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Effect of mixed NiO-CuO in soda lime silicate glasses

Nattapon Srisittipokakun[1,2,*], Anon Angnanon[1,2] and Jakrapong Kaewkhao[1,2]

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

Abstract

Ni/Cu co-doped in soda lime silicate (SLS) glasses were prepared by using normal melt quenching technique at 1200°C for 3 h, and annealed at 500 °C for 3 h. The current composition was prepared based on the proposed ratio: (64.98-x)SiO_2: 10CaO: 25Na_2O: 0.02NiO: xCuO where x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 mol%. The physical and optical properties of Ni/Cu co-doped in SLS glasses such as density, molar volume, refractive index and optical absorption were measured and discussed. The optical absorption spectrum of Ni/Cu co-doped in SLS glasses measured at room temperature in the wavelength region 200–1100 nm were presented.

Keywords: soda lime silicate glasses, NiO, CuO, co-doped, optical properties

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1. Introduction

Glasses containing transition metal oxide can be expected to possess interesting and unusual properties arising from the fact that transition metal ion can exist in more than one valence state in glasses [1]. Transition metal ions are characterized by partially filled d-shell that can frequently exist in a number of oxidation states and the electro-optical behavior can occur as a result of electron transfers from ions in a lower to those in a higher oxidation state [2 - 4]. Nickel oxide (NiO) is used extensively in many areas, such as catalysis, battery electrodes, electrochromic film, gas sensors and magnetic materials [5 - 8]. Copper oxide (CuO) have an interesting and varied structural chemistry due to their flexibility, which is a result of the ability of copper to adopt different geometries [9-12]. In the silicate glass matrices this ion is expected to exist as metallic Cu, cuprous Cu^{+}, or cupric Cu^{2+} ions as per the following redox reaction [13]. The aim of the present work is to investigate the physical and optical properties of co-doped NiO based with variation of CuO concentration of soda lime silicate glasses.

2. Materials and methods

Samples were prepared by awell-known melt quenching technique. The current composition was prepared based on the proposed ratio:(64.98-x)SiO_2: 10CaO: 25Na_2O: 0.02NiO: xCuO where x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 mol%. The CuO was doped in the range of 0.0-0.5 mol%, because of glass still transparent and not opaque. If it was doped too much, it will be opaque. The starting raw materials such as silicon dioxide (SiO_2), calcium carbonate ($CaCO_3$), sodium carbonate (Na_2CO_3), copper oxide (CuO) and nickel oxide (NiO) were obtained from Sigma Aldrich having a purity of 99.99%. All the chemicals were weighted according to the stoichiometric amount and thoroughly mixed. The well mixed powder were loaded in porcelain crucible and melted in an electric furnace at 1200°C for 3 h. The melt glass samples were obtained by pouring on a graphite mold. The obtained transparent glass samples were finally annealed at 500°C for 3 h. The temperature of the annealing furnace was reduced to the room temperature with a cooling rate of 10°C/min to reduce thermal stress, and cool down to the room temperature. Finally, good qualities of clear and transparent glasses were formed. For optical and spectroscopic measurements, the samples were cut and polished by diamond clay for 30 min for each sample. Figure 1 shows the photographs of the cut and polished glass samples.

All the developed glass samples were characterized using various characterization techniques. Absorption spectra and color coordinates system (CIE L*a*b*) were recorded using a UV – visible spectrophotometer (cary-50), working in 200 – 1,100 nm at room temperature. The refractive indices were measured by an Abbe refractometer (ATAGO) with a sodium vapor lamp as a light source having a wavelength of 589.3 nm (D line) with monobromonaphthalene as a contact layer between the sample and prism of the refractometer. The glass samples densities were determined by Archimedes method. Water was selected as an immersive fluid. For all samples, the measurement

*Corresponding author; e-mail: Nattapon2004@gmail.com

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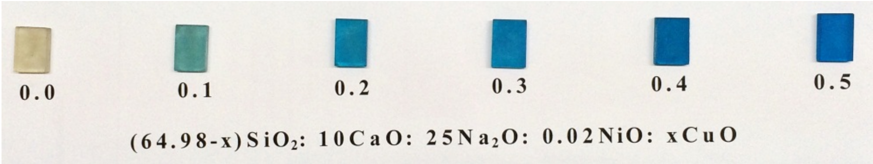

Figure 1 Digital photograph of Ni/Cuco-doped in SLS glasses

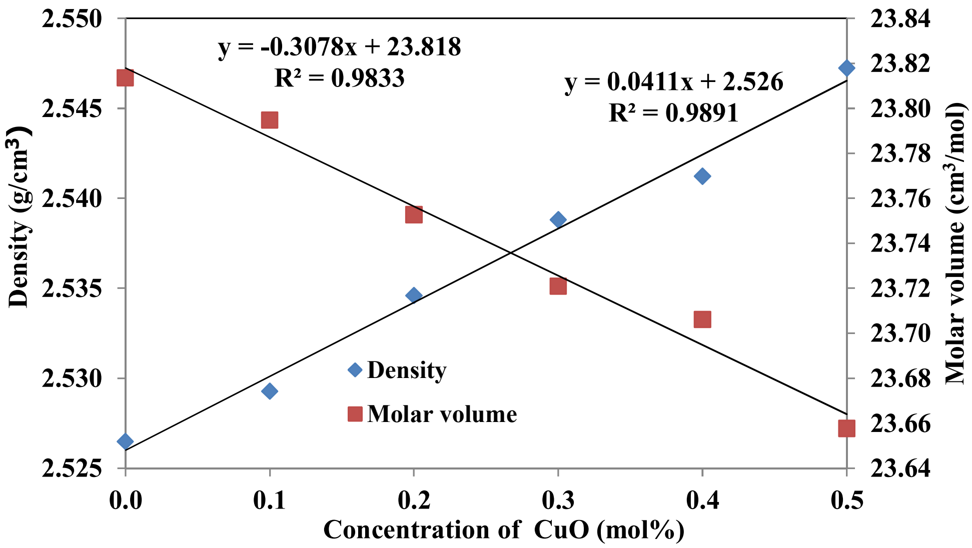

Figure 2 Density and molar volume of glass samples

was done at room temperature and repeated three times to reduce the error. Consequently, the molar volumes of the glass samples were calculated based on the density values according to the following equation.

3. Results and discussion

3.1 Density and molar volume

The density of the materials is an important quantity of the physical parameters to determine the change of the structural softening/compactness, change in geometrical configuration, coordination number, cross-link density and dimension of interstitial spaces of the glass [14]. The density of glass samples increase with the increasing Cu^{2+} concentration. In the present glass compositions, the molecular mass of CuO is greater than SiO_2 that is why the molecular mass of the present glasses increases and their density also increases. The molar volume decreases and the density increases as copperion content increases. This agrees with the density definition that is the mass of glass sample divided by the molar volume of the glass sample. Besides that, there might be ion copper substituted inside the glass network and make the glass matrix become denser, the intermolecular spacing decreases and a decrease in molar volume and an increase in density [15]. Density and molar volume of glass samples are shown in Figure 2. Refractive index is the most significant property of the optical glasses. Therefore the relation between refractive index and glass composition have been investigated by most researchers [16]. Figure 3 shows that the refractive index of glass samples increases with concentration of Cu^{2+} ion, it is because of the increasing density of the prepared glass samples. When the density of the developed glass samples increases the structure of the glass will be compact and velocity of light in these materials will be less which cause the refractive index increases.

3.2 Ion concentration

By using equation (1) the ion concentration (N) was determined [17]. The distance between the Cu^{2+} ion (r_i), polaron radius (r_p) and field strength (F) of Cu–O bond in the glass system were also measured and are shown in Table 1.

$$N\,(\text{ion/cm}^3) = (\%\text{mol of CuO})\ \text{x}\ \frac{(\text{Avogadro's number})(\text{glass density})}{(\text{glass average molecular weight})} \quad (1)$$

Ni^{2+} ion concentration, refractive index and density were used to calculate the physical properties of the glasses such as polaron radius (r_p), electronic polarizability (α_e), molecular refractivity (R_m), inter nuclear distance (r_i), field strength (F) and reflection losses (R), using the relevant expressions and the results are collected in Table 1 for glass samples.

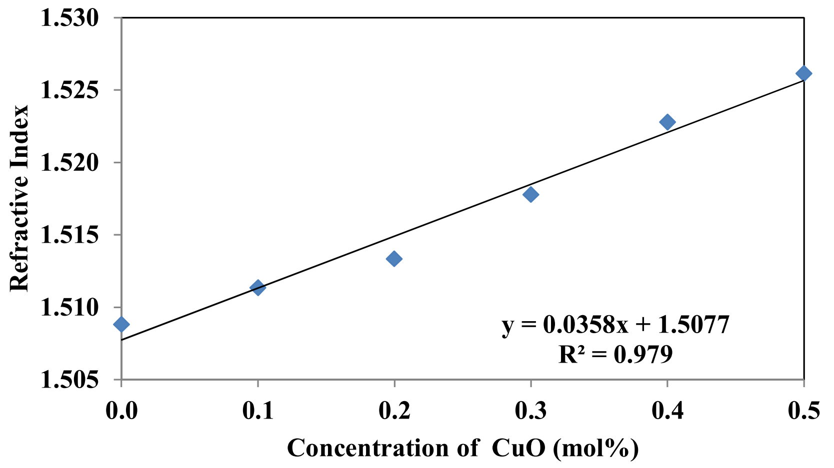

Figure 3 Refractive index of glass samples

Table 1 Physical parameters of SiO_2-CaO-Na_2O-NiO glass doped with different CuO (concentration)

Physical properties	Dopant concentration (mol%)					
	0.0	0.1	0.2	0.3	0.4	0.5
Density, ρ (g/cm^3)	2.5265	2.5293	2.5346	2.5388	2.5412	2.5472
Thickness (cm)	0.3500	0.3500	0.3500	0.3500	0.3500	0.3500
Refractive index, n	1.5088	1.5113	1.5133	1.5178	1.5228	1.5261
Molecular weight, M (g/mol)	60.1642	60.1836	60.2031	60.2225	60.2420	60.2614
Molar volume (cm^3/mol)	23.8134	23.7948	23.7527	23.7209	23.7060	23.6576
Ion concentration (N $x10^{20}$ ion/cm^3)	-	0.2531	0.5071	0.7616	1.0161	1.2727
Polaron radius r_p (Å)	-	13.7280	10.8895	9.5086	8.6373	8.0127
Inter-nuclear distance r_i (Å)	-	34.0602	27.0176	23.5915	21.4299	19.8802
Field strength, F ($x10^{12}$ cm^{-2})	-	0.2122	0.3373	0.4424	0.5362	0.6230
Molar refraction R_m (cm^3/mol)	7.1080	7.1323	7.1431	7.1853	7.2390	7.2632
Molar polarizability α_m (Å^3)	2.8167	2.8263	2.8306	2.8474	2.8686	2.8782
Metallization criteria (M)	0.7015	0.7003	0.6993	0.6971	0.6946	0.6930

The result from equation 1 shows that with increasing CuO concentration the ion concentration (N) were also increased in the present glass matrix. This result indicates that the Cu^{2+} ions are expected to be uniformly distributed in the present glass matrix. Due to the presence of cobalt oxide, in order to confirm this compaction of our glasses, the inter ionic separation (r_i) and polar on radius (r_p) have been determined by equation (2) and (3), respectively.

$$r_i(\overset{o}{A}) = \left(\frac{1}{N}\right)^{1/3} \quad (2)$$

$$r_p(\overset{o}{A}) = \left(\frac{1}{2}\right)\left(\frac{\pi}{6N}\right)^{1/3} \quad (3)$$

where N is the ion concentration. The values are listed in Table 1, which clearly indicate that with increasing concentration of CuO a continuous decreases the polaron radius and inter ionic separation. It means the compact structure of our prepared glass samples. So the Cu-O bond strength increases and producing a stronger field around the Cu^{2+} ions. The field strength (F) around Cu^{2+} ion was calculated according to the following relation.

$$F(cm^2) = \left(\frac{Z}{r_p^2}\right) \quad (4)$$

where r_p is the polaron radius and Z is the atomic mass of Cu^{2+} ion. Refractive index (n), density (ρ) and molecular mass were used to measure the molar refractivity (R_m) by the relation [18].

$$R_m = \frac{(n_o^2 - 1)}{(n_o^2 + 2)}\left(\frac{m}{\rho}\right) \quad (5)$$

The molar refractivity is related to the structure of the glass network. The molar refractivity of glass samples

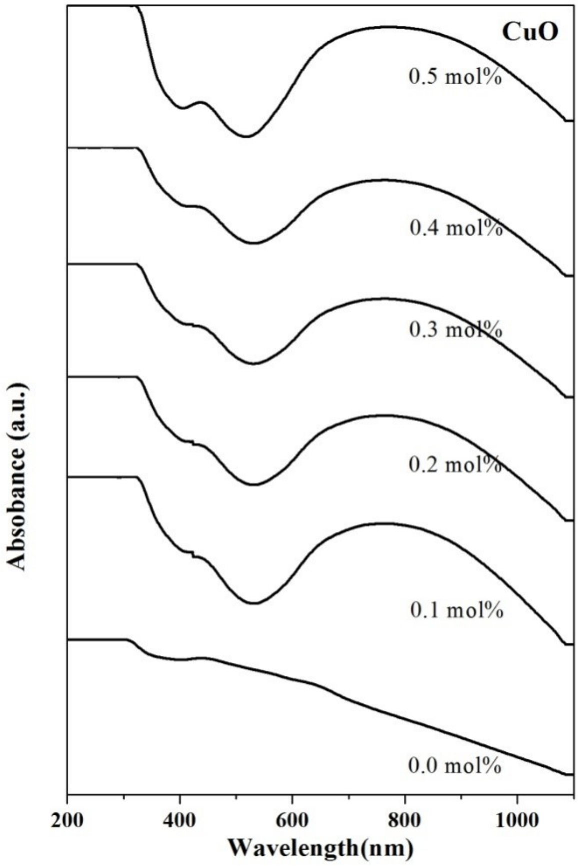

Figure 4 Absorption spectra of glass samples

increase with concentration of Cu^{2+} ion. It is proportional to the molar electronic polarizability of the material (α_m) by the Clasius-Mosotti relation [19, 20].

$$\alpha_m = \frac{3}{4\pi N_A} R_m \qquad (6)$$

where N_A is Avogadro's number. The value $\left(\frac{3}{4\pi N_A}\right)$ is known as Lorentz function. From Table 1, it was observed that the molar electronic polarizability of the material increases with molar refractivity and refractive index which indicate that the refractive index of the prepared glass samples depends not only on the density but also on the polarizability of the glass. The metallization criterion, which gives the information about the non-metallic nature of the solid and was calculated by the relation [20].

$$M=1 - R_m/V_m \qquad (7)$$

The values of R_m/V_m are useful in measuring the metallic or non-metallic nature of the materials, $R_m/V_m< 1$ is non-metal whereas $R_m/V_m> 1$ is metal. The measured values of metallization criterion are collected in Table 1, which clearly indicate that with increasing concentration of CuO a continuous decrease in metallization criterion shows that the developed samples are non-metallic in nature.

3.3 Absorption spectra

The typical optical absorption spectra of glass samples in the wavelength range 200-1100 nm are recorded and given in Figure 4. There are 2 peaks at 468 nm, and 790 nm. The observed visible peaks are related to the presence of nickel ions in the divalent state in the tetrahedral coordination at 468 nm. The energy level structure of the Ni^{2+} (d^7) ion in tetrahedral site is similar to the energy level structure of d^3 ions in octahedral site. Using Tanabe–Sugano diagrams for the d^3 configuration, which is conjugate to (d^7) ion, the absorption peak observed near to 468 nm are assigned to $^3A_2 \rightarrow ^1T_2$ [21]. Broad absorption around 790 nm corresponds to $^2B_{1g}$–$^2B_{2g}$ transition of Cu^{2+} ions [22].

4. Conclusions

In the present work, SiO_2-CaO-Na_2O-NiO doped with different concentrations of Cu^{2+} ions were prepared using normal melt quenching technique. In this work, the structural and optical properties of Cu^{2+} doped glass samples were investigated. Optical absorption, density, molar volume, refractive index, and other physical parameters were measured and discussed for Cu^{2+} doped glass samples. The density and refractive index results show usual behaviour with particular trend in the increase with increasing CuO concentration. The molar volume decreases and the density increases as Cu^{2+} ion content increases. This agrees with the density definition that is the mass of glass sample divided by the molar volume of the glass sample. Besides that, there might be ion copper substituted inside the glass network and make the glass matrix become denser, the intermolecular spacing decreases and a decrease in molar volume and an increase in density. From optical absorption spectra, there are three broad band transitions were observed. The absorption peak observed near468 nm, and 790 nm are assigned to ${}^3A_2 \rightarrow {}^1T_2$ and ${}^2B_{1g}$–${}^2B_{2g}$, respectively.

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