Ceramics International **21** (1995) 159–167

Crystallization Characteristics of Some Lithia Calcia Magnesia Borosilicate Glasses

Samia N. Salama, S. M. Salman & Hussein Darwish

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

(Received 4 January 1994; accepted 9 March 1994)

Abstract: The crystallization process of the glasses based on the lithium–borosilicate system containing CaO and/or MgO has been investigated by X-ray diffractometry, DTA and scanning electron microscopy (SEM).

Lithium metasilicate was formed as a major phase constituent during the crystallization of the glasses. However, lithium disilicate and α-quartz were crystallized as well. On the addition of CaO at the expense of B_2O_3, calcium silicate (wollastonite) and calcium borate were crystallized together with varieties of lithium borate phases including lithium diborate, lithium tetraborate and lithium pyroborate, which were mostly formed as functions of the CaO/B_2O_3 and Li_2O/B_2O_3 ratios in the glasses, as well as the heat treatment applied. Pyroxene phase of diopsidic [$CaMgSi_2O_6$] type was also formed due to the replacement of CaO and MgO instead of B_2O_3 and Li_2O, respectively.

The role played by the glass oxide constituents in determining the crystallization characteristics of the glasses, as well as the conditions at which the crystallized phase assemblages were formed, are discussed.

1 INTRODUCTION

Glass-ceramic materials are interesting solid substances that are especially useful, due to their exceptional technical parameters, including a wide range of unusual combinations of properties.[1] Recently, a new technique for preparing glass-ceramics with an oriented polar phase has been investigated with the objective of fabricating inexpensive large area sensor elements for application in pyroelectric detectors, compared with ferroelectric single crystals and PZT ceramics.[2]

Borate-based glass compositions containing large concentrations of R_2O (e.g. Li_2O) are of potential technological importance due to their fast ionic conductivity.[3] The conductivity of these phases is greatly enhanced as the alkali concentration is increased.[4] Lithium borate glasses are of particular interest because it has been found that they can form over a very broad range of Li_2O/B_2O_3 ratio.[5] Lithium borate compositions could be used for containerless processing in microgravity experiments.[6]

A number of studies[7] have also shown that the properties of some alkali-borosilicate glasses can be improved substantially by choosing the optimum composition of glass and using suitable heat treatments, causing phase separation with the formation of conducting chemically unstable phase enclosed in drops and a high-silica matrix. It has been shown[7] that low alkali-borosilicate glass have a good ensemble of the most valuable physico-chemical properties. Their high electrical resistivity, low dielectric loss, and increased chemical stability are due to the localization of the alkali-borate phase enclosed region surrounded primarily by a high-silica matrix.

Extensive research is reported on the crystallization process of alkali-borosilicate glass systems. However, the reported data concerning the role played by CaO and/or MgO in glass-ceramic formation based on lithium borosilicate glasses are relatively scarce.[7]

Therefore, in the light of the above features, lithium borosilicate glasses containing various proportions of CaO and/or MgO could be potential candidate compositions to obtain glass-ceramics. It was the objective of this work to provide a qualitative examination of the crystallization characteristic of Li_2O (MgO)–B_2O_3 (CaO)–SiO_2 glass. Emphasis was placed upon the study of the crystallization-temperature process, the temporal sequence and nature of the crystal phase formation, as well as the microstructure developed in relation to the glass oxide constituents and heating conditions.

2 EXPERIMENTAL

2.1 Glass composition and preparation

Glasses of composition expressed in the following formula were prepared: $(33{\cdot}33\text{-}X)Li_2O\text{–}XMgO\text{–}(28{\cdot}04\text{–}Y)B_2O_3\text{–}YCaO\text{–}38{\cdot}63\ SiO_2$ mol%, where $X = 0$, 12 and $Y = 0$, 4, 8, 12 and 16 were chosen in the present study. The effect of CaO replacing B_2O_3 and/or MgO replacing Li_2O were considered. The glass batches were prepared from acid-washed pulverized quartz sand, and Analar grade Li_2O_3, H_3BO_3, $MgCO_3$ and $CaCO_3$ were used as starting materials. The weighed batch materials were melted in a Pt–2% Rh crucible, covered with Pt foil to minimize the evaporation, in an electric furnace, with an SiC heating element, at 1200°C for 3 h. The homogeneity of the melt was achieved by swirling the melt-containing crucible several times at about 20 min intervals. The melt was cast into rods and as buttons which were then properly annealed in a muffle furnace to minimize the strain.

2.2 Differential thermal analysis

The thermal behaviour of the glasses was followed using the DTA technique. A weighed amount of the sample, in powder form, was heated in the DTA apparatus of Shimadzu type against the same amount of Al_2O_3 standard. A uniform rate of heating of 20°C/min was adopted up to the appropriate temperature of the glasses.

2.3 Heat treatment

The glasses were heated according to the DTA data. At the endothermic temperature of each glass composition, the glass sample was soaked for 3 h, and then the temperature was raised up to the exothermic temperature recorded on the DTA of each glass for 20 h. In some cases, however, the glasses were heated through single step heat treatment in the 550–600°C temperature range for 10 h.

2.4 Material investigation

To investigate the crystallizing samples, the powder X-ray diffraction patterns were obtained using a Philips-type diffractometer (P.W. 1730) with Ni-filtered Cu-radiation. The crystallization characteristics and internal microstructures of the resultant materials were examined by scanning electron microscopy (SEM), where representative electron micrographs were obtained using a Semco-Nanolab 7-scanning electron microscope.

3 RESULTS

3.1 Differential thermal analysis

The DTA traces of the glasses (Fig. 1) showed endothermic effects in the 480–595°C temperature

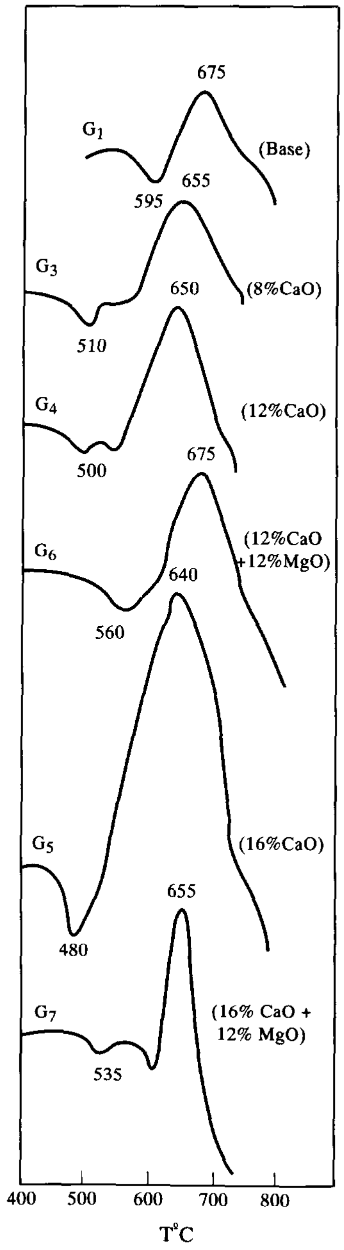

Fig. 1. DTA of the studied glasses.

range. These endothermic effects are to be attributed to the glass transition, at which the atoms begin to arrange themselves in preliminary structural elements subsequent to crystallization. Various exothermic effects in the 640–675°C temperature range, indicating crystallization reaction in the glasses, are also recorded.

3.2 Crystallization characteristics

The progress of crystallization in the glasses, the type and proportions of the resulting crystalline phase assemblages were markedly dependent on the variation of the glass oxide constituents, the extent of CaO/B_2O_3 and MgO/Li_2O replacements, as well as the effect of thermal treatment.

The DTA data (Fig. 1) revealed that the addition of CaO instead of B_2O_3 led to a shift, both of the endothermic dips and the onset of crystallization exotherms to lower temperatures (e.g. G_1–G_5). However, the MgO/Li_2O replacement moved the endothermic dips and exothermic peak towards higher temperature (e.g. G_4–G_7).

SEM micrographs of fractured surfaces (Figs 2–5) showed the crystallization characteristics and microstructures of the crystallizing glasses from which it is seen that fine feathery growths were developed in the sample of G_1, with some glassy phase

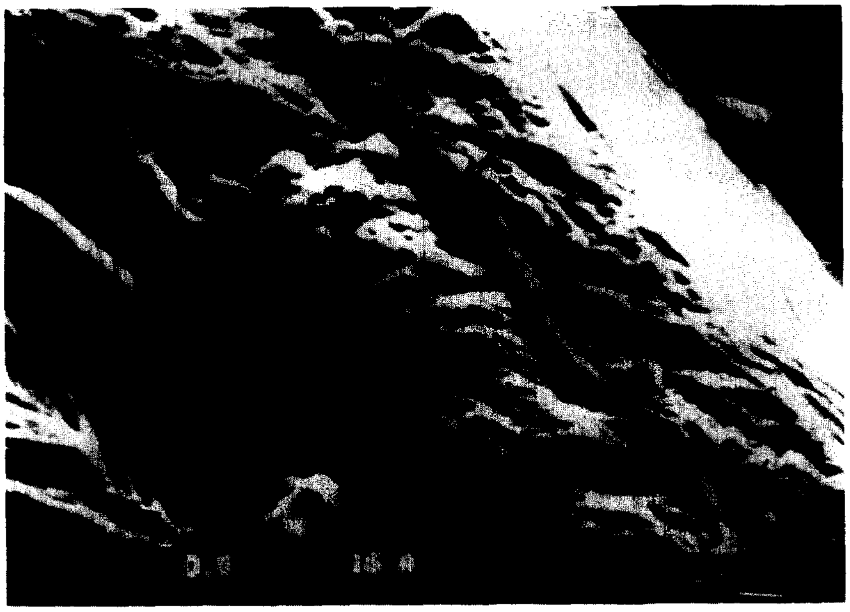

Fig. 2. SEM micrograph of the fractured surface of G_1, crystallized at 680°C/30 h, showing feathery-like growths of lithium disilicate, lithium diborate, lithium metasilicate and α-quartz, with some glassy matrix in between (bar = 2 μm).

Fig. 3. SEM micrograph of the fractured surface of G_4 (12% CaO), crystallized at 650°C/30 h, showing numerous prismatic growths of lithium metasilicate, calcium silicate and tiny growths of calcium borate, α-quartz, lithium tetraborate with a minor amount of lithium disilicate phase (bar = 2 μm).

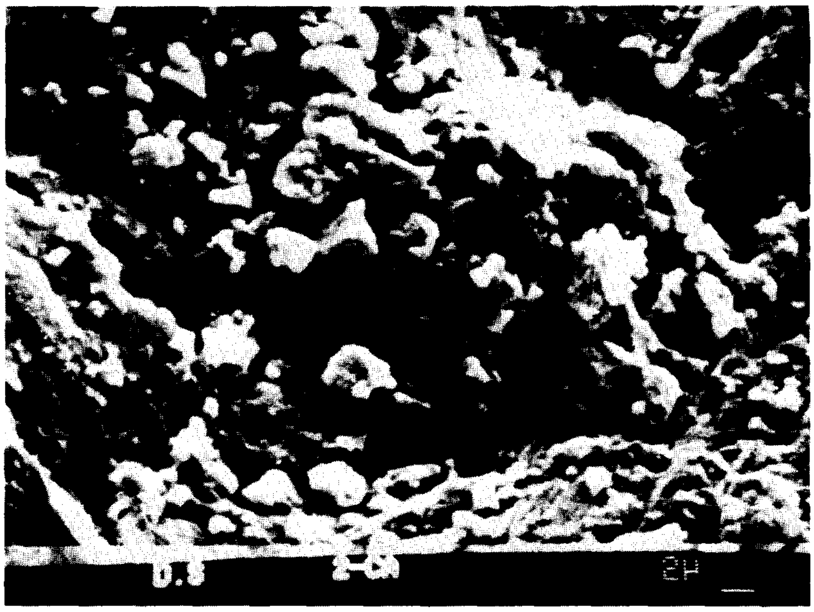

Fig. 4. SEM micrograph of the fractured surface of G_5 (16% CaO), crystallized at 640°C/30 h, showing rounded growths with some fine fibrous and tiny aggregates of lithium metasilicate, calcium silicate and calcium borate phases (bar = 2μm).

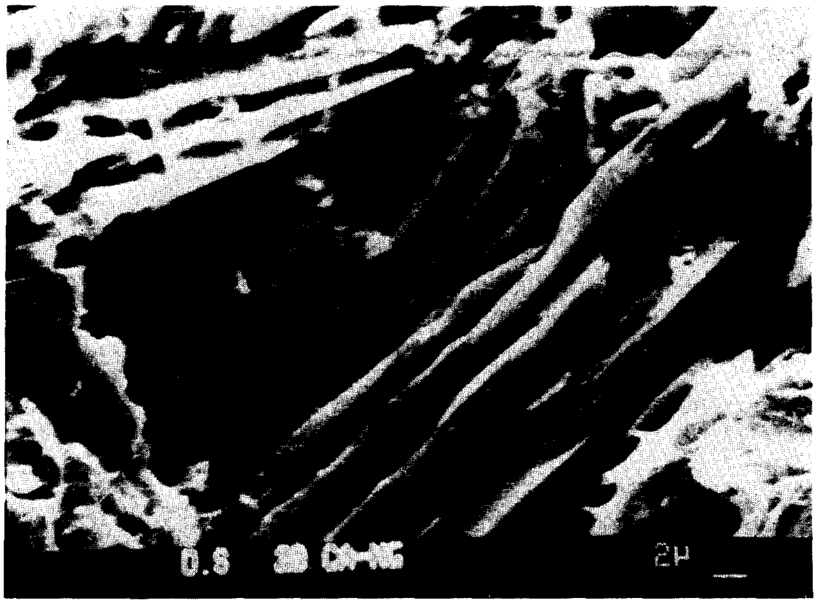

Fig. 5. SEM micrograph of the fractured surface of G_7 (with 16% CaO, 12% MgO), crystallized at 660°C/30 h, showing a well developed prismatic microstructure of lithium metasilicate and diopside, with intergrowths of lithium tetraborate and lithium pyroborate (bar = 2 μm).

(Fig. 2). The crystallization proceeded inwards, without great difficulty, on CaO/B_2O_3 replacement, exhibiting a microstructure of numerous prismatic and tiny growths in the sample of G_4 (Fig. 3), while rounded and tiny aggregates were developed in the sample of G_5 (Fig. 4). A well-developed prismatic microstructure was developed in glasses modified by MgO/Li_2O replacement (e.g. G_7, Fig. 5).

3.2.1 Effect of CaO/B_2O_3 replacements

The X-ray analysis (Fig. 6, Pattern I) revealed that lithium disilicate [$Li_2Si_2O_5$] (lines 5·46, 3·76, 3·67, 3·58 Card No. 17–447), lithium diborate [$Li_2B_4O_7$] (lines 4·09, 3·50, 2·60 Card No. 22–1140) with minor amounts of lithium metasilicate [Li_2SiO_3] