

## Gamma ray interaction with lithium borate glasses containing WO<sub>3</sub>

Fatma H ElBatal\*

Glass Research Department, National Research Center Dokki, Cairo, Egypt

\*E-mail: fh\_elbatal@yahoo.co.uk

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Glasses from the system of undoped lithium diborate and WO<sub>3</sub>-doped were synthesized by the usual melting and annealing techniques. UV-visible absorption spectra of the prepared sample were measured before and after successive gamma irradiation. Undoped glass reveals strong UV absorption spectrum which is related to the presence of unavoidable trace iron impurity. The presence of tungsten ions in this glass system is observed to impart no colour or marked changes in the absorption spectrum of the host glass suggesting the presence of tungsten ions mostly as W<sup>6+</sup> species. Gamma irradiation produces extended induced bands in the UV-visible regions in the undoped and WO<sub>3</sub>-doped glasses. These induced bands are related to the presence of intrinsic defects already present in the host lithium diborate glass and extrinsic defects due to the presence of both trace iron impurity and tungsten ions. Infrared absorption spectra reveal specific vibrational bands due to characteristic borate network beside modifier lithium ions (Li<sup>+</sup>) and tungsten groups. Raman spectra confirm the IR results regarding the presence of tungsten ions mainly as WO<sub>6</sub> groups due to the oxidizing nature of the host glass. Tungsten ions are seen to cause shielding or retardation of the growth of the induced bands by gamma irradiation.

**Keywords:** Lithium diborate glass, WO<sub>3</sub>, UV-visible spectroscopy, Gamma rays, IR-Raman, ESR spectroscopy

### 1 Introduction

Tungsten oxide containing glasses are of great interest because they can exhibit unusual electrochromic or photosensitive properties related to the ability of tungsten atoms<sup>1</sup> to exhibit various oxidation states (W<sup>6+</sup>, W<sup>5+</sup> or W<sup>4+</sup>). Tungsten ions can generate special bronzes which could result in interesting laser-active materials<sup>2</sup>. Tungsten oxide with lithium diborate glass could be used for electro-optic and related applications<sup>3</sup>. Glasses offer larger number of advantages over crystalline electrolytes including physical isotropy, absence of grain boundaries, continuously variable composition, ease of thin film formation for device application and good stability.

WO<sub>3</sub> and MoO<sub>3</sub> are two transition metal oxides which do not form glasses by themselves but do so readily in combination with other glass formers<sup>4,5</sup> such as P<sub>2</sub>O<sub>5</sub>. They can be added to alkali borate and lead borate with considerable amounts<sup>6,7</sup>. Experimental results indicate that tungsten ions occupy mainly in glasses two possible valencies W<sup>6+</sup> and W<sup>5+</sup> with different local sites depending on the host glass composition and concentration of tungsten ions<sup>1,8</sup>.

Gamma ray irradiation is accepted to affect glass producing induced defects which can be identified by UV-visible spectroscopic measurements<sup>6,9,10</sup>. The principal effect of ionizing radiation results from

almost purely electronic processes<sup>10</sup>. Specifically, these effects occur because electrons are excited to leave their normal positions and move or travel through the glass network. The net result is production of pairs of electrons and positive holes. In glasses containing transition metal ions, there is a marked possibility that most transition metal ions may change their valences through photochemical reactions by accepting or releasing electrons. Also, some transition metal ions reveal shielding behaviour towards the action of successive gamma irradiation<sup>11,12</sup>.

The optical UV-visible, infrared and Raman spectra of some lithium borate glasses containing varying WO<sub>3</sub> contents before and after successive gamma ray irradiation have been studied in the present paper. The electron spin resonance of some samples has been studied and the collective data with structural evolution caused by the introduction of WO<sub>3</sub> in such host lithium borate glass has been correlated. A further aim of the paper is to characterize the effect of gamma irradiation on the prepared glasses and elucidate the induced damages generated by continuous gamma irradiation.

### 2 Experimental Details

#### 2.1 Preparation of glasses

The glasses were prepared from chemically pure orthoboric acid, (H<sub>3</sub>BO<sub>3</sub>, s.d.fine-chem.Ltd., Mumbai,

India, 99.5%) and lithium carbonate (Fluka, Germany, >98.5 %, 0.005 Fe) and the transition metal,  $\text{WO}_3$  was added as such. The weighed batches were melted in platinum crucibles in an electric furnace at  $1100^\circ\text{C}$  for 90 min with rotating of the melts several times to achieve homogeneity. The melts were cast into preheated stainless steel molds and the prepared samples were immediately transferred to a muffle temperature regulated at  $400^\circ\text{C}$  and the muffle was left to cool after 1 hour at a rate of  $25^\circ\text{C}/\text{h}$  to room temperature.

## 2.2 UV-visible absorption measurements

The optical absorption of highly polished samples of the undoped and  $\text{WO}_3$ -doped glasses of the dimensions  $1 \times 4 \times 0.1 \text{ cm}^3$  were recorded at room temperature before and after each successive gamma dose by a recording spectrophotometer in the range 200-1100 nm type JASCO, Corp., V-570, Rel-00, Japan.

## 2.3 Infrared absorption measurements

The infrared absorption spectra of the undoped and  $\text{WO}_3$ -doped glasses were measured at room temperature in the wave number range  $400\text{-}4000 \text{ cm}^{-1}$  by a Fourier Transform computerized infrared spectrometer type JASCO Corp., FT/IR-430, Japan. The samples were investigated as fine powders which were mixed with KBr in the ratio (2.200 mg glass powder to KBr, respectively). The weighed mixture was then subjected to a pressure of  $5 \text{ tons}/\text{cm}^2$  to produce clear homogeneous discs. The IR spectra were measured immediately after preparing the discs.

## 2.4 Raman measurements

Raman spectra were measured for fine glass powder using a Fourier transform Raman spectrometer (model Nexus 760 Nicolet-Madison-WI, USA) equipped with a 2W Nd:YAG laser ( $1064 \text{ nm}$ ), which eliminates the problem of samples fluorescence and photo-decomposition. The spectra were measured using a 0.7 W laser power, 64 scans and  $4 \text{ cm}^{-1}$  resolution in the wavelength range  $3700\text{-}100 \text{ cm}^{-1}$ .

## 2.5 Irradiation facility

A  $^{60}\text{Co}$  gamma cell (2000 Ci) was used as a gamma ray source with a dose rate of  $1.5 \text{ Gy}/\text{s}$  ( $150 \text{ rad}/\text{s}$ ) at a temperature of  $30^\circ\text{C}$ . The investigated glasses were subjected to the same gamma dose every time. Using a Fricke dosimeter, the absorbed dose in glass is expressed in terms of absorbed dose in water, rather than in terms of dose in glass. No cavity theory correction was made.

## 2.6 Electron spin resonance measurements

Electron spin resonance spectra were recorded at room temperature on an ESR spectrometer (Bruker, E 500; Germany) operating at  $9.808 \text{ Hz}$  and using  $100 \text{ kHz}$  field modulation. The magnetic field was scanned from 480 to 6480 Gauss. The ESR spectra were measured as an evidence for the presence of the states of tungsten containing unpaired electrons.

## 3 Results

### 3.1 UV-visible absorption spectra

#### 3.1.1 UV-visible spectrum of host undoped lithium diborate glass

Figure 1 shows the spectrum of the undoped base lithium diborate glass. The spectrum shows high intense charge transfer absorption broad band extending from the beginning of measurements at 200 to about 300 nm with a peak at about 230 nm and no visible bands could be identified. With the introduction of increasing amounts of  $\text{WO}_3$ , the UV peak is observed (Fig. 2) to shift progressively to reach about 275 nm with the highest  $\text{WO}_3$  10% content and no visible absorption could be identified. On subjecting the host base glass to successive gamma irradiation, the UV absorption becomes broader (Fig. 1) and extends from the beginning of measurement at 200 to about 400 and showing four small split apex peaks at about 205, 220, 240 and 270 nm in the final gamma dose (5 MR) (Fig. 1). Also, the visible spectrum reveals the successive gamma irradiation, the resolution of a broad band centered at about 550 nm.

#### 3.1.2 UV-visible absorption spectra of $\text{WO}_3$ -doped glasses

Figure 2 shows the UV-visible absorption of  $\text{WO}_3$ -doped lithium diborate glasses before and after successive gamma irradiation. With the introduction of increasing amounts of  $\text{WO}_3$ , the UV peak is

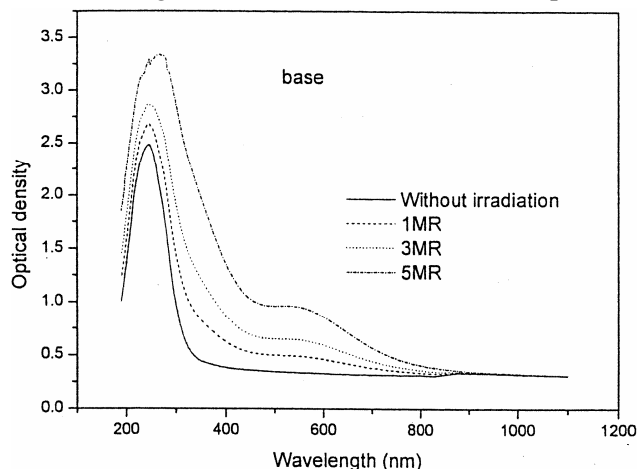


Fig. 1 — Absorption spectrum of base undoped lithium diborate glass before and after successive gamma irradiation

