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Effect of Nd_2O_3 content on the optical band gap, density and electronic polarizability of SiO_2-Na_2O-CaO-Nd_2O_3 glasses

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ABSTRACT

Glasses with compositions (65-x)SiO_2:25Na_2O:10CaO:xNd_2O_3 with 0.0≤x≤5.0 (in mol%) have been prepared using the normal melt-quenching technique. The optical absorption spectra of the glasses have been recorded in the wavelength range 300-900 nm. The fundamental absorption edge has been identified from the optical absorption spectra. The values of optical band gap for indirect allowed and indirect forbidden transitions have been determined using available theories. Besides the spectral property analysis, different important physical properties have also been investigated from the measured density and refractive indices. The density and molar volume studies indicate that Nd_2O_3 in these glasses is acting partly as network modifier and partly as network former. The substitution of Nd_2O_3 with SiO_2 increases the refractive index of the glass with an increase in the electronic polarizability.

KEYWORDS

Nd_2O_3;
Optical properties;
Density;
Electronic polarizability.

INTRODUCTION

Glass is a promising host to investigate the influence of chemical environment on the optical properties of the rare-earth ions. The physical and spectroscopic properties of silicate, borate and phosphate glasses doped with various rare earth (RE^{3+}) ions have been extensively investigated in the past, and many technological and commercial applications have been realized[1-4]. Rare-earth ions are used as dopants in glasses mainly for two reason: firstly, their well defined and sharp energy levels may serve as structural probes for the environment of the dopant and secondly, the modifications of the energy level structure of the rare earth ions caused by the glassy environment may lead to interesting applications[5]. The spectroscopic behaviour of rare-earth ions are strongly affected by the local structure at the rare-earth sites and the distribution of the doped ions in the glass matrix[6].

The relationship between the structure of the host glass and the properties of the doped ions is useful for designing the glasses for different applications. Most of the work on rare earth metals in glasses has been performed on silicate glasses, due to their tech-

nological applications and stability[4]. 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 nonbridging 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[7].

Among all the rare-earth ions, neodymium has been most widely studied as doping agent and has come out to be most applicable for laser action, since neodymium lasers can operate with high efficiency, even at room temperature. However, to the best of our knowledge, rare earth doped soda-lime-silicate glasses have not been studied in any great detail. Motivated by these considerations we have prepared soda-lime-silicate glasses doped with Nd^{3+}, and studied the effects of the Nd^{3+} concentration on physical and spectroscopic properties.

Methodology

A series of Nd^{3+} doped soda-lime-silicate glasses of the type $(65-x)SiO_2$-$25Na_2O$-$10CaO$-xNd_2O_3, where x=0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 mol% were prepared by the melt quenching technique. Appropriate amounts of the raw materials, SiO_2, Na_2O, CaO and Nd_2O_3 of 99.9% purity, were thoroughly mixed and ground in porcelain crucibles and were later melted in an electrical muffle furnace for 3 h, at 1200°C. After complete melting, the melts were then cast into a preheated stainless steel mould before immediately transferred to an annealing furnace at 500°C for 3 h in order to eliminate internal mechanical stress. Finally, the as-prepared glass samples were cut and then finely polished in order to study their spectroscopic properties. The chemical compositions of the glasses are summarized in TABLE 1.

TABLE 1: Chemical compositions of the glasses

Sample	Nd_2O_3 (mol%)	Glass composition (mol%)
S65ND0	0.00	$65SiO_2$-$25Na_2O$-$10CaO$
S64ND1	1.00	$64SiO_2$-$25Na_2O$-$10CaO$-Nd_2O_3
S63ND2	2.00	$63SiO_2$-$25Na_2O$-$10CaO$-$2Nd_2O_3$
S62ND3	3.00	$62SiO_2$-$25Na_2O$-$10CaO$-$36Nd_2O_3$
S61ND4	4.00	$61SiO_2$-$25Na_2O$-$10CaO$-$4Nd_2O_3$
S60ND5	5.00	$60SiO_2$-$25Na_2O$-$10CaO$-$5Nd_2O_3$

The density (ρ) of each sample was calculated by the Archimedes' method using xylene as the immersion liquid. The corresponding molar volume (V_M) was calculated using the relation, $V_M=M_T/\rho$, where M_T is the average molecular weight of the multi-component glass system given by

$$\mathbf{M_T = x_{SiO_2} Z_{SiO_2} + x_{Na_2O} Z_{Na_2O} + x_{CaO} Z_{CaO} + x_{Nd_2O_3} Z_{Nd_2O_3}} \quad (1)$$

where x_{SiO_2}, x_{Na_2O}, x_{CaO}, and $x_{Nd_2O_3}$ are the mole fractions of the constituent oxides and Z_{SiO_2}, Z_{Na_2O}, Z_{CaO} and $Z_{Nd_2O_3}$ are the molecular weights of the different oxides.

The refractive indices were measured at room temperature using an Abbe refractometer (ATAGO) and mono-bromonaphthalene as an adhesive coating. Optical absorption spectra were recorded at room temperature using a spectrophotometer (Hitachi, U-1800), working in the UV-visible range.

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[8-10,14,17].

Optical band gap

Optical absorption spectra of Nd^{3+} doped soda-lime silicate glasses in wavelength range 300-900nm are shown in Figure 1. The optical absorption edge is not sharply defined in glass samples under study, in accord with their amorphous nature[8].

A comparison of the optical absorption spectra of the present glass series with many reported in literatures[3-6,11-13], result in the identification of following spectroscopic transitions:

$^4F_{3/2}$, $^4F_{5/2}+^2H_{9/2}$, $^4S_{3/2}+^4F_{7/2}$, $^4F_{9/2}$, $^4G_{5/2}+^2G_{7/2}$, $^2K_{13/2}+^4G_{7/2}+^4G_{9/2}$, $^2K_{15/2}+^2D_{3/2}+^2G_{9/2}$, $^2P_{1/2}$, $^4D_{3/2}+^4D_{5/2}+^4D_{1/2}\leftarrow{}^4I_{9/2}$.

Full Paper

TABLE 2: Physical properties of soda-lime-silicate glasses containing varying amounts of Nd^{3+} ions

Physical property	Glass Sample					
	S65ND0	S64ND1	S63ND2	S62ND3	S61ND4	S60ND5
Average molecular weight, M(g)	60.1573	62.9212	65.6852	68.4491	71.2130	73.9770
Density, ρ(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)	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
Molecular electronic 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 energy E_g^{ind} (eV)	3.5673	3.3357	3.2376	3.2343	3.1720	2.9548
Direct optical band gap energy E_g^{dir} (eV)	3.9167	3.9081	3.9049	3.8653	3.6940	3.6243
Cut-off wavelength (nm)	296.99	302.86	296.65	306.58	310.05	306.61
Optical basicity, Λ_{th}	0.6288	0.6430	0.6571	0.6710	0.6847	0.6982
Oxide electronic polarizability, α_{o2-} (A°^{3})	1.6544	1.6629	1.6682	1.6803	1.6820	1.7009

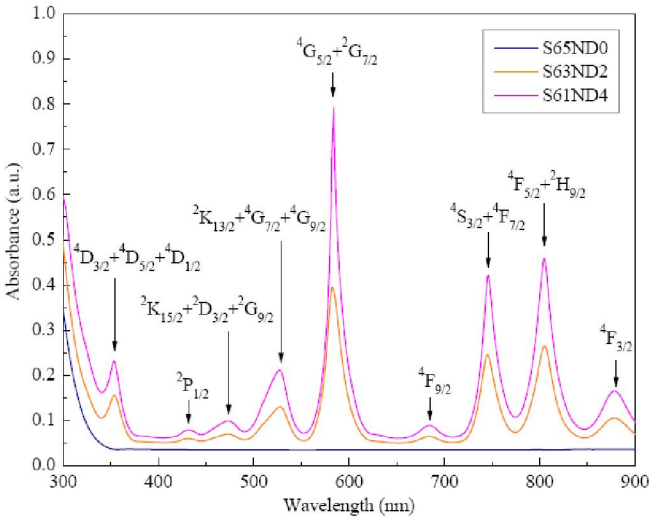

Figure 1 : A typical absorption spectrum of SiO2-Na2O-CaO-Nd2O3 glass systems

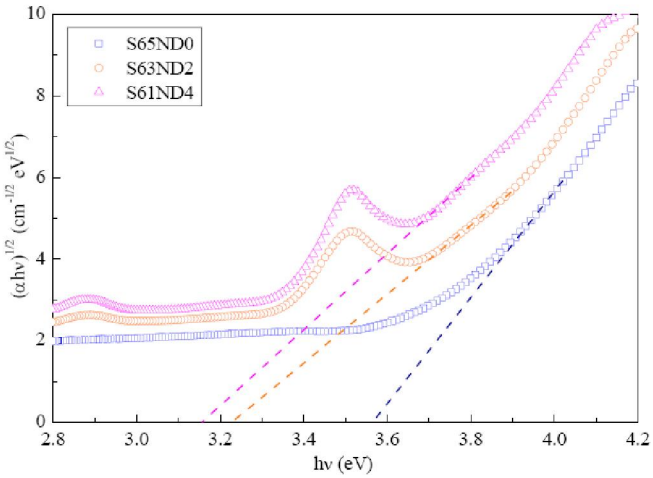

Figure 2 : Determination of the optical energy band gap for indirect transition (E_g^{ind})

Optical band gaps for direct and indirect transitions have been obtained following Mott and Davis[8], using the equation

$$\alpha h\upsilon = B[h\upsilon - E_g]^n \quad (2)$$

where B is a constant, α is the absorption coefficient, υ is the angular frequency and values of n are 1/2 and 2 for direct and indirect transitions respectively.

The values of optical band gap energies can be obtained from the above relation by extrapolating the absorption coefficient to zero absorption in the $(\alpha h\upsilon)^{1/2}$-hυ and $(\alpha h\upsilon)^2$-hυ plots (Tauc's plots), as shown in Figure 2 and 3. The direct and indirect optical band gap energy are list in TABLE 2 (row 9,10) respectively.

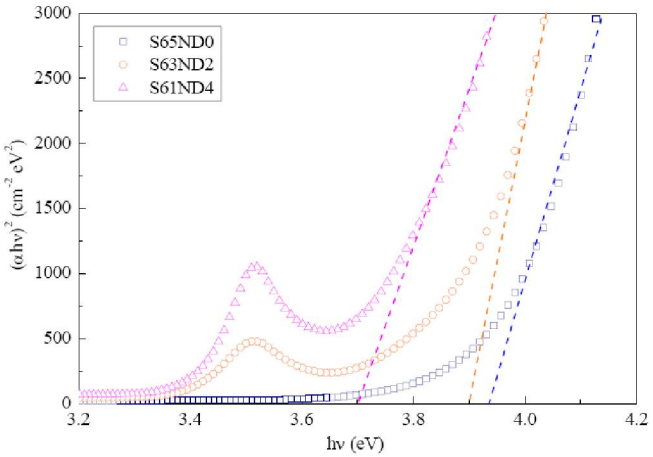

Figure 3 : Determination of the optical energy band gap for direct transition (E_g^{dir})

Electronic polarizability

Dimitrov and Sakka[9] calculated the average electronic polarizability of oxide ions in numerous single component oxides on the basis of linear refractive index and energy gap. For multi-component oxide glasses with a general formula $x_1A_pO_q : x_2B_rO_s : x_3C_nO_m$, where x denoted the molar fraction for each oxide, the electronic polarizability of oxide ion α_o^{2-}, is calculated using following equation:

$$\alpha_o^{2-}(n_o) = [\frac{R_m}{2.52} - \Sigma\alpha_{cat}]/N_o^{2-} \quad (3)$$

where $\Sigma\alpha_{cat}$ denotes the molar cation polarizability given by $x_1p\alpha_A+x_2r\alpha_B+x_3n\alpha_C$ and denotes the number of oxide ions in the chemical formula given by $x_1q+x_2s+x_3m$. The molar cation polarizability of the glasses is calculated using data on the polarizability of cations collected from references 14 and 15. The electronic polarizability of Si^{4+}=0.033 $A^{\circ 3}$, Na^{+}=0.181 $A^{\circ 3}$, Ca^{2+}=0.469 $A^{\circ 3}$[15] and Nd^{3+}=2.546 $A^{\circ 3}$[14].

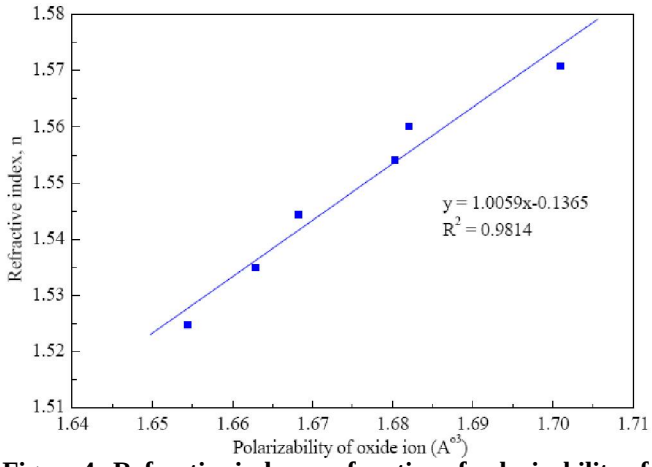

Figure 4 : Refractive index as a function of polarizability of the oxide ion

The calculated electronic polarizability of the oxide ion listed in TABLE 2, was plotted against refractive index as shown in Figure 4. It is seen that the electronic 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 figure. 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.

CONCLUSION AND DISCUSSION

From the present study of SiO_2-Na_2O-CaO-Nd_2O_3 glasses, the data presented in TABLE 2 show that an increase in the average molecular weight (M_T) influences significantly both the refractive index and density and also various other physical parameters. The behavior of molar volume mainly depends upon the density of glasses and as expected in the present case, it follows a trend similar to density.

Density and molar volume

It is seen from the TABLE 2 (row 2) that the density increases with increase in Nd_2O_3 content. Since Nd_2O_3 has a high relative molecular mass, therefore, it is an expected result. 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 (row 5). The molar volume of the glass systems under study 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[10].

Optical band gap and electronics polarizability

The optical spectra data use to evaluate the values of in indirect allowed and direct allowed transitions. It can be noticed that the optical band gap energy (E_g) value are slightly decreasing with increase of the Nd_2O_3 concentration of both divalent contents and results in the increase of bonding defect and non-bridging oxygen[8]. 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. This observation must be attributed to the average bond energy of the glass system which leads to decrease in the energy of conduction band edge and thereby E_g decrease[9]. It is established that there is a general trend of increasing electronic polarizability with increasing refractive index and

decreasing energy gap[14]. Furthermore, 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[16].

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