Gamma ray interaction, crystallization and infrared absorption spectra of some glasses and glass-ceramics from the system \( \text{Li}_2\text{O}.\text{B}_2\text{O}_3.\text{Al}_2\text{O}_3 \)

H A El-Batal, F A Khalifa & M A Azooz
Glass Research Department, National Research Centre, Dokki, Cairo, Egypt

Received 23 January 2001; accepted 26 June 2001

The infrared absorption spectra of some selected ternary glasses and their glass-ceramic derivatives from the system \( \text{Li}_2\text{O}.\text{B}_2\text{O}_3.\text{Al}_2\text{O}_3 \) have been measured in the spectral range 200-4000 cm\(^{-1}\) before and after successive gamma rays irradiation. Vibrational and crystallization techniques are employed to investigate the structure and phases which are found in this system by controlled crystallization. The role of \( \text{Al}_2\text{O}_3 \) in the structure and the crystallization behaviour of the system has been discussed. The effect of gamma rays on the surface of the glasses and glass-ceramics as revealed from infrared spectroscopy is discussed.

1 Introduction

Glass-ceramics are materials prepared by the controlled crystallization of glasses and have a variety of established used dependent on their uniform reproducible fine-grain microstructures, absence of porosity and wide range properties which can be tailored by changes in composition and heat treatment.

Glass-ceramics are frequently produced by inducing volume nucleation in melt-derived bulk silicate glasses, usually by the addition of nucleating agents. More recently, glass-ceramic processing has been greatly extended to include non-silicate and even non-oxide compositions, and to include the preparation of the precursor glasses by sol-gel techniques. The established compositions and uses of glass-ceramics are extensive and include silicate compositions containing \( \text{Li}_2\text{O} \) and \( \text{Al}_2\text{O}_3 \) used in both transparent and opaque cooking ware, cooker range tops, heat-resistant windows and telescope mirror blanks. These aspects of applications are covered at length in various textbooks.

An interesting new ranges of glass-ceramics include phosphate-containing and aluminoborate-containing systems. The Lithia-boric oxide system is known for both ease of melting and crystallizing behaviour but shows poor chemical durability. Additions of oxides acting as network formers and modifiers can greatly improve the chemical and physical properties and enable glass-ceramics to be obtained having acceptable properties.

Vibrational and crystallization techniques were employed to investigate the structure and sequence of crystallization of glasses in the system \( \text{Li}_2\text{O} \), \( \text{B}_2\text{O}_3 \), and \( \text{Li}_2\text{O}.\text{B}_2\text{O}_3.\text{Al}_2\text{O}_3 \). Infrared spectra have been measured and analyzed in order to elucidate the role of \( \text{Al}_2\text{O}_3 \) in such glasses and in correlation between vibrational groups and variations in glass composition was made. X-ray analysis was also done to investigate the crystalline phases formed during thermal treatment conversion of the glasses to their corresponding glass-ceramics.

It was previously shown that gamma irradiation of glasses from the system \( \text{B}_2\text{O}_3.\text{SiO}_2.\text{BaO} \), progressively decreases with the intensity of the infrared absorption bands to a measurable extent. In the present investigation, the effect of progressive increasing gamma rays on the infrared spectra and of X-ray diffraction patterns of some selected glasses and their glass-ceramic derivatives from the ternary \( \text{Li}_2\text{O}.\text{B}_2\text{O}_3.\text{Al}_2\text{O}_3 \) system, was studied.

2. Experimental Details

2.1 Glass preparation

The parent glasses of the chemical compositions listed in Table 1 were prepared from melting chemical pure raw materials. Boric oxide was introduced as orthoboric acid \( (\text{H}_3\text{BO}_3) \), while lithium oxide was added in the form of anhydrous lithium...
carbonate. Alumina was added as pure calcined Al₂O₃. Melting was carried out in platinum 2 % Rh crucibles in an electrically-heated furnace at 1200 ± 20 °C. Melting was continued for 3 h after the last traces of batches and rotating of the melts was done to promote complete mixing and homogeneity. The melts were cast in rectangular stainless steel moulds 1 × 1 × 4 cm. The prepared glasses were transferred to be annealed in a muffle furnace regulated at 430 °C which was then left to cool to room temperature at a rate of 30 °C/h.

