

## Influence of $\gamma$ -Irradiation on the Optical Properties of Sodium Silicate Glasses Doped With Iron Oxide

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**Abstract:** Sodium silicate glasses doped with 1 and 3 mol% iron oxide have been prepared by the melt quenching technique. The obtained X-ray diffraction (XRD) patterns confirmed the amorphous structure of all samples. The UV-VIS spectra of the doped glasses have been recorded in the range from 200 to 800 nm, before and after  $\gamma$ -irradiation with various doses. The cut off wavelength of the doped glasses was found to decrease with increasing Fe<sub>2</sub>O<sub>3</sub> content, while it increased by increasing  $\gamma$ -irradiation dose. The analysis of the optical absorption spectra revealed that all the glass samples exhibited indirect optical transition. The optical band gap energy (E<sub>g</sub>) was found to decrease with increasing  $\gamma$ -irradiation dose, while the Urbach energy (Eu) increased. The decrease in the optical band gap and consequently the increase in Urbach energy confirmed more extension of the localized states within the band gap which indicated an increase in the disorder of the glass network.

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### 1. Introduction

Recently, the study of the irradiation effects on glasses has drawn the attention of many researchers because of the increasing use of different radio-active sources in various daily life fields [1, 2]. Since glasses are usually transparent to visible light, so they represent a good alternative of concrete which is usually used for  $\gamma$ -energy shielding purposes [2, 3]. In this sense, sodium based silicate glasses are supposed to have good radiation shielding properties due to their high atomic number. These glasses find their use in the nuclear engineering applications such as nuclear reactors, hot cells and encapsulating the radioactive wastes [4-6].

From another point of view, doping is an important technique for developing functional materials, where it imparts various functions to the parent materials, or improves their properties. Material properties are drastically modified by the addition of small amounts of dopants. It was found that transparent oxide glasses, which are intrinsically insulating and optically inactive, are changed to be electronically and/or optically active materials by doping. Also, doping has remarkable effects on crystalline materials such as silicon and perovskite-type materials [7].

Oxide glasses doped with small quantities of transition metal oxides have been extensively investigated for their coloring properties [8]. Moderate to large quantities of transition metal oxides have been also introduced in glasses for their

interesting electrical and magnetic properties [9, 10]. The control of the oxidation state of iron in commercial glasses with a special application is very important [11], and the effects of iron on the optical properties of glass have been widely studied [12–15]. It has been found that the change in the melting point results in different ferrous to ferric ratio in glasses [16, 17].

However, the purpose of the present article is to prepare some sodium silicate glasses doped with different concentration of Fe<sub>2</sub>O<sub>3</sub> (1 & 3 mol%) and to study the structural and the optical properties of the prepared glass samples as well as to investigate the influence of  $\gamma$ -irradiation on the studied properties.

### 2. Experimental

Two sodium silicate glass samples doped with (1 & 3 mol%) Fe<sub>2</sub>O<sub>3</sub>, (namely S1 and S2 respectively) have been prepared by the melt quenching technique. All the glass batches were prepared using analytical raw materials. Silicon dioxide was introduced in the form of ortho-silicic acid (H<sub>4</sub>SiO<sub>4</sub>) and sodium oxide was introduced in the form of bicarbonate (NaHCO<sub>3</sub>) while ferric oxide was introduced as such (Fe<sub>2</sub>O<sub>3</sub>).

The batches were melted in platinum 2% rhodium crucibles at 1100°C for 2 hs in an electrically heated muffle furnace. The melts were stirred several times during melting to obtain glasses of high uniformity. Then the melts were poured on a

stainless-steel plate and were directly transferred to the annealing furnace at 350°C.

All glasses were examined visually, where they appeared free from any visible inhomogeneities or air bubbles. After that, the glasses were cut into sheets of 25×25×1 mm, and all surfaces were well polished using 400 mesh ceria powder.

