

Optical Investigation and Electronic Polarizability of Nd³⁺ Doped Soda-Lime-Silicate Glasses

¹P. Chimalawong, ²J. Kaewkhao and ¹P. Limsuwan

¹Department of Physics, Faculty of Science,

King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

²Glass and Materials Science Research Unit, Faculty of Science and Technology,
Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand

Abstract: Problem statement: This study researched on different physical and optical properties of Nd³⁺ doped soda-lime-silicate glass. The glasses containing Nd³⁺ in (65-x)SiO₂: 25Na₂O: 10CaO: xNd₂O₃ (where x = 0.0-5.0 mol%) had been prepared by melt-quenching method. The density and molar volume increase with increasing of Nd₂O₃ concentration due to increasing of Non Bridging Oxygen (NBOs) in glass matrix. The optical spectra were measured and evaluated their optical band gap and found to decrease with increasing of Nd₂O₃ concentration. 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. The values of polarizability of oxide ions, theoretical optical basicity were also determined. **Approach:** This study investigated the effect of Nd₂O₃ content on optical band gap, density, molar volume, optical basicity and polarizability in soda-lime silicate glass. Series of Nd³⁺ doped soda-lime silicate glasses (in mol%): (65-x)SiO₂-25Na₂O-10CaO-xNd₂O₃ (x = 1-5 mol%) were prepared by the normal melt-quenching technique. Analytical reagent grade chemicals of SiO₂, Na₂O, CaO and Nd₂O₃ 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 of 3 mm. The 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 refractometer (ATAGO) and mono-bromonaphthalene as an adhesive coating. The optical absorption spectra of Nd³⁺ doped soda-lime silicate glasses were recorded at room temperature using a UV-VIS spectrophotometer (Hitachi, U-1800), working in 300-700 nm. **Results:** By addition of Nd₂O₃ into the SiO₂-Na₂O-CaO glass network, the density increases with increase in Nd₂O₃ content. The molar volume of the glass systems under study increases with increase in Nd₂O₃ content, which is attributed to increase in the number of Non Bridging Oxygen (NBOs). The optical band gap slightly decreases with the increase of Nd₂O₃ and results in the increase of bonding defect and non-bridging oxygen. The optical basicity of the glasses are increasing with Nd₂O₃ content change with the increasing of polarizability and consequently the increase in refractive index. **Conclusion:** The study of SiO₂-Na₂O-10CaO-Nd₂O₃ glass systems showed that the density and refractive index increase with increasing concentration of Nd₂O₃. The increase of molar volume with Nd₂O₃ content indicates that the extension of glass network is due to the increase of the number of NBOs. The optical band gap slightly decreases with in Nd₂O₃ 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.

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; Maumita *et al.*, 2006; Mohana *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 an 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 (Bonamartini *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. CaO and Nd_2O_3 were used in the glasses preparation.

MATERIALS AND METHODS

Glass preparation: Series of Nd^{3+} doped soda-lime silicate glasses (in mol%): $(65-x)\text{SiO}_2\text{-}25\text{Na}_2\text{O-}10\text{CaO-xNd}_2\text{O}_3$ ($x = 1\text{-}5$ mol%) were prepared by the normal melt-quenching technique and there compositions in mole percent are given in Table 1. Analytical reagent grade chemicals of SiO_2 , Na_2O , 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 .

Table 1: Glass composition (mol%)

Glass ID	Nd_2O_3 (mol %)	Glass composition (mol %)
S65ND0	0	$65\text{SiO}_2\text{-}25\text{Na}_2\text{O-}10\text{CaO}$
S64ND1	1	$64\text{SiO}_2\text{-}25\text{Na}_2\text{O-}10\text{CaO-}1\text{Nd}_2\text{O}_3$
S64ND2	2	$63\text{SiO}_2\text{-}25\text{Na}_2\text{O-}10\text{CaO-}2\text{Nd}_2\text{O}_3$
S64ND3	3	$62\text{SiO}_2\text{-}25\text{Na}_2\text{O-}10\text{CaO-}3\text{Nd}_2\text{O}_3$
S64ND4	4	$61\text{SiO}_2\text{-}25\text{Na}_2\text{O-}10\text{CaO-}4\text{Nd}_2\text{O}_3$
S64ND5	5	$60\text{SiO}_2\text{-}25\text{Na}_2\text{O-}10\text{CaO-}5\text{Nd}_2\text{O}_3$

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 of 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 refractometer (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 AND DISCUSSION

Physical properties: Based on the determined density, refractive index values and the molecular weight of $\text{SiO}_2\text{-Na}_2\text{O-CaO-Nd}_2\text{O}_3$ 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; Zhaoa *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. As can be seen from the Fig. 2 that, by addition of Nd_2O_3 into the $\text{SiO}_2\text{-Na}_2\text{O-CaO}$ 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.

