Gamma-irradiation Effect on Optical Properties of $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ glass

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The effect of gamma irradiation doses (5-45 kGy) has been studied on the optical properties of $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ glass. The glass densities are determined using Archimedes principle, while UV-VIS Spectrophotometer was used to evaluate the changes in the optical properties before and after irradiation. Gamma irradiation causes structural changes which due to the breaking of the network bonding. The decrease in optical band gap and shift of absorption edge towards longer wavelength is attributed to the increment of NBO atoms and increase of defect in the glass sample.

INTRODUCTION

Gamma rays are one of the most significant type of radiations emitted from the radiation sources and also nuclear reactor for which the shielding is mandatory. Gamma rays have highly penetrating capability and negligible heat production [1]. Glasses are known to have pre-existing intrinsic defects like oxygen vacancies or Non-Bridging Oxygens (NBOs) or any imperfections caused by any high energy electrons, and the irradiations impact the distinct structural units together with modifier ions [2]. An electron displaced from its lattice site due to prolonged irradiation falls into an interstitial position, if in case it did not migrate to the surface. Irradiation affects the vitrified network with free electrons and positive holes creating vacancies and lattice defects. Minimum thermodynamic free energy in the glass matrix increases the disorders and defects. There are chances whereby defects like vacancies, interstitial electrons, multivalent impurities or NBOs in built in the glass lattice could be recovered by modifying into other defects or by recombination of Hole Center (HC) with Electron Center (EC) [3,4]. The interaction of radiations on glasses rely on type of radiation and energy of the same ionizing radiations (gamma rays, X-rays) or matter waves (electron beam, alpha rays), type of glass and intrinsic defects of the amorphous network.

Radiations induced atomic or electronic defects, like, displacements by momentum and energy transfer (valency), charge trapping (ionization) and radiolysis (photochemical effects) [5]. This is majorly observed when visible color of the glass samples changes after irradiation. Defect centers causing this are referred as color or absorption or Farbe centers/F Centers. Electrons initially in its lattice position (in valence band) excited only if the energy of the incident radiation (E) is greater than the energy band gap (E_g) [$E > E_g$]. That is, if E > 1 keV, the electrons are excited by Compton effect. This effect depends on the atomic number of the element (higher the metal element content, the cross section for the Compton effect increases) as well.

Gamma irradiation also may affect the optical properties of various glasses with varying degrees depending on the type and composition of glass including the presence of transition metal ions even if present as impurities. Gamma irradiations affect the structure of the glass matrix, resulting in changes in the optical, physical and electrical properties [6,7]. Defect centers induced by ionizing radiation in borate glasses are described by microscopic models constructed on the basis of local information obtained from studies using several spectroscopic techniques, such as optical absorption, infrared or Raman spectroscopy [8]. The knowledge of the glass structure before and after irradiation is a prerequisite for understanding the structural evolution of glasses under long term irradiation.

The present work aims to assess the radiation response toward gamma irradiation on a glass sample with chemical composition $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$. The structural and optical properties for studied glass sample after gamma exposure will be analyze using Fourier Transform Infrared (FTIR) and UV-Vis spectroscopy measurement. This work is a continuation of previous studies [9] with the addition information on exploring the fundamental understanding of gamma irradiation induced structural modifications in glass material.

Methodology

Glass with chemical composition of $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ was prepared by using a melt quenching technique. The chemicals such as tellurium (IV) dioxide TeO_2, boron oxide B_2O_3 and barium oxide from Assay, Alfa Aesar were mixed together and ground thoroughly by using an agate mortar for about 20 minutes. The mixture was preheated at 350°C for 30 minutes and then melted at 900°C for 1 hour. The molten glass was poured into a stainless steel mould which was preheated at 400°C and annealed at 400°C for 1 hour. All glasses were cut (about 2 mm thickness) and then polished until its surfaces become smooth. The glasses were prepared in powder form for the (FTIR) analysis in the range of 200–2000 cm^{-1}. The glass density, ρ, was determined using Archimedes principle. A UV-Visible spectroscopy SIMADSU Model UV-1650PC was used to observe the optical absorption at the range of 200-800 nm. Optical absorption coefficient, α, was determined using:

$$\alpha = 2.303\left(\frac{A}{d}\right) \qquad (1)$$

where d is thickness of glass sample and A is absorbance. The band gap energy, E_{opt} (indirect transition) was measured using:

$$(\alpha\hbar\omega)^{1/2} = B\left(\hbar\omega - E_{opt}\right) \qquad (2)$$

where B is a constant and ω is the photon energy. Urbach energy, ΔE is define as the width of tailed of localized states in the band gap and was determined by taking the reciprocal of the slope of the plot ln α against $\hbar\omega$ curve. The decrease or increase value of ΔE can describe defect in the glass network. The gamma irradiation process was conducted using gamma rays with Co-60 source using operating dose of 5.52 kGy/h at MINTec SINAGAMA-PARK, Malaysia Nuclear Agency. All glasses placed at 100 cm from the source were subjected to gamma irradiation dose between 5 to 45 kGy.

