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Physical and optical properties of the SLS glass doped with low Cr₂O₃ concentrations

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Abstract

The aim of this work is to study the physical properties of Cr₂O₃ -doped soda lime silicate glass in batch of 25Na₂O : 10CaO : (65-x)SiO₂ : xCr₂O₃ where 0.00 ≤ x ≤ 0.05 mol%. The glass samples were prepared by normal melt-quenching technique with 1500°C melting-temperature. The amorphous structure of glass samples were confirmed by X-Ray Diffractometer (XRD) analysis. The density of glass samples were increased with increasing of Cr₂O₃ concentration due to the higher molecular weight of Cr₂O₃ (Mw.=151.9904 g/mol) than SiO₂ (Mw.=60.0843 g/mol). On the other hand, the molar volumes were decreased. It means that network of glasses were compressed because of the substitution of Cr₂O₃ in the place of SiO₂. The refractive index of glass samples was increased. The optical spectra of glass samples were also investigated.

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Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).*Keywords:* Soda-lime-silicate; Cr₂O₃; density; refractive index

1. Introduction

Glass is fusion product of inorganic material which has been cooled to a rigid condition without crystallization [1-2]. The glass can exist color when doped transition metal. The color of glass depends on electron structure as well as on the chemical composition and structure of the base glass which

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determined the local site of these elements [3]. For this paper present, chromium which is a transition metal was doped soda lime silicate glass system.

The doped transition metal in glasses affect to color and physical properties (eg. density, molar volume, refractive index, etc.). The atomic number and atomic weight of chromium are 24 and 51.996 g/mol, respectively. The chromium $3d^5 4s^1$ electron configuration is a paramagnetic transition ion. It is known that the chromium has various oxidation number; Cr^{3+} , Cr^{4+} , Cr^{5+} , Cr^{6+} . Usually, stability chromium ion are Cr^{3+} and Cr^{6+} ions [4]. The Cr^{3+} and Cr^{6+} ions doped in glass system created color in glasses which can be observed by UV-VIS spectra. The aim of this work was to investigate physical and optical properties of soda-lime silicate glass dope with different Cr_2O_3 concentrations and under quenching temperature $1500^\circ C$.

2. Experimental details

Soda lime silicate doped Cr_2O_3 were prepared by mixed chemical reagent, SiO_2 , Na_2O , CaO and Cr_2O_3 due to Na_2O is unstable in the air so the reagent was added as the Na_2CO_3 form. The mixture was melted in alumina crucible at $1500^\circ C$ for 3 hours and cooled down to room temperatures. The composition is $25Na_2O : 10CaO : (65-X) SiO_2 : X Cr_2O_3$ (where $0.00 \leq X \leq 0.05$ mol%). The chemical composition was shown in Table 1.

Table 1. Chemical composition of glass samples

Glass ID	Cr_2O_3 (mol%)	Glass composition (mol%)
S65Cr0	0	65SiO ₂ -25Na ₂ O-10CaO
S65Cr1	0.01	64.99SiO ₂ -25Na ₂ O-10CaO-0.01Cr ₂ O ₃
S65Cr2	0.02	64.98SiO ₂ -25Na ₂ O-10CaO-0.02Cr ₂ O ₃
S65Cr3	0.03	64.97SiO ₂ -25Na ₂ O-10CaO-0.03Cr ₂ O ₃
S65Cr4	0.04	64.96SiO ₂ -25Na ₂ O-10CaO-0.04Cr ₂ O ₃
S65Cr5	0.05	64.95SiO ₂ -25Na ₂ O-10CaO-0.05Cr ₂ O ₃

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

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

where ρ and ρ_w are density of samples and water ($\rho_w = 1.0000$ g/cm³), respectively, W_A is the weight of the sample 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, $M = X_{SiO_2}Z_{SiO_2} + X_{Na_2O}Z_{Na_2O} + X_{CaO}Z_{CaO} + X_{Cr_2O_3}Z_{Cr_2O_3}$ where X, Z is the mole fraction and molecular weight of each composite.

The refractive index was measured by Abbe refractometer (ATAGO) and use monobromonaphthalene for adhesive coating. It measured a unitless number between 1.3000 to 1.7000. The wavelength of light source is the sodium D line at 589.3 nm so we use symbol D is subscript of refractive index. Then calculated the molar refraction by Lorentz-Lorentz formula :

$$R_m = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) V_m \quad (2)$$

where $R_m =$ molar refraction by $(n^2-1)/(n^2+2)$ is known as the refraction loss, n is refractive index, V_m is called the molar volume ($V_m = M/\rho$). Thereafter we calculate molar refraction and molar electronic polarizability of the material from the relation

$$\alpha_m = \left(\frac{3}{4\pi N} \right) R_m \quad (3)$$

where N represents Avogadro's number or more strictly, the number of polarisable ions per mole. The structure of glass samples were confirmed by X-Ray Diffractometer.

The absorption spectra were measured by UV-VIS spectrophotometer (Hitachi, U-1800) at room temperature and were recorded in range 300-800 nm. The color of glass samples were investigated using CIE $L^*a^*b^*$ system.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction pattern (XRD) of 0.05 mol% Cr_2O_3 -doped soda-lime silicate glass was shown in Fig. 1. The XRD pattern showed a widely spread scattering at low angle (30 deg.) which indicated amorphous of glass samples.

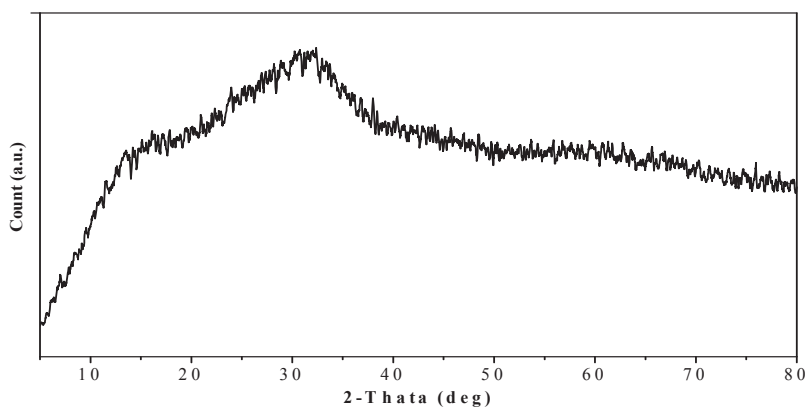


Fig. 1. XRD pattern of 0.05 mol% Cr_2O_3 -doped soda lime silicate glass

3.2. Physical properties

The density and molar volume of glass samples with different Cr_2O_3 concentration were presented in Table 2. The density and molar volume with Cr_2O_3 concentration is shown in Fig. 2. When added Cr_2O_3 into the soda-lime silicate glass network, the density of glass samples increase because of the substitution molecular weight of Cr_2O_3 (Mw. = 151.9904 g/mol) higher molecular weight of SiO_2 (Mw. = 60.0843g/mol). The relation of density with chromium concentration is linearity. The molar volume of the glass sample were decrease with chromium concentration increase due to the shorter bond length of Cr_2O_3 compared to that of SiO_2 . The Cr-O and Si-O distance is 1.61 and 1.62 Å respectively. These distances are ionic radii [5]. This indicate that the network of glass samples were compressed because of the substitution of Cr_2O_3 in the place of SiO_2 .

Table 2. The various physical properties of the glass sample.

Parameters	Cr ₂ O ₃ concentration (mol%)					
	0	0.01	0.02	0.03	0.04	0.05
Density, ρ (g/cm ³)	2.5498	2.5531	2.5579	2.5594	2.5637	2.5672
Molar volume, V _m (cm ³ /mol)	23.5931	23.5658	23.5252	23.5153	23.4797	23.4510
Refractive index, n _D (589.3 nm)	1.5269	1.5272	1.5277	1.5279	1.5282	1.5285
Molar refractivity, R _m (cm ³)	7.2524	7.2479	7.2407	7.2400	7.2331	7.2273
Refraction losses, R (%)	0.3073	0.3075	0.3077	0.3078	0.3080	0.3081
Molar electronic polarizability, α _m (Å ³)	2.8775	2.8757	2.8725	2.8726	2.8698	2.8675

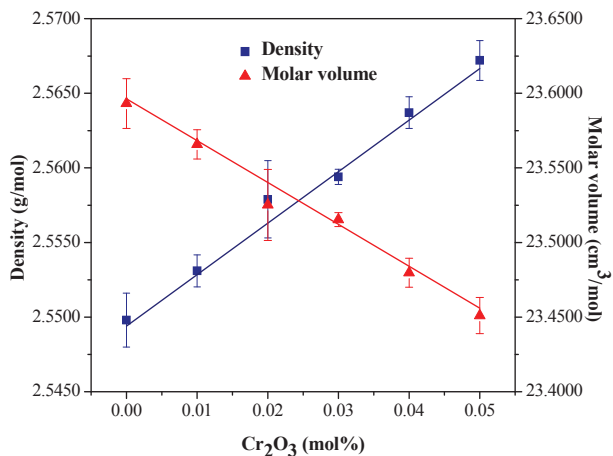


Fig. 2. The density and molar volume of glass sample as a function of Cr₂O₃ content

