



# Shielding behavior of $V_2O_5$ doped lead borate glasses towards gamma irradiation

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## ABSTRACT

Undoped lead borate glass of the composition  $PbO$  70%– $B_2O_3$  30% together with samples of the same composition and doped with varying  $V_2O_5$  contents were prepared. UV–visible absorption spectra were measured out in the range 200–1500 nm before and after successive gamma irradiation. Infrared absorption measurements within the range 4000–400  $cm^{-1}$  were carried out for the undoped and  $V_2O_5$  doped samples before gamma irradiation and after being irradiated with a dose of 6 Mrad. All the glass samples are observed to absorb strongly in the UV region due to the combined contributions of absorption due to trace iron impurities and that from the divalent lead  $Pb^{2+}$  ions. The  $V_2O_5$ -doped glasses reveal extra visible absorption bands which are attributed to the existence of  $V^{3+}$  ions in measurable content but not neglecting the other valence states of vanadium ions ( $V^{4+}$ ,  $V^{5+}$ ). Infrared absorption spectra indicate the presence of both triangular and tetrahedral borate groups besides the sharing of lead ions in network forming and network modifying sites.

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## 1. Introduction

Lead glasses are extensively used for various applications including crystal glass and optical glasses, low-melting solder glasses and glass–ceramics, numerous optical and electronic applications, radiation protection and in immobilization of hazardous radioactive wastes [1–4].

Lead oxide is well known to show interesting physical and chemical properties upon glass formation with many systems such as silicates, borates and phosphates. The structural role of  $Pb^{2+}$  ions in the glass network has already been the subject of numerous studies [5–12]. In binary lead glasses, lead atoms are often described as glass former at high lead oxide content and as network modifier at low lead oxide content. Such differences in the structural role of  $Pb^{2+}$  ions would imply significant modifications of their local environments and of their coordination. Earlier studies [5–7] consider that the glass forming groups are the  $[PbO_4]$  units while recent studies [12] claim that  $PbO_3$  units or a mixture of the two structural units ( $PbO_4$ ,  $PbO_3$ ) are the basic building units in high  $PbO$  content glasses.

The optical absorption spectra of vanadium ions in cabal, silicate, phosphate and borate glasses before and after gamma irradiation have been reported by several investigators [13–18]. Vanadium

ions are accepted to exist in glasses in three possible valencies, namely, the trivalent, tetravalent and pentavalent states. The trivalent vanadium ( $V^{3+}$ ) ions exist in distorted octahedral coordination with oxygens and show two characteristic absorption bands at 350–400 nm (3.54–2.69 eV), 580–680 nm (2.13–1.82 eV) and a third possible band in the UV region originating from electron transfer within the vanadium ion itself. The tetravalent vanadium ( $V^{4+}$ ) ions seem to exist normally as vanadyl ions ( $VO^{2+}$ ) and exhibit four characteristic weak bands at about 420 nm (2.95 eV), 760–860 nm (1.63–1.44 eV) and  $\sim 1000$  nm (1.239 eV) in addition to a possible UV band. The pentavalent vanadium ( $V^{5+}$ ) ions correspond to the  $d^0$  configuration and thus will not give rise to d–d transitions but give a charge transfer band at  $\sim 380$  nm. In a series of recent studies on gamma irradiation of 3d-doped soda lime phosphate [19], cabal [20], bioglass [21], borosilicate [22] and lithium diborate [23] glasses, it is established that transition metal ions compete with both trace impurities and host glass in producing induced radiation defects. While intrinsic defects arise after irradiation from the glass matrix itself, extrinsic defects are due to dopants or impurities [24–26]. Some of the transition metal dopants within the glasses capture negative electrons or positive holes causing changes in their valencies through photochemical reactions during the exposure of the glasses to successive gamma irradiation.

The main objective of this present work is to study the UV–visible and infrared absorption spectra of some undoped and  $V_2O_5$  doped lead borate glasses before and after successive gamma irradiation. This work will enable us to specify the existing

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**Table 1**  
Chemical composition of the studied glasses.

Glass no.	PbO (wt%)	B <sub>2</sub> O <sub>3</sub> (wt%)	V <sub>2</sub> O <sub>5</sub> added (dopant)
G0	70	30	0
G1	70	30	0.5
G2	70	30	1.5
G3	70	30	2
G4	70	30	3
G5	70	30	4

valencies of vanadium ions in such glass system. Also, this study aims to justify the effect of gamma irradiation on the base lead borate glass and V<sub>2</sub>O<sub>5</sub> containing samples and deduce the radiation induced defects generated upon gamma irradiation.

## 2. Experimental details

### 2.1. Preparation of glasses

The studied glasses were prepared using reagent grade chemical materials. Pb<sub>3</sub>O<sub>4</sub> was used for PbO and H<sub>3</sub>BO<sub>3</sub> for B<sub>2</sub>O<sub>3</sub> and vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) was added as such with different successive percents. All the weighed batches were melted in platinum crucibles at 1000 °C for 2 h. The crucibles were covered with platinum lids during melting to avoid loss of the constituents at high temperature.

The melts after homogenizing with stirring at fixed time intervals were cast in slightly preheated stainless steel molds to the required dimensions and the prepared specimens were immediately transferred for annealing in a muffle furnace adjusted at 380 °C. The muffle was left to cool after 1 h to room temperature at a rate of 20 °C h<sup>-1</sup>.

The melts after homogenizing with stirring at fixed time intervals were cast in slightly preheated stainless steel molds to the required dimensions and the prepared specimens were immediately transferred for annealing in a muffle furnace adjusted at 380 °C. The muffle was left to cool after 1 h to room temperature at a rate of 20 °C h<sup>-1</sup> (Table 1).

### 2.2. UV-visible absorption spectra measurements

The optical absorption spectra before and after gamma irradiation were measured at room temperature in the range from 200 to 1500 nm using a computerized recording spectrophotometer (type JASCO corp., V-570, Rel-00, Japan). Polished samples of equal thickness (2 ± 0.1 mm) were used in these measurements.

### 2.3. Infrared absorption measurements

The infrared absorption spectra of the prepared samples were measured at room temperature in the range 4000–400 cm<sup>-1</sup> by an infrared spectrometer (type Mattson 5000, USA) using the KBr disc technique. The samples were pulverized into fine powder, and then mixed with potassium bromide powder with a weight ratio of 1:100 (0.002 g sample; 0.2 g KBr). The mixture was subjected to a load of 5 tons cm<sup>-2</sup> in an evocable die for 2 min to produce clear homogenous discs. The IR absorption spectra were measured immediately after preparing the discs.

### 2.4. Irradiation facility

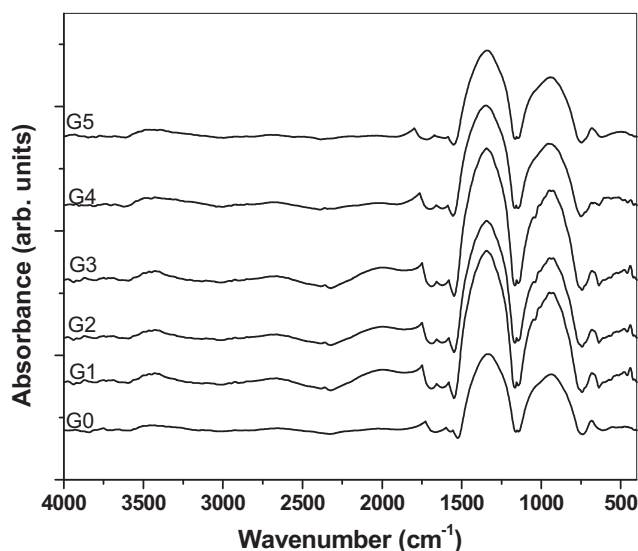
A <sup>60</sup>Co gamma cell (2000 Ci) was used as a gamma ray source with a dose rate of 1.5 Gy s<sup>-1</sup> (150 rad s<sup>-1</sup>) at a temperature of 30 °C. The investigated glasses were subjected to the same required gamma dose every time.

## 3. Results

### 3.1. Infrared absorption spectra

Fig. 1 illustrates the infrared absorption spectrum of the undoped and V<sub>2</sub>O<sub>5</sub> doped lead borate glasses. The infrared spectrum of the base undoped lead borate glass is seen to possess the following spectral characteristics:

- A sharp small peak at about 472 cm<sup>-1</sup>.
- A broad band at about 966 cm<sup>-1</sup>.
- A sharp band with a peak at about 1349 cm<sup>-1</sup>.
- A sharp band with a peak at about 1475 cm<sup>-1</sup>.
- A sharp band peaks at about 1578 cm<sup>-1</sup>.
- A sharp band peaks at about 1758 cm<sup>-1</sup>.



**Fig. 1.** IR absorption spectra of the prepared glasses.

- Two successive small kinks at about 2362 and 2925 cm<sup>-1</sup>.
- Two broad medium bands at about 3434 and 3399 cm<sup>-1</sup>.

The main characteristic absorption bands due to borate network groups are identified as four intense IR bands at about 650, 966, 1349 and 1578 cm<sup>-1</sup>.

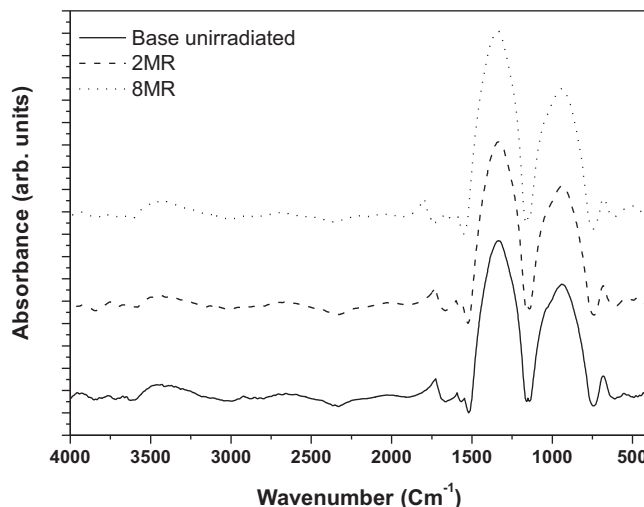
The effects of introducing different concentrations of V<sub>2</sub>O<sub>5</sub> (0.5 g, 1.5 g, 2.0 g, 3.0 g and 4.0 g) on the IR spectra are shown also in Fig. 1 and can be summarized as follows:

All glasses containing varying concentrations of V<sub>2</sub>O<sub>5</sub> reveal in general the following spectral characteristics;

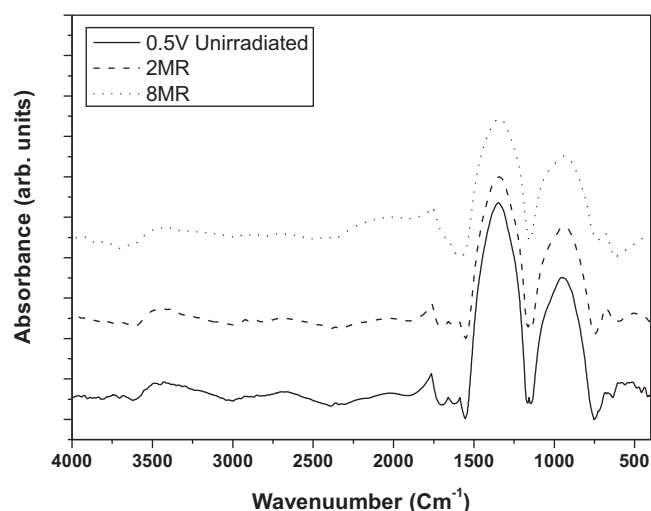
- The depression of the band at about 684 cm<sup>-1</sup>.
- Resolution of three far-infrared kinks at about 422, 543 and 686 cm<sup>-1</sup>.
- The other IR absorption characteristic bands observed in the undoped sample remain almost unchanged.

### 3.2. Effect of gamma irradiation on the IR spectra

Figs. 2–4 illustrate the IR spectra of the undoped and V-doped glasses after gamma irradiation with 2 Mrad and 8 Mrad. The results indicate the following variations.



**Fig. 2.** Infrared spectra of undoped lead borate glass after successive gamma irradiation.

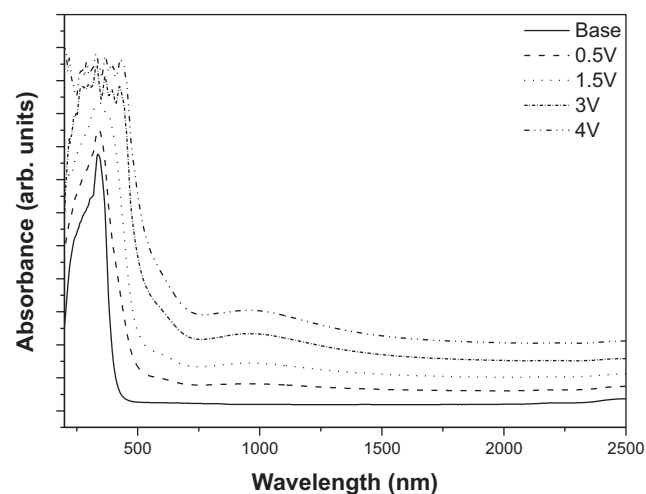


**Fig. 3.** Infrared spectra of 0.5%  $\text{V}_2\text{O}_5$  doped glass before and after successive gamma irradiation.

- The IR bands of the undoped glass remain unchanged in their number and intensity with progressive irradiation.
- The IR absorption bands of the 0.5%  $\text{V}_2\text{O}_5$  doped glass show the maintenance of the bands in their number and position but with slight decrease with progressive gamma irradiations.
- The IR absorption bands of the 1.5%  $\text{V}_2\text{O}_5$  doped glass show the maintenance of the bands in their position and number but the intensities reveal obvious increase with gamma irradiations.

### 3.3. UV–visible absorption spectra before gamma irradiation

Fig. 5 reveals the optical absorption spectra of undoped lead borate glasses together with samples containing increasing  $\text{V}_2\text{O}_5$  contents. The undoped glass reveals strong ultraviolet absorption comprising four successive peaks at about 250, 275, 310 and 350 nm and no visible bands could be identified: With the introduction of increasing  $\text{V}_2\text{O}_5$  contents, the first three UV peaks remain unchanged while the last fourth peak is slightly decreased and new visible bands are identified at about 400 and 440 nm and followed by a small broad band centered at about 580 nm. The visible absorption bands are observed to be more intensified with the increase of



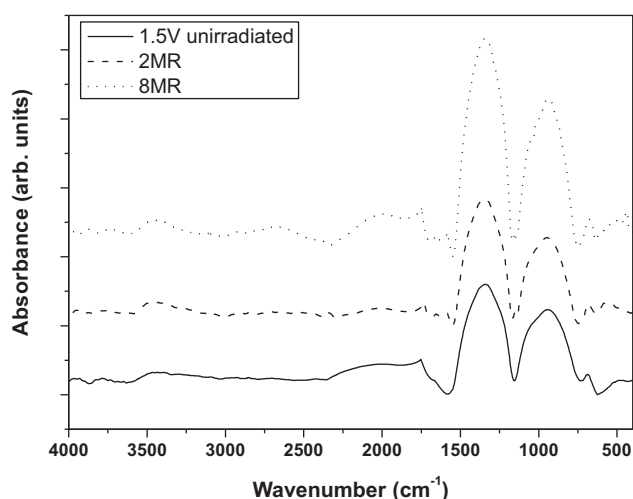
**Fig. 5.** UV–visible absorption spectra of undoped and  $\text{V}_2\text{O}_5$  doped glasses before irradiation.

$\text{V}_2\text{O}_5$  content and with a resolution of a new broad band centered at about 850 nm.

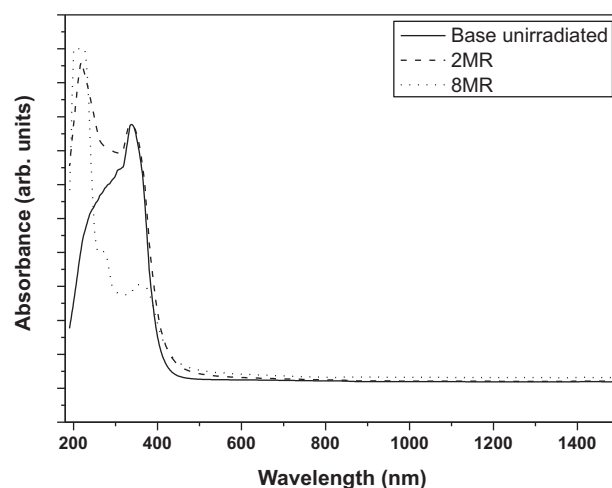
### 3.4. Effect of gamma irradiation on UV–visible spectra

Figs. 6–9 illustrate the optical absorption of the undoped and  $\text{V}_2\text{O}_5$  doped lead borate glasses after gamma irradiation with 2 and 8 Mrad. The undoped lead borate glass shows upon gamma irradiation the resolution of an induced high intense UV absorption band at about 225 nm which attains saturation on prolonged irradiation from 2 Mrad to 8 Mrad. The absorption band at about 340 nm attains constancy with 2 Mrad but with increasing the dose to 8 Mrad a marked decrease in the intensity and with the resolution of two peaks, at 285 and 380 nm. It is evident that the spectrum extending from about 400 nm to the rest of measurement shows no induced bands and with continuous irradiation the spectral curves reveal no variations but remain very close to each other.

The vanadium doped glasses show similar behavior irrespective of the  $\text{V}_2\text{O}_5$  content. All the studied glasses reveal a continuous decrease of the intensities with progressive irradiation in the UV region of the spectrum while within the rest visible region; the spectral curves show no variations and remain very close with irradiation.



**Fig. 4.** Infrared spectra of 1.5%  $\text{V}_2\text{O}_5$  doped glass before and after successive gamma irradiation.



**Fig. 6.** UV–visible spectra of undoped lead borate glass before and after successive gamma irradiation.

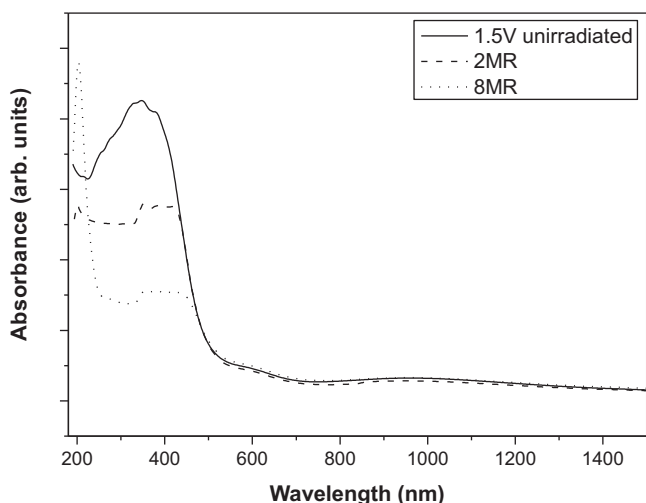


Fig. 7. UV-visible spectra of 1.5% V<sub>2</sub>O<sub>5</sub> doped lead borate glass before and after successive gamma irradiation.

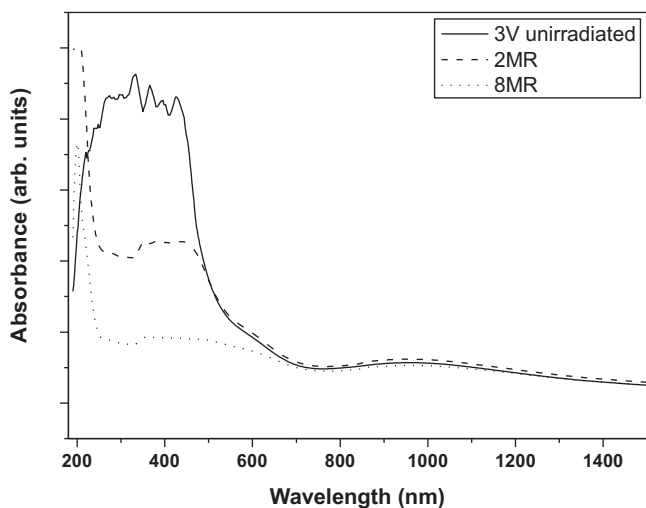


Fig. 8. UV-visible spectra of 3% V<sub>2</sub>O<sub>5</sub> doped lead borate glass before and after successive gamma irradiation.

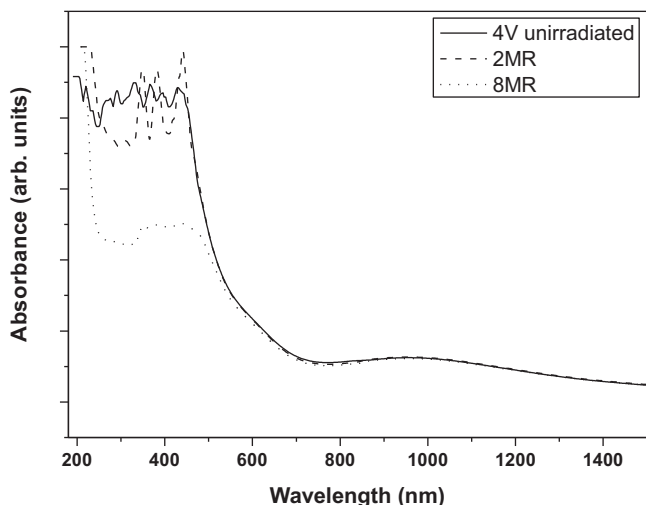


Fig. 9. UV-visible spectra of 4% V<sub>2</sub>O<sub>5</sub> doped lead borate glass before and after successive gamma irradiation.

## 4. Discussion

### 4.1. Interpretation of the infrared absorption spectra

Infrared spectroscopic data of the studied lead borate glasses have been used as a basis for the qualitative identification of glass forming structural units in this type of glass [24–28]. Lead borate glass belongs to an interesting system because PbO unlike alkali and alkaline earth oxides can enter the glass network in dual situation both as network modifier and network former. Hence, the network structure of the lead borate glasses is expected to be different from that of alkali borate glasses. Bray and co-workers [5,29] have carried out NMR investigations of lead borate glasses and related crystalline compounds and their studies indicate that  $N_4$  (the fraction of the four coordinated boron atoms in the glass) increases with the PbO content up to 50%. Further increase of PbO decreases the value of  $N_4$  (ratio of  $BO_4$ /total boron content). The lead oxide enters the glass network originally at ( $0 \leq R \leq 0.33$ ), where  $R$  is the ratio of PbO, it does so as a modifier [5]. In the case of lead (II) ions, each ion acts as a dual charge balance providing the positive charge necessary for the formation of the two tetrahedral  $(BO_4)^{-1}$  units. The bonding of lead is strongly ionic and the cations enter the network in an interstitial manner. The change in coordination number of boron from three to four leading to an obvious compacting of the glass network structure. The glass network remains fairly open at low PbO concentration, thus allowing void filling. Beginning at  $R = 0.33$ , however, the role of lead cations begins to change. The lead ions are likely to form compact structural  $PbO_3$  and/or  $PbO_4$  pyramidal units assuming on a more covalent arrangement. The participation of lead cations (and their associated oxygens) in these pyramidal units reduces the availability of such ions for ionic charge balance, thus reducing the formation rate of the four coordinated tetrahedral boron units. The typical back conversion to three coordination by boron must be to a  $(BO_{1.5})$  units bridging to an even increasing number of lead cations [8–11].

Careful inspection of the infrared absorption bands which are observed in the region  $1200\text{--}1600\text{ cm}^{-1}$  reveals distinct comparable intensities which indicate that the ratios of  $BO_3$  and  $BO_4$  groups are approximately reaching constancy or equality. The base studied composition of PbO 70 wt% and B<sub>2</sub>O<sub>3</sub> 30 wt% equivalent to 42.1 and 57.9 mol%, respectively, supports this IR result. It is expected that the studied base host glass contains  $BO_3$  groups in sufficient quantity to be easily identified in equivalent to the formed  $BO_4$  groups. It is also expected that PbO behaves in dual functions assuming the role of modifier and former in such studied high lead borate glass [24]. In accordance with the interpretation of most authors [20,24–28], the infrared absorption in the region  $800\text{--}1200\text{ cm}^{-1}$  can be assigned to  $BO_4$  groups while the absorption extending from  $1200$  to  $1600\text{ cm}^{-1}$  can be related to  $BO_3$  groups. The infrared bands in the wavenumber region  $530\text{--}630\text{ cm}^{-1}$  and  $690\text{--}770\text{ cm}^{-1}$  are assumed to be due to bending vibrations of various borates including isolated  $BO_3^{3-}$  groups. The near-infrared bands in the wavenumber range  $3000\text{--}4000\text{ cm}^{-1}$  are related to vibrations due to water, OH or BOH groups [20,28].

The small far-infrared peak at about  $472\text{ cm}^{-1}$  observed in the undoped and V<sub>2</sub>O<sub>5</sub> doped glasses seems to be related to vibrations of  $Pb^{2+}$  ions. Extensive studies of Witke et al. [11,30] on IR and Raman spectra of lead borate glasses have reached the conclusion that at low PbO content, PbO predominantly acts as modifier (ionic Pb–O bond with IR band in the region at  $10\text{--}150\text{ cm}^{-1}$ ). With increasing PbO content, it behaves as network modifier as well as glass former (covalent Pb–O bonds, with IR band at about  $300\text{ cm}^{-1}$ ). By careful examination of the published figures of Witke et al. [11,30], some peaks could be identified in the region  $400\text{--}500\text{ cm}^{-1}$  which are very close to the observed peak at about  $472\text{ cm}^{-1}$  in this study.

**Table 2**IR vibrational absorption bands wavenumber ( $\text{cm}^{-1}$ ) and their corresponding vibrational mode assignment in undoped and  $\text{V}_2\text{O}_5$  doped lead borate glasses.

Band position ( $\text{cm}^{-1}$ )	Associated vibrational mode	Ref.
467, 491, 563, 498, 567	Loose $\text{BO}_4$ units, Pb–O vibrations	[11,30,32]
704, 744	B–O–B bending vibrations	[11,30]
912, 960, 972	B–O bond stretching of $\text{BO}_4$ units with PbO bonds overlapping	[28]
1284, 1288	B–O stretching vibrations of $(\text{BO}_3)^{3-}$ units in meta, orthoborate chains.	[28]
1300	Vibrations of boron–oxygen rings	[28,33]
1505, 1559, 1611	Asymmetric stretching relaxation of the B–O bond of trigonal $\text{BO}_3$ units	[28,30,32]
1640, 3446, 3565, 3747	Molecular water groups	[30,40,46,48]

Recent studies by Pisarski et al. [31] have shown that the IR spectra of lead borate glasses in the range  $400\text{--}1400\text{ cm}^{-1}$  are connected with vibrations of the network of different borate units together with the sharing of Pb–O groups. They assumed that the IR spectra consist of four characteristic groups at  $400\text{--}650\text{ cm}^{-1}$  identified as B–O–B and Pb–O–B bending vibrations and borate ring deformation, at  $650\text{--}700\text{ cm}^{-1}$  due to  $\text{BO}_3$  bending, at  $950\text{--}1050\text{ cm}^{-1}$  due to stretching vibration of tetrahedral  $\text{BO}_4$  groups and the fourth main broad IR absorption region existing at about  $1200\text{--}1400\text{ cm}^{-1}$  reveals two absorption bands due to stretching of trigonal  $\text{BO}_3$  ( $\approx 1200\text{ cm}^{-1}$ ) and tetrahedral  $\text{BO}_4$  ( $\approx 1320\text{ cm}^{-1}$ ) groups, respectively.

Table 2 gives the experimental IR bands and their assignments with related References

#### 4.2. Interpretation of the UV–visible absorption spectra

##### 4.2.1. Origin of UV absorption in base undoped lead borate glass

It was previously assumed [34,35] that the charge transfer ultraviolet bands generally observed in some commercial glasses originated from the presence of unavoidable trace iron impurities within the raw materials used for the preparation of such glasses.