In this research, the irradiated glass samples were packed in a small box and then placed in an automatic product carrier system. The carrier system carries the samples with radiation batch number and routine dosimeter to the irradiation room and then brings them to the processed product area. After the irradiation process, the dosimeter are sent to the quality control (QC) laboratory to measure the absorbed dose by Ceric Cerous meter and is then issued the certification for maximum and minimum dose delivery for each radiation batch. The requested radiation dose for glass samples are from 5 kGy to 45 kGy with intervals of 5 kGy. However, the actual dose measured by Ceric Cerous meter shown in the certificate is difference with the request radiation dose in the range ± 1 kGy. Within one week, all irradiated samples were then analyzed for structural (XRD and FTIR) and optical (UV-VIS) measurements.

Results and Discussion

The data on the density of glass material before and after irradiation is important in order to study the structural changes that occur inside the material. It can affect the structural compaction, expansion or/and changes in the geometrical configuration and the dimension of interstitial spaces of the glass [10]. The values of glass density with their molar volume with variation of gamma radiation dose of (0, 5, 15, 25, 35 and 45 kGy) for $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ glass presented in Figure 1. This values have been determined using Archimedes principle after gamma exposure. The connected line from one point to another point drawn in this graph does not resemble any significant descriptions rather than to show the increasing and decreasing pattern of density and molar volume values.

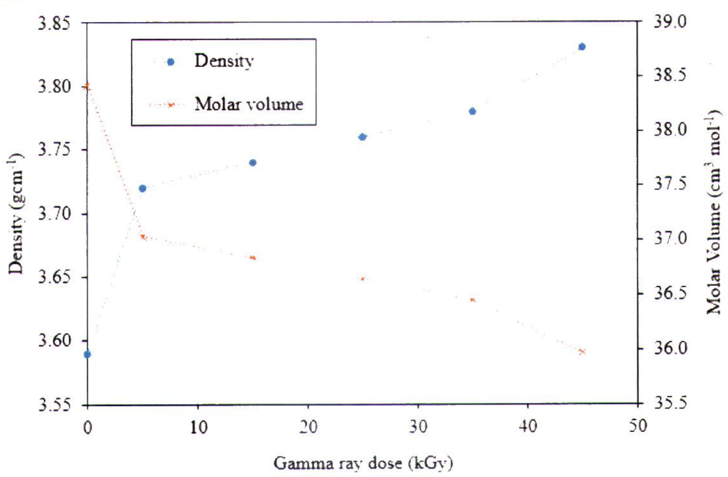

Figure 1. The variation of density and molar before and after gamma irradiation.

From Figure 1, the density of studied glass increased greatly after exposed to 5 kGy gamma ray. The further effect of 15 kGy to 35 kGy of gamma irradiation dose on $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ glass produces only slight changes in the density and molar volume values. As gamma dose increases to maximum (45 kGy), more increment is shown in the density value. It is expected that the density and the molar volume opposite behaviour with each other. This opposite trend between density and molar volume is also observed by [11,12]. Density and molar volume related to how tightly the atoms and atomic groups are placed together in the glass network.

Generally, it can be observed that gamma irradiation leads to an increase in density of glass sample. This increment can be attributed to the change in the structure after irradiation. There are some expected causes of increment in glass density observed by previous researchers after gamma irradiation which can be summarized as below:

1. density change depends on the composition or state of aggregation;
2. density increase is caused by the compact state which is produced from the decreasing in bond angle;
3. gamma ray induced damage which is responsible for induced colour centers [13].

At higher irradiation doses, the irradiated sample can cause the compaction of B_2O_3 by breaking the bonds between trigonal groups thus allowing the formation of tetrahedral [BO_4]. [14] & [15] suggested that the irradiation affected the boron–oxygen bond. Displacement of atoms from their position in the glass network caused by irradiation can give rise to a number of structural changes which cause change in density.