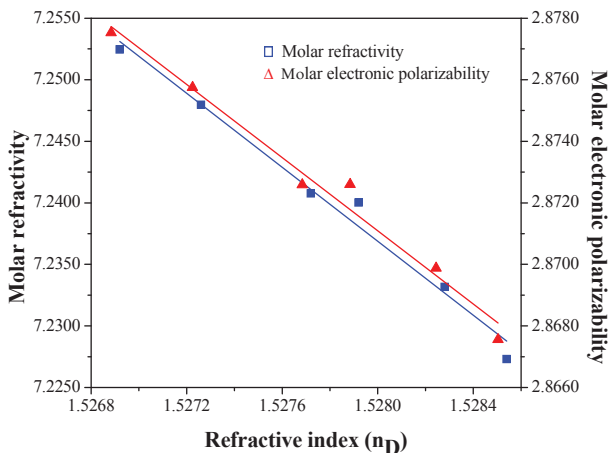


Fig. 3. The relation between molar electronic polarizability and refractive index

The refractive indices are given in Table 2 and will be used for the determination of molar refractivity and molar electronic polarizability. The molar refractivity and the molar electronic polarizability of oxide ions showed tendency linear decrease with refractive index. The linearity of molar refractivity has slope more than linearity of molar electron polarizability about 2.52 times when compared with refractive

index. The linear decrease of the both parameter indicated that the refractive index of glass does not only depend on the density [4,6].

3.3. Optical properties

The 0.05 mol% Cr₂O₃ -doped were color glass at greenish-yellow color (-a*, b*) as fig shown in Fig. 4. Fig. 5 show that the optical absorption spectra of Cr₂O₃ -doped glass samples. The spectra exhibited absorption band at around 330, 350 and 370 nm for Cr⁶⁺ ion [1,7]. In addition there are a slightly peak absorption broadband at around 650 nm [8,9] for Cr³⁺ ion. The ratio intensity between Cr⁶⁺ and Cr³⁺ is about 60 times which indicate that Cr⁶⁺ ion strong band than Cr³⁺. A. Fatma H El-Batal et al. report [10], The color of Cr₂O₃ -doped glass were green and gives four absorption band; ultraviolet region at 350 nm and visible at 430 nm, 660 nm and 880 nm. The Cr³⁺ ion correspond with the first two visible absorption band. The absorption band at 880 nm is not previously shown in glasses melt under atmosphere condition.

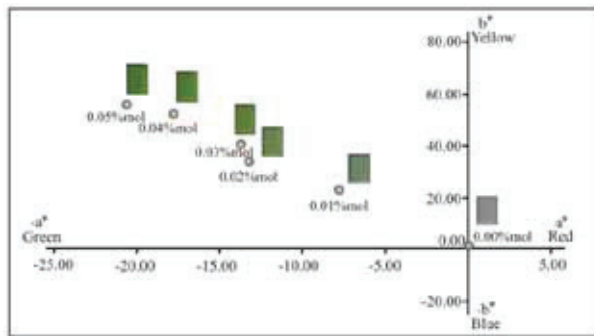


Fig. 4. The CIE L*a*b* color scale of undoped and doped Cr₂O₃ in soda lime silicate glass samples

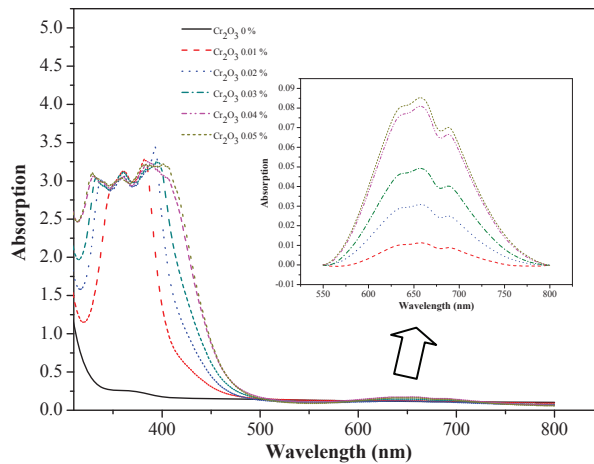


Fig. 5. The optical spectra of undoped and Cr₂O₃-doped glass samples at room temperature

4. Conclusion

Cr₂O₃ -doped soda lime silicate glass in batch of 25Na₂O : 10CaO : (65-x)SiO₂ : xCr₂O₃ where 0.00 ≤ x ≤ 0.05 mol% at 1500°C melting temperature show that the density and refractive index with increasing concentration of Cr₂O₃. The density and molar volume was opposite when Cr₂O₃ concentration increase due to the increase of the molecular weight of glass system. The both of molar electron polarizability and molar refraction decrease when refractive index increase. This indicate that the refractive index has affect in both properties. In addition, the glass sample have peak at 330, 350 and 370 nm of hexavalent and a slightly peak at 641, 660 and 688 nm of trivalent. These band absorptions was confirm colour of the glass samples which glass samples have greenish-yellow color.

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