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Effect of Gamma Irradiation on High Lead Borate Glass Doped with Tungsten Oxide

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X-ray, Ultraviolet and Fourier Transform infrared spectral properties of tungsten ions doped in a host lead borate glass have a composition [60% PbO and 40% B_2O_3 wt %] are studied. Effect of gamma irradiation on the prepared glass samples was surveyed. Amorphization of the studied glass samples have been checked by X ray. Deep inspection for density, molar volume, UV and FTIR for base glass and tungsten oxide with different concentrations (0.15- 2.28) wt% proved that the tungsten ions are pronounced as structural groups mostly in the hexavalent W^{6+}. The constancy of optical absorption spectral curves reverse the shielding behavior for this combined glass towards successive gamma irradiation. Glasses containing high lead oxide content are extensively used for multi-applications including lead crystal glass and some special optical glasses, low-melting solder glasses and radiation protection windows and even in immobilization of radioactive nuclear wastes.

Keywords: Lead borate glass, Density and molar volume, FT-IR spectroscopy, Gamma irradiation, Optical characteristics, Gamma attenuation.

Introduction

In lead glasses, lead atoms are often described as glass former at high lead oxide content. Several studies (1) declared that PbO_3 units or a mixture of PbO_4 and PbO_3 are the basic building units specially in high lead oxide glasses. Tungsten oxide, WO_3 can exhibit six different states 0,+2,+3,+4,+5,+6 in its compounds (2). In glasses, tungsten is admitted to be found as trivalent W^{3+}, tetravalent W^{4+}, pentavalent W^{5+} or as hexavalent W^{6+} states or a combination of some of them (3-5). It has been established that silicate and alkali borate glasses favor the dominance of the hexavalent state of molybdenum and tungsten ions while phosphate glasses generally initiate the trivalent, tetravalent and pentavalent states(6,7).

Glass materials doped with heavy metal oxides such as lead are used in wide range for radiation shielding (8-10). The present work reports UV-visible, infrared spectroscopic studies on lead borate glasses of the basic composition [60% PbO and 40% B_2O_3 wt %] with different concentrations of WO_3 up to 2.28wt % in order to study the effect of successive gamma irradiation on them. The final goal of this study is to justify the effect of tungsten ions in this host lead borate glass beside investigation for possibility of using this combined glass as gamma radiation shielding.

Experimental

Sample preparation

Tungsten oxide doped lead–borate glasses were prepared from analar grade powders of H_3BO_3, PbO_2 and pure WO_3 was added. The combined materials for final preparation of [60% PbO and 40%B_2O_3 wt %] were doped with different concentrations of WO_3 (0.15, 0.45, 0.76 and 2.28 wt %). Melt quenching technique was used where the appropriate amount of chemicals

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were mixed and heat treated in a porcelain crucible at 1100°C for 90 minutes in an electric furnace. The melts were rotated several times to achieve homogeneity. The homogenized melts were poured into stirred stainless steel molds with the required dimensions. The prepared samples were immediately transferred to an annealing muffle regulated at 350°C.The muffle was switched off after 1h, left to cool to room temperature inside the muffle at a rate of 30°C/hr. Table (1) gives the chemical compositions of the studied glass systems which were cut in dimensions of 1 x 1 x 0.2 cm to be easily measured by different techniques.

X-ray diffraction analysis

The amorphous state of prepared samples was checked by X-ray diffraction spectra recorded at Shimadzu (Japan) diffractometer type XD-D1 with copper target and applied voltage of 40 kV and 30 mA anode current.

Irradiation facility

The samples were exposed in calibrated (^{60}Co-based gamma chamber 4000 A with a dose rate of 1.5 Gy s^{-1}) at a temperature of 30°C with different doses. Using Fricke dosimeter, the absorbed dose in glass is expressed in terms of absorbed dose in water, no correction needed.

Density and molar volume

The density of the prepared glasses before and after gamma irradiation was determined using the Archimedes method. Each sample was weighed in air and then when immersed in xylene at room temperature. All measurements were repeated twice. The density was calculated according to the formula:

$$\rho= \{w_a / (w_a-w_x)\}* \rho_x \quad (1)$$

where: **(ρ)** is the density of the glass sample,

$\mathbf{w_a}$ and $\mathbf{w_x}$ are the weight of the glass samples in the air and in xylene respectively

$\boldsymbol{\rho_x}$ is the density of xylene and equal (0.86 gm / cm^3).

The accuracy of the results in duplicate measurements is ± 0.01 g/cm^3 .The molar volume of the prepared glass samples, V_m , was calculated by means of the following relation:

$$V_m = M/ \rho \quad (2)$$

Where (**M**) is the molar weight of glass sample and (**ρ**) is the sample density.

Infrared measurements

The FTIR absorption spectra were registered at room temperatures using a Fourier Transform computerized infrared spectrometer type, Vertex-7o, German. The IR absorption spectra measurements were recorded through wavenumber range 400-4000 cm^{-1} before and after gamma irradiation.