XRD analysis was firstly carried out at RT in order to confirm the amorphous nature of the studied glasses. A Philips (Type X Pert) X-ray diffractometer with Ni-filtered and CuK $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) operated at 30 mA and 40 KV was used.

The optical absorption of the glass samples was measured at RT with un-polarized light at normal incidence in the wavelength range from 200 to 800 nm, using a double beam spectrophotometer (Type JASCO Corp. Model V – 570) with an estimated error of  $\pm 0.5 \%$ . All measurements were performed on the as prepared samples as well as those  $\gamma$ -irradiated at different doses (0.5, 1.5 and 3 MRad).

Irradiation of the glass samples was performed at RT using  $^{60}\text{Co}$  gamma source. The dose rate for irradiation was ranging from 2.4787 to 2.2709 kGy/hr. The glass samples were placed in the gamma cell in a manner that each sample was subjected to the same dose. This has been achieved by putting the glass samples in the same place around a cylinder placed inside the chamber. The glass samples were irradiated for the necessary time interval to achieve the desired overall dose. All samples under investigation exposed to successive doses of 0.5, 1.5 and 3 MRad.

### 3. Results and Discussion

#### 3.1. The amorphous nature

The obtained XRD patterns of the powdered glass samples, S1 and S2 are shown in Figs. (1, a & b) respectively. These patterns did not show any sharp Bragg peaks confirming the amorphous nature of all the investigated samples.

#### 3.2. Optical Band Gap

The optical properties of the prepared glasses doped with 1% and 3% of  $\text{Fe}_2\text{O}_3$  and  $\gamma$ -irradiated with different  $\gamma$ -doses (0.5, 1.5 and 3 M Rad) were studied. Fig. (2), represents the optical absorption spectra of the un-irradiated doped glasses recorded at RT in the wave length region of 200-800 nm. It was clear from this figure that, the fundamental absorption edges are nearly sharp. This is a characteristic feature of all amorphous and glassy materials. The cutoff wavelength of the doped glass is found to decrease with increasing the concentration of  $\text{Fe}_2\text{O}_3$ , and it shifts to the red range at 412 nm i.e. to higher wavelength as shown from Fig. (2).

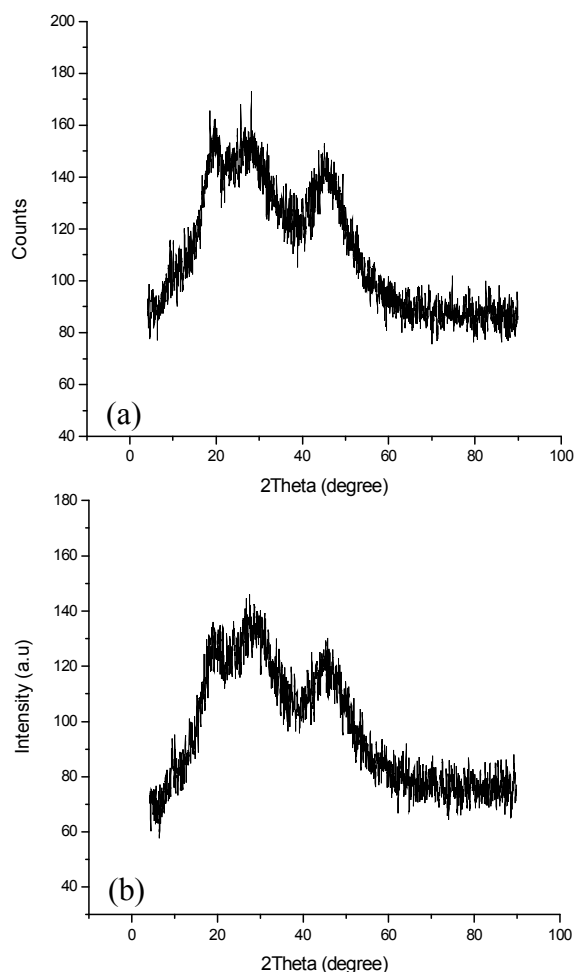


Figure 1. XRD pattern of produced glasses a- S1 contains 1 mol%  $\text{Fe}_2\text{O}_3$ , b- S2 contains 3 mol%  $\text{Fe}_2\text{O}_3$