Figure 2 show the variation of color changes before and after exposed to gamma irradiation for $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ glass. From this figure, the gamma irradiation effects were clearly observed through the color changes seen in the glass sample. The light yellow of $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ glass sample turned to dark yellow color after exposed to 5 – 25 kGy and later changed to yellow-brownish color after irradiated with 35 and 45 kGy doses. This color changes are the indicative of lattice defects. Referring to [12], it was suggested that Farbe centers (F_{centre}) or color centers, also named as "Absorption Center" are induced in the samples as resulted of irradiation. This is a type of lattice defect in which an anionic vacancy is filled by one or more electrons. Electrons in such a vacancy tend to absorb light in the visible spectrum such that a material that is usually transparent becomes colored. These vacancies capture available electrons, e, to maintain charge neutrality, forming F-centers; that is, the electrons released in this process diffuse to occupy the vacant sites. The greater the number of F-centers, the more intense is the color of the compound.

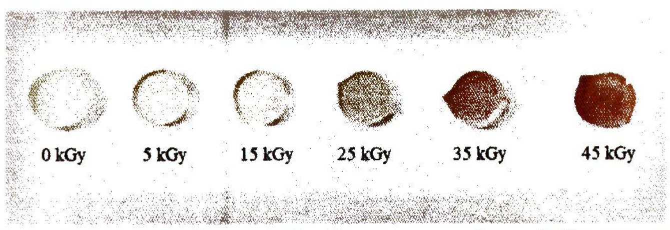

Figure 2 Color changes before and after exposed to different gamma doses

X-ray diffraction patterns of studied glasss before and after gamma irradiation, were obtained, with a broad diffracted peak, confirming the amorphous nature as shown in Figure 3. This graph shows the presence of a broad halo around $2\theta \cong 24\text{-}30^\circ$.

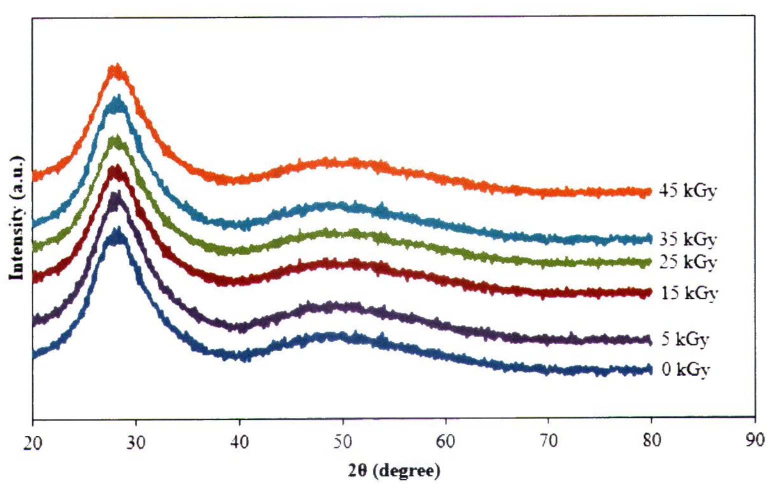

Figure 3 XRD pattern before and after irradiated with different doses of gamma ray.

In Figure 4, it has been shown that the FTIR spectra changes effected by gamma irradiation on $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ glass. Before gamma irradiation, the absorption bands are shown in the area from 1200 to 1400 cm^{-1}, ~1070, 900 cm^{-1}, 800 cm^{-1} and another band lies at about 700 cm^{-1}. The bands at 1200 to 1400 cm^{-1}, ~1070 and 800 - 900 cm^{-1} were assigned due to stretching relaxations of B–O bonds of the trigonal BO_3 units, vibrations of the BO_4 structural units, and bending vibrations of B–O–B linkages, respectively. The presence of band ~700 cm^{-1} is due to bending vibrational modes of B-O-B linkages of $[BO_3]$ groups. Most of the absorption peak are increased as gamma dosage increases. The increase in the intensity of absorption band near 1200 cm^{-1} after gamma irradiation is due to the transformation of BO_4 groups into BO_3 groups along with the non-bridging oxygen's. The changes of band intensity are more pronounced in the case of 15 kGy dose and thereafter. The replacement of broad absorption bands with sharp peaks (500 – 700 cm^{-1}) are probably due to the high degeneracy of the lattice vibrational states and/or broadening of the lattice dispersion band [16]. Similarly, [14] has concluded that irradiation causes a compaction of B_2O_3 by breaking the bonds between the trigonal elements, allowing the formation of BO_4 tetrahedra. The absorption band in this range are due to the vibrations of BO_4 overlape with TeO_3 [2,11].