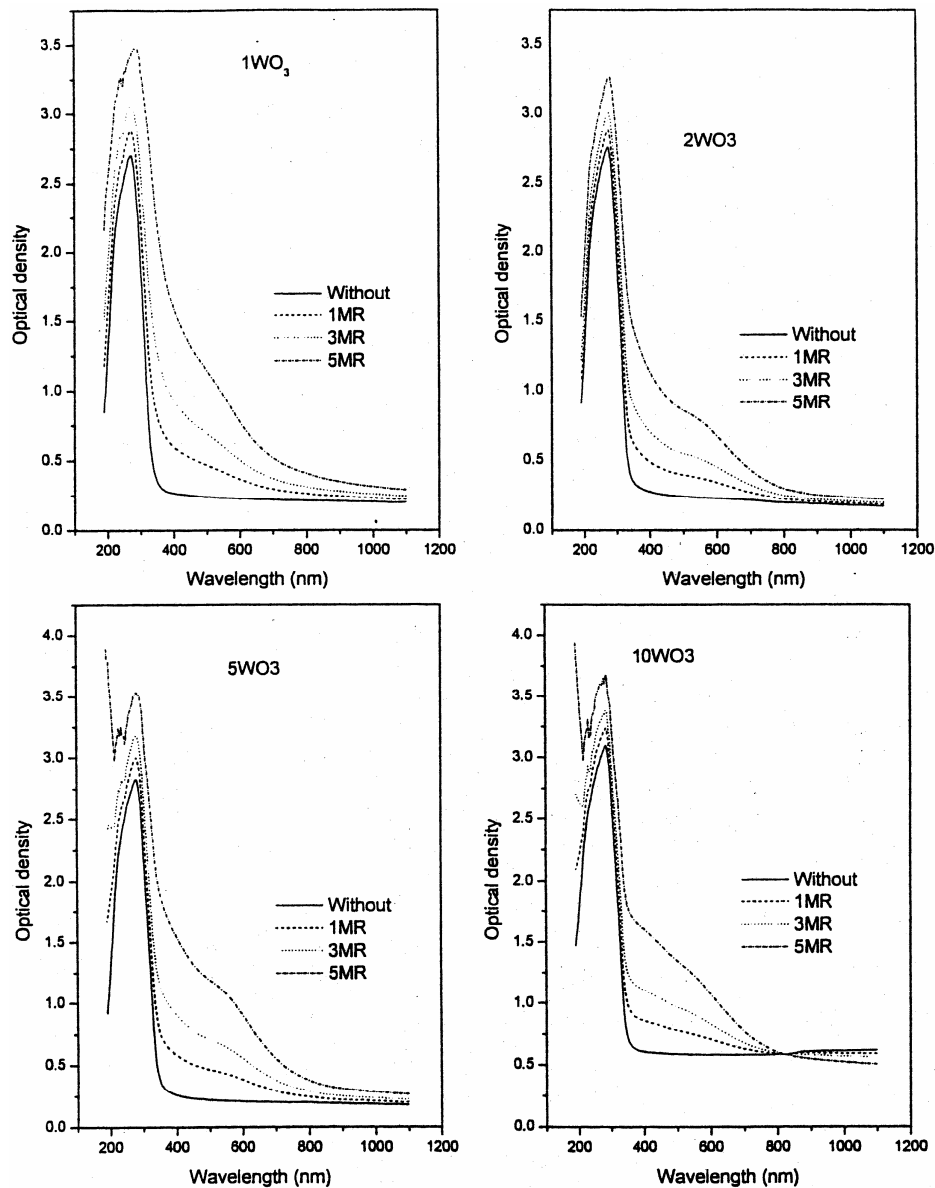


Fig. 2 — Absorption spectra of  $\text{WO}_3$ -doped lithium diborate glasses before and after successive gamma irradiation

observed (Fig. 2) to shift progressively to reach about 275 nm with the highest  $\text{WO}_3$  10% content and no visible absorption could be identified. The UV absorption spectra in all the studied  $\text{WO}_3$ -doped samples exhibit broadness and the intensities progressively increase with gamma gamma irradiation. The glasses containing higher  $\text{WO}_3$  contents (5% and 10%) reveal obvious splitting of the UV spectrum with gamma irradiation especially with the highest dose (5MR) at which several component splitted peaks could be identified in the UV region. The visible spectra of the  $\text{WO}_3$ -doped glasses show a broad visible band centered at about 540 nm together with a small curvature around 400 nm.

### 3.1.3 Induced spectra

Figures 3 and 4 shows the induced spectra of the undoped host lithium diborate glass and  $\text{WO}_3$ -doped glasses.

The induced spectra are obtained by subtracting the optical density from each glass sample before exposed to gamma irradiation from that of the same sample after each specified dose of gamma rays. Thus, the induced results given express the net results of undoped and each  $\text{WO}_3$ -doped glasses showing change in optical density (or  $\Delta D$ ) which is the difference in optical density against wavelength (in nm). The induced results can be summarized as follows:

### 3.1.4 Induced spectrum of the undoped glass

Figure 3 shows the induced spectrum of the undoped glass which consists of two induced UV bands, the first band is small at about 205 nm and the second band is strong at about 290 nm and followed by a broad induced visible band centered at about 540 nm. It is evident that with progressive gamma irradiation, the induced UV and visible bands sharply increase in intensity.

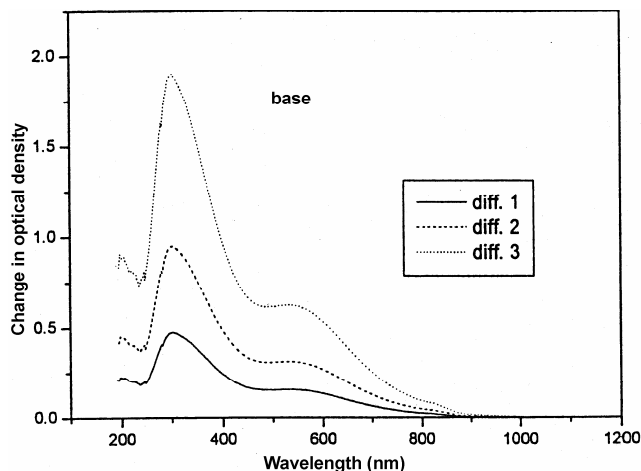


Fig. 3 — Induced spectra of  $\text{WO}_3$ -doped lithium diborate glasses

### 3.1.5 Induced spectra of $\text{WO}_3$ -doped glasses

Figure 4 shows the induced spectra of the  $\text{WO}_3$ -doped glasses which reveal some changes produced by the introduction of  $\text{WO}_3$ . With the progressive increase of the  $\text{WO}_3$  content, it is observed that two small peaks are identified at about 210 and 250 nm and the strong band at 290 nm in the undoped glass decreases in intensity with shifting to about 340 nm and the visible induced band becomes less identified with irradiation.

## 3.2 Infrared absorption spectra

### 3.2.1 Infrared absorption spectrum of base lithium diborate glass

Figure 5 shows the infrared absorption spectrum of the base lithium diborate glass. This IR spectrum is, generally, observed to be characterized by the three absorption regions which are distinguished in various publications concerning borate glasses<sup>6,7</sup>. The first region is extending from 1200 to 1600  $\text{cm}^{-1}$  which is due to B-O stretching of  $\text{BO}_3$  units, the second region extends from 800 to 1200  $\text{cm}^{-1}$  which is due to B-O stretching of  $\text{BO}_4$  units, the third region lies around 700  $\text{cm}^{-1}$  which is due to bending vibration of B-O-B linkages.

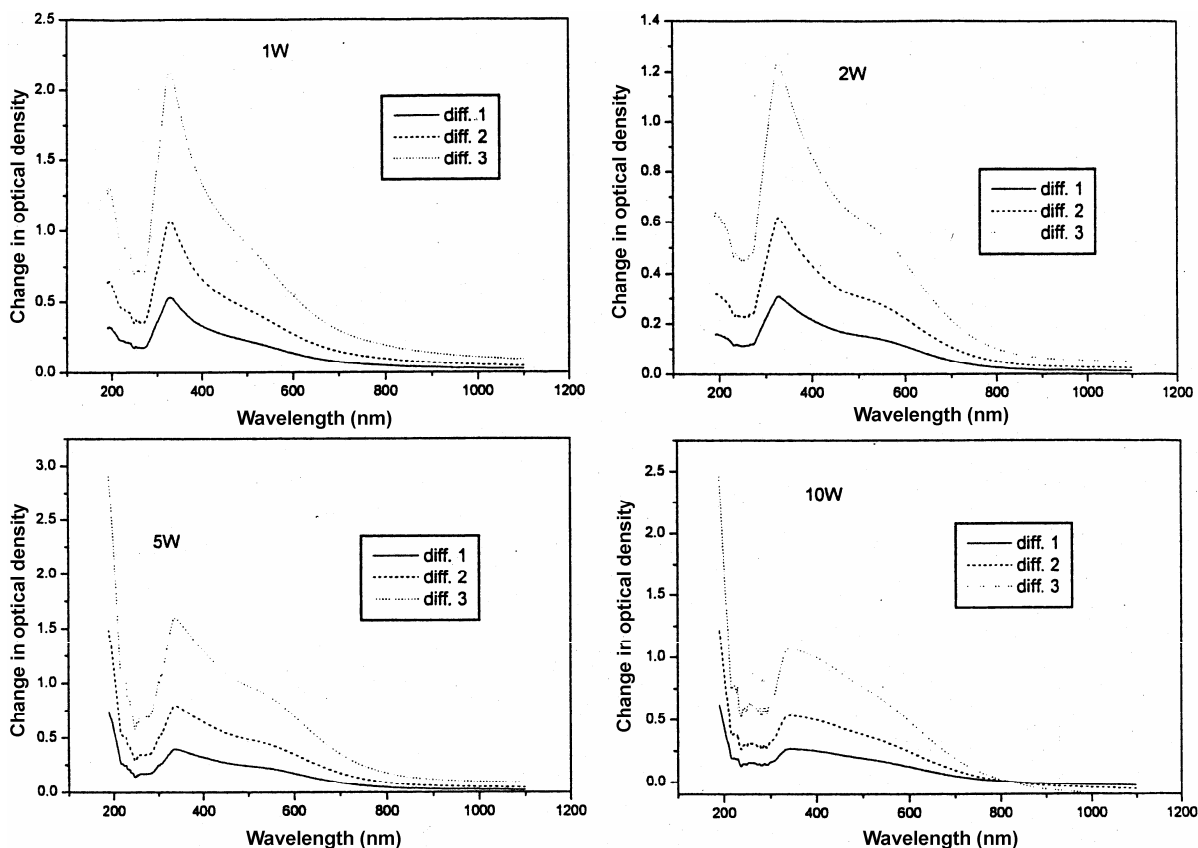


Fig. 4 — Induced spectra of  $\text{WO}_3$ -doped lithium diborate glasses

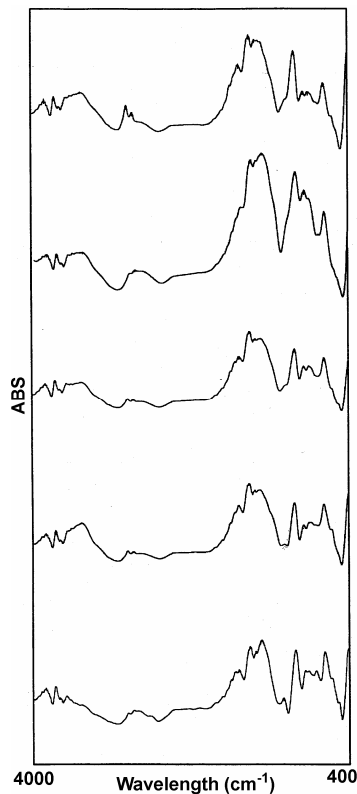


Fig. 5 — Infrared absorption spectra of undoped and  $\text{WO}_3$ -doped lithium borate glasses

In the mid region, Fig. 5 shows four prominent absorption bands at about 673, 1008, 1390, 1523  $\text{cm}^{-1}$  and six other medium bands at about 774, 850, 899, 1145, 1460 and 1652  $\text{cm}^{-1}$ . Also, the IR spectrum shows in the far-infrared region, a prominent band at about 410 and two other peaks at about 520 and 580  $\text{cm}^{-1}$ . It is also obvious in the near-infrared region, some small bands at about 2420, 2857 followed by other small kinks at about 3450, 3618, 3745 and 3855  $\text{cm}^{-1}$ .

### 3.2.2. Infrared absorption of $\text{WO}_3$ -doped lithium diborate glasses

Careful inspection of Fig. 5 indicates that the successive addition of  $\text{WO}_3$  to the level studied (1-10% wt%) to the host lithium diborate glass, has only minor effect on the IR spectra of the studied glasses. The main vibrational characteristic bands remain prominent but it is obvious that some alterations in some of the absorption bands intensities are noticed. The absorption band at about 1145  $\text{cm}^{-1}$  in the base glass is observed to decrease in intensity with the addition of  $\text{WO}_3$  while the band at about 1016  $\text{cm}^{-1}$  is highly persistent in all the samples together with all the other main bands. Also, the

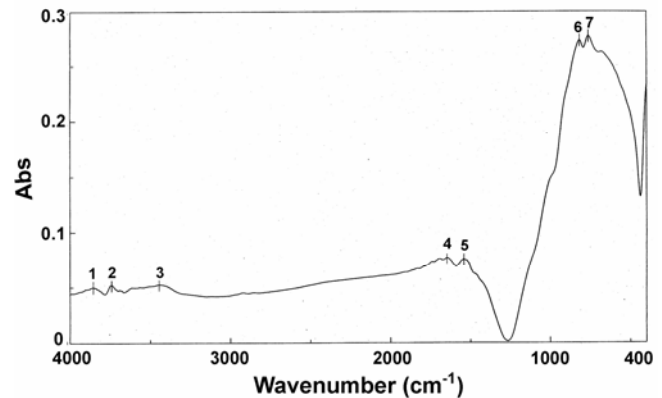


Fig. 6 — Infrared absorption of crystalline  $\text{WO}_3$

bands in the region 1390-1640  $\text{cm}^{-1}$  are still highly distinguished.

Figure 6 shows the IR spectrum of pure crystalline  $\text{WO}_3$  in the same condition of measurements. It is obvious that three absorption peaks could be identified at about 680, 760, 818  $\text{cm}^{-1}$  followed by two other peaks in the mid-region at about 1541 and 1647  $\text{cm}^{-1}$ . In the near-region, three small peaks are observed at about 3445, 3741 and 3855  $\text{cm}^{-1}$ .

### 3.3. Raman spectra

Figure 7 shows the Raman spectra of undoped lithium diborate glass together with some samples of  $\text{WO}_3$ -containing lithium borate glasses. The base lithium diborate glass reveals Raman spectrum consisting of three distinct bands at about 323, 784 and 957  $\text{cm}^{-1}$  together with some minor ones at about 1109, 1438, 1834, 2035  $\text{cm}^{-1}$ . The second sample containing 2%  $\text{WO}_3$  shows Raman spectrum consisting of three sharp bands at about 721, 780 and 1029 together with some other peaks at about 186, 191, 259, 349, 484 and 967  $\text{cm}^{-1}$ . When the concentration of the  $\text{WO}_3$  reaches 4%, the Raman spectrum reveals one sharp band at about 781  $\text{cm}^{-1}$  together with some other medium bands at about 307, 453, 973, 1156, 1458, 1869  $\text{cm}^{-1}$ . The glass sample containing 8%  $\text{WO}_3$ , produces Raman spectrum with three sharp bands at about 344, 779 and 953 and other five medium bands at about 484, 850, 1078, 1464, 1747  $\text{cm}^{-1}$ . The last studied glass sample which contains 10%  $\text{WO}_3$  shows three bands at about 333, 775 and 945  $\text{cm}^{-1}$  and after 2000  $\text{cm}^{-1}$  the Raman spectrum shows fluorescence effect.

### 3 Electron spin resonance (ESR) spectrum

No ESR spectral signals could be detected for the undoped glass. Figure 8 shows the ESR spectrum of

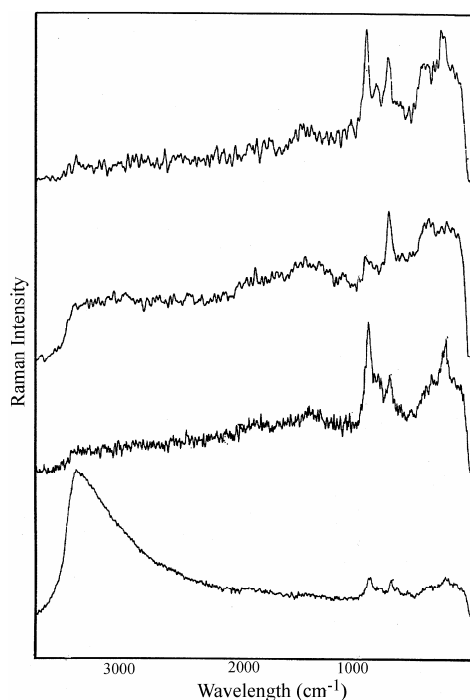


Fig. 7 — Raman spectra of undoped and  $\text{WO}_3$ -doped lithium borate glasses

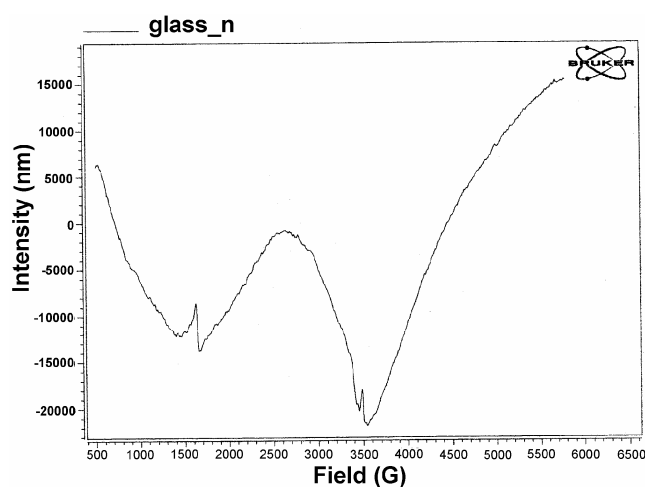


Fig. 8 — Electron spin resonance of selected sample of  $\text{WO}_3$ -doped glasses

$\text{WO}_3$ -doped glass. The spectrum shows no sharp signals indicating that the tungsten ions are mainly present in the hexavalent  $\text{W}^{6+}$  state which belongs to the  $d^0$  state possessing no unpaired electrons and this explains the expected observed result.