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Li₂O (wt %)</th>
<th>B₂O₃ (wt %)</th>
<th>Al₂O₃ (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>75</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>70</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>65</td>
<td>20</td>
</tr>
</tbody>
</table>

### 2.2 Process of conversion to glass ceramics
Controlled thermal heat treatment of the prepared glass samples was carried out in a controlled tube furnace. Each glass sample was subjected to two-steps heat treatment schedule. The determination of both the first nucleation and the second subsequent crystal growth temperatures was done by carrying differential thermal analysis (DTA). The data obtained from the exothermic peaks were used for heat-treatment regimes. The main objective in this heat-treatment is to achieve many nuclei growing to polycrystalline small crystals. It is accepted that the investigated Lithia-containing glass system can exhibit self-internal nucleation without the addition of any nucleating agents. The adopted procedure is believed to give satisfactory glass-ceramic products.

### 2.3 Infrared measurements
Infrared absorption spectra of powdered glasses and their glass-ceramic derivatives were measured before and just after gamma-rays irradiation in the range 200-4000 cm⁻¹ using the KBr technique at room temperature. A recording spectrometer type Jasco FT/IR – 300 E (Japan) was used. The ratio of the sample powder to KBr in the measured discs was 2:200.

### 2.4 X-ray investigations
Identification of crystalline phases was carried out by X-ray diffraction using a Philips powder camera (type CPM 9920/05), through the examination of fine powder of the glasses before and after thermal heat-treatment and the conversion to the corresponding glass-ceramics. Cu-K₀ radiation with Ni filter was used.

### 2.5 Gamma irradiation
An Indian ⁶₀Co gamma cell (2000 Ci) was used as a gamma-ray source with a dose rate of 1.50 Gy/s at a temperature of ≈ 30 °C. The investigated samples were placed in the γ-cell in a manner that each sample was subjected to the same gamma dose. By using a fricke dosemeter, 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.

### 3 Results
The experimental results can be summarized as follows:

#### 3.1 Infrared spectra of parent glasses
(i) The spectrum of glass no. 1 of the composition (15 wt % Li₂O-85 wt% B₂O₃) is illustrated in Fig. 1 and reveals five main absorption bands: one in near infrared at ~3200 cm⁻¹, one in the range (1200-1600 cm⁻¹), one in the range (800-1200 cm⁻¹), one at 700 cm⁻¹ and the last one in the far infrared in the range (200-500 cm⁻¹).
(ii) The intensity of the peaks at (1200-1600 cm⁻¹) is lower than the intensity of the peaks at (800-1200 cm⁻¹).
(iii) On replacing B₂O₃ by Al₂O₃, the splitting of the peaks at (1200-1600 cm⁻¹) and at (800-1200 cm⁻¹) is disappeared and the sharper peaks are overlapped and newly formed broad peaks are observed.
(iv) Also, on replacing B₂O₃ by Al₂O₃, the intensity of the peaks at (1200-1600 cm⁻¹) is increased than that at (800-1200 cm⁻¹) until the concentration of Al₂O₃ reached to 20 wt %.

(b) After irradiation:
Fig. 2 shows the effect of gamma irradiation on the infrared spectra of all the glasses under
The intensities of all the mid- and near-bands at 3200 cm\(^{-1}\), (1200-1600 cm\(^{-1}\)), (800-1200 cm\(^{-1}\)) and 700 cm\(^{-1}\) drastically decrease but the far infrared bands obviously remain sharp.

### 3.2 Infrared spectra of the glass-ceramic derivatives

#### (a) Before irradiation

All the absorption spectra which are previously obtained from the parent glasses before irradiation are repeatedly shown in the corresponding glass-ceramic derivatives (Fig. 3), except that the splitting of the peaks at (800-1200 cm\(^{-1}\)) 700 cm\(^{-1}\) and (200-500 cm\(^{-1}\)) remains with minor changes in their positions and intensities, while the peaks at (1200-1600 cm\(^{-1}\)) are overlapped as shown with parent glasses.

![Fig. 1 — IR absorption spectra of Li_2O.B_2O_3.Al_2O_3 glasses before irradiation](image1)

![Fig. 2 — IR absorption spectra of Li_2O.B_2O_3.Al_2O_3 glasses after irradiation](image2)

#### (b) After irradiation

The effect of increasing gamma-rays on the glass-ceramics is completely different from that on the parent glasses. Fig. 4 reveals that the action of gamma rays on the glass-ceramic derivatives which results in the same number and identity of the absorption bands with minor change. The intensities of the absorption bands at (1200-1600 cm\(^{-1}\)), at (800-1200 cm\(^{-1}\)) and at 700 cm\(^{-1}\) are shown to be slightly increase after irradiation by gamma rays but the positions of all bands remain unchanged. In brief, successive gamma rays irradiation on this type of glass-ceramic system have not introduced any new absorption bands or cause marked changes of the spectra as it is observed in the case of the base parent glass.

Figs 5 and 6 depict the X-ray diffraction patterns obtained from the glass-ceramic derivatives before
and after being subjected to gamma-rays irradiation. The results indicate that the main phases separated on controlled crystallization are lithium borate of the formula LiB₂O₃ (card index 32-549) and lithium diborate (Li₂O·2B₂O₃) card index (18-717).

simplified especially in the range of 2θ from 20 to 50 where it can be observed that the diffraction peaks which are very close in position of both the two phases are replaced by the diffraction peaks of the lithium diborate phase alone.

Fig. 3—IR absorption spectra of Li₂O·B₂O₃·Al₂O₃ glass-ceramics before irradiation

Before the introduction of Al₂O₃, the two phases are almost apparent in equal ratio but on increasing the Al₂O₃ in replacement of B₂O₃, the diborate phase becomes more prominent and the other phase progressively decreases in intensity. Fig. 6 illustrates that gamma irradiation does not produce any noticeable effect on both the type or intensity of the phases precipitated in the glass-ceramic derivatives.

Also, it is apparent that on increasing the Al₂O₃ content, the X-ray diffraction patterns become more

Fig. 4—IR absorption spectra of Li₂O·B₂O₃·Al₂O₃ glass-ceramics after irradiation

On increasing the Al₂O₃ content, a new crystallize phase (beta-Li₂B₂O₅) is observed, and in this phase the ratio of Li: B is higher than the ratio of the diborate phase.

4 Discussion

It is found helpful to introduce summary of the structure and arrangement of the structural groups in the parent cabal glass to understand the significance and correlation between infrared spectroscopy and structure. Boroaluminate glasses are generally...
assumed to consist of random networks formed by oxygens bridging two network-forming cations namely, B" or Al". Most glass structural models\textsuperscript{8,13} assume that in pure B\textsubscript{2}O\textsubscript{3} glass, all boron is present in neutral sites in which B" is coordinated to three oxygens. Recent studies\textsuperscript{2,14} indicate that B\textsubscript{2}O\textsubscript{3} glass consists mainly of boroxyl groups in the ratio (87 %) and the rest is existing as free BO\textsubscript{3} groups. As modifier cations such as alkali or alkaline earth cations are added, it is assumed that all modifiers are charge compensated by the creation of ionic, tetrahedrally coordinated boron sites at low modifier contents and by the formation of non-bridging oxygens at higher modifier contents. For Al-containing glasses, it is generally believed that Al in neutral sites is 6-coordinate, whereas anionic Al sites (charge compensated by modifier cations) and are all 4-coordinated.

