Journal of Thai Interdisciplinary Research
Volume 13, Number 2, Pages 37 - 41

# Effect of $Cr_2O_3$ concentration on physical and optical properties of sodium barium bismuth silicate glasses

Piyachat Meejitpaisan[1,3,*], Nattapon Srisittipokakun[1,3] and Jakrapong Kaewkhao[2,3]

[1]Industrial Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand
[2] Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand
[3]Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand

## Abstract

$Cr_2O_3$ doped sodium barium bismuth silicate glasses have chemical composition (30-x)$SiO_2$ : 30$Na_2O$ : 10 $Bi_2O_3$ : 30BaO : x$Cr_2O_3$ 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 $Cr_2O_3$ 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 $Cr_2O_3$ doped glasses appear broadband around 630 and 690 nm in an octahedral site due to $Cr^{3+}$ ions which corresponding to $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^2T_1$ transition, respectively by Tanabe-Sukano diagram. Nevertheless, the absorbance decreased with $Cr_2O_3$ concentration since $Cr^{3+}$ may be transfer electron. The optical band gaps were studied with Urbach plot. It found that $Cr_2O_3$ 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 $3d^3$ 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: $Cr^{3+}$, $Cr^{4+}$, $Cr^{5+}$ and $Cr^{6+}$ ions [9-10]. Nevertheless, stability chromium ions are exist $Cr^{3+}$ and $Cr^{6+}$ ion in nature [11]. Commonly, the $Cr^{3+}$ ions possess octahedral sites [12] and the efficiency of the most common lasing transition $^4T_2 \rightarrow {}^4A_2$ of this ion is found to be very sensitive to the internal structure of the silicate glass, while the $Cr^{6+}$ ions exhibit tetrahedral site of $^4T_{1g}(P) \rightarrow {}^4A_2$ lasing transition [9]. In this paper, the physical and optical properties of $Cr_2O_3$ doped $Na_2O$-$Bi_2O_3$-BaO-$SiO_2$ glasses have been investigated by varying $Cr_2O_3$ concentrations from 0.0 to 1.0 mol%.

## 2. Materials and methods

2.1 *The preparation of glasses*

$Cr_2O_3$ doped sodium barium bismuth silicate glasses have chemical composition (30-x)$SiO_2$ : 30$Na_2O$ : 10 $Bi_2O_3$ : 30BaO : x$Cr_2O_3$ 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

*Corresponding author; e-mail: piyachat_mee@hotmail.com
DOI 10.14456/jtir.2018.17

**Table 1** Chemical composition of glasses

| Glass ID | $Cr_2O_3$ (mol%) | Glass Composition |
|---|---|---|
| C0 | 0.0 | $30.0SiO_2 : 30Na_2O : 10Bi_2O_3 : 30BaO$ |
| C1 | 0.1 | $29.9SiO_2 : 30Na_2O$ : 10Bi2O3 : 30BaO : $0.1Cr_2O_3$ |
| C3 | 0.3 | $29.7SiO_2 : 30Na_2O$ : 10Bi2O3 : 30BaO : $0.3Cr_2O_3$ |
| C5 | 0.5 | $29.5SiO_2 : 30Na_2O$ : 10Bi2O3 : 30BaO : $0.5Cr_2O_3$ |
| C7 | 0.7 | $29.3SiO_2 : 30Na_2O$ : 10Bi2O3 : 30BaO : $0.7Cr_2O_3$ |
| C10 | 1.0 | $29.0SiO_2 : 30Na_2O$ : 10Bi2O3 : 30BaO : $1.0Cr_2O_3$ |

**Table 2** Molecular weights (g/mol), densities (g/cm$^3$), molar volumes of glasses (cm$^3$/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 $SiO_2$, $Na_2CO_3$, $Bi_2O_3$ and $BaCO_3$ and mixed in crucible. Then, the combined compounds were melted at 1400 $^oC$ for 3 hours and annealed at 500 $^oC$ for 3 hours before cooled down at room temperature. Finally, the glasses were cut and finely polished to a dimension of 1x1.5x0.3 cm$^3$

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 $\rho_w$ are density of glass and water ($\rho_w$ = 1.0000 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/ ρ where M is total molecular weight of composition, $M = X_{SiO2}Z_{SiO2} + X_{Na2O}Z_{Na2O} + X_{CaO}Z_{CaO} + X_{Cr2O3}Z_{Cr2O3}$ 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 bad 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 $Cr_2O_3$ concentrations because the molecular weight of $Cr_2O_3$ ($Mw_{Cr2O3}$ = 151.9904 g/mol) which replace $SiO_2$ ($Mw_{SiO2}$ = 60.0843 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 $Cr_2O_3$ 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 $Cr_2O_3$ to $SiO_2$. The relation of densities and molar volumes with $Cr_2O_3$ 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 $Cr_2O_3$ 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 ($3 \times 10^8$ 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 $Cr^{3+}$ ions [13]. From using Tanabe-Sugano diagrams for $d^3$ ion, the spectra have been analyzed which correspond to $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^2T_1$ transition [14], respectively.

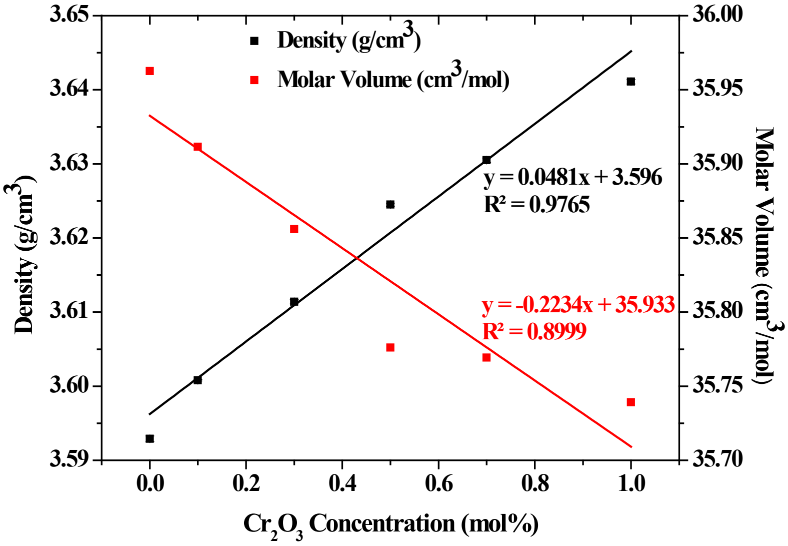


**Figure 1** Densities and molar volumes of glasses as a function of $Cr_2O_3$ concentrations

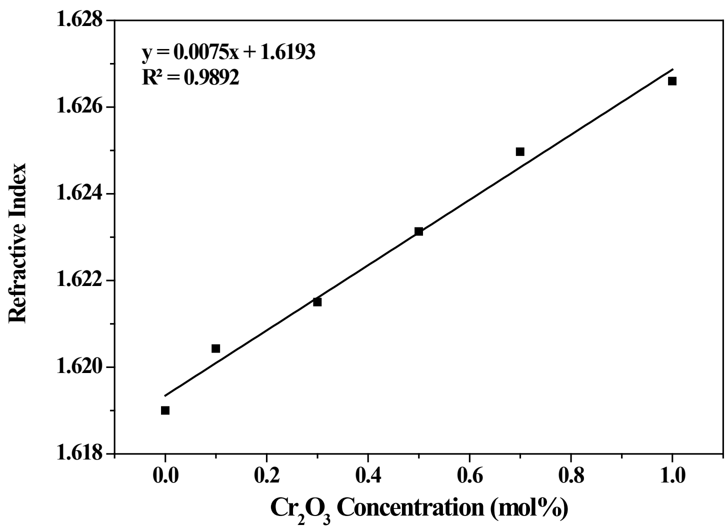


**Figure 2** Refractive indexes of glasses as a function of $Cr_2O_3$ concentrations

However, the spectrum at 370 (due to $Cr^{6+}$ ion) [15], 450 and 712 nm which related with $^4T_{1g}(P)$, $^4T_{1g}(F)$ [8] and $^2E_g(G)$ [10] start from $^4A_2$ ground state was not observed. Besides, the band at 880 nm was not reported in $Cr_2O_3$ doped glass that melted under atmospheric condition, yet it was observed under reducing condition [7]. When 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. The reduction of absorbance indicated that the $Cr^{3+}$ ions may be transfer electron as a represent by the oxidation-reduction equilibrium equation [16]:

$$4Cr^{6+} + 6O^{2-} \leftrightarrow 4Cr^{3+} + 3O^{2-} \quad (2)$$

Even so, $Cr_2O_3$ doped silicate glasses absorb light in UV region owing to the electronic transition in interior molecules which in order to the band of $Cr^{6+}$ ion was not observed. From the observed absorption edges found to shift rarely toward longer wavelength with increasing of $Cr_2O_3$ concentrations. The optical band gap has been discussed by the Urbach plot between $(\alpha h\upsilon)^{1/2}$ and $h\upsilon$ [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 $Cr_2O_3$ 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 $Cr_2O_3$ concentrations because the molecular weight

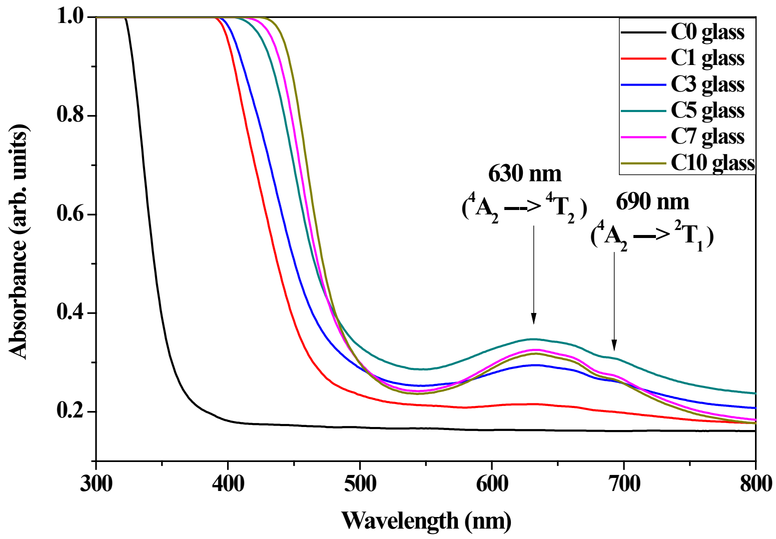


**Figure 3** Optical absorption spectra of $Cr_2O_3$ doped glasses

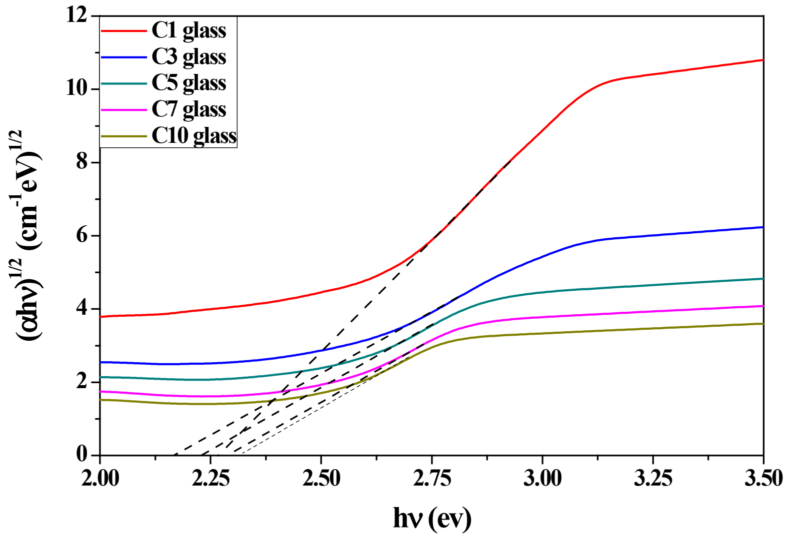


**Figure 4** Urbach plot for glass doped with various concentrations of $Cr_2O_3$

**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.

## References


[1] Manal AB, Fouad ED. Optical properties of oxide glasses containing transition metals: Case of titanium- and chromium-containing glasses. **Curr. Opin. Solid St. M** 2006;**10**: 217-229.

[2] Meejitpaisan P, Insiripong S, Kedkaew C, Kaewkhao J. Radioluminescence and optical studies of gadolinium calcium phosphate oxyfluoride glasses doped with $Sm^{3+}$. **Radiat. Phys. Chem** 2017;**137**: 62-67.

[3] Stara-Janakova S, Spirkova J, Svecova B, Mika M, Oswald J, Mackova A. Chromium (IV) ions containing novel silicate glasses. **Opt. Mater** 2009; **32**: 85-88.

[4] Rakpanich S, Meejitpaisan P, Ravangvong S, Kaewkhao J. Effect of $Nd^{3+}$ ion on bismuth borosilicate glass properties. **Key. Eng. Mat** 2016; **702**: 13-17.

[5] Yoshiyuki K, Hirohiko A, Masahiro T, Tsutomu M. Electronic states of transition metal ions in silicate glasses. **J. Non-Cryst Solids** 1995; **192 & 193**: 316-320.

[6] Kanth CL, Reddy YR, Babu KR, Anjaiah J. Study on certain physical properties of $ZnF_2$-$CdO$-$TeO_2$:$Cr_2O_3$ glasses. **African Physical Review** 2010; **4**: 73-85.

[7] Fatima HEB, Sherief MAN, Fathy ME. Spectroscopic studies of gamma-irradiated transition metals-doped soda lime phosphate glass. **Indian J. Pure Ap. Phy** 2005; **43**: 579-590.

[8] Reddy MR, Reddy MS, Veeraiah N. Physical properties of PbO-Al2O3-B2O3 glasses doped with $Cr_2O_3$. **Indian J. Pure Ap. Phy** 2006; **44**: 446-454.

[9] Flower GL, Reddy MS, Baskaran GS, Veeraiah N. The structural influence of chromium ions in lead gallium phosphate glasses by means of spectroscopic studies. **Opt. Mater** 2007; **30**: 357-363.

[10] Kiran N, Kesavulu CR, Kumar AS, Rao JL. Spectral studies on $Cr^{3+}$ ions doped in sodium-lead borophosphate glasses. **Physica B** 2011; **406**: 1897-1901.

[11] Shigeki M. Optical absorption of Cr-Containing $Li_2O$-$SiO_2$ system transparent glass-ceramics. **J. Ceram. Soc. Jpn** 2004; **112**: 130-132.

[12] Casalboni M, Ciafardone V, Giuli G, Lzzi B, Paris E, Prosposito P. An optical study of silicate glass containing $Cr^{3+}$ and $Cr^{6+}$ ions. **J. Phys. Condens** 1996; **8**: 9059-9069.

[13] Hongping M, Ping L, Degang D, Shiqing X. Spectroscopy and crystal-field analysis of $Cr^{4+}$-doped transparent silicate glass-ceramics. **J. Non-Cryst Solids** 2011; **357**: 2294-2297.

[14] Rao GV, Veeraiah N. Study on certain physical properties of $R_2O$-$CaF_2$-$B_2O_3$:$Cr_2O_3$ glasses. **J. Alloy Comd** 2002; **339**: 54-64.

[15] Meejitpaisan P, Kaewkhao J, Limsuwan P, Kedkaew C. Physical and optical properties of the SLS glass doped with low $Cr_2O_3$ concentrations. **Procedia. Engineer** 2012; **32**: 787-792.

[16] Duffy JA. Redox equilibria in glass. **J. Non-Cryst Solids** 1996; **196**: 45-50.

[17] Krishna GM, Kumari BA, Reddy MS, Veeraiah N. Characterization and physical properties of $Li_2O$-$CaF_2$-$P_2O_5$ glass ceramics with $Cr_2O_3$ as a nucleating agent-physical properties. **J. Solid State Chem** 2007; **180**: 2747-2755.