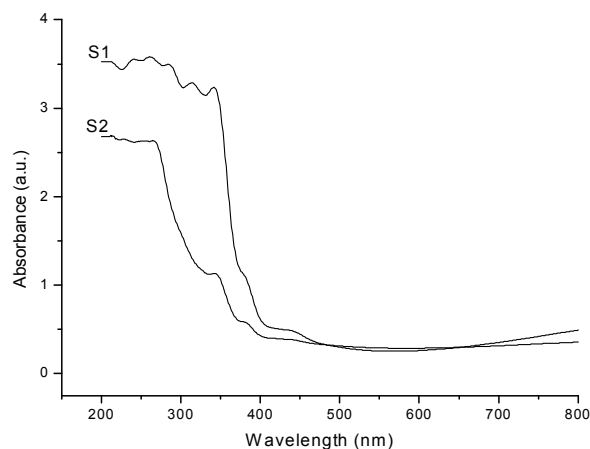


Figure 2. the obtained optical absorption spectra of the un-irradiated glass samples S1 and S2

The optical absorption spectra of the glass sample doped with 3% Fe<sub>2</sub>O<sub>3</sub> (S2), before and after  $\gamma$ -irradiation with various doses, are shown in Fig. (3), as representative example. From this curve it is clear that no characteristic band are present in both

ultraviolet and visible region and exhibited only an UV cutoff extending from the beginning of the measurement up to 330 nm. The UV absorption edge values for all the doped and  $\gamma$ -irradiated glass samples are presented in Table (1).

Table 1.  $\lambda_{cutoff}$  values of the studied glasses

Samples	Mol% Fe <sub>2</sub> O <sub>3</sub>	$\lambda_{cutoff}$ (0 MR)	$\lambda_{cutoff}$ (0.5 MR)	$\lambda_{cutoff}$ (1.5 MR)	$\lambda_{cutoff}$ (3 MR)
S1	1% Fe <sub>2</sub> O <sub>3</sub>	363.62nm	365.64 nm	373.89 nm	377.95 nm
S2	3% Fe <sub>2</sub> O <sub>3</sub>	308.23 nm	310.25 nm	312.28 nm	375.91 nm

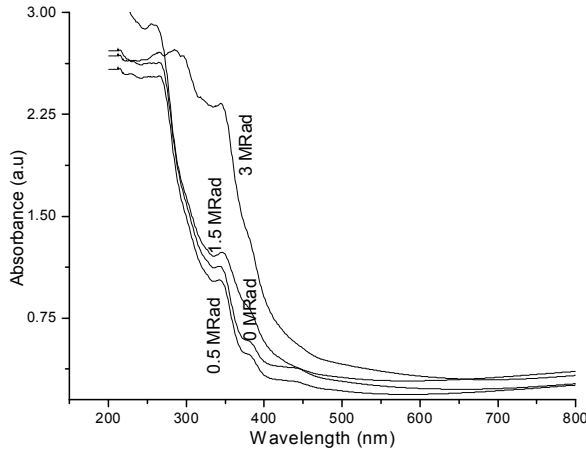


Figure 3. the obtained optical absorption spectra of the un-irradiated and irradiated glass S2 (3% Fe<sub>2</sub>O<sub>3</sub>) at different  $\gamma$ -ray doses, as representative curve

It is well known that, the interaction of ionizing radiation with solids including glasses depends on the type of radiation, the type of solid itself and the defects within its matrix. However, it can be supposed that, the radiation interaction may cause a displacement of lattice atoms or electronic defects which involve changes in the valance state of the lattice or impurity atoms. Also it may involve ionization and charge trapping and radiolytic or photo-channel reactions [18, 19].

