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Effect of neutron-irradiation on optical properties of SiO_2-Na_2O-MgO-Al_2O_3 glasses

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Abstract : Silica based glasses are used as nuclear shielding materials. The effect of radiation on these glasses varies as per the constituents used in these glasses. Glasses of different composition of SiO_2-Na_2O-MgO-Al_2O_3 were made by melt casting techniques. These glasses were irradiated with neutrons of different fluences. Optical absorption measurements of neutron-irradiated silica based glasses were performed at room temperature (RT) to detect and characterize the induced radiation damage in these materials. The absorption band found for neutron-irradiated glasses are induced by hole type color centers related to non-bridging oxygen ions (NBO) located in different surroundings of glass matrix. Decrease in the transmittance indicates the formation of color-center defects. Values for band gap energy and the width of the energy tail above the mobility gap have been measured before and after irradiation. The band gap energy has been found to decrease with increasing fluence while the Urbach energy shows an increase. The effects of the composition of the glasses on these parameters have been discussed in detail in this paper.

Keywords : Silicate glass, neutron irradiation, UV-VIS spectra, color-centers, optical energy gap, Urbach energy.

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1. Introduction

Study of optical absorption has been one of the most productive methods in understanding the band structure and energy gap of both crystalline and amorphous materials. The measurement of optical absorption coefficients, particularly near the fundamental absorption edge, is a standard method for the investigation of optically induced electronic transitions.

Interaction of radiations with glasses results in the profound structured changes, affecting their optical and physical properties [1]. Effects of irradiation on the optical properties of glasses are important, since they are related to the formation and accumulation of radiation-

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induced defects and hence the existence of characteristic color-centers [2]. Electronic transitions in color-centers may cause absorbance in the UV and visible spectral range.

This paper reports experimental results of an effort undertaken to identify and characterize the radiation induced defects created during thermal neutron irradiation of artificially made silicate glasses on the basis of optical absorption measurements performed before and after irradiation. Also the work is extended to investigate the effect of the variation of composition on the optical energy gap, E_{opt}, of the glasses.

2. Experimental details

Table 1 gives the chemical composition of the quaternary silicate glasses studied. Silica was introduced in the form of quartz granules of the highest grade available. Sodium oxide was introduced in the form of its anhydrous carbonates of analytical (AR) grade. MgO and Al_2O_3 were added as AR quality of their respective oxides. Dried ingredients were ball milled in acetone medium and after drying acetone, the mixed powder was heated in alumina crucible in a resistance-heating furnace at a temperature of 1560 ^oC, afterwards the melt was casted into a preheated graphite mold and annealed at 300 ^oC for one hour. The annealed specimen was cut in to the samples of thickness 2 mm by using low speed saw diamond cutter. Grinding of the samples was performed using SiC abrasives and aluminum oxide and the polishing was done with cerium oxide. These samples were than irradiated with thermal neutrons in CIRUS Reactor with varying neutron fluence of 10^{14}, 10^{15}, 10^{16} and 10^{17} n/cm^2 from BARC, Mumbai.

Table 1. Chemical composition of quaternary silicate glasses studied.

Sample Code	SiO_2	Na_2O	MgO	Al_2O_3 (mole %)
Comp-I	75	15	5	5
Comp-II	70	20	5	5
Comp-III	65	25	5	5
Comp-IV	60	30	5	5

Optical transmittance measurements before and after irradiation were performed using a UV-VIS spectrophotometer (Shimadzu, Model 160A) in the wavelength range of 200–600 nm at normal incidence.

3. Results and discussion

3.1. Coloration of glass :

The melted unirradiated glass is colorless, with no characteristic absorption bands to be observed in both the ultraviolet and visible regions. On subjecting the glasses to neutron irradiation, their color changes to bright amber at low doses that afterwards deepens to dark brown on further exposure to prolonged doses of neutrons.

Figure 1 shows the absorption spectra of the base glass of Comp-I before and after neutron irradiation. The spectrum reveals a slight shift of the beginning of the absorption edge to a longer wavelength with increasing irradiation. In addition, several other induced absorption bands are observed which become slightly pronouncd with irradiation. These absorption bands are located at about 360 and 430 nm. It is apparent that only the intensities of the peaks increase with irradiation with no change in the band peak-position.

