American Journal of Applied Sciences 7 (4): 584-589, 2010
ISSN 1546-9239

Optical Properties of the SiO_2-Na_2O-CaO-Nd_2O_3 Glasses

[1]P. Chimalawong, [2]J. Kaewkhao, [3]T. Kittiauchawal, [1]C. Kedkaew and [1,4]P. Limsuwan
[1]Department of Physics, Faculty of Science,
King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand
[2]Center of Excellence in Glass Technology and Materials Science, Faculty of Science and Technology,
Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand
[3]Department of Physics, Faculty of Science and Technology,
Thepsatri Rajabhat University, Lopburi 15000, Thailand
[4]Thailand 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_2O: 10CaO: xNd_2O_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_2O_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_2O_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_2O_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_2O_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_2O-10CaO-xNd_2O_3 (x = 1-5 mol%) were prepared by the normal melt-quenching technique and there compositions in mole percent are given in Table 1.

Table 1: Glass composition (mol%)

Glass ID	Nd_2O_3 (mol %)	Glass composition (mol %)
S65ND0	0	65SiO_2-25Na_2O-10CaO
S64ND1	1	64SiO_2-25Na_2O-10CaO-Nd_2O_3
S63ND2	2	63SiO_2-25Na_2O-10CaO-2Nd_2O_3
S62ND3	3	62SiO_2-25Na_2O-10CaO-3Nd_2O_3
S61ND4	4	61SiO_2-25Na_2O-10CaO-4Nd_2O_3
S60ND5	5	60SiO_2-25Na_2O-10CaO-5Nd_2O_3

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

Analytical reagent grade chemicals of SiO_2, Na_2O, CaO and Nd_2O_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_2O-CaO-Nd_2O_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_2O_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.

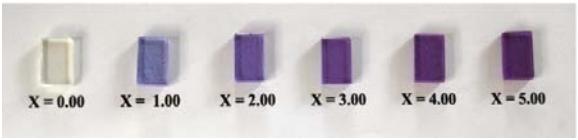

Fig. 1: Photographs of Nd^{3+} doped soda-lime silicate glasses

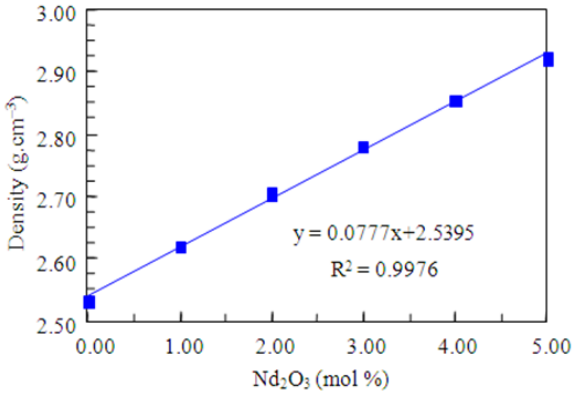

Fig. 2: Variation of the density with Nd_2O_3 concentration

Table 2: Various physical properties of SiO_2-Na_2O-CaO-Nd_2O_3 glasses

	Nd_2O_3 (mol %)					
Parameters	0.0	1.0	2.0	3.0	4.0	5.0
Average molecular weight, M(g)	60.1573	62.9212	65.6852	68.4491	71.2130	73.9770
Density, ($g.cm^{-3}$)	2.5314	2.6175	2.7031	2.7789	2.8526	2.9194
Thickness of the glass, d (cm)	0.3880	0.3580	0.3550	0.3680	0.3630	0.3530
Refractive index n_d (589.3 nm)	1.5247	1.5350	1.5444	1.5542	1.5601	1.5709
Molar volume V_M (cm^3 mol^{-1})	23.7644	24.0387	24.2999	24.6317	24.9643	25.3398
Molar refractivity, R_m (cm^{-3})	7.2793	7.4840	7.6758	7.8965	8.0031	8.3246
Molar polarizability, α_m ($Å^3$)	2.8858	2.9669	3.0429	3.1304	3.1727	3.3001
Refraction losses, R (%)	4.3192	4.4540	4.5779	4.7079	4.7865	4.9312
Indirect optical band gab, E_g (eV)	3.5673	3.3357	3.2376	3.2343	3.1720	2.9548
Glass optical basicity, (Λ)	0.6288	0.6430	0.6571	0.6710	0.6847	0.6982
Glass oxide polarizability, α_{o2-} ($Å^3$)	1.6544	1.6629	1.6682	1.6803	1.6820	1.7009

The general formula for the optical absorption coefficient $\alpha(\omega)$ is given as:

$$\alpha(\omega) = 1 / \ln I_o / I_t \quad (1)$$

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:

$$\alpha = 2.303 \times (OD)/d \quad (2)$$

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:

$$\alpha(\nu) = B/h\nu(h\nu - E_g)^n \quad (3)$$

Where:
B = A constant
$h\nu$ = The incident photon energy
E_g = The optical band gap

The values of n are ½ 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 ($^4F_{9/2}$, $^2G_{7/2}$+$^4G_{5/2}$, $^2K_{13/2}$+$^4G_{7/2}$+$^4G_{9/3}$, $^2K_{15/2}$+$^2D_{3/2}$+$^2G_{9/2}$, $^2P_{1/2}$, $^4D_{3/2}$+$^4D_{5/2}$+$^4D_{1/2}$) inside the $4f^3$ 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).