Optical absorption spectral measurements

UV–visible spectrophotometer [Evolution 600, Japan] was used in measuring the optical absorption spectra in the range 200-900 nm of highly polished samples of the undoped and doped with WO_3 were measured before and after successive gamma irradiation.

Results and Discussion

X-ray diffraction analysis

X-ray investigation of the prepared glasses revealed no diffraction peaks in lines or any crystalline phases, and the results as shown in Fig. (1) indicate that the prepared samples were revealed broad humps characteristics of the amorphous structure formed.

Density and molar volume

Effect of concentration on density and molar volume

TABLE 1. Chemical compositions of investigated glass samples.

Glass No.	PbO %	B_2O_3 %	WO_3	
			wt (%)	wt (gm)
G0	60	40	------------	-------
G1	60	40	0.15	0.1
G2	60	40	0.45	0.3
G3	60	40	0.76	0.5
G4	60	40	2.28	1.5

The density is a powerful tool capable of exploring the changes in the structure of glasses. The density is affected by the structural softening/ compactness (11), change in geometrical configuration, coordination number, cross-link density and dimension of interstitial spaces of the glass. It is noted that the density of studied glasses increases with the increasing of tungsten concentrations, which is shown in Fig. (2). In B_2O_3 –PbO–WO_3 glasses samples density increases with the increase of tungsten contents. The increasing in density may be due to the formation of tetrahedral borate groups, which helps to compact the glass network, due to the availability of more oxygen from WO_3 which shifts the coordination of boron from trigonal BO_3 to tetrahedral BO_4 groups. The tetrahedral BO_4 groups are more strongly bonded as compared to the triangular BO_3 groups and therefore this factor helps to compact the structure of glasses. This leads to increase the density of glasses. Another factor may be responsible for increase in density of glasses is also due to presence of WO_4 or WO_6 structural groups of tungsten ions in glass network (12).

Molar volume is also an important physical property, it is noted that, the density increases, with a decrease in the molar volume as the WO_3 content increasing as shown in Fig. (2). A decrease in molar volume may be related to the decrease in bond length which is responsible for compaction of glass network. This may be explained by considering the formation of B–O–W linkages (13,14) with strong covalent B and W oxygen bond.

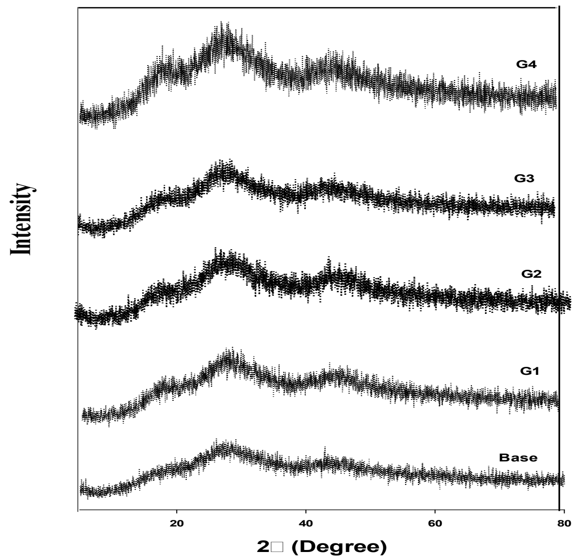


Fig. 1. XRD pattern for lead borate glass doped with different concentrations of WO_3

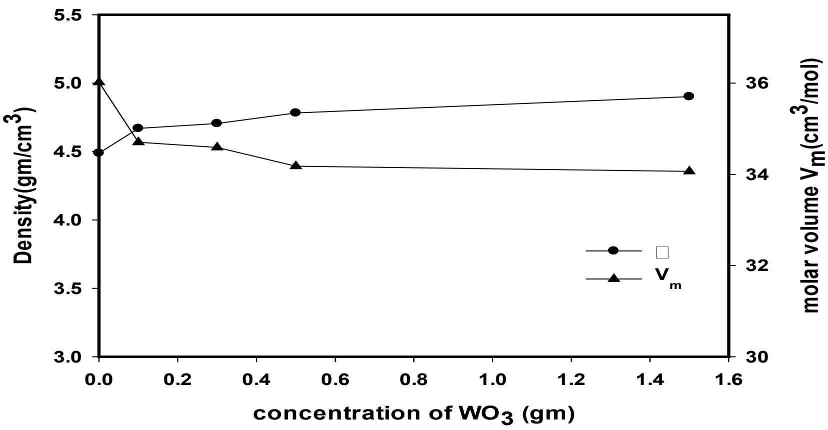


Fig. 2. Density and molar volume of PbO– B_2O_3–WO_3 glasses.

Effect of gamma irradiation on density and molar volume

As shown from Fig.(3) the densities of the glasses increase with the increase of irradiation dose, while the molar volume decrease . Some workers have been explained the interaction with gamma radiation is as follows :

Irradiation with gamma are assumed to create displacements, electronic defects and/or breaks in the network bonds, which allow the structure to relax and fill the relatively large interstices that exist in the interconnected network of boron and oxygen atoms causing expansion followed by compaction of the volume (15).