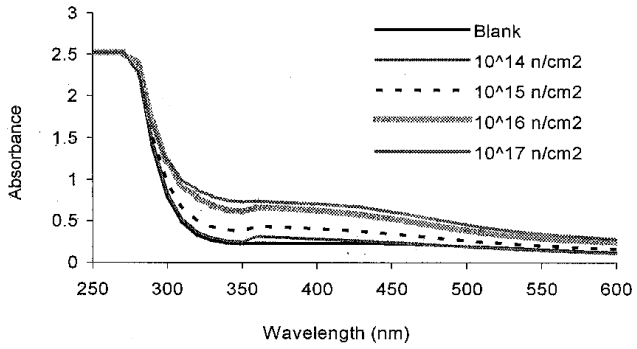

Figure 1. UV-VIS spectra of blank and neutron irradiated glass of Comp-I.

The ionizing radiation produces electron-hole pairs which individually become trapped at various defect sites in the glass structure. Accordingly, new optical absorption bands may develop. In general, these absorption bands are associated with either oxygen deficiency or oxygen excess in the glass network [2,3]. The most fundamental radiation induced defects in glasses are the non-bridging oxygen hole center (NBOHC: ≡Si-O*), the *E'* center (≡Si*), the peroxy radical (POR: ≡Si-O-O*), and the trapped electron (TE), where the notation "≡" represents three bonds with other oxygens in the glass network and "*" denotes an unpaired electron [2–4]. In the glass exposed to radiations, hole trapped color centers with characteristic absorption bands around 430 nm were formed upon irradiation, leading to the development of the brown color. The intensity of the induced color increased with increasing exposure time. Thus, the absorption band at 430 nm was identified as absorption of NBOHCs, and the band of 360 nm was attributed to the trapped electron [5,6].

3.2. Optical properties :

The absorption coefficient, $\alpha(\nu)$, in amorphous materials, in the optical region near the absorption edge, at a particular temperature, obeys an empirical relation known as Urbach rule [7] given by

$$\alpha(\nu) = \alpha_0 \exp(h\nu/E_e) \tag{1}$$

where *hv* is the photon energy, α_0 is a constant and E_e an energy which is interpreted as the width of the localized state in the normally forbidden band gap and which is also

known as the Urbach energy. Urbach plots for glass of Comp-I irradiated with neutrons of different fluences are shown in Figure 2.

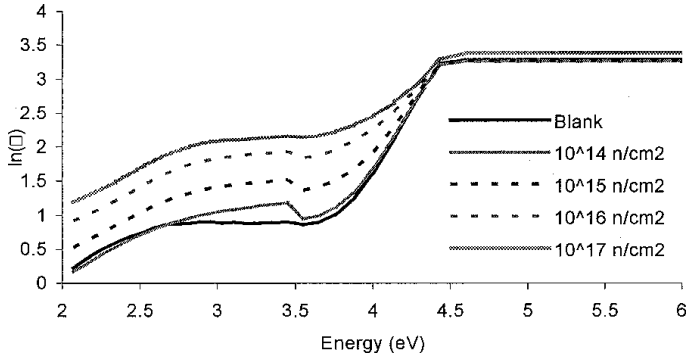

Figure 2. Urbach plot for blank and neutron irradiated glass of Comp-I.

The absorption coefficient, $\alpha(\nu)$, for the amorphous materials is given by Tauc [8] equation :

$$\alpha(\nu) = \text{const}\left[\frac{\left(h\nu - E_{\text{opt}}\right)^2}{h\nu}\right]. \qquad (2)$$

where $h\nu$ is the photon energy and E_{opt} is the optical energy gap. The values of optical energy gap (E_{opt}) which is the extrapolation of the linear region of the plots of $(\alpha h\nu)^{1/2}$ against $h\nu$ to $(\alpha h\nu)^{1/2} = 0$ and Urbach energy (E_e) which is the slope of the Urbach plots, for the blank and neutron irradiated samples of different fluences for Comp-I are given in Table 2. The variations of the optical energy gap (E_{opt}) with varying the composition for the unirradiated and irradiated glass samples with neutrons is reported in Table 3 and shown in Figure 3.

Table 2. The variation of band gap energy and Urbach energy with increasing neutron fluence in glass of Comp-I (75%SiO_2; 15%Na_2O; 5%MgO; 5%Al_2O_3).

Neutron fluence (n/cm^2)	Optical energy gap E_{opt} (eV)	urbach energy E_e (eV)
0	4.204 ± 0.007	0.262 ± 0.002
10^{14}	4.187 ± 0.007	0.267 ± 0.001
10^{15}	4.095 ± 0.007	0.323 ± 0.001
10^{16}	4.073 ± 0.007	0.483 ± 0.001
10^{17}	4.051 ± 0.007	0.473 ± 0.001

Table 3. The variation of optical energy gap with composition for unirradiated and irradiated glass samples with lowest dose (10^{14} n/cm^2)

Sample code	Optical energy gap, E_{opt} (eV)	
	Blank	10^{14}
Comp-I	4.204 ± 0.007	4.187 ± 0.007
Comp-II	4.164 ± 0.007	4.141 ± 0.007
Comp-III	4.007 ± 0.007	3.876 ± 0.006
Comp-IV	3.986 ± 0.006	3.849 ± 0.006

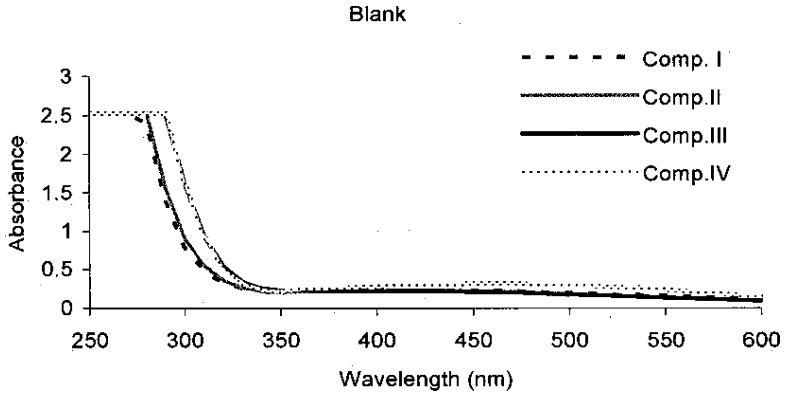

Figure 3. UV-VIS spectra of unirradiated glasses of varying compositions from I-IV.

As can be seen in Figure 1 that with the increasing fluence of neutrons, the tail of the band is tailing into the visible region. Also with the increasing content of Na_2O, from Comp-I to Comp-IV, the absorption edge is shifting towards the longer wavelength side as shown in Figure 3. According to Stevals [9], the absorption edge in oxide glasses corresponds to the transition of an electron belonging to an oxygen ion to an excited state. The more weakly these electrons are bound, the more easily absorption occurs. As reported in Table 2, the band gap energy decreases with increasing neutron fluence. Similar is the results obtained in the microscopic glass slide irradiated with neutrons in one of our previous works [10]. Some of the workers [9,11,12] suggested that in oxide glasses, the shift of energy gap to lower energies could be related to the formation of non-bridging oxygen that binds excited electrons less tightly than bridging oxygen. The high-dose of neutron irradiation break up the normal silicon-oxygen bonds in the glass network and displace oxygen out of its normal position, resulting in NBOs. With increasing percentage of Na_2O from Comp-I to Comp-IV, the band gap energy decreases due to the production of two non-bridging oxygens per Na_2O molecule and Na ion going into the interstitials. The negative charges on the NBOs have larger magnitude than that on the bridging oxygens. Increasing the ionicity of oxygen ions, by converting them from bridging

to non-bridging oxygen (NBO) ions, raises the top of the valence band resulting in the reduction of the optical energy gap (E_{opt}) [13].

The Urbach plot for Comp-I is shown in Figure 2. The random fluctuations in the potential associated with any lattice distortions, like thermal vibrations, dislocations, electric fields of defects, *etc.* can affect the energy band and cause tailing of energy states in the forbidden gap. The Urbach rule for absorption coefficient is an attempt to explain the observed exponential tail in terms of internal electric field generated within a solid. This internal electric field leads to the exponential broadening of the energy states. Some of the workers [14,15] have reported that such a tailing off of states could modify the direct band transition and cause an exponential energy dependence of the intrinsic edge. As shown in Table 2, with increasing neutron fluence, the Urbach energy (E_e) increases from 0.26–0.48 eV with a slight decrease at the highest fluence for the glass sample of Comp-I. This increase in the Urbach energy, with increasing irradiation may be related to the increase in the amorphousity of the glass structure. Similar results have been reported with gamma irradiation of the microscopic glass slide [16].

4. Conclusions

The neutron irradiation of silicate glasses results in the development of optical absorption bands at 360 and 430 nm due to the formation of NBOHC. The increasing concentration of broken oxygen-silicon bridge due to deformation modifies the number of sites for color-center creation as well as the quantity of the recombination sites. The variation in the optical energy gap with increase in mole percentage of network modifier Na_2O and with increasing neutron fluence is discussed on the basis of the formation of non-bridging oxygen.

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