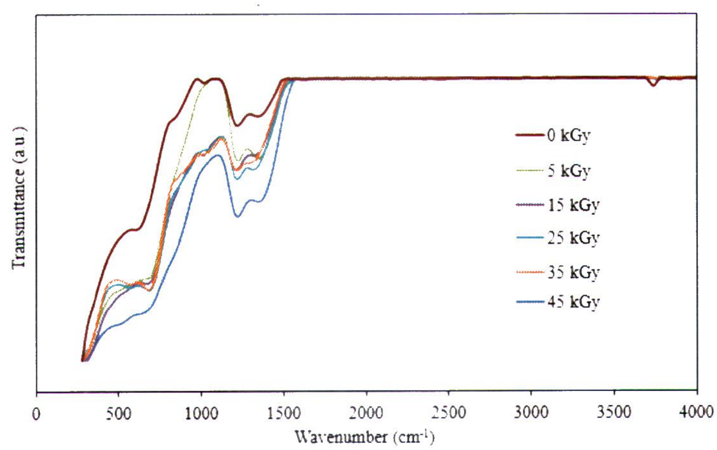

Figure 4 FTIR spectra before and after irradiated with different doses of gamma ray

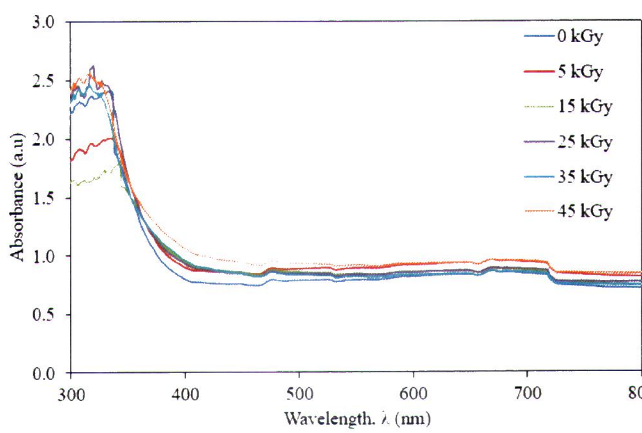

Figure 5 Optical absorption for $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ glasses before and after irradiated with different doses of gamma ray

Table 1 Optical band gap, E_{opt}, urbach energy, ΔE Refractive index, n, molar refraction, R_m, molar polarizability, α_m, and oxide polarizability, α_o^{2-} value.

γ-ray dose (kGy)	$E_{opt,direct}$ (eV)	$E_{opt,indirect}$ (eV)	ΔE (eV)	n	R_m	α_m (Å³)	α_o^{2-} (Å³)
0	3.44	2.62	0.528	1.839	16.452	6.521	4.251
5	3.42	2.54	0.571	1.849	16.512	6.544	4.417
15	3.32	2.50	0.626	1.867	16.541	6.556	4.522
25	3.30	2.54	0.788	1.879	16.771	6.647	4.602
35	3.28	2.55	0.849	1.901	16.981	6.730	4.613
45	3.18	2.53	0.869	1.904	16.998	6.737	4.628

It is well known that the effect of gamma irradiation may result in compaction or expansion of the glass material. In borate-based glass, radiation induced expansion can be due to increase in B-O bond length due to hole trapping by bridging oxygen. Radiations can also break B-O bonds and allows the structure to fill the large interstices in the interconnected network of boron and oxygen atoms, consequently causing compaction of glass [17]. In the case of zinc lead borate glass system, gamma irradiation causes of decrement in band gap value for all the samples. The separation between BO_4 tetrahedra and a neighbouring BO_3 should be less than the separation between two adjacent BO_3 triangles. Thus, the conversion of three co-ordinated boron to four coordinated boron is the cause of network contraction. This signifies that a decrease in band gap after gamma exposure in this glass system is due to breakage of bonds in the trigonal elements, allowing the formation of BO_4 units ([18].

Analysis form present results in Figure 5 and Table 1 show that the gamma irradiation effect the absorption spectra as well as the optical band gap. Gamma irradiation may increase the network disorder and consequently the extension of the localized states within the gap. More likely, increasing irradiation dosage will be breaking up the B–O–B and Te–O–Te bonds as proven in FTIR spectra result and introduces coordinate defects known as dangling bonds along with non-bridging oxygen [11]. The shift of the bands and shoulders (in FTIR spectra around 500 – 600 cm^{-1}) ascribed to the TeO_2 because the incorporation of the glass modifier to higher wavenumber indicates the conversion of some TeO_4 to $[TeO_{3+1}]$ then to trigonal pyramids $[TeO_3]$ (tp) structural units which increases the formation of non-bridging oxygen atoms [19].

Previous research reports that gamma irradiation effect on glasses depends on several factors such as radiation dose, type of glass and the essential defects which are already present in the glass before irradiation [20] & [12] agreed that the decrease in E_{opt} values after irradiation due to the displacements of ions, electronic defects and breaking of B-O bond, resulted the compacting in glass network. The very small decrement of band gap value after irradiation (from 25 to 45 kGy) shows that the glass becomes resistant even while increasing gamma dose. When gamma irradiation interacts with the host glass, it can cause the electronic defects or displacement of lattice atoms. This mechanism involved changes in the valence state of the lattice or impurity atoms and also involve ionization and charge trapping and/or radiolytic [16].

In addition, the decreasing values of optical band gap observed after being exposed to gamma irradiation can be explained on the basis of the increase in spin density and the density of the unpaired electrons in unfilled bands [21]. After gamma irradiation exposure, the defects centers formed from the charge trapping of the radiolytic electrons or holes which often have electronic states in the gap between the valence and the conduction bands. Hence, optical photons can induce transitions from the valence band to the defects level or from the defects level to the conduction band [22].

Most of previous work have reported that the optical band gap, E_{opt} values are inversely proportional to the Urbach energy, ΔE. It is found similar result for studied glass, which is the E_{opt} values are found to decrease while the ΔE value are shown increment pattern as gamma dosage increases up to 45 kGy. The increased value might be due to increasing of structural disorder and consequently the more extension of the localized states. Structural disorder consists of both of intrinsic and induced external sources (radiation and conditions of preparation) [6]. The Urbach energy value after irradiation reported by [16] are higher than present the work. The values of ΔE are found to lie in the range of 0.528–0.869 eV after irradiation.

Furthermore, when $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ glass were subjected to different gamma ray dosage, their refractive index, n, molar refraction, R_m, and molar polarizability, α_m, and oxide ion polarizability, α_o^{2-}, values were observed to increase as shown in Table 1. These parameters were found to have the same trend which opposes the trend of the optical band gap. After gamma irradiation, the increasing value of refractive index, molar refraction and polarizabilities are due to the breaking bonds and the structural damaged as well as the transformation of BO_4 to BO_3 and TeO_4 to TeO_3 structural units, resulting in the formation of non-bridging oxygen in the glass system.

As reported earlier by [2], non-bridging oxygen ions have higher polarizability compared to bridging oxygen ions because they held less tight electrons. As a result, the electron clouds will be easily distorted with the presence of electric field. The rises in the polarizability then will cause the molar refraction as well as the refractive index to increase. The same trend of molar refraction and refractive index specifies that molar refraction plays a significant role in the overall refractive index of the glass samples. The increment of refractive index shows that the velocity of light that passes through the glass is decreasing and vice versa. The increase of the refractive index of the glasses with increasing gamma irradiation dosage may be due to the ionization or atomic displacements resulted from gamma rays collision with the glass composition, which may materially alter or change the internal structure of the glass.

The optical basicity value for studied glass after gamma exposure increase from 0.888 to 0.951 while the metallization criterions are decrease from 0.379 to 0.333 after exposure. The positive and decreasing values of this metallization criterion suggest that the all glasses are metalizing [23]. Upon gamma irradiation, amount of disorderness and defects present in the glass structures are increase, which can be seen in increasing value of Urbach energy. The structural disorderness and defects are due to the displacements of ions, electronic defects and breaking of bond between atoms, compacting the glass network. Bonds breaking of O-Te-O and B-O-B after gamma irradiation may cause increasing of non-bridging oxygen (NBO) number. NBOs will result in the widening of the valence band as they have higher energy orbital than bridging oxygen. Besides that, the extension of the bands might also due to the formation of band tails [11]. Band tails are produced in the mid-gap states, which are produced because of the induced disorder in the glass network that overlaps with the conduction and valence bands. As a result, this overlapping will cause the bands to become wider and extend into the band gap region. This in turn leads to reduction of the metallization criterion.

Conclusion

Exposure of gamma irradiation on glass samples have effected their structural and optical properties. The decrease in optical band gap and shift of absorption edge towards longer wavelength is attribute to the increment of non-bridging oxygen atoms. Increasing gamma irradiation leads to changes in the glass structure. FTIR study confirms the increment formation of non-bridging oxygen atoms was existing from the transformation of TeO_4 to TeO_3 structural unit after gamma ray exposure. After gamma irradiation, the color of $[(TeO_2)_{0.7}(B_2O_3)_{0.3}]_{0.75}(BaO)_{0.25}$ glass sample have become darken due to lattice defect.

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