasses doped with transition metal oxide have been investigated optical absorption properties. It well known that the transition metal ions dissolved in silicate glass matrix even in so amount, may affect the optical absorption

due to the different oxidation state and coordination [5] which described by ligand field theory. The change of oxidation state and coordination depend on transition oxide concentration and melting temperature [6-8]. Among transition ions, chromium ion with 3d³ configuration is of interest for cathode materials in rechargeable battery because of their very high energy density and high capacitance. Normally, chromium consists of various oxidation states: Cr³⁺, Cr⁴⁺, Cr⁵⁺ and Cr⁶⁺ ions [9-10]. Nevertheless, stability chromium ions are exist Cr³⁺ and Cr⁶⁺ ion in nature [11]. Commonly, the Cr³⁺ ions possess octahedral sites [12] and the efficiency of the most common lasing transition ⁴T₂ → ⁴A₂ of this ion is found to be very sensitive to the internal structure of the silicate glass, while the Cr⁶⁺ ions exhibit tetrahedral site of ⁴T_{1g}(P) → ⁴A₂ lasing transition [9]. In this paper, the physical and optical properties of Cr₂O₃ doped Na₂O-Bi₂O₃-BaO-SiO₂ glasses have been investigated by varying Cr₂O₃ concentrations from 0.0 to 1.0 mol%.

2. Materials and methods

2.1 The preparation of glasses

Cr₂O₃ doped sodium barium bismuth silicate glasses have chemical composition (30-x)SiO₂ : 30Na₂O : 10 Bi₂O₃ : 30BaO : xCr₂O₃ where x is 0.0, 0.1, 0.3, 0.5, 0.7 and 1.0 mol% which shown in Table 1. All glasses were prepared by melt quenching

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Table 1 Chemical composition of glasses

Glass ID	Cr ₂ O ₃ (mol%)	Glass Composition
C0	0.0	30.0SiO ₂ : 30Na ₂ O : 10Bi ₂ O ₃ : 30BaO
C1	0.1	29.9SiO ₂ : 30Na ₂ O : 10Bi ₂ O ₃ : 30BaO : 0.1Cr ₂ O ₃
C3	0.3	29.7SiO ₂ : 30Na ₂ O : 10Bi ₂ O ₃ : 30BaO : 0.3Cr ₂ O ₃
C5	0.5	29.5SiO ₂ : 30Na ₂ O : 10Bi ₂ O ₃ : 30BaO : 0.5Cr ₂ O ₃
C7	0.7	29.3SiO ₂ : 30Na ₂ O : 10Bi ₂ O ₃ : 30BaO : 0.7Cr ₂ O ₃
C10	1.0	29.0SiO ₂ : 30Na ₂ O : 10Bi ₂ O ₃ : 30BaO : 1.0Cr ₂ O ₃

Table 2 Molecular weights (g/mol), densities (g/cm³), molar volumes of glasses (cm³/mol) and refractive indexes

Glass ID	Molecular weight(g/mol)	Density (g/cm ³)	Molar Volume (cm ³ /mol)	Refractive index
C0	129.21	3.5929	35.9626	1.6190
C1	129.31	3.6008	35.9115	1.6204
C2	129.49	3.6114	35.8559	1.6215
C3	129.67	3.6245	35.7760	1.6231
C4	129.86	3.6305	35.7692	1.6250
C5	130.13	3.6411	35.7392	1.6266

technique. The chemical use in the present study made up of SiO₂, Na₂CO₃, Bi₂O₃ and BaCO₃ and mixed in crucible. Then, the combined compounds were melted at 1400 °C for 3 hours and annealed at 500 °C for 3 hours before cooled down at room temperature. Finally, the glasses were cut and finely polished to a dimension of 1x1.5x0.3 cm³

2.2 Properties measurement

The densities were measured by Archimedes's method which using water as working liquid at room temperature. The density of glass was calculated from formula:

$$\rho = \left(\frac{W_A + W_B}{W_B} \right) \rho_w \quad (1)$$

where ρ and ρ_w are density of glass and water ($\rho_w = 1.0000 \text{ g/cm}^3$), respectively, W_A is the weight of the glass in air, W_B is the weight of the sample in water. After that the molar volumes were calculated from relation $V_m = M/\rho$ where M is total molecular weight of composition, $M = X_{\text{SiO}_2}Z_{\text{SiO}_2} + X_{\text{Na}_2\text{O}}Z_{\text{Na}_2\text{O}} + X_{\text{CaO}}Z_{\text{CaO}} + X_{\text{Cr}_2\text{O}_3}Z_{\text{Cr}_2\text{O}_3}$ where X , Z is the mole fraction and molecular weight of each composite.

The refractive indexes were measured by Abbe refractometer (ATAGO) and used monobromonaphthalene for adhesive coating. It was measured values from 1.3000 to 1.7000 with an accuracy of 0.0001. The wavelength of light source is the sodium D line at 589.3 nm so we use symbol D is subscript of refractive index. The UV-VIS absorption spectra of glass samples were recorded between 300-800 nm by UV-VIS spectrophotometer (Hitachi, U-1800) at room temperature. The optical band gaps have been discussed by the Urbach plot.

3. Results and discussion

The molecular weights, densities and molar volumes of glasses were shown in Table 2. Normally, the physical properties of glass depend on composition proportion. The densities of glasses were increased with a function of Cr₂O₃ concentrations because the molecular weight of Cr₂O₃ ($M_{\text{Cr}_2\text{O}_3} = 151.9904 \text{ g/mol}$) which replace SiO₂ ($M_{\text{SiO}_2} = 60.0843 \text{ g/mol}$) was higher. It was causes of molecular weights of glasses were increase as well. On the other hand, the molar volumes of glasses were decrease with increasing of Cr₂O₃ concentrations. The molar volumes of glasses depend on the ratio of molecular weight and density as follows: $V_m = M_T/\rho$. This was indicated that the network of glasses was compressed thanks to substitution of Cr₂O₃ to SiO₂. The relation of densities and molar volumes with Cr₂O₃ concentrations was linearity which was shown in Figure 1.

The refractive indexes results of glasses were reported on Table 1. The refractive indexes were increased with Cr₂O₃ concentrations. Generally, the refractive indexes depended on the densities of glasses. Increasing of densities was lead to light travel slower due to the change of direction and more refraction. This phenomenon can explain from equation: $n = c/v$, where n was refractive index, c was speed of light ($3 \times 10^8 \text{ m/s}^2$) and v was speed of light in glass. The refractive indexes of glasses were shown in Figure 2.

The optical absorption spectra of glasses were measured in the wavelength range of 300 - 800 nm as shown in Figure 3. The spectra appear broadband around 630 and 690 nm in an octahedral site due to Cr³⁺ ions [13]. From using Tanabe-Sugano diagrams for d³ ion, the spectra have been analyzed which correspond to ⁴A₂ → ⁴T₂ and ⁴A₂ → ²T₁ transition [14], respectively.

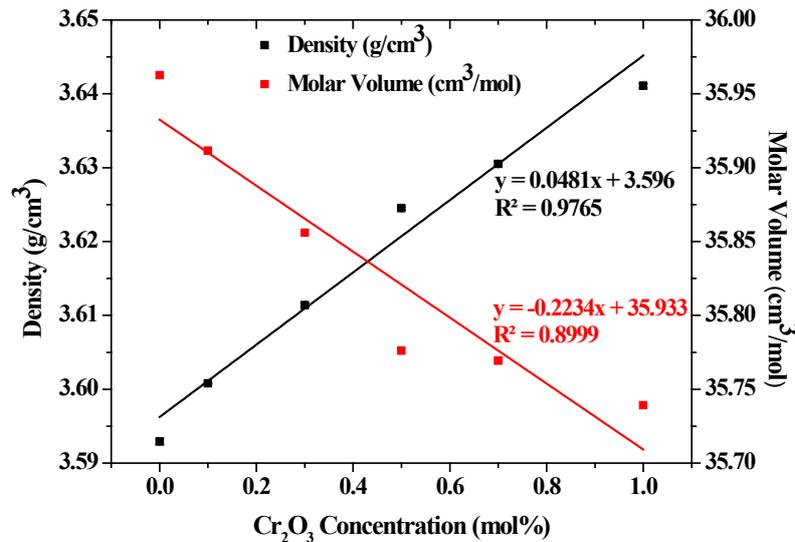


Figure 1 Densities and molar volumes of glasses as a function of Cr₂O₃ concentrations

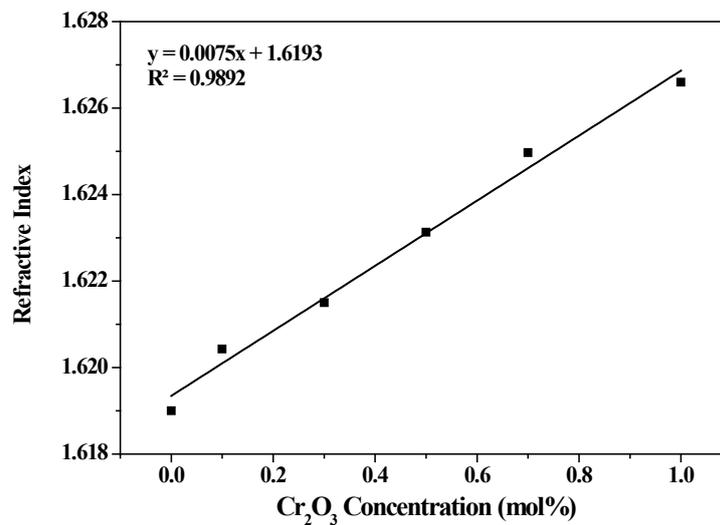
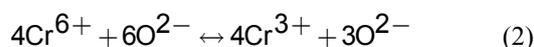


Figure 2 Refractive indexes of glasses as a function of Cr₂O₃ concentrations

However, the spectrum at 370 (due to Cr⁶⁺ ion) [15], 450 and 712 nm which related with ⁴T_{1g}(P), ⁴T_{1g}(F) [8] and ²E_g(G) [10] start from ⁴A₂ ground state was not observed. Besides, the band at 880 nm was not reported in Cr₂O₃ doped glass that melted under atmospheric condition, yet it was observed under reducing condition [7]. When considering the absorbance with Cr₂O₃ concentrations, it found that the absorbance increased up to 0.5 mol% of Cr₂O₃ and beyond it was decreased. The reduction of absorbance indicated that the Cr³⁺ ions may be transfer electron as a represent by the oxidation-reduction equilibrium equation [16]:



Even so, Cr₂O₃ doped silicate glasses absorb light in UV region owing to the electronic transition in interior molecules which in order to the band of Cr⁶⁺

ion was not observed. From the observed absorption edges found to shift rarely toward longer wavelength with increasing of Cr₂O₃ concentrations. The optical band gap has been discussed by the Urbach plot between $(\alpha h\nu)^{1/2}$ and $h\nu$ [17] as present in Figure 4. The optical band gap values were showed in Table 3. The C10 glass was found to have maximum optical band gap.