The absorption intensity of the incident light by a glass sample follows Beer-Lambert law. In the near absorption edge, the optical absorption coefficient  $\alpha(\omega)$  of such glass sample of thickness “t” can be calculated from the relation

$$\alpha(\omega) = \frac{1}{t} \ln \left( \frac{I_0}{I_t} \right) \quad [1]$$

Where  $\ln(I_0/I_t)$  is the absorption,  $I_0$  and  $I_t$  are the intensities of the incident and transmitted light respectively. The optical absorption of the disordered materials ( $\alpha_0 \geq 10^4 \text{ m}^{-1}$ ) follows Taue’s rule [9].

$$\alpha(\omega) = \frac{1}{t} \alpha_0 (h\nu - E_g)^r \quad [2]$$

Where  $\alpha_0$  is a constant related to the extent of the band tailing and  $E_g$  is the optical band gap energy [20], the exponent  $r = 1/2$ , indicates an allowed direct transition, while  $r = 2$ , indicates an allowed indirect transition. It is observed that the measured absorption data shows the best fit to equation (2) when  $r = 2$ , which corresponds to an indirect allowed transitions. The plot of  $(\alpha h\nu)^{1/2}$  versus  $(h\nu)$  for the doped glasses before and after  $\gamma$ -irradiated with different doses are represented in Fig.s, (4 & 5). The values of the energy gaps  $E_g$  can be estimated by the extrapolation of the linear portion of the curve to the x-axis, that is,  $(\alpha h\nu)^{1/2} = \text{zero}$ .

From these figures, it is observed that, the energy gaps for all glass samples decreased with increasing the doping concentration of Fe<sub>2</sub>O<sub>3</sub> as well as the increase of  $\gamma$ -ray irradiation dose. All the obtained data are listed in Table (2).

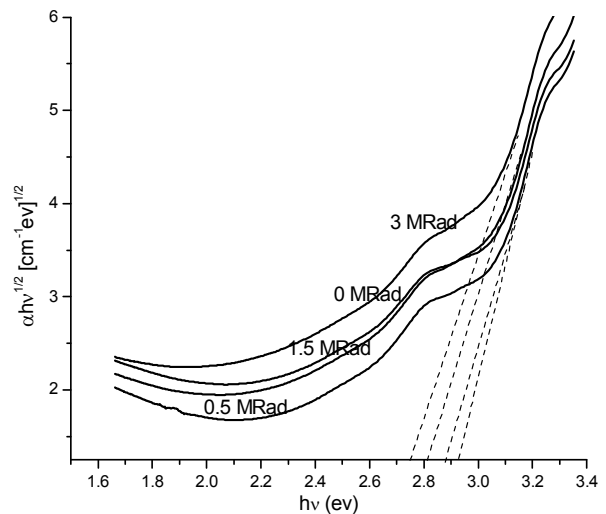
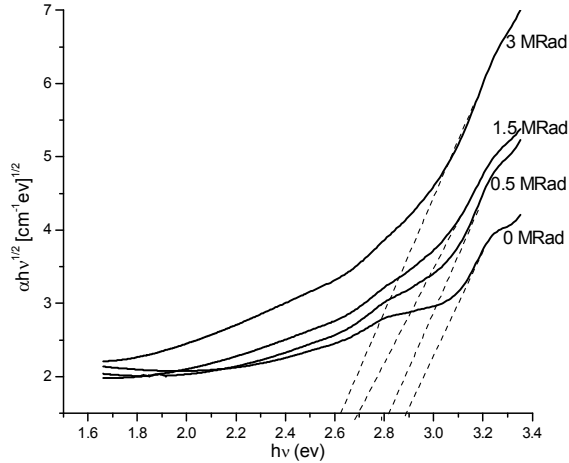
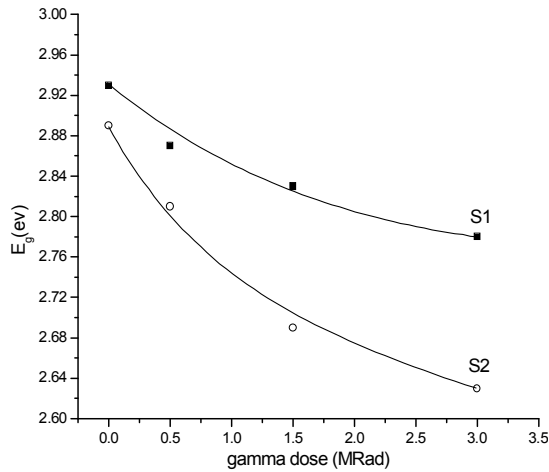