![Fig. 5 - XRD of Li\textsubscript{2}O-B\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} glass-ceramics before irradiation](image)

![Fig. 6 - XRD of Li\textsubscript{2}O-B\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} glass-ceramics after irradiation](image)

The oxygen ions donated by Lithia (in the present Li\textsubscript{2}O-B\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} system) will be largely claimed by the Al" and B" ions. Most or all of the alumina present is previously assumed\textsuperscript{10,11} to be present as Al\textsubscript{2}O\textsubscript{3} tetrahedra, and some of the boron ions become tetrahedrally coordinated till one fifth of the boron ions have formed tetrahedral groups, with the rest of the boron in three-fold coordination.

With more Lithia introduced than is required for the four-coordination of aluminium ions and the permissible part of the boron ions, the excess Lithia will create non-bridging oxygens. The portion of non-bridging oxygen would certainly be expected to increase with the Lithia content. De Waal\textsuperscript{14} suggested that not all the aluminium ions in aluminoborate glasses were in four-fold coordination with bridging oxygen ions. The dilemma about the “lodging” of alumina in glass...
could be solved by assuming the occurrence of tricliners, as proposed by Lacy\textsuperscript{15} who pointed out that in glasses with a low number of non bridging ions, some of the aluminium ions might be surrounded by three bridging oxygen ions and one "tripod" or "inactive" oxygen ion, touching three network-forming cations instead of two. The excess oxygen ions, resulting from these structural units may be used partly to form BO\textsubscript{4} groups and partly to raise the number of non-bridging oxygen ions.

Bunker et al.\textsuperscript{16} assumed that Al may exist in 5-coordination like in crystals beside the 4- and 6-coordinated aluminium.

4.1 Contribution of the infrared spectra

It is evident that by obtained infrared absorption spectra appear more complex due to their close and overlapping bands. The vibrational modes of the binary lithium borate glass are seen to be mainly active in three infrared spectra regions which are similar to those reported previously by several workers\textsuperscript{17-19}. The first one can be attributed to be due to the vibrations of OH groups or water and lies\textsuperscript{20} in the region 3000-3200 cm\textsuperscript{-1}. The second set of bands may be related to the vibrations of the borate network, and their absorption peaks are located\textsuperscript{21} at (1200-1600 cm\textsuperscript{-1}), (800-1200 cm\textsuperscript{-1}) and at 700 cm\textsuperscript{-1}. The third one which is located in the far infrared region may be assigned to be due to the vibrations of the alkali cations located\textsuperscript{22} in interstitial position (Li\textsuperscript{+} cations in this work).

The intensities of the bands which lie in the region (1200-1600 cm\textsuperscript{-1}) are observed to be less than the intensities of the bands located at the region (800-1200 cm\textsuperscript{-1}). This observation confirms with that obtained in previous literature\textsuperscript{18,20} where the bands at (1200-1600 cm\textsuperscript{-1}) are assigned to be due to the stretching vibration of the BO\textsubscript{4} groups and the bands at (800-1200 cm\textsuperscript{-1}) are related to the stretching vibration of the BO\textsubscript{3} groups. In the glass system studied, the concentration of the alkali cations (Li\textsuperscript{+} ions) is enough to satisfy the formation of the maximum BO\textsubscript{4} groups permissible in this glass system.

On replacing B-O by Al-O, the intensities of the absorption bands at (1200-1600 cm\textsuperscript{-1}) begin to increase more than the intensities of the absorption bands at (800-1200 cm\textsuperscript{-1}). This can be rationalized by considering that Al-O, is assumed to enter in the glass network mainly as both AlO\textsubscript{4} tetrahedral in modifying positions and also as AlO\textsubscript{4} tetrahedral groups by obtaining the excess oxygen from Lithia in preference to the formation of BO\textsubscript{4} groups.

It can be assumed that the vibrations of AlO\textsubscript{4} and AlO\textsubscript{3} groups lie in the (500-680 cm\textsuperscript{-1}) and 775 cm\textsuperscript{-1} respectively\textsuperscript{23} and their locations are close to the positions due to the borate groups composing the main network building units.

On increasing AlO\textsubscript{4} in replacement of B-O, while the concentration of Li\textsubscript{2}O remains constant, leads to a situation that the amount of BO\textsubscript{4} is reduced because alumina consumes the available oxygen ions from Li\textsubscript{2}O and the concentration of BO\textsubscript{3} slightly increases, but the overall B-O content decreases.

The absorption bands due to AlO\textsubscript{4} or AlO\textsubscript{3} groups are located in the same positions as the position of borate groups.

4.2 Crystallization behaviour in borate glasses

The crystallization behaviour of the glasses in the system Li\textsubscript{2}O-B\textsubscript{2}O\textsubscript{3} was shown by Sastry and Hummer\textsuperscript{24} to proceed mainly in accordance with the phase diagram. Inspection of the diagram reveals that lithium diborate and lithium metaborate phases will form at all temperatures. Studies on the sequences of crystalline phase formation have indicated\textsuperscript{25} that the processes are sensitive to temperature, thermal history, and batch composition. It was shown\textsuperscript{26} that there was no evidence for metastable phase separation, even for the rapidly cooled samples. The phases were produced are those corresponding to the equilibrium phase diagram. The relative amounts of the two phases which formed, namely, lithium metaborate and lithium diborate, reflect the thermal histories as well as the differing crystallization rates of the two crystalline species.

Chryssikos et al.\textsuperscript{26} had studied, by spectroscopic techniques the crystallization of glassy lithium metaborate and revealed the formation of three different lithium metaborate polymorphs. The networks are found to consist of BO\textsubscript{3} triangles in chain configuration (α-LiBO\textsubscript{3}), of alternating BO\textsubscript{2} triangles and BO\textsubscript{3} tetrahedral (β-LiBO\textsubscript{3}), or solely of BO\textsubscript{2} tetrahedral (γ-LiBO\textsubscript{3}). All three compounds are kinetically stable at ambient conditions, but undergo very solid transformations of reconstructive nature at higher temperatures.
4.3 Contribution of the crystallization data

The data obtained from X-ray diffraction investigation of the base lithium borate glass-ceramic indicate that the main phases separated on controlled crystallization are microcrystalline species of lithium borate of the formula \( \text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3 \) and \( \text{LiB}_2\text{O}_4 \) with equal ratio. This result is quietly expected with the lithium diborate phase. The appearance of the phase \( \text{LiB}_2\text{O}_4 \) (with the ratio \( \text{Li}_2\text{O} : \text{B}_2\text{O}_3 = 1:1.5 \)) instead of the lithium metaborate (with ratio 1:1) might be due to the specific studied glass composition and conditions of heat-treatment schedule. To interpret the observation that on introducing \( \text{Al}_2\text{O}_3 \), the diborate phase becomes the dominant one, it can be assumed that detailed crystallization studies of lithium borate glasses have reached the conclusion that at least a small amount of diborate phase is formed first when heated from below. The other \( \text{LiB}_2\text{O}_4 \) phase may be considered as metastable one.

The appearance of a new phase of the formula (beta-\( \text{Li}_2\text{B}_2\text{O}_4 \)) with the further addition of \( \text{Al}_2\text{O}_3 \) can be interpreted by assuming that the replacement of \( \text{B}_2\text{O}_3 \) by \( \text{Al}_2\text{O}_3 \) results in the decrease of the total \( \text{B}_2\text{O}_3 \) content in the parent glass. Controlled thermal crystallization of such glass is hence expected to give a crystalline phase with the ratio of \( \text{Li}_2\text{O} : \text{B}_2\text{O}_3 \) to be higher than the ratio of the diborate.

4.4 Effect of radiation on glasses

It has been established that when subjected to ionizing radiation, most glasses acquire radiation-induced defects. Radiation may cause the displacement of lattice atoms or cause electron defects which involve changes in the valence state of lattice or impurity atoms. The displacement of one atom creates a point which is the simplest disturbance of the lattice. It is possible to produce groups of vacancies by prolonged irradiation and usually the atom that left its lattice site will lie settled in an interstitial position if it does not mount to the surface. Irradiation may also cause what are called thermal and displacement of network spikes including a sequences of decreasing the bond angles of network forming cations and oxygens are described by Primak. However, the expected resultant effects of radiation on glasses have been summarized by Friebele to fall into three categories: (1) atomic displacement by momentum and energy transfer, (2) ionization and charge trapping, and (3) radiolytic or photochemical effects. The obvious effect of irradiation usually results in the occurrence of all three processes (or at least in the second and third); the relative contribution to the net damage depends on the type and energy of the radiation, as well as on the total dose. Griscom has summarized that there are three possible boron-oxygen hole centers in alkali borate glasses beside two other generic defect types which appear to be of the trapped electron type.

Bake and Kinser and Ruller and Friebele studied the radiation-induced changes in density of different silicas, both natural and synthetic and reported much more complex behaviour, consisting of both expansion and compaction. These results were demonstrated to depend in part in their fabrication technique, impurity and OH contents.

Radiation-induced expansion may include hole trapping by bridging oxygen causing the Al-O bond to increase, and also radiolytic electrons and holes can be trapped by Si-OH. Radiation compaction may include displacements, electronic defects and/or breaks in the Si-O-Si bonds, which allow the structure to relax and fill the relatively large interstices that exist in the interconnected network between glass-forming cation and oxygen atoms causing compaction.

4.5 Contribution of the effect of gamma irradiation

To explain the different effect of gamma rays on crystalline glass-ceramic derivatives than their effect on the parent glass, it can be assumed that glass-ceramics are characterized by having polycrystalline texture with well-defined microcrystals. It seems that the microcrystals are closely packed in their arrangements and the mutual bonding is so strong to give the expected superior chemical and physical properties of the glass-ceramic derivatives. The resultant effect due to gamma rays is not sufficient to cause marked changes in bond angles or bond lengths of the fully crystalline closely packed microcrystals in the glass ceramic. It can be suggested that the bond strengths in the already random network in glasses are believed to be some what weak to be affected or overcome by the resultant energy due to gamma irradiation. Another postulation can be advanced which suggested that gamma rays radiation causes some disruption of the already distorted or random
network and the group arrangement becomes more unsymmetrical leading to the possible weakness of the network grouping vibrations and this explains the observation that the characteristic absorption peaks are progressively diminished in their intensities with prolonged gamma rays irradiation. The present experimental results on glasses from the system Li₂O.B₂O₅.Ai₂O₃.SiO₂ systems or conformed or goes parallel to the previous results obtained by some of the present authors on the BaO.B₂O₅.SiO₂ system.

Several authors had shown that for lower gamma-irradiation the superconductivity properties of ceramic superconductors are improved and this was ascribed to the ability of ionizing radiation to stimulate some equilibrium ordering in the irradiated crystal lattice. At higher dose, the observed change could be related to the destruction of chains and that the superconducting properties must be influenced by a long-range interaction phenomenon.

However, in the present work, progressive gamma rays irradiation continuously decreases the intensity of the absorption bands of the glasses but the fully crystalline glass-ceramic derivatives have retained their intensity with variation of gamma dose.

The exact detailed defects or radiation damage is not clear by this work and it is born in mind that these effects are temporary and can be recovered by thermal treatment and/or bleaching of the formed induced defects. Further work is still needed to judge about the extent of damage processes and whether it only involves more disruption of the network or changes of bond angles or bond lengths.

References