## 4 Discussion

### 4.1 Origin of ultraviolet absorption in base lithium diborate glass

It is earlier assumed by several researchers<sup>13,14</sup> that the ultraviolet absorption bands usually observed in

commercial glasses and several undoped glasses are related to the presence of an unavoidable trace transition impurities and specifically originate from trace iron impurities present in the raw materials or contaminated in glass by contact of molten oxides with refractories during glass preparation. The same postulation was also reconsidered by Duffy<sup>15</sup> who assumes that charge transfer absorption originates from traces of impurities such as Fe, Cu, Pb etc. Ehrt and her coworkers<sup>16-18</sup> in searching for ultra pure glasses for special optical applications confirm that trace iron impurities even in the ppm level could impair the application of glasses for high quality optical applications.

In a series of continuous studies, ElBatal and her coworkers have confirmed through investigating undoped phosphate<sup>19,20</sup>, cobalt<sup>21</sup>, borosilicate<sup>22</sup>, bioglass<sup>23</sup>, lithium diborate<sup>24</sup> glasses that trace iron impurities present in the raw chemicals for their preparation and specifically  $\text{Fe}^{3+}$  ions, produce charge transfer strong ultraviolet bands. The present studied base lithium diborate glass reveal strong and high intense ultraviolet absorption extending from 200 to 300 nm and centered at about 230 nm and no visible bands could be identified. Therefore, it is assumed that this charge transfer absorption observed in the undoped glass virtually originates from the contamination with trace iron impurities from the raw chemical materials used for the preparation of the studied glasses.

### 4.2 Contribution of the effect of gamma irradiation

Ionizing radiation including gamma ray has been observed to produce variable induced defects<sup>24,25</sup>. Defects caused by radiation in pure materials originate at imperfections present before irradiation. Glasses have normally short range order and do contain numerous defects sites such as vacancies, interstitial atoms, multivalent impurity ions and non-bridging oxygen ions.

Experimental results indicate that gamma irradiation of the host lithium diborate glass produces four strong UV peaks at about 205, 220, 240 and 270 nm especially at high gamma dose level beside a broad visible centered at about 550 nm.

Bishay<sup>27</sup> in 1970 assumed that it is, generally accepted that visible induced bands are due to positive hole traps while UV induced bands are due to electron traps. Worldwide review published papers<sup>25-27</sup> agreed and recognized three induced bands in alkali borate glasses at 2.2 eV ( $\sim 550$  nm), 3.0 eV ( $\sim 400$  nm) and at 5.1 eV (235 nm).

Friebele<sup>26</sup> assumed that although the details of the induced defect centers are different in alkali borate, alkali phosphate and alkali silicate glasses, bands associated with holes trapped on oxygen atoms have been identified in all these systems in the 2.0-2.6 and 2.5-3.0 eV ranges. Also, alkali electron center bands arising from a defect similar to the F-center in alkali halides have been found in all three systems in the 1.5-2.4 eV range. An electron trap perhaps similar to the  $E_2'$  center in irradiated silica has been identified in all glasses near 5.1 eV (~235 nm), and it seems to comprise an electron trapped in an anti-bonding orbital of the glass former with a neighbouring alkali ion.

Later Shkrob *et al.*<sup>28</sup> have identified by modified electron paramagnetic resonance studies the following defects in alkali borate glasses:

- (a) All variants of boron oxygen hole centers (BOHC) are holes trapped on the bridging oxygen in a  $b_3$  unit.
- (b) Boron electron centers (BEC or  $BE^-$ ) represent an electron trapped on over-coordinated oxygen (the " $O_3^+$ " defect). If it is coordinated with an alkali cation or a compensated  $b_3$  unit, the (BEC) is formed.
- (c) The peroxy radicals are likely to be formed by hole trapping at the ( $b_4$ -O O- $b_4$ ) linkage.

Shkrob *et al.*<sup>28</sup> further added that more work is still needed to establish the structure of the formed defects and the mechanism of their generation by combined techniques.

#### 4.3 Contribution of the effect of tungsten ions

It is well known that transition metal ions present as dopants or impurities in glass can influence the processes and mechanisms responsible for the formation of radiation induced colour centers<sup>25-27</sup>. The transition metal ions can compete with the intrinsic defects already present in the glass to trap the liberated electrons and holes produced by irradiation. The capturing process depends strongly on the nature of the transition metal ion and its concentration as well as on the type and composition of the host glass.

The effect of transition metal ions can be understood by assuming that these transition metal ions are available as potential traps for the radiolytic electrons and holes<sup>25-27</sup>. In most of the cases, the trapping of charges by the transition metal ions seems to be favoured and the response of the 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. Rather, by providing alternate sites, they affect the formation rate and the recovery or annihilation rate of the intrinsic colour centers.

The experimental results shown in Figs 1-4 reveal that careful inspection and comparison of the effect of successive gamma irradiation on the base host lithium diborate glass and the same effect on  $WO_3$ -doped samples indicate that the presence of tungsten ions and especially at high concentrations causes marked resolution and splitting of the UV absorption to several component peaks at the highest gamma dose (5MR) while the induced visible band observed in the base host glass at about 540 nm shows obvious decrease in intensity. These observed changes could be interpreted in accordance with the assumption of Moncke and Ehrh<sup>17,18</sup> who postulated that the formed extrinsic defects are possibly due to photochemical processes (photo-oxidation or photo-reduction) of the transition metal ions (even that present as impurities) by the effect of successive gamma irradiation.

It is generally accepted that tungsten ions exist in glasses in three possible valencies:  $W^{6+}$ ,  $W^{5+}$  and  $W^{4+}$  and the first two states are the predominate<sup>1,29-32</sup> and could participate in the glass network itself. Recent postulations<sup>1,32</sup> state that tungsten ions participate in the glass network with different structural units like:  $WO_4$  (Td) and  $WO_6$  (Oct) of hexavalent  $W^{6+}$  ions and ( $W^{5+}O_3$ ) (Oct) of pentavalent  $W^{5+}$  ions.

High PbO content in lead borate glasses favours the presence of high valence hexavalent tungsten ions ( $W^{6+}$ ) in appreciable amounts<sup>7</sup>. But, sodium metaphosphate glass is found to initiate the existence of pentavalent tungsten ( $W^{5+}$ ) ions in noticeable bluish colour and imparting two visible absorption bands<sup>33</sup> at about 500 and 830 nm especially with high concentration of  $WO_3$ .

In the present studied lithium diborate glasses containing progressive  $WO_3$  content, all the specimens are colourless and impart no obvious visible absorption bands. It is believed that tungsten ions are present mostly in the hexavalent state as ( $W^{6+}$ ) ions as indicated and initiated by the presence of appreciable alkali oxide  $Li_2O$  content.

The obvious splitting of  $WO_3$ -containing glasses with irradiation can be related to the first generation of induced defects with progressive irradiation reach to some saturation<sup>25-27</sup>. The addition of increasing  $WO_3$  causes splitting of the UV absorption bands which can be correlated with the introduction of  $WO_3$

in the structural network by forming W-O-W or W-O-B units or compete with trace iron impurities as a further transition metal.

#### 4.4. Interpretation of the infrared absorption data in relation to glass structure

The potential of infrared spectroscopy for investigation of glass structure has been well documented for numerous glass compositions<sup>34,35</sup>. In particular, the studies in the mid infrared region (~400-1700 cm<sup>-1</sup>) have proved valuable progress in determining the local structural arrangements constituting the borate glass network<sup>34-37</sup>.

For many years, the structure and properties of borate glasses have been studied because of their interesting and intriguing peculiarities. Among the facts which seem to be firmly supported by experimental data<sup>35-37</sup> are: (1) the presence in pure B<sub>2</sub>O<sub>3</sub> glass of boroxol rings and some isolated BO<sub>9</sub> triangles, (2) the conversion of the coordination number (CN) of boron from 3 to 4 and back under the effect of the modifier oxides.

The realization and interpretation of the IR spectra have been carried out in agreement with the concept adopted by Tarte<sup>38</sup> and Condrate<sup>39</sup> about the independent vibrations of different groups. From the infrared reflectance<sup>34-37</sup> and absorption<sup>6,24</sup> spectra of lithium borate glasses, it can be concluded that:

- (1) The observed IR absorption spectra of lithium diborate glasses are somewhat complex than the corresponding Raman spectra due to their extensively numerous overlapping bands.
- (2) Careful identification and comparison of the observed IR absorption bands with the published IR spectra of crystalline and glassy borates indicates that the obtained vibrations are virtually due to diborate, pentaborate and triborate groups. The studied base glass is the lithium diborate composition which is equivalent to about (0.33 Li<sub>2</sub>O.0.67 B<sub>2</sub>O<sub>3</sub>) in mol ratio. It is evident that the asymmetric stretching vibrations of tetrahedral borate (BO<sub>4</sub><sup>-</sup>) units are active in the 800-1200 cm<sup>-1</sup> range as evidenced by the quite appearance of the strong IR band in the wavelength range 1009-1016 cm<sup>-1</sup> together with a small peak at about 850 cm<sup>-1</sup>.
- (3) The high frequency absorption at (1350-1550) cm<sup>-1</sup> cannot easily be attributed to specific borate units, because most of the borate groups absorb in this region with various degrees. However, the modes of boron-oxygen triangular units (BO<sub>3</sub> and

BO<sub>2</sub>O<sup>-</sup>) are absorbing in the wavelength range 1200-1600 cm<sup>-1</sup> and specifically the IR absorption bands at about 1250, 1400, 1460, 1510, 1525 and 1638 cm<sup>-1</sup>.

- (4) The low-frequency region of the mid infrared (550-800) cm<sup>-1</sup> is dominated by the bending vibrations or deformation modes of various borate units and the quite strong band at about 673-686 cm<sup>-1</sup> represents this mode.
- (5) The far-infrared bands at about 405-420, 520 and 560 cm<sup>-1</sup> are correlated with lithium ions in two residing sites as bridging and non-bridging as deduced by Kamitsos<sup>37</sup>.
- (6) The rest of the IR bands induced by the base lithium diborate glass in the region from about 2400 to 4000 cm<sup>-1</sup> are generally correlated with the bands due to OH, water and B-OH vibrations as have been suggested by Doremus *et al.*<sup>41,42</sup> and other researchers<sup>6,24,40</sup>.
- (7) Concerning the effect of the introduction of WO<sub>3</sub> on IR spectra of WO<sub>3</sub>-doped lithium borate glasses it is evident from the IR data obtained and shown in Fig. 5 that no new separate bands could be identified until the maximum addition of WO<sub>3</sub> (10 wt%). Previous infrared absorption studies on WO<sub>3</sub>-doped glasses<sup>1-8</sup> showed that WO<sub>6</sub> units exhibit asymmetric vibrations in the range 900-950 cm<sup>-1</sup> while WO<sub>4</sub> units show asymmetric vibrations at about 880 cm<sup>-1</sup> while the asymmetric stretching of M-O-O bridges lies at about 630-640 cm<sup>-1</sup>. Experimental results reveal that the glass containing 5% WO<sub>3</sub> shows the relative growth of the band at about 916 cm<sup>-1</sup> which may be taken due to the quite appearance of WO<sub>6</sub> units in this composition in noticeable appreciable amounts. When more WO<sub>3</sub> content is added (10 wt %), the intensity of the band at 915 cm<sup>-1</sup> is in equivalence ratio to the band at about 855 cm<sup>-1</sup>.
- (8) All the prepared WO<sub>3</sub>-doped glasses are colourless which indicate the possible absence of W<sup>5+</sup> ions which are known to give bluish colour and observed in WO<sub>3</sub>-doped phosphate glasses<sup>33</sup>. The studied lithium diborate glass composition seems to favour the hexavalent tungsten W<sup>6+</sup> ions due to the presence of appreciable Li<sub>2</sub>O content. No indication is noticed of any IR bands due to W<sup>5+</sup> ions.
- (9) Maczka *et al.*<sup>43</sup> observed new very sharp IR bands at about 420 and 510 cm<sup>-1</sup> in tungsten glasses and



attributed them to  $W_4$  (of  $WO_6$ ) mode. However, the base undoped glass reveals a prominent band at  $410\text{ cm}^{-1}$  and two other peaks at about  $520$  and  $580\text{ cm}^{-1}$  and they are attributed by various researchers to be due to  $Li^+$  ions in different sites<sup>6,35,37</sup>. It seems that further work is needed to study lithium borate glasses containing high  $WO_3$  contents to justify this postulation.

Table 1 presents detailed IR bands and their assignments.

#### 4.5 Interpretation of Raman spectra

Raman spectroscopy is accepted to be as an analytical tool sensitive to the nearest local structure in glasses<sup>34</sup>. Like infrared spectroscopy, it is possible to attribute Raman vibrational modes to specific structural units or groups present in the glass network based on data from crystalline analogues.

The observed Raman peaks in base lithium diborate glass can be interpreted as follows:

- (a) The main Raman peaks at  $320\text{--}550\text{ cm}^{-1}$  can be attributed to tetrahedral borate groups mainly pentaborate and triborate groups<sup>44-47</sup>.
- (b) The main peak at about  $780\text{--}785\text{ cm}^{-1}$  is related to the presence of tetrahedral borate groups<sup>44-47</sup> (tri-tetra-, penta borate units) or generally three membered rings possessing one or more four-coordinated borons<sup>48</sup>.
- (c) The main peak at about  $955\text{--}970\text{ cm}^{-1}$  can be related to diborate groups<sup>45,47</sup>.
- (d) The other minor peaks can be related to
  - (i) The small peaks at about  $1100$  and  $1438\text{ cm}^{-1}$  are attributed to borate groups in tetrahedral coordination<sup>46,47</sup>.
  - (ii) The small peaks at about  $1834$  and  $2035$  can be related to hydroxyl related bands<sup>49</sup>.

When the introduced  $WO_3$  reaches 4%, a new additional Raman peak is induced at about  $721\text{ cm}^{-1}$  which can be assigned to symmetric stretching vibrations of W-O-W linkages suggesting the presence of tungsten as distorted  $WO_6$  octahedra<sup>1</sup> and the weak Raman peak at about  $349\text{ cm}^{-1}$  is assigned to bending vibration of  $WO_3$  groups which becomes prominent together with the two peaks at  $775$  and  $945\text{ cm}^{-1}$  which can be related to combined contribution of both tetrahedral borate groups and  $WO_6$  groups. Boudlich *et al.*<sup>8</sup> assumed that the Raman vibrations at  $340\text{ cm}^{-1}$  are attributed to W-O stretching associated with  $WO_4$  units. However, Poirier *et al.*<sup>1</sup> assumed that the Raman bands around

Table 1 — Assignments of the infrared absorption bands obtained from the studied undoped and  $WO_3$ -doped lithium diborate glasses

| Peak position ( $\text{cm}^{-1}$ ) | Assignments  |
|------------------------------------|--|
| Borate network                     |  |
| (a) $BO_3$ stretching              |  |
| 1652, 1523                         | B-O bonds  |
| 1460, 1390                         | B-O vibrations of various borate rings                             |
| 1145                               | pyroborate, diborate   |
| (b) $BO_4$ stretching              |  |
| 1008                               | Tri-, Penta-, tetraborate groups                                   |
| 899                                | Diborate, tetraborate units  |
| 850                                | Tri-, Penta-, and diborate   |
| (c) B-O-B bending                  |  |
| 774                                | Diborate groups  |
| 673                                | Oxygen bridges between one and one trigonal boron atom tetrahedral |
| (d) Metal ions( $Li^+$ )           |  |
| 586, 520                           | Vibrations of lithium cations                                      |
| 410                                | Vibrations of lithium cations                                      |
| (e) Other ions                     |  |
| 3855, 3745, 361                    | 8 B-OH   |
| 3450                               | Molecular water  |
| 2857                               | Hydrogen bending   |
| 2420                               | water or hydrogen bonding  |

$930$  and  $810\text{ cm}^{-1}$  in sodium tungstate cannot be assigned to stretching vibrations of  $WO_4$  units but are assumed to be due to asymmetric and symmetric vibrations of terminal W-O bonds, respectively. Sekiya *et al.*<sup>50</sup> previously suggested that the position of these Raman bands is independent of the tungsten coordination number and thus, does not allow to fully identifying the tungsten environment. It is obvious that further studies are needed to justify the proper assignments for Raman peaks in tungsten-containing glasses.

## 5 Conclusions

Induced defects generated in undoped and  $WO_3$ -doped lithium diborate glasses by gamma-ray irradiation were investigated. UV-visible spectra were measured for the prepared samples before and after each successive gamma dose of irradiation. The host base lithium diborate glass produces before gamma irradiation strong UV absorption which is related to the presence of trace iron impurity. Undoped and  $WO_3$ -doped glasses reveal numerous radiation-induced ultraviolet and visible spectra which are attributed to both intrinsic and extrinsic defects.

Infrared absorption spectra of undoped and WO<sub>3</sub>-doped samples indicate the presence of triangular and tetrahedral borate groups together with tungstate WO<sub>6</sub> groups.

Raman and ESR spectra support the assumption of the presence of tungsten in lithium diborate glass mainly as [W<sup>6+</sup>] or WO<sub>6</sub> groups.

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