Figure 4. Tauc plots of sample S1 (1% Fe<sub>2</sub>O<sub>3</sub>) before and after irradiation with different  $\gamma$ -ray doses

Table 2. the obtained energy gap ( $E_g$ ) values of the studied glasses, before and after  $\gamma$ -ray irradiation

Sample	Mol% $\text{Fe}_2\text{O}_3$	$E_g$ (0MR)	$E_g$ (0.5MR)	$E_g$ (1.5MR)	$E_g$ (3MR)
S1	1% $\text{Fe}_2\text{O}_3$	2.93 eV	2.87 eV	2.83 eV	2.78 eV
S2	3% $\text{Fe}_2\text{O}_3$	2.89 eV	2.81 eV	2.69 eV	2.63 eV

Figure 5. Tauc plots of sample S2 (3% $\text{Fe}_2\text{O}_3$ ) at different  $\gamma$ -ray dosesFigure 6. relation between  $\gamma$ -ray dose (MRad) and energy gap ( $E_g$  eV) for samples S1 & S2

As the  $\gamma$ -ray irradiation dose was gradually increased, a shift of  $\lambda_{\text{cutoff}}$  to a higher wavelength and a decrease in the values of  $E_g$  has been observed (see Fig. (6)). This indicated an increase in the non-bridging oxygen atoms in the glass network. It is known that, oxygen ions that connect two structural units in the glass network are called bridging oxygen, and the addition of some network modifier breaks these bridges and creates non-bridging oxygens. These oxygen ions carry a partial negative charge and

are connected to structural unit only at one end in the glass network [21].

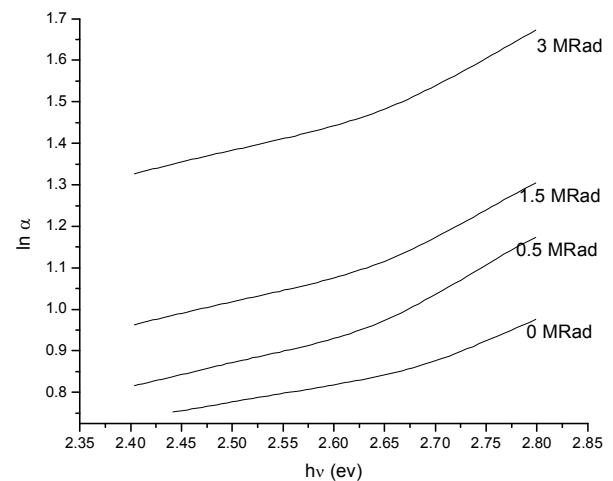
### 3.3. Urbach Energy

The main feature of the absorption edge of amorphous materials is an exponential increase of the absorption coefficient with photon energy. When the energy of the incident photon is less than the band gap, the increase in absorption coefficient is followed with an exponential decay [22]. The lack of crystalline long-range order in amorphous or glassy materials is associated with a tailing of density of states through the forbidden energy gap [22]. Urbach energy characterizes the extent of exponential tail of the absorption edge. The exponential absorption tail and Urbach energy is given in accordance with the empirical relation [23]

$$\alpha(\nu) = B \exp(h\nu / E_u) \quad [3]$$

Where B is a constant,  $E_u$  is the Urbach energy, which can be taken as an indication to the width of the band tails of the localized states and ( $\nu$ ) is the frequency of radiation.