Table 2: Various physical properties of SiO₂-Na₂O-CaO-Nd₂O₃ glasses

Parameters	Nd ₂ O ₃ (mol %)					
	0	1	2	3	4	5
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)	0.3000	0.3000	0.3000	0.3000	0.3000	0.3000
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 gap, 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

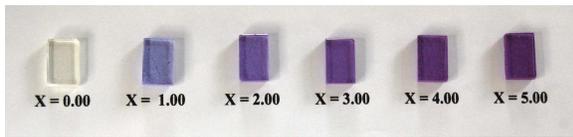


Fig. 1: Photographs of Nd³⁺ doped soda-lime silicate glasses

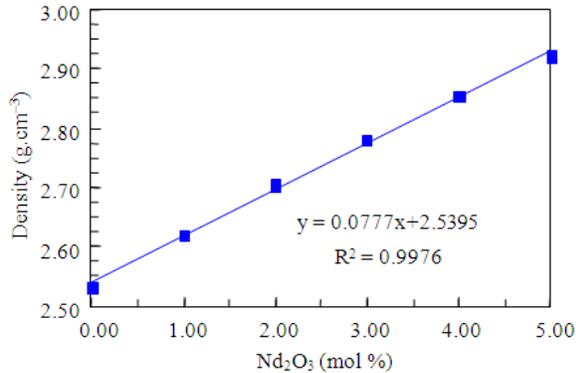


Fig. 2: Variation of the density with Nd₂O₃ concentration

As shown in Table 2, the molar volume increases with increase in Nd₂O₃ content, which is attributed to increase in the number of Non Bridging Oxygen (NBOs).

It can be also be observed that by addition of Nd₂O₃ 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, as can be seen from Table 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. The general formula for the optical absorption coefficient α(ω) is given as:

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

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
hν = The incident photon energy
E_g = The optical band gap

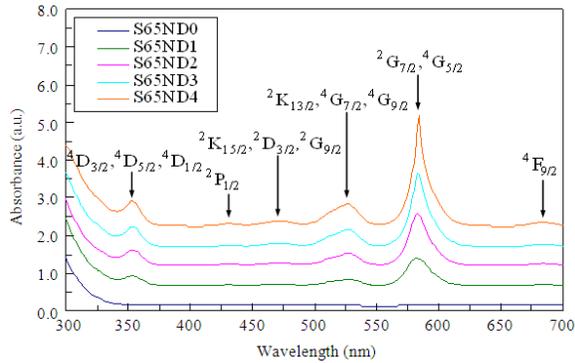


Fig. 3: Optical absorption spectra of SiO₂-Na₂O-CaO-Nd₂O₃ glass systems

The values of n are $\frac{1}{2}$ and 2 for direct and indirect transitions, respectively.

The UV-VIS absorption spectra of Nd³⁺ doped glasses are shown in Fig. 3. 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 (Karthikeyana *et al.*, 2003). It is observed that the absorption intensity of the observed bands increases with the increase of Nd₂O₃ concentration. 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_{9/2}, ²K_{15/2}+²D_{3/2}+²G_{9/2}, ²P_{1/2}, ⁴D_{3/2}+⁴D_{5/2}+⁴D_{1/2}) inside the 4f³ electronic configuration of the Nd³⁺ ions. The transitions were assigned by comparing the band positions in the absorption spectra with those reported in literatures (Maumita *et al.*, 2006; Mohana *et al.*, 2008; Karthikeyana *et al.*, 2003; Karthikeyana and Mohanb, 2004; Ratnakaram *et al.*, 2004).

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.

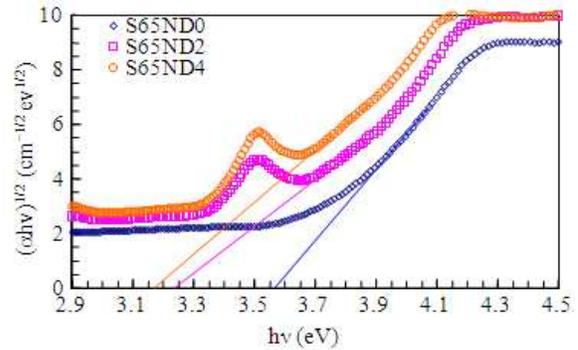


Fig. 4: Tauc's plot for SiO₂-Na₂O-CaO-Nd₂O₃ glasses

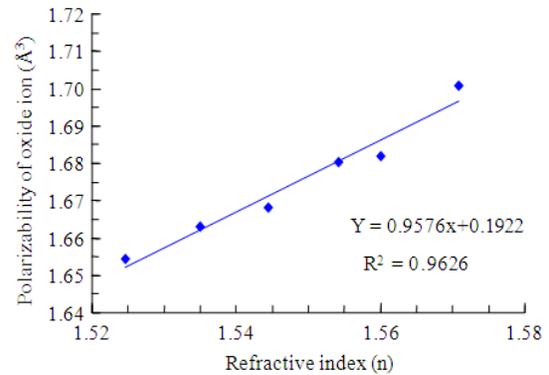


Fig. 5: Polarizability of the oxide ion as a function of refractive index

The values of the optical band gap obtained are listed in Table 2. It can be noticed that the optical band gap slightly decreases with the increase of Nd₂O₃ 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.

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 index. 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, 2006).

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 have been calculated as:

$$\Lambda = x_1\Lambda_1 + x_2\Lambda_2 + x_3\Lambda_3 + \dots$$

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 (Rao, 2002).

The optical basicity and electronic polarizability of the oxide species of the glass compositions are evaluated (Zhaoa *et al.*, 2007) and listed out in 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:

$$\Lambda = 1.67 \left[1 - \left(\frac{1}{\alpha_{o2}} \right) \right] \quad (4)$$

where, α_{o2} is the polarizability of oxide ions. Equation 4 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 $(65-x)\text{SiO}_2: 25\text{Na}_2\text{O}: 10\text{CaO}: x\text{Nd}_2\text{O}_3$ (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 financially supported by the Department of Physics, Faculty of Science, King Mongkut's University of Technology Thonburi and P. Chimalawong would like to thank the Glass and Materials Science Research Unit (GMSRU), Faculty of Science and Technology, Nakhon Pathom Rajabhat University for instrument and facilities.

Kaewkhao would like to thank the National Research Council of Thailand (NRCT) for funding this research.

REFERENCES

- Abdel-Baki, M. and F. El-Diasty, 2006. 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
- Bonamartini, C.A., 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.JNONCRY SOL.2005.03.002

- 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.*, 178: 831-846. DOI: 10.1016/J.JSSC.2004.12.013
- 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 $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$. *J. Non-Crystal. Solids*, 231: 189-199. DOI: 10.1016/S0022-3093(98)00375-5
- Karthikeyana, B. and S. Mohanb, 2004. Spectroscopic and glass transition investigations on Nd^{3+} -doped $\text{NaF-Na}_2\text{O-B}_2\text{O}_3$ glasses. *Mater. Res. Bull.*, 39: 1507-1515. DOI: 10.1016/J.materresbull.2004.04.025
- Karthikeyana, B., S. Mohanb and M.L. Baesso, 2003. Spectroscopic and glass transition studies on Nd^{3+} -doped sodium zincborate glasses. *Phys. B.*, 337: 249-254. DOI: 10.1016/S0921-4526(03)00411-3
- Maumita, D., K. Annapurna, P. Kundu, R.N. Dwivedi and S. Buddhudu, 2006. Optical spectra of Nd^{3+} : $\text{CaO-La}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses. *Mater. Lett.*, 60: 222-229. DOI: 10.1016/J.MATLET.2005.08.022
- Mohana, S., K.S. Thind, G. Sharma and L. Gerward, 2008. Spectroscopic investigations of Nd^{3+} doped fluoro-and chloro-borate glasses. *Spectrochimica Acta Part A.*, 70: 1173-1179. PMID: 18068421
- Moorthy, L.R., T.S. Rao, M. Jayasimhadri, A. Radhapythy and D.V.R. Murthy, 2004. Spectroscopic investigations of Nd^{3+} -doped alkali chloroborophosphate glasses. *Spectrochimica Acta Part A*, 60: 2449-2458. DOI: 10.1016/J.SAA.2003.12.022
- Pisarski, W.A., T. Goryczka, B.W. 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*. Elsevier Sci. Ltd.
- Ratnakaram, Y.C., A.V. Kumar, D.T. 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 $\text{MO.Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ ($\text{M} = \text{Ba,Sr}$) glasses. *Mater. Chem. Phys.*, 90: 83-89.
- 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-
- Zhaoa, X., X. Wangb, H. Lina and Z. Wanga, 2007. Electronic polarizability and optical basicity of lanthanide oxides. *Phys. B.*, 392: 132-136. DOI: 10.1016/J.PHYSB.2006.11.015