It can also may be due to that damage by an irradiation species can cause the compaction of B_2O_3 by the breaking of bonds between trigonal elements, allowing the formation of different ring configurations. This can explain the increase in the density of the glass with irradiation. This result is in agreement with the results obtained by El-Batal et al. (16) where they found that nuclear irradiation is believed to cause noticeable structural changes which may comprise :

a) Some bond angles become smaller, i.e. a compact state are produced.
b) Increase or decrease in density depending on composition or state of aggregation.

Infrared absorption spectra "IR"

Effect of composition

The infrared absorption spectra of lead borate glass is an interesting system because PbO, unlike alkali oxides can enter the glass network as network modifier or network former. Fig. (4) shows the infrared absorption spectra of lead borate glasses of the base composition [60% PbO and 40% B_2O_3 wt %] with different

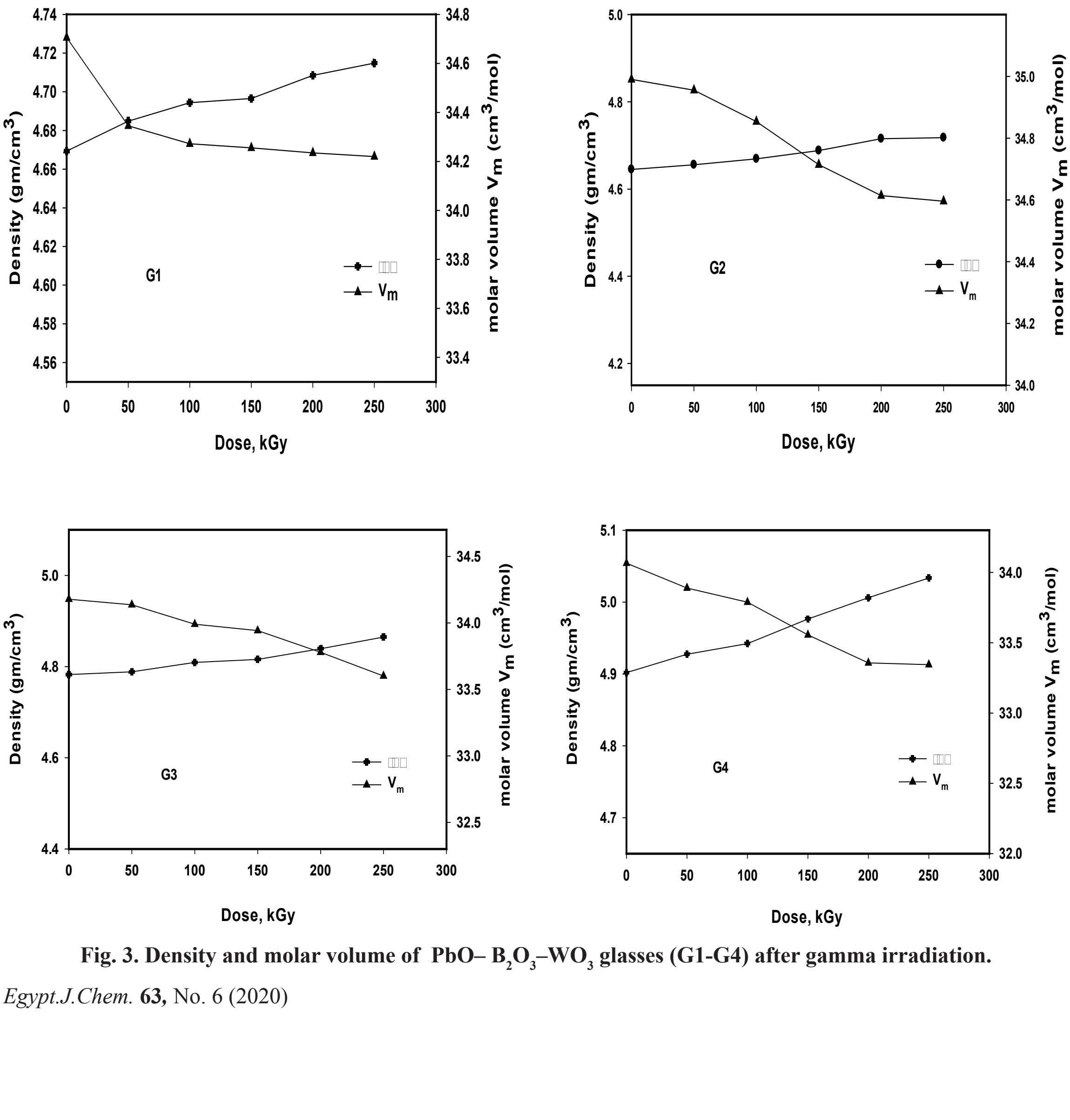


Fig. 3. Density and molar volume of PbO– B_2O_3–WO_3 glasses (G1-G4) after gamma irradiation.

concentrations of WO_3 from (0.15-2.28 wt%). The absorption spectra of all the glasses reveal some characteristic peaks located at 460-473, 625-700, 925, 1260, 1340, 1610 and 2110 cm^{-1}.The detailed IR absorption spectra of base lead borate glass can be summarized as follows: Table (1) shows the experimental IR bands and their assignments with related references.

After doping with different concentrations of WO_3 all the spectral curves shown in Figure (4) reveal the same previous absorption bands which reflect the main structural borate chains and their arrangement which are nearly the same except a small shoulder at about 600 cm^{-1} appears in samples concentrations 0.1 and 0.3gm of WO_3. The IR spectral characteristics of the doping glasses are summarized as follows :

a) The introduction of WO_3 with concentrations in glass samples G1 and G2 causes an appearance of a small band at 625cm^{-1}. The first two bands at (965-1040cm^{-1}) are centered at 925cm^{-1} and (1270-1355cm^{-1}) also shifted to (1260-1340cm^{-1}).
b) By increasing the concentrations of WO_3 no noticeable change occurred except the small band at 625cm^{-1} was almost vanished. In glass samples G4 a small shift occurred to the band at 460 cm^{-1} to 473cm^{-1}.

Experimental results indicate that three main IR absorption regions of borate glasses can be identified: the first region at 400-800 cm^{-1} which is due to bending vibration of various borate arrangements beside the bending group of lead oxide, the second at 800-1200 cm^{-1} which is due to B-O stretching tetrahedral units as well as the vibration group of lead oxide appears at about and overlap with the vibration group of borate in this region, and the third at 1200-1600 cm^{-1} which is due to B-O stretching of trigonal BO_3 units. According to(17) the band at about 700 cm^{-1} is due to the presence of B-O-B bending vibrations present in borate glass. There are one in the far infrared ranging from 500-400 cm^{-1} which is due to the bending vibrations of borate groups as well as the vibration of lead cations in their oxygen sites (18,19).

To interpret the effect of WO_3 on the IR spectra, it is assumed that the introduction of tungsten ions causes the formation of new structural units or at least the formation of B-O-W bonding. This assumption is supported by the decrease of the intensity of main broad bands at about 960 cm^{-1} due to BO_4 groups together with a slight decrease of the bending band of B-O-B grouping.

Effect of gamma radiation

Effect of gamma radiation on the base lead borate glass

Figure (5) shows the effect of exposing the base lead borate glass to gamma radiation at doses of 10,50 and 100 kGy. The figure illustrates that the range of doses used have no significance effect on peak intensity, but only slight changes

TABLE 1. IR vibrational absorption band wavenumber (cm^{-1}) and their corresponding vibrational mode assignment in doped lead borate glasses.

Band position (cm^{-1})	Associated vibrational mode	Ref.
460	Loose BO_4 units, Pb-O vibrations	[17,118,19,20]
700	B-O-B bending vibrations	[19,21]
925	B-O bond stretching of BO_4 units with PbO bonds overlapping	[17,18,19,20,22]
1260	B-O stretching vibrations of $(BO_3)^{3-}$ units in meta, orthoborate chains	[17,19]
1340	Vibration of boron oxygen rings	[18,22]
1600-3000	Molecular water groups	[19]