Figs. (7 & 8), show the relation between  $h\nu$  (eV) and  $\ln(\alpha)$  of the doped glasses (S2 & S1) respectively before and after  $\gamma$ -ray irradiation with different doses. From both figures, Urbach energy values can be calculated from the slopes of the linear regions of  $\ln(\alpha)$  versus  $h\nu$  plot for all the doped glasses before and after  $\gamma$ -irradiation.

Figure 7.  $h\nu$  (eV) versus  $\ln(\alpha)$  of sample S2 at different  $\gamma$ -ray doses

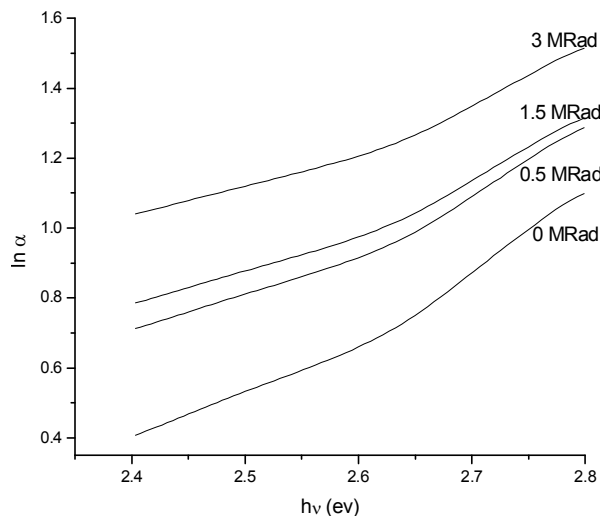


Figure 8.  $h\nu$  (eV) versus  $\ln(\alpha)$  of sample S1 at different  $\gamma$ -ray doses

It is clear that, Urbach energy increased by increasing the doping concentration as well as the increase of  $\gamma$ -ray doses from zero to 3 MRad for all glass samples under investigation. These values are represented in Table (3) and Fig. (9).

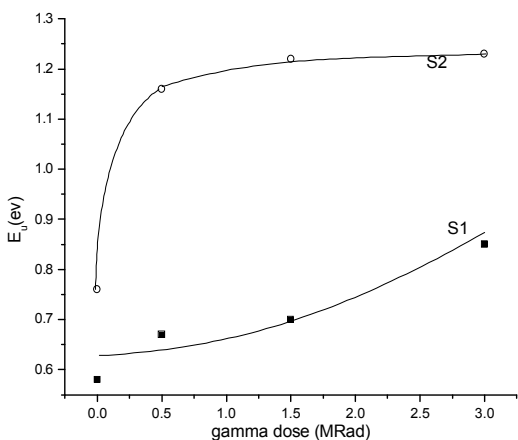


Figure 9. relation between  $\gamma$ -ray irradiation doses (MRad) and energy gap  $E_u$  (eV) for samples S1 & S2

The decrease in  $E_g$  values and the increase of  $E_u$  values indicated an increase of disorder in the glass network of the studied glasses and consequently there will be more extension of the localized states within the band gap as suggested by Mott and Davis [9].

### 3.4. Refractive index (n) and Extinction Coefficient (k)

The optical constants  $n$  and  $k$  of the investigated glass samples were determined for all glasses before and after  $\gamma$ -ray irradiation. Figs. (10 & 11) represent the relation between the refractive index ( $n$ ) and extinction coefficient ( $k$ ) versus the wavelength from 390-600 nm for the 1%  $\text{Fe}_2\text{O}_3$  doped glass as a representative curve. From these figures it is clear that,  $n$  increased, while  $k$  decreased with the gradual increase of the wavelength, for the un-irradiated and irradiated samples with different  $\gamma$ -ray doses.