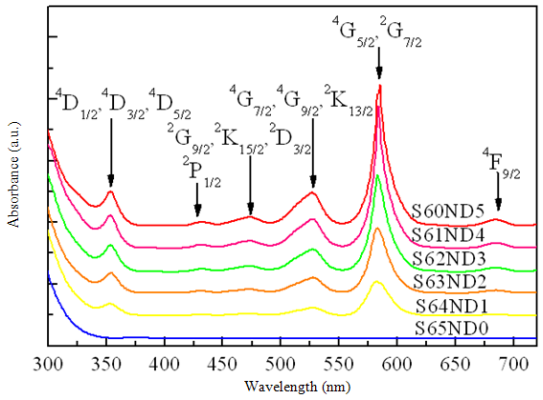

Fig. 3: Optical absorption spectra of SiO_2-Na_2O-CaO-Nd_2O_3 glass systems

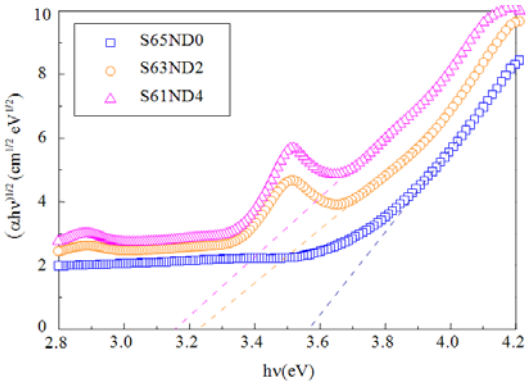

Fig. 4: Tauc's plot for SiO_2-Na_2O-CaO-Nd_2O_3 glasses

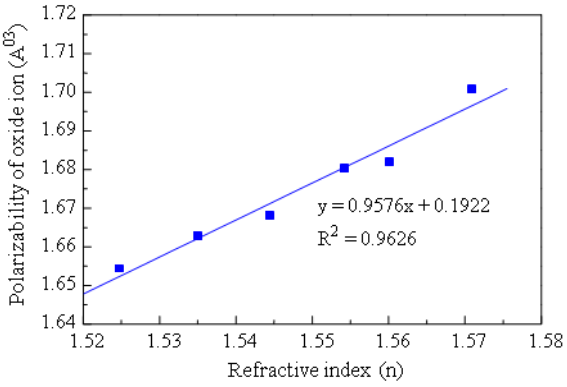

Fig. 5: Polarizability of the oxide ion as a function of refractive index

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 polarizbility 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:

$$\Lambda = x_1 + x_2\Lambda_2 + x_3\Lambda_3 + ... \quad (4)$$

Where:

Λ_1, Λ_2 and Λ_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 and 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_2O_3 into the SiO_2-Na_2O-CaO glass network, the density increases with increase in Nd_2O_3 content. This indicate that increasing the molecular weight of oxide ions used in the glass, replacing SiO_2 by Nd_2O_3, might be expected increase the density of these glasses. The molar volume of the glass systems under study changes with Nd_2O_3 content. As shown in Table 2, the molar volume increases with increase in Nd_2O_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_2O_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_2O_3 concentration.

The value of optical band gap slightly decreases with the increase of Nd_2O_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 polalizabilty and optical basicity: From the Table 2, it is observed that the optical basicity values of the glasses are increasing with Nd_2O_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:

$$\Lambda = 1.67\left[1 - \left(\frac{1}{\alpha_{o2-}}\right)\right] \quad (5)$$

where, α_{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_2O_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_2O: 10CaO: xNd_2O_3 (where x = 0.0-5.0 mol%) glass systems shows that the density and refractive index increase with increasing concentration of Nd_2O_3. The increase of molar volume with Nd_2O_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_2O_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_2O_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.

ACKNOWLEDGEMENT

This research is thanks to Commission of Higher Graduation under National Research University (NRU) Project and J. Kaewkhao would like to thank the National Research Council of Thailand (NRCT) for funding. P. Chimalawong would like to thank the Nakhon Pathom Rajabhat University (NPRU) for instrument and facilities.

REFERENCES

Abdel-Baki, M. and F. El-Diasty, 2007. Optical properties of oxide glasses containing transition metals: Case of titanium and chromium-containing glasses. Curr. Opin. Solid State Mater. Sci., 10: 217-229. DOI: 10.1016/j.cossms.2007.08.001

Abdel-Baki, M., F.A. Abdel-Wahab, A. Radi and F. El-Diasty, 2007. Factors affecting optical dispersion in borate glass systems. J. Phys. Chem. Solids, 68: 1457-1470. DOI: 10.1016/j.jpcs.2007.03.026

Corradi, A.B., V. Cannillo, M. Montorsi, C. Siligardi and A.N. Cormack, 2005. Structural characterization of neodymium containing glasses by molecular dynamics simulation. J. Non-Crystal. Solids, 351: 1185-1191. DOI: 10.1016/j.jnoncrysol.2005.03.002

Das, M., K. Annapurna, P. Kundu, R.N. Dwivedi and S. Buddhudu, 2006. Optical spectra of Nd^{3+}: CaO-La_2O_3-B_2O_3 glasses. Mater. Lett., 60: 222-229. DOI: 10.1016/j.matlet.2005.08.022

Davis, E.A. and N.F. Mott, 1970. Conduction in non-crystalline systems V. conductivity, optical absorption and photoconductivity in amorphous semiconductors. Philosophic. Mag., 22: 903-922. DOI:10.1080/14786437008221061

Dimitrov, V. and T. Komatsu, 2002. Classification of simple oxide glasses: A polarizability approach. J. Solid State Chem., 163: 100-112. DOI: 10.1006/jssc.2001.9378

Eraiah, B. and S.G. Bhat, 2007. Optical properties of samarium doped zinc-phosphate glasses. J. Phys. Chem. Solids, 68: 581-585. DOI: 10.1016/j.jpcs.2007.01.032

Gatterer, K., G. Pucker, W. Jantscher, H.P. Fritzer and S. Arafa, 1998. Suitability of Nd(III) absorption spectroscopy to probe the structure of glasses from the ternary system Na_2O-B_2O_3-SiO_2. J. Non-Crystall. Solids, 231: 189-199. DOI: 10.1016/S0022-3093(98)00375-5

Karthikeyan, B. and S. Mohan, 2004. Spectroscopic and glass transition investigations on Nd^{3+}-doped NaF-Na_2O-B_2O_3 glasses. Mater. Res. Bull., 39: 1507-1515. DOI: 10.1016/j.materresbull.2004.04.025

Karthikeyan, B., S. Mohan and M.L. Baesso, 2003. Spectroscopic and glass transition studies on Nd^{3+}-doped sodium zincborate glasses. Phys. B: Condensed Matter, 337: 249-254. DOI: 10.1016/S0921-4526(03)00411-3

Mohan, S., K.S. Thind, G. Sharma and L. Gerward, 2008. Spectroscopic investigations of Nd^{3+} doped flouro-and chloro-borate glasses. Spectrochim. Acta Part A: Molecular and Biomolecular Spectroscopy, 70: 1173-1179. DOI: 10.1016/j.saa.2007.10.038

Moorthy, L.R., T.S. Rao, M. Jayasimhadri, A. Radhapathy and D.V.R. Murthy, 2004. Spectroscopic investigations of Nd^{3+}-doped alkali chloroborophosphate glasses. Spectrochim. Acta Part A: Molecular and Biomolecular Spectroscopy, 60: 2449-2458. DOI: 10.1016/j.saa.2003.12.022.

Pisarski, W.A., T. Goryczka, B. Wodecka-Dus, M. Plonska and J. Pisarska, 2005. Structure and properties of rare earth-doped lead borate glasses. Mater. Sci. Eng. B, 122: 94-99. DOI: 10.1016/j.mseb.2005.05.002

Rao, K.J., 2002. Structural Chemistry of Glasses. 1st Edn., Elsevier Science Ltd., ISBN: 0080439586, pp: 237.

Ratnakaram, Y.C., A. Vijaya Kumar, D. Thirupathi Naidu, R.P.S. Chakradhar and K.P. Ramesh, 2004. Optical absorption and luminescence properties of Nd^{3+} in mixed alkali borate glasses-spectroscopic investigations. J. Luminescence, 110: 65-77. DOI: 10.1016/j.jlumin.2004.04.004

Sindhu, S., S. Sanghi, A. Agarwal, V.P. Seth and N. Kishore, 2005. Effect of Bi_2O_3 content on the optical band gap, density and electrical conductivity of $MO.Bi_2O_3.B_2O_3$ (M = Ba,Sr) glasses. Mater. Chem. Phys., 90: 83-89. DOI: 10.1016/j.matchemphys.2004.10.013

Yanbo, Q., D. Ning, P. Mingying, Y. Lyun and C. Danping *et al*., 2006. Spectroscopic properties of Nd^{3+}-doped high silica glass prepared by sintering porous glass. J. Rare Earths, 24: 765-770. DOI: 10.1016/S1002-0721(07)60026-X

Zhao, X., X. Wang, H. Lina and Z. Wang, 2007. Electronic polarizability and optical basicity of lanthanide oxides. Physica B, 392: 132-136. DOI: 10.1016/j.physb.2006.11.015