Optical Properties of the SiO$_2$-Na$_2$O-CaO-Nd$_2$O$_3$ Glasses

1P. Chimalawong, 2J. Kaewkhao, 3T. Kittiauchawal, 4C. Kedkaew and 1,4P. Limsuwan
1Department of Physics, Faculty of Science, King Mongkut’s University of Technology Thonburi, Bangkok 10140, Thailand
2Center of Excellence in Glass Technology and Materials Science, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand
3Department of Physics, Faculty of Science and Technology, Thespatri Rajabhat University, Lopburi 15000, Thailand
4Thailand Center of Excellence in Physics, Chiang Mai University, Chiang Mai 50202, Thailand

Abstract: Problem statement: This study researched on different physical and optical properties of Nd$^{3+}$ doped soda-lime-silicate glass. The glasses containing Nd$^{3+}$ in (65-x) SiO$_2$: 25Na$_2$O: 10CaO: xNd$_2$O$_3$ (where x = 0.0-5.0 mol%) had been prepared by melt-quenching method. The density and molar volume increase with increasing of Nd$_2$O$_3$ concentration due to increasing of Non Bridging Oxygens (NBOs) in glass matrix. Approach: The optical spectra were measured and evaluated their optical band gap and found to decrease with increasing of Nd$_2$O$_3$ concentration. Results: Moreover, these results showed that the refractive index of glass does not only depend on the density but also depend on the electronic polarizability of the glass. Conclusion: The values of polarizability of oxide ions, theoretical optical basicity were also determined.

Key words: Nd$_2$O$_3$, optical band gap, optical properties, NBOs

INTRODUCTION

Rare earth containing glasses have attracted a great deal of interest due to their macroscopical properties such as high mechanical resistance, chemical stability and heat-resistance (Gatterer et al., 1998). Moreover their optical and magnetic properties justify the wide use of these glasses as optical amplifiers in telecommunication fibers network, as new miniature optical devices and as component for laser technology (Pisarski et al., 2005; Das et al., 2006; Mohan et al., 2008). Among the conventional glasses, soda-lime silicate glasses have attracted much attention because of their good glass forming nature compared to several other conventional systems (Moorthy et al., 2004; Yanbo et al., 2006). As well as erbium doped glass materials, the main application of neodymium containing glasses is as optical amplifiers for long distance telecommunication. The addition of an extra cation to the glass network exerts an influence on the glass structure leading to the local change of the Bridging Oxygen (BO) and Non Bridging Oxygen (NBO) distribution. In particular the addition of a high field strength modifier, promoting the increase of the NBO species in the glass matrix, leads to the general depolymerization of the network that can be related to the modifications of the chemical and physical properties (Corradi et al., 2005).

However, a little information is available on structure and properties of the multi-component soda-lime silicate glasses containing rare earth ions. Therefore, the aim of the present study has been to investigate the effect of Nd$_2$O$_3$ content on optical band gap, density, molar volume, optical basicity and polarizability in soda-lime silicate glass.

MATERIALS AND METHODS

Glass preparation: Series of Nd$^{3+}$ doped soda-lime silicate glasses (in mol%): (65-x) SiO$_2$:25Na$_2$O:10CaO-xNd$_2$O$_3$ (x = 1-5 mol%) were prepared by the normal melt-quenching technique and their compositions in mole percent are given in Table 1.

| Glass ID | Nd$_2$O$_3$ (mol %) | Glass composition (mol %) |
|----------|---------------------|---------------------------|
| S65ND0   | 0                   | 65SiO$_2$:25Na$_2$O:10CaO |
| S64ND1   | 1                   | 64SiO$_2$:25Na$_2$O:10CaO-Nd$_2$O$_3$ |
| S63ND2   | 2                   | 63SiO$_2$:25Na$_2$O:10CaO-2Nd$_2$O$_3$ |
| S62ND3   | 3                   | 62SiO$_2$:25Na$_2$O:10CaO-3Nd$_2$O$_3$ |
| S61ND4   | 4                   | 61SiO$_2$:25Na$_2$O:10CaO-4Nd$_2$O$_3$ |
| S60ND5   | 5                   | 60SiO$_2$:25Na$_2$O:10CaO-5Nd$_2$O$_3$ |

Corresponding Author: P. Chimalawong, Department of Physics, Faculty of Science, King Mongkut’s University of Technology Thonburi, Bangkok 10140, Thailand

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Analytical reagent grade chemicals of SiO$_2$, Na$_2$O, CaO and Nd$_2$O$_3$ were used in the glasses preparation. Each batch of chemical was powdered finely and mixed thoroughly in porcelain crucibles and was later melted in an electrical muffle furnace for 3 h, at 1200°C.

After complete melting, the homogenized melt was quickly poured onto a stainless steel mould that was heated at 500°C to form the glasses. The glass blocks thus resulted were immediately transferred to the annealing furnace that and were annealed at 500°C for 3 h and then slowly cooled down to the room temperature in order to remove possible thermal stains in the glasses. Finally, the as-prepared glass samples were cut and then finely polished to a thickness about 3 mm.

**Measurements:** Glass densities were measured by using xylene as an immersion liquid based on the Archimedes’s principle. Glass refractive indices were measured at room temperature using an Abbe refractor meter (ATAGO) and mono-bromonaphthalene as an adhesive coating. The optical absorption spectra of Nd$^{3+}$ doped soda-lime silicate glasses were recorded at room temperature using a UV-VIS spectrophotometer (Hitachi, U-1800), working in 300-700 nm.

**RESULTS**

**Physical properties:** Based on the determined density, refractive index values and the molecular weight of SiO$_2$-Na$_2$O-CaO-Nd$_2$O$_3$ glass, the various physical properties relating to the glass studied, are present in Table 2. The necessary formulae of these factors are reported already in the literatures (Sindhu et al., 2005; Abdel-Baki et al., 2007; Eraiah and Bhat, 2007; Zhao et al., 2007). The color of the transparent Nd$^{3+}$ doped soda-lime silicate glasses changes with Nd$_2$O$_3$ content between colorless and dark violet, as shown in Fig. 1. The measured densities of these glasses are shown in Fig. 2.

**Optical band gap:** The study of optical absorption edge is useful information for understanding the optically induced transitions and optical band gaps of materials. In order to understand the optically induced transition, optical band gaps have been computed from the UV absorption spectra of these glasses. The principle of the technique is that a photon with energy greater than the band gap energy will be absorbed. There two kind of optical transitions at the fundamental absorption edge: direct and indirect transitions, both of which involve the interaction of an electromagnetic wave with an electron in valence band.

![Fig. 1: Photographs of Nd$^{3+}$ doped soda-lime silicate glasses](image1)

![Fig. 2: Variation of the density with Nd$_2$O$_3$ concentration](image2)

| Parameters                        | Nd$_2$O$_3$ (mol %) |
|-----------------------------------|---------------------|
|                                   | 0.0                 |
| Average molecular weight, M(g)    | 60.1573             |
| Density, (g.cm$^{-3}$)            | 2.5314              |
| Thickness of the glass, d (cm)    | 0.3880              |
| Refractive index $n_d$ (589.3 nm) | 1.5247              |
| Molar volume $V_m$(cm$^3$ mol$^{-1}$) | 23.7644             |
| Molar refractivity, $R_m$ (cm$^{-1}$) | 7.2793              |
| Molar polarizability, $\alpha_m$ (Å$^3$) | 2.8858              |
| Refraction losses, R (%)          | 4.3192              |
| Indirect optical band gap, $E_g$ (eV) | 3.5673              |
| Glass optical basicity, $\Lambda$  | 0.6288              |
| Glass oxide polarizability, $\alpha_o$ (Å$^3$) | 1.6544              |
|                                   | 1.0                 |
|                                   | 62.9212             |
|                                   | 2.6175              |
|                                   | 0.3580              |
|                                   | 1.5350              |
|                                   | 24.0387             |
|                                   | 7.4840              |
|                                   | 2.8669              |
|                                   | 4.5400              |
|                                   | 3.3357              |
|                                   | 0.6430              |
|                                   | 1.6629              |
|                                   | 65.6852             |
|                                   | 2.7031              |
|                                   | 0.3550              |
|                                   | 1.5444              |
|                                   | 24.2999             |
|                                   | 7.6758              |
|                                   | 3.0429              |
|                                   | 4.5779              |
|                                   | 3.2376              |
|                                   | 0.6571              |
|                                   | 1.6682              |
|                                   | 68.4491             |
|                                   | 2.7789              |
|                                   | 0.3680              |
|                                   | 1.5542              |
|                                   | 24.6317             |
|                                   | 7.8965              |
|                                   | 3.1304              |
|                                   | 1.5601              |
|                                   | 24.9643             |
|                                   | 8.0031              |
|                                   | 3.1727              |
|                                   | 1.5709              |
|                                   | 25.3398             |
|                                   | 8.3246              |
|                                   | 3.3001              |
|                                   | 4.3192              |
|                                   | 4.4540              |
|                                   | 4.5779              |
|                                   | 4.7079              |
|                                   | 4.7865              |
|                                   | 4.9312              |
|                                   | 3.5673              |
|                                   | 3.3357              |
|                                   | 3.2376              |
|                                   | 3.2343              |
|                                   | 3.1720              |
|                                   | 2.9548              |
|                                   | 0.6288              |
|                                   | 0.6430              |
|                                   | 0.6571              |
|                                   | 0.6710              |
|                                   | 0.6847              |
|                                   | 0.6982              |
|                                   | 1.6544              |
|                                   | 1.6629              |
|                                   | 1.6682              |
|                                   | 1.6803              |
|                                   | 1.6820              |
|                                   | 1.7009              |

Table 2: Various physical properties of SiO$_2$-Na$_2$O-CaO-Nd$_2$O$_3$ glasses
The general formula for the optical absorption coefficient \( \alpha(\omega) \) is given as:

\[
\alpha(\omega) = \frac{1}{\ln I_o / I_t}
\]

(1)

Where:

- \( I_o \) and \( I_t \) = The intensities of the incident and the transmitted light, respectively
- \( d \) = The thickness of the sample

According to literature (Rao, 2002), the optical absorption coefficient can be also be given as:

\[
\alpha = 2.303 \times \frac{(OD)}{d}
\]

(2)

Where:

- OD = Optical Density
- D = The thickness of the glass

The optical absorption at the fundamental edge in terms of the theory given by Davis and Mott (1970) and Eraiah and Bhat (2007) in general form is as follows:

\[
\alpha(\nu) = B/h\nu \left( h\nu - E_g \right)^n
\]

(3)

Where:

- \( B \) = A constant
- \( h\nu \) = The incident photon energy
- \( E_g \) = The optical band gap

The values of \( n \) are \( \frac{1}{2} \) and 2 for direct and indirect transitions, respectively. The UV-VIS absorption spectra of Nd\(^{3+}\) doped glasses are shown in Fig. 3.

The absorption coefficients, \( \alpha(\nu) \), were determined near the absorption edge at different photon energies for all glass samples. It is observed that for many amorphous materials, a reasonable fit of Eq. 3 with \( n = 2 \) are achieved. Therefore, the typical plot of \( (\alpha h\nu)^{1/2} \) versus photon energy \( (h\nu) \) (Tauc’s plot) is shown in Fig. 4, for indirect allowed transitions to find the values of optical band gap, \( E_g \). It can be seen that there exists a linear dependence of \( (\alpha h\nu)^{1/2} \) in the photon energy. This suggests that at higher photon energies the transitions occurring in the present glass samples are of indirect type. The values of the optical band gap obtained are listed in Table 2.

From the Fig. 3, the spectra consists of various absorption levels corresponding to the transitions between the ground state and higher energy states \( (^{4}F_{9/2}, ^{2}G_{7/2}, ^{2}G_{5/2}, ^{5}K_{13/2}, ^{4}G_{7/2}, ^{4}G_{9/2}, ^{5}K_{15/2}, ^{4}D_{3/2}, ^{2}D_{3/2}, ^{2}G_{9/2}, ^{2}F_{1/2}, ^{4}D_{5/2}, ^{4}D_{7/2}, ^{4}D_{1/2}) \) inside the \( 4f^6 \) electronic configuration of the Nd\(^{3+}\) ions. The transitions were assigned by comparing the band positions in the absorption spectra with those reported in literatures (Das et al., 2006; Mohan et al., 2008; Karthikeyan et al., 2003; Ratnakaram et al., 2004).
Electronic polarizability: The calculated polarizability of the oxide ion listed in Table 2, was plotted against refractive index as shown in Fig. 5. It is seen that the oxide ion polarizability increases linearly with increase of refractive. The correlation equation and the square of the correlation coefficient $R^2$, which can be used to measure the effectiveness of the least-squares fitting, are also shown in the Fig. 5. The results show that the refractive index of glass does not only depend on the density but also depend on the electronic polarizability of the glass (Abdel-Baki et al., 2007; Abdel-Baki and El-Diasty, 2007).

Optical basicity of the glasses: The optical basicity of an oxide glass defines the ability of the glass to donate negative charge to the probe ion. An optical basicity of glass can also be predicted from its composition. In multi-component oxide glasses, the basicity has been calculated as:

$$
\Lambda = x_1 \Lambda_1 + x_2 \Lambda_2 + x_3 \Lambda_3 + \ldots.
$$

(4)

Where:

- $\Lambda_1$, $\Lambda_2$ and $\Lambda_3$ = Basicities of the component oxides
- $x_1$, $x_2$ and $x_3$ = Their equivalent fractions (fraction of the total oxygen provided by the component oxide glass)

In context of modification, therefore, we may note the following: modifier oxides should be more basic than the glass forming oxides. When modifier oxides are added to glass-forming oxides, the resulting modification reaction is like an acid-base reaction in which the sites in the acidic (glass forming) oxide are approached by the oxide ion (of the modifier) in the order of decreasing acidities (Zhao et al., 2007).

The optical basicity and electronic polarizability of the oxide species of the glass compositions are evaluated (Karthikeyan and Mohan, 2004) and listed out in Table 2.

DISCUSSION

Physical properties: By addition of Nd$_2$O$_3$ into the SiO$_2$-Na$_2$O-CaO glass network, the density increases with increase in Nd$_2$O$_3$ content. This indicate that increasing the molecular weight of oxide ions used in the glass, replacing SiO$_2$ by Nd$_2$O$_3$, might be expected increase the density of these glasses. The molar volume of the glass systems under study changes with Nd$_2$O$_3$ content. As shown in Table 2, the molar volume increases with increase in Nd$_2$O$_3$ content, which is attributed to increase in the number of Non Bridging Oxygen (NBOs). It can be also be observed that by addition of Nd$_2$O$_3$ may accordingly result in an extension of glass network (Abdel-Baki et al., 2007). The change in molar volume depends on the rates of change of both density and molecular weight.

However, the rate of increasing in molecular weight is greater than the rate of increase in density. This would be accompanied by an increase in molar volume.

Optical band gap: As can be seen from the Fig. 3 that, the optical absorption edge is not sharply defined in glass samples under study, in accordance with their amorphous nature (Eraiah and Bhat, 2007). It can be seen that the transition energy levels vary with the concentration and depend on covalency and the asymmetry of Nd-O local structure among these host matrices (Karthikeyan et al., 2003). It is observed that the absorption intensity of the observed bands increases with the increase of Nd$_2$O$_3$ concentration.

The value of optical band gap slightly decreases with the increase of Nd$_2$O$_3$ and results in the increase of bonding defect and non-bridging oxygen. This leads to an increase of the degree of localization of electrons thereby the increase of donor center in the glass matrix. The increase of presence of donor center, leads to the decrease of optical band gap, therefore, the shift of absorption edge toward the longer wavelength was observed.

Electronic polarizability and optical basicity: From the Table 2, it is observed that the optical basicity values of the glasses are increasing with Nd$_2$O$_3$ content change. The optical basicity evaluated for the glasses increase when SiO$_2$ is replaced by one of the trivalent metal neodymium oxide. The increase of optical basicity in this work means to increase of ability of oxide ions to transfer electrons to the surrounding cations (Abdel-Baki et al., 2007). Since the polarizability of oxide ions is closely to the optical basicity of oxide materials. On the basis of refraction data, Duffy (Dimitrov and Komatsu, 2002) proposed the following correlation:

$$
\Lambda = 1.67 \left[ 1 - \frac{1}{\alpha_{o2-}} \right]
$$

(5)

where, $\alpha_{o2-}$ is the polarizability of oxide ions. Equation 5 shows that the increase of polarizability results in increase of optical basicity and consequently the increase in refractive index. Because Nd$_2$O$_3$ has a higher optical basicity than that of SiO$_2$, therefore, an increase of the glass refractive indices is expected.
CONCLUSION

The study of (65-x) SiO$_2$: 25Na$_2$O: 10CaO: xNd$_2$O$_3$ (where x = 0.0-5.0 mol%) glass systems shows that the density and refractive index increase with increasing concentration of Nd$_2$O$_3$. The increase of molar volume with Nd$_2$O$_3$ content indicates that the extension of glass network is due to the increase of the number of NBOs. The optical spectra data was used to evaluate the values of in indirect allowed transitions. It was found that the optical band gap slightly decreases with in Nd$_2$O$_3$ content due to an increase in the degree of localization of electrons thereby increase of the donor center in the glass matrix. The electronic polarizability and optical basicity increase with the increase of mol% of Nd$_2$O$_3$, which is in agreement with the decrease of optical band gap. Moreover, the results found in this study show that the refractive index of glass does not only depend on the density but also depend on the electronic polarizability of the glass. However, very slight variation in the values of optical band gap, refractive index, optical basicity and polarizability of oxide ions have been observed in the present glass systems.

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