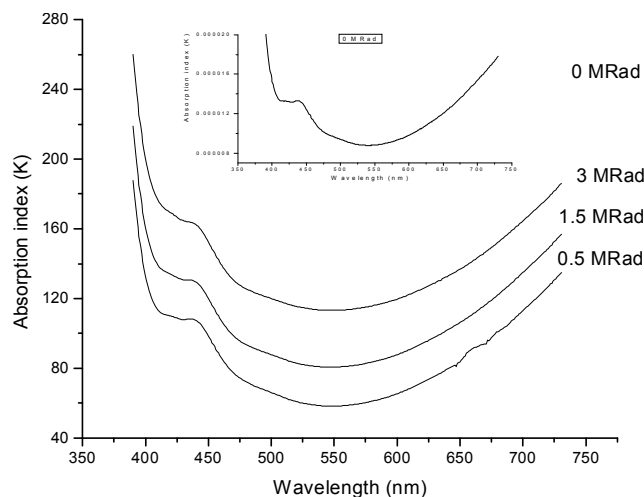


Figure 10. relation between the wavelength (nm) and refractive index ( $n$ ) for sample S1 (1% $\text{Fe}_2\text{O}_3$ ) at different  $\gamma$ -ray doses, as representative figure

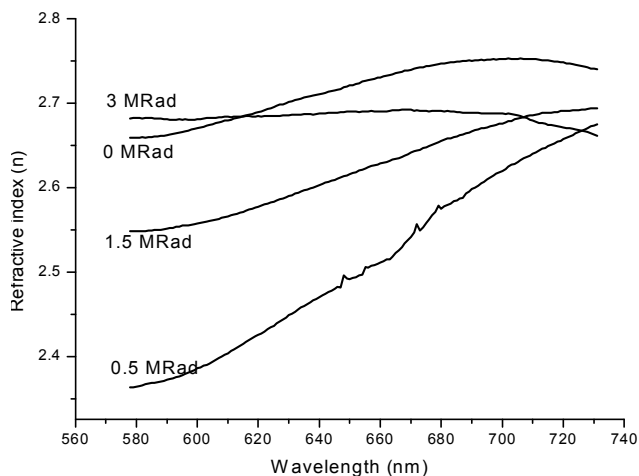


Figure 11. relation between the wavelength (nm) and absorption index ( $k$ ) for sample S1 (1% $\text{Fe}_2\text{O}_3$ ) at different  $\gamma$ -ray doses, as representative figure

A linear refractive index ( $n$ ) and its dispersive wavelength dependence are important parameters that determine the suitability of an oxide glasses to be used as an optical material [24]. The

increase in refractive index with  $\gamma$ -irradiated may be due to the increase of the disordered and hence the increase of the intensity of dielectric constant in these glasses.

Table 3. Urbach energy  $E_u$  values of the studied glasses

oncn of $Fe_2O_3$	$E_u$ (0MR)	$E_u$ (0.5MR)	$E_u$ (1.5MR)	$E_u$ (3MR)
1% $Fe_2O_3$	0.58 ev	0.679 ev	0.702 ev	0.853 ev
3% $Fe_2O_3$	0.76 ev	1.16 ev	1.22 ev	1.23 ev

The decrease in the optical energy gap and the increase in refractive index values with the increase of the doping concentration are in agreement with other reported values [25].

It can be observed that the presence of iron ions additives increases the refractive index and the transmission range. A higher refractive index is desirable to increase glass reflectivity (appear shiny).

#### 4. Conclusion

Sodium silicate glasses doped with 1 and 3 mol%,  $Fe_2O_3$ , were prepared by the melt quenching technique. The influence of doping and gamma irradiation on the optical properties of these glasses had been studied. XRD analysis revealed that all the glass samples have amorphous structure.

From the UV-VIS optical absorption spectra of the studied glasses, it can be concluded that, the red shift of  $\lambda_{cut-off}$  values increased as the dopant concentration was decreased. It can be concluded also that, all the glass samples exhibited indirect optical transition with relatively higher Urbach tail. The energy gap ( $E_g$ ) decreased, while Urbach energy ( $E_u$ ) increased with the increase of the doping concentration. The increase of the Urbach energy values as well as the energy gap ( $E_g$ ), with increasing  $Fe_2O_3$  concentration confirmed the extension of more tails of the localized states into the band gap of the glass samples.