4. Conclusions

Several of Cr₂O₃ concentration doped sodium barium bismuth silicate glasses were prepared by melt quenching-technique and characterize their density, molar volume, refractive index and optical absorption. The densities of glasses were increased with a function of Cr₂O₃ concentrations because the molecular weight

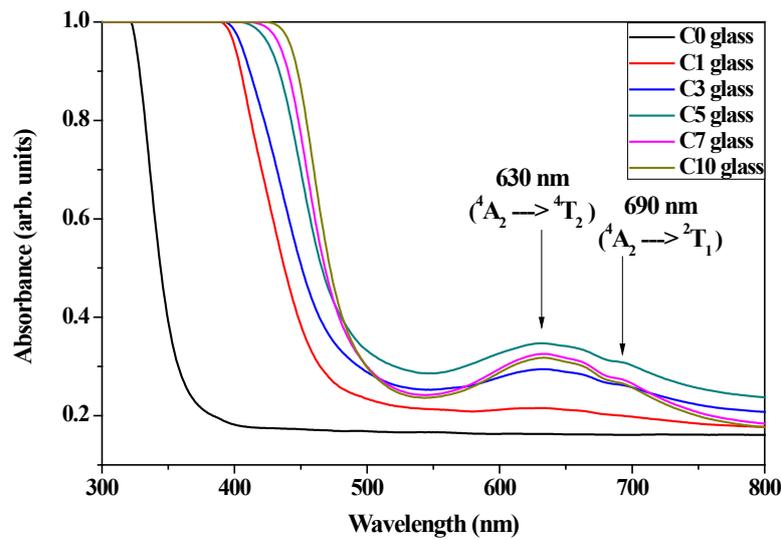


Figure 3 Optical absorption spectra of Cr_2O_3 doped glasses

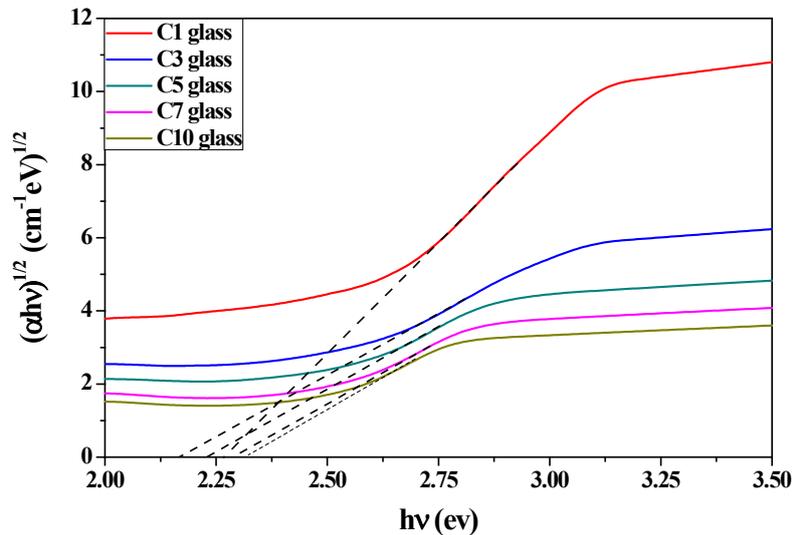


Figure 4 Urbach plot for glass doped with various concentrations of Cr_2O_3

Table 3 Cut off wavelength (nm) and optical band gap (eV) of Cr_2O_3 doped glass

Glass ID	Cut-off wavelength (nm)	Optical band gap (eV)
C1	393	2.27
C3	397	2.17
C5	412	2.23
C7	422	2.29
C10	432	2.32

of Cr_2O_3 which replace SiO_2 was higher. The molar volumes of glasses were decrease with increasing of Cr_2O_3 concentrations while the refractive indexes were increased since increasing of densities was lead to light travel slower due to the change of direction and more refraction. From optical absorption results, the spectra appear broadband around 630 and 690 nm in an octahedral site due to Cr^{3+} ions. However, considering the absorbance with Cr_2O_3 concentrations, it found that the absorbance increased up to 0.5 mol% of Cr_2O_3 and

beyond it was decreased as the Cr^{3+} ions may be transfer electron to Cr^{6+} ions. The optical band gap values were discussed by Urbach plot. The concentration at 1.0 mol% of Cr_2O_3 was maximum optical band gap value.

Acknowledgements

The authors would like to express sincere gratitude toward Nakhon Pathom Rajabhat University (NPRU) and National Research Council of Thailand (NRCT) to support this work.

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