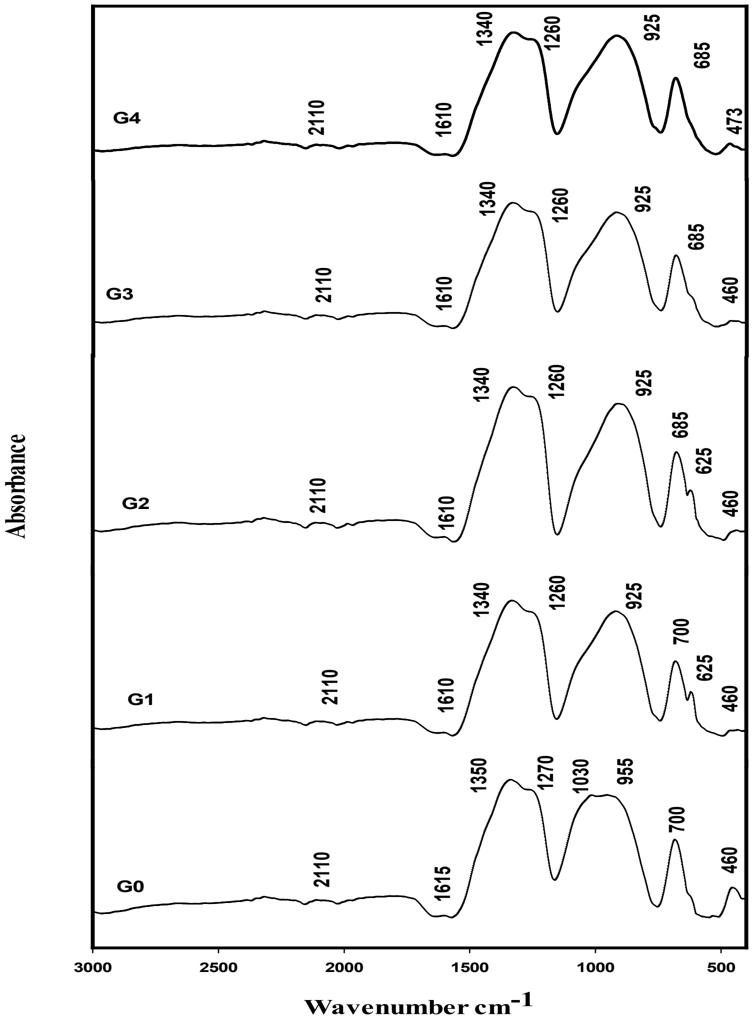


Fig. 4. Infrared absorption spectra of lead borate glass doped with different concentrations of WO_3.

in the positions of some bands was recorded. This changes return back to action of lead oxides towards resulting species emerging through absorbing the gamma photons. The heavy metal oxides (such as PbO, Bi_2O_3, BaO) prohibit the free passage of liberated electrons or positive holes through the glass matrix (20).

Figures (6 & 7) showed IR spectrums for G1 and G4 before and after gamma irradiation to the same dose ranges. No significance changes were noticed which reversed the shielding behavior against gamma irradiation.

It has been reached by some researchers[(21-25)] that the presence of transition metal ions as dopants or even as impurities compete to react with the generated electrons and positive holes during the irradiation process. Some of the transition metal ions (V^{5+}, Cu^{2+}, W^{6+}, Mo^{6+}) show shielding effects toward successive gamma irradiation and the net result is that the optical spectral curves or IR spectra remain almost parallel without distinct variations after gamma irradiation.

Optical absorption spectra of unirradiated glass

Effect of different concentrations of WO_3 on the optical absorption

Figure (8) showed a comparable shift in intensities to lesser wavelength which are detectable for different concentrations of WO_3 that can be referred to the rearrangement of the housing ions of W^{+3} ions in stable sites by allowing the structure to relax and fill the large

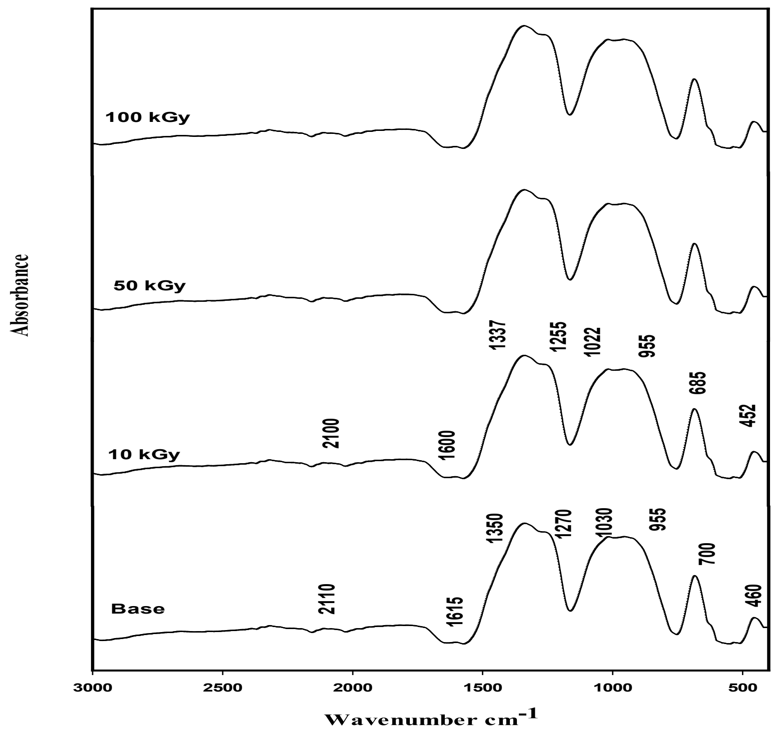


Fig. 5. Infrared absorption spectra of the base glass before and after gamma irradiation.

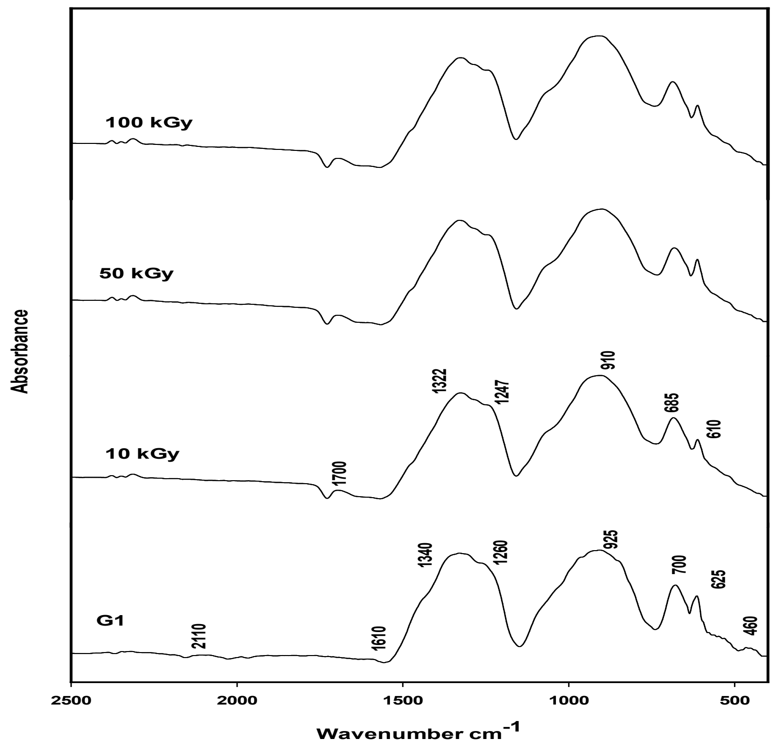


Fig. 6. Infrared absorption spectra of the lead borate glass doped with WO_3 (G1) before and after gamma irradiation

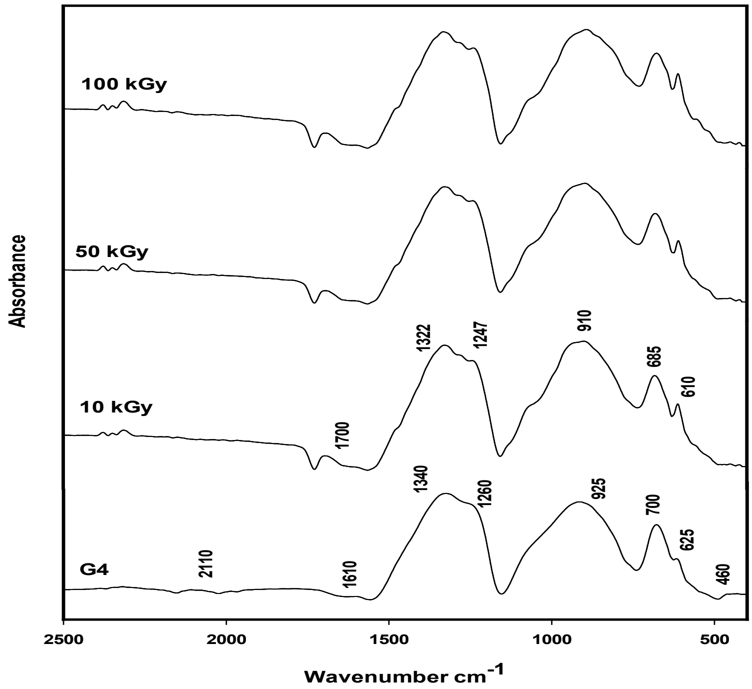


Fig. 7. Infrared absorption spectra of the lead borate glass doped with WO_3 (G4) before and after gamma irradiation.

interstices in the network (21) .

Effect of gamma irradiation on the optical absorption of lead borate glass doped with WO_3

Effect of gamma irradiation on the base lead borate glass

Figure (9) illustrates the UV–visible absorption spectra of the undoped lead borate glass before and after successive gamma irradiation. The optical spectrum reveals no absorbed peaks in the visible region. On subjecting this base undoped lead borate glass to different doses of 10,18,25 and 75 kGy, the spectrum shows a small decrease in the intensity and also no visible peaks registered as before irradiation which indicating a shielding behavior or resistance to successive gamma irradiation. Duffy(26) has assumed that certain metal ions (such as Pb^{2+}, Bi^{3+}, …) absorb radiation through electronic transitions involving orbitals essentially of the metal ions. Recent study on lead borate glass (5) has experimentally confirmed this postulation for the sharing of Pb^{2+} ions in the UV spectra of lead borate glass. It is therefore suggested that the charge transfer ultraviolet absorption observed in the present studied high lead borate glass is attributed to the co-sharing of absorption by both trace iron impurities and lead Pb^{2+} ions.

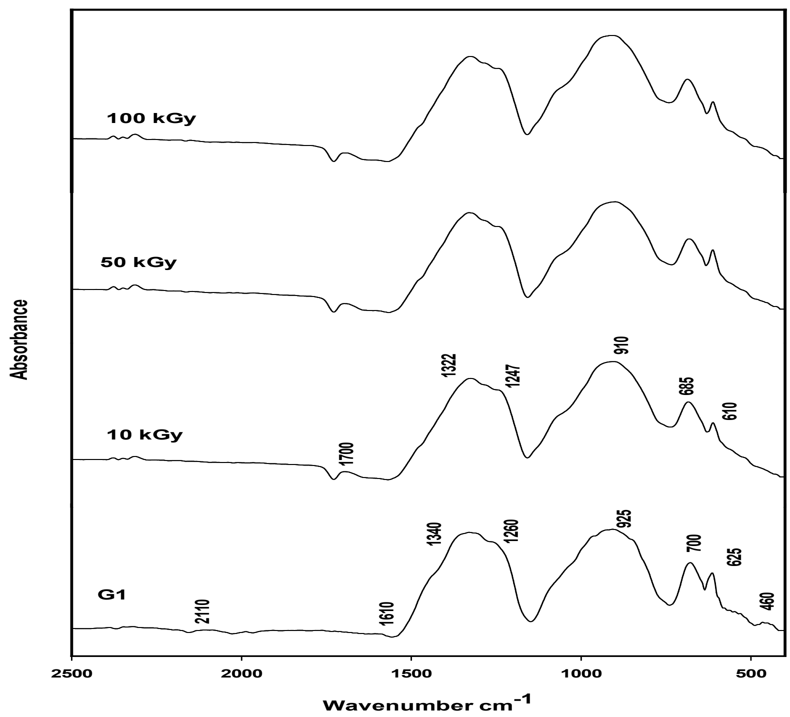
Effect of gamma irradiation on the optical absorption of lead borate glass doped with different concentrations of WO_3

Figure (10) illustrates the optical absorption spectra of WO_3- doped lead borate glasses with increasing WO_3 contents (G1, G2, G3 and G4) before and after successive gamma irradiation (0, 10, 50, 100, 150, 200 and 250 kGy). The spectrum indicates unaffected by gamma irradiation, also no peaks recorded in the visible region which reverse the action of WO_3 ions in shielding works in these combined glass towards gamma irradiation.

It is accepted (2) that tungsten can exist in different oxidation states ranging from +2 to +6 in its various compounds. However, in glasses, tungsten is believed to exhibit hexavalent (W^{6+}), pentavalent (W^{5+}) or tetravalent (W^{4+}) states(27,28). Also, the measured optical spectra did not contain any visible bands and this indicates that the tungsten ions are present mostly as colorless hexavalent W^{6+} state. Also, the absorption of the irradiated WO_3-doped samples did not show any induced visible bands and the glasses reveal obvious shielding behavior.

Conclusion

A new combined glass consists of [60%PbO and 40%B_2O_3 wt %] with different concentrations of WO_3 was studied for possible using as shielding material in dose range 0-100kGy. The prepared glass density increases due to the action of tungsten which act as oxygen donor transfer the basic building unit BO_3 into BO_4 leading to compactness of the glass matrix. Optical studies



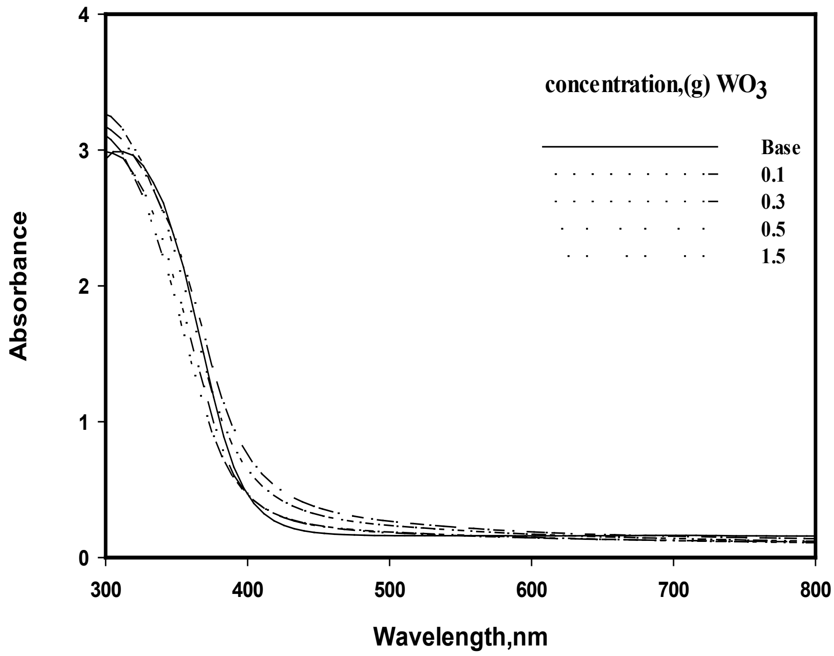


Fig. 8. UV–visible absorption spectra of undoped and doped lead borate glass with different concentrations of WO_3.

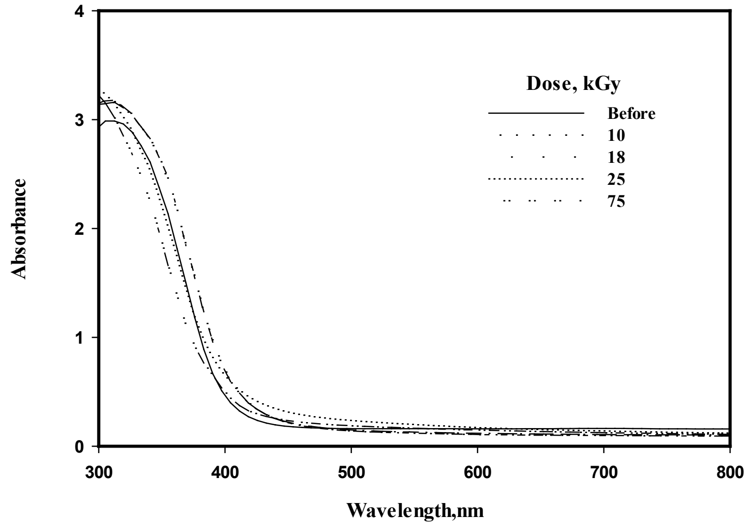


Fig. 9. UV–visible absorption spectra of undoped lead borate glass before and after successive gamma irradiation.

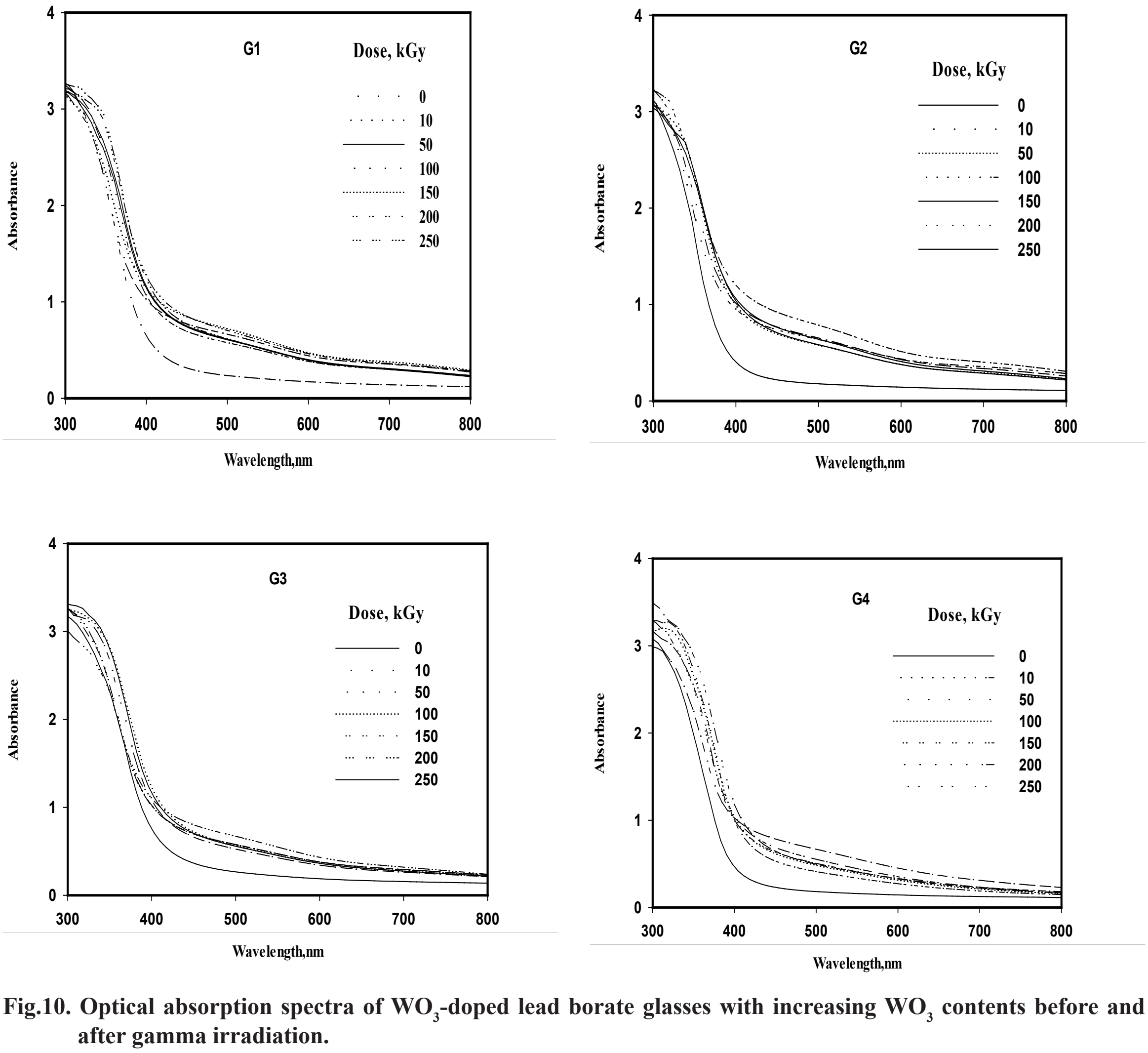


Fig.10. Optical absorption spectra of WO_3-doped lead borate glasses with increasing WO_3 contents before and after gamma irradiation.

proved no peaks detected in the visible region nominated the presence of tungsten in WO_5 or WO_6 which considered as structural group in glass network. The amorphous nature of this new combined glass have shielding behavior due to the action of lead and tungsten against gamma irradiation ascertained through FTIR and UV-Vis spectra measurements, no significance change in assignment peaks recorded in the examined dose range.

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