The influence of the  $\gamma$ -irradiation with different doses (0, 0.5, 1.5, & 3 MRad) on all the optical parameters ( $E_g$ ,  $E_u$ ,  $n$  &  $k$ ) indicated that the energy gap ( $E_g$ ) decreased, while Urbach energy ( $E_u$ ), refractive index ( $n$ ) and the extinction coefficient ( $k$ ) increased for the investigated samples. This behavior confirms the increase of the disorder in the glass network and consequently there will be more extension of the localized states within the band gap.

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#### References

1. S.Y. El-Kameesy, S. Abd El-Ghany, M. Abd El-Hakam Azooz, Y. Abd Allah El-Gammam, World J. of Condensed Matter Physics, 3, (2013), 198.
2. R. Kaur, S. Singh, O. P. Pandey, Physica B, 407, (2012), 4765.
3. H. Singh, K. Singh, L. Gerward, H. S. Sahota, R. Nathuram, Nuclear Instruments and Methods in Physics Research Section (B): Beam Interactions with Materials and Atoms, 207, No. 3, (2003), 257.
4. M.A. Marzouk, F. H. El Batal, Appl. Phys (A), 115, (2014), 903.
5. M.A. Marzouk, J. of Molecular Structure, 1019, (2012), 80.
6. A.M Abdelghany, H. A. El Batal, L. K. Marei, 167 (1), (2012), 49.
7. F. Funabiki, T. Kamiya, H. Hosono, Ceramic Society Japan 120 (11), (2012), 447.
8. C.R. Bamford, "Color Generation and Control in Glasses", Elsevier Scientific Publishing Co., Amsterdam and New York, (1977).
9. N.F. Mott, and E. A Davis, "Electrical Processes in Non-Crystalline materials", 2<sup>nd</sup> Edition, Oxford University Press, London, (1979).
10. H.O. Hooper, A.M. de Graff (Eds.), Plenum Press, New York, (1973).
11. F.V. Tolly, Foundation of Glass Industry,, Qazvin glass Co, Qazvin, 3, (1991), 1316.
12. K.R. Kukadapu, G. L. Li, H. Smith, J. Non-Cryst. Solids, 317 [3] (2003), 301.
13. M. Yamashita, T. Akai, R. Sawa, J. Non-Cryst. Solids, 354 [40-41] (2008), 4534.
14. K. Sakaguchi, T. Uchino, J. Non-Cryst. Solids, 353 [52-54] (2007) 4753.

15. S.B. Donald, A.M. Swink, H.D. Schreiber, J. Non-Cryst. Solids, 352 [6-7] (2006) pp. 539–543.
16. W.A. Weyl, Dawson's of Pall Mall, London, UK, 1, (1959), 89.
17. B. Mirhadi, B. Mehdikhani, J. Korean Ceram. Soc., 48[2], (2011), 117.
18. D. Ehrhart, P. Ebeling, Glass Technol. 44 (2003) 46.
19. H.A. El Batal, N. Abd-El-Shafi, M.A. Azooz, Nucl. Sci. J. 35 (1998) 331.
20. E.A. Davis, N.F. Mott, Phil Mag., 22, (1970), 903.
21. Ch. Rajasree and D.Krishna Rao., J. Non-Crystalline Solids, 325, (2011), 836.
22. B. Abay, H. S. Guder, Y. K. Yogurtchu. Solid State Commun, 112, (1999), 489.
23. M.A. Hassan, C.A. Hogarth. J. Mater Sci, 23, (1988), 2500.
24. S.S. Rao, G. Ramadevudu, M. D. Shreefuddin, A. Hameed, M. N. Chary and M.L. Rao, International J. of Engineering, Science and Technology, 4, (4) (2012), 25.
25. S.M. Abo-Naf, M.S. El-Amiry and Abdel-Khalek, J. Optical Materials, (6), (30), (2008), 900.

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