Duffy and Ingram [36] and Duffy [37] have classified differently originated ultraviolet absorption bands in glasses. Some transition metal ions (e.g.  $\text{Fe}^{3+}$ ,  $\text{Cr}^{6+}$ ) exhibit characteristic charge transfer UV absorption in glasses even if present in the ppm level. Such metal ions in glass owe their UV absorption to an electron transfer mechanism. But certain other metal ions including  $\text{Ce}^{3+}$  and  $\text{V}^{4+}$  as well as  $d^{10} s^2$  ions (e.g.  $\text{Pb}^{2+}$  and  $\text{Bi}^{3+}$ ) absorbed radiation through electronic transition involving orbital essentially of the metal ion only, and the name “Rydberg” has been suggested for such spectra to distinguish them from the common electron transfer spectra.

Ehrt et al. [22,23,38,39] have postulated that small amounts of transition metal ions (especially trace iron impurities even in the ppm level) cause deterioration of the UV transmission of optical glasses. They have claimed the need of ultrapure chemicals for the preparation of special optical glasses for specific recent diverse applications. They also assumed that the UV bands identified by the deconvolution of the spectra are related to trace iron impurities.

Recently, ElBatal et al. [15–20,40–42] have specified experimentally that the charge transfer UV absorption bands observed in undoped varieties from phosphate, silicate and borate glasses are related to trace iron impurities present within the raw materials used for the preparation of such various glasses.

On the basis of previous arguments, it is suggested that the observed UV absorption bands obtained from undoped lead borate glass are due to trace iron impurities present within the raw chemicals used for preparation of such glasses beside the contribution from absorption due to  $\text{Pb}^{2+}$  ions as previously mentioned by Duffy et al. [36,37].

##### 4.2.2. Contribution of the effect of vanadium ions on the optical spectra

The base lead borate host glass seems to favor the high oxidation state of vanadium, viz. pentavalent ions [2,13–16].  $\text{V}^{5+}$  ions belong to the  $d^0$  configuration and thus possess only UV absorption and without visible bands [13–20]. The visible bands around 400, 440 and 580 nm seems to indicate the existence of  $\text{V}^{3+}$  ions in measurable amount. The existence of  $\text{V}^{4+}$  ions are not clearly identified as their visible spectra are known to be forbidden with low intensities and the absorption spectrum of trivalent vanadium ions are expected to mask them except when high concentrations  $\text{V}_2\text{O}_5$  are added. The same situation is to be expected for the spectra of  $\text{V}^{5+}$  ions in the UV region which includes also spectra due to trace iron impurities and  $\text{Pb}^{2+}$  ions.

Fig. 5 shows a band near 850 nm is resolved at high concentration of  $\text{V}_2\text{O}_5$ . Previous study of vanadium doped alkali silicate, alkali borate, and alkali phosphate glasses [13] indicated the appearance of a band at 850 nm in phosphate glass and it was attributed to tetragonally distorted octahedral  $\text{V}^{4+}$  ions. It is assumed that the studied lead borate glass contains the three vanadium species  $\text{V}^{3+}$ ,  $\text{V}^{4+}$  and  $\text{V}^{5+}$  with ratio depending on the type, composition of glass, condition of melting and concentration of vanadium ions.

##### 4.2.3. Interpretation of gamma irradiation on UV–visible spectra

It is accepted that [43,44] radiation can induce numerous changes in the physical properties of glass, one of the most obvious is visible coloration, and for this reason the defect centers causing this are often referred to as “color centers”. The nature of radiation damage in glass depends on the type (i.e. ionizing radiation vs. particle) and energy of radiation impinging on the material. The resultant effects may be divided into three categories:

- (1) atomic displacement by momentum and energy transfer.
- (2) ionization and charge trapping, and
- (3) radiolysis or photochemical effects.

The irradiation of glass usually results in the occurrence of all three processes (or at least in the second and third); the relative contributions to the net damage depend on the type and energy of the radiation, as well as the total dose.

When ionizing radiation such as gamma rays, X-rays, electrons, UV-radiation, and so on impinges on the glass, electrons are initially excited from the valence band if the incident energy is greater than the band if the incident energy is greater than the band gap. If  $E > 1\text{ keV}$ , the electrons are excited by the Compton effect. The excess energy is converted to kinetic energy and, as these electrons travel through the material, they will either recombine with positively charged holes, become trapped to form color centers, or if the energy is sufficiently high produce a secondary electron cascade by knock-on collisions with other bound electrons.



Additional bound electrons are ionized by the secondary electrons through Coulombs interactions, the secondaries losing approximately 20 eV for each ionization. Finally, when the electrons energy become too low to ionize other electrons, they will either be trapped or recombine with holes.

It is accepted that when a glass that contains transition metal ions is irradiated, these TM ions are available as potential traps for the released electrons and formed holes during the irradiation process [43,46].

In most cases, the trapping of charges by TM ions seems to be favored and the behavior of such glass depends primarily on the type and concentration of these dopants (or impurities). It is important to note that the presence of the dopants does not alter the intrinsic trapping sites of the glass, they sometimes retard the formation rate of color center (or cause annihilation) of the intrinsic color center [43,46].

Some scientists [45–47] have remarked that glasses containing heavy metal ions such as  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$  shield gamma irradiation to a measurable extent and such glasses can be used in windows in nuclear reactors, hot cells or other radiation environments and even in encapsulation of radioactive wastes.

The observed optical results in such high lead borate glasses which indicate that gamma irradiation only affects UV absorption and the visible absorption spectra remain unchanged which can be realized and interpreted as follows;

- The host high lead borate glass is expected to show resistance or shielding towards successive gamma irradiation. This is due to the presence of  $\text{Pb}^{2+}$  ions in the glass in high percent because these ions possess heavy mass and thus retard the passage and ease of electron ionization [45,48].
- The ultraviolet absorption is related to charge transfer bands due to trace iron impurities and in the host base glass it is assumed that gamma irradiation initiate the transformation of iron by photochemical reactions to higher or lower valencies for the iron species. Moncke and Ehrhart [22,23] have assumed that the iron states even when present as impurities in the glass, can be affected.  $\text{Fe}^{2+}$  ions can be photo-oxidized to  $(\text{Fe}^{2+})^+$  ions and  $\text{Fe}^{3+}$  ions can be photo-reduced to  $(\text{Fe}^{3+})^-$  ions. The experimental optical spectra of the undoped glass after successive gamma irradiation, show first stabilization of the UV band at about 340 nm with irradiation, which is related to divalent lead ( $\text{Pb}^{2+}$ ) ions indicating the stability of these ions, then it shows a decrease with high dose (8 Mrad). The UV absorption in the region 200–310 nm related to iron impurities reveals increase in intensity with irradiation which can be related to the conversion of some  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by capturing holes during the irradiation process and the high dose (8 Mrad) shows slight increase.
- The V-doped samples show different behavior on the effect of gamma irradiation within the UV absorption region revealing continuous decrease with progressive irradiation and the visible absorption curves show stability and obvious shielding effect. It seems that in the presence of another extra transition metal ion (vanadium ions) the decrease of the intensity of the UV absorption can be related to the conversion of some  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by photochemical reaction through capturing electrons. This comes from the competition between transition metal ions (V ions) and the trace iron impurities ( $\text{Fe}^{3+}$  ions) have the direction to be photo reduced to lower valence ions ( $\text{Fe}^{2+}$ ) which have its preferred absorption in the near IR at about 1100 nm.

#### 4.2.4. Interpretation of the effect of gamma irradiation on IR spectra

The overall effects of gamma irradiation on the IR spectra are visualized by the maintenance of the number and position of the

main IR bands observed in the glasses before irradiation and only minor variations in the intensity of some bands are identified after irradiation.

Some scientists have noticed the same observations in other glasses [48,49], and they have related them to the weakening of the already nonperiodic network structure or to changes in the bond angles and/or bond lengths between the building structural units as recently suggested by various authors [50,51].

The observed results can thus be interpreted by assuming that gamma irradiation causes some variations in the bond angles and/or bond lengths within the structural groups as suggested before.

## 5. Conclusion

Lead borate glass of the composition  $\text{PbO}$  70%– $\text{B}_2\text{O}_3$  30% and other samples with the same composition with added  $\text{V}_2\text{O}_5$  (0.5–4%) have been prepared and their optical absorption has been examined before and after successive gamma irradiation. The undoped sample shows strong UV absorption bands due to the presence of  $\text{Pb}^{2+}$  ions and unavoidable trace iron impurities.  $\text{V}_2\text{O}_5$ -doped samples reveal additional visible bands due to the presence of various states of vanadium ions namely  $\text{V}^{3+}$  and  $\text{V}^{4+}$ .

The prepared samples have been examined by FTIR spectral measurements which show characteristic IR bands due to triangular and tetrahedral borate groups beside Pb–O vibrations. The addition of  $\text{V}_2\text{O}_5$  in the doping level produces minor variations which are related to the depolymerization of the network. Gamma irradiations produces induced optical bands which are related to positive holes in the visible region and electron defects in the UV region. Gamma irradiation causes minor changes in the IR spectral bands which are related to variations of the bond lengths and/or bond angles within the structural groups.

## References

- [1] C.F. Leiser, *Glass Ind.* 44 (1963) 630, 509, 574, 594.
- [2] E.M. Rabinovich, *J. Mater. Sci.* 11 (1976) 925–948, and references therein.
- [3] R.R. Fummala, in: L.D. Pye, V.D. Frechette, N.J. Kreidl (Eds.), *Borate Glasses*, Plenum Press, New York, USA, 1978.
- [4] N. Shenkai, R.C. Bradt, G.E. Rindone, *J. Am. Ceram. Soc.* 65 (1982) 123–126.
- [5] M. Leventhal, P.J. Bray, *Phys. Chem. Glasses* 6 (1965) 113–125.
- [6] M.F. Mydlar, N.J. Kreidl, J.K. Hendren, G.T. Clayton, *Phys. Chem. Glasses* 11 (1970) 196–201.
- [7] R. Dupree, N. Ford, D. Holland, *Phys. Chem. Glasses* 28 (1987) 78–84.
- [8] B.N. Meera, A.K. Sood, N. Chandrabhas, J. Ramakrishna, *J. Non-Cryst. Solids* 126 (1990) 224–230.
- [9] B.N. Meera, J. Ramakrishna, *J. Non-Cryst. Solids* 159 (1993) 1–21.
- [10] Y. Akasaka, I. Yasui, T. Nanba, *Phys. Chem. Glasses* 34 (1993) 232–237.
- [11] T. Hubert, U. Harder, G. Mosel, K. Witke, in: A.C. Wright, S.A. Feller, A.C. Hannon (Eds.), *Proc. 2nd Int. Conf. Borate Glasses Crystals and Melts*, Society of Glass Technology, Sheffield, UK, 1997, pp. 156–163.
- [12] K.J. Singh, N. Singh, R.S. Kaundal, K. Singh, *Nucl. Instrum. Meth. Phys. Res. B* 226 (2008) 944–948.
- [13] A.M. Nassar, N.A. Ghoneim, *J. Non-Cryst. Solids* 46 (1981) 181–195.
- [14] N.A. Ghoneim, H.A. ElBatal, M.A. Azooz, *Nucl. Sci. J.* 33 (1996) 289–298.
- [15] F.M. EzzElDin, N.A. Elalaily, H.A. ElBatal, N.A. Ghoneim, *Radiat. Phys. Chem.* 48 (5) (1996) 659–664.
- [16] F.H. ElBatal, S.M. AboNaf, F.M. EzzElDin, *Indian J. Pure Appl. Phys.* 43 (2005) 579–590.
- [17] S.Y. Marzouk, F.H. ElBatal, H.M. Salem, S.M. AboNaf, *Opt. Mater.* 29 (2007) 1456–1466.
- [18] F.H. ElBatal, M.A. Azooz, S.Y. Marzouk, *Phys. Chem. Glasses Eur. J. Glass Sci. Technol.* 47 (2006) 588–598.
- [19] F.H. ElBatal, M.A. Azooz, S.Y. Marzouk, M.S. Selim, *Physica B* 398 (2007) 126–134.
- [20] F.H. ElBatal, A.A. Elkheshen, M.A. Azooz, S.M. AboNaf, *Opt. Mater.* 30 (2008) 881–891.
- [21] D. Ehrhart, P. Ebeling, U. Natura, *J. Non-Cryst. Solids* 240 (2000) 263–264.
- [22] U. Natura, D. Ehrhart, *Nucl. Meth. Phys. Res. B* 174 (2001) 143–151.
- [23] D. Moncke, D. Ehrhart, *Opt. Mater.* 25 (2004) 425–437.
- [24] J. Wong, C.A. Angel, *Glass Structure by Spectroscopy*, Marcel Dekker, New York, USA, 1976.
- [25] L.D. Pye, V.D. Frechette, N.J. Kreidl (Eds.), *Borate Glasses, Structure, Properties and Applications*, Plenum, New York, USA, 1978.

- [26] A.C. Wright, S.A. Feller, A.C. Hannon (Eds.), Proc. 2nd Int. Conf. on Borate Glasses, Crystals and Melts, Society of Glass Technology, Sheffield, UK, 1997.
- [27] Y.B. Dimitriev, A.C. Wright (Eds.), Proc. 3rd Int. Conf. on Borate Glasses, Crystals and Melts, Society of Glass Technology, Sheffield, UK, 2001.
- [28] E.I. Kamitsos, Phys. Chem. Glasses 44 (2003) 79–87.
- [29] P.J. Bray, M. Leventhal, H.O. Hooper, Phys. Chem. Glasses 4 (1963) 47–52.
- [30] K. Witke, U. Harder, M. Willfahrt, T. Hubert, P. Reich, Glastechn. Ber. Glass Sci. Technol. 69 (1996) 143–153.
- [31] W.A. Pisarski, J. Pisarski, G. Domniak-Dzik, W. Ryba-Romanowski, J. Phys.: Condens. Matter 16 (2004) 6171–6184.
- [32] G. Lakshminarayana, S. Buddhudu, Spectrochim. Acta A 63 (2006) 295.
- [33] Y. Cheng, Physica B 404 (2009) 1230.
- [34] G.H. Sigel, R. Ginther, Glass Technol. 9 (1968) 66.
- [35] L. Cook, K.H. Mader, J. Am. Ceram. Soc. 65 (1982) 109.
- [36] J.A. Duffy, M.D. Ingram, Phys. Chem. Glasses 15 (1974) 34.
- [37] J.A. Duffy, Phys. Chem. Glasses 38 (1997) 289.
- [38] W. Seeber, D. Ehrt, Glastechn. Ber. Glass Sci. Technol. 70 (1997) 312.
- [39] U. Natura, D. Ehrt, Glastechn. Ber. Glass Sci. Technol. 72 (1999) 295.
- [40] F.H. ElBatal, S.Y. Marzouk, N. Nada, S.M. Desouky, Physica B 391 (2007) 88.
- [41] F.H. ElBatal, J. Mater. Sci. 43 (2008) 1070.
- [42] E.M.A. Khalil, F.H. El-Batal, Y.M. Hamdy, H.M. Zidan, M.S. Aziz, A.M. Abdelghany, Physica B 405 (5) (2010) 1294.
- [43] E.J. Friebele, D.L. Griscom, in: M. Tomozawa, R.H. Doremus (Eds.), Treatise on Materials Science and Technology, Vol. 17, Academic Press, New York, 1979, p. 257.
- [44] E.J. Friebele, Optical Properties of Glass, in: D.R. Uhlmann, N.J. Kreidl (Eds.), American Ceramic Society, Westerville, OH, 1991, p. 205.
- [45] F.H. ElBatal, Nucl. Instrum. Meth. Phys. Res. B 254 (2007) 243.
- [46] A.M. Abdelghany, Silicon, [in press](#).
- [47] N. Singh, K.J. Singh, K. Singh, H. Singh, Nucl. Instrum. Meth. Phys. Res. B 275 (2009) 305.
- [48] F.H. El-Batal, E.M.A. Khalil, Y.M. Hamdy, H.M. Zidan, M.S. Aziz, A.M. Abdelghany, Physica B 405 (12) (2010) 2648.
- [49] F.H. El-Batal, E.M.A. Khalil, Y.M. Hamdy, H.M. Zidan, M.S. Aziz, A.M. Abdelghany, Silicon 2 (2010) 41.
- [50] L.W. Hobbs, A.N. Sreeram, C.E. Jesurum, B.A. Beger, Nucl. Instrum. Meth. Phys. Res. B 116 (1996) 18.
- [51] P. Piao, W.G. Oldham, E.E. Haller, J. Non-Cryst. Solids 276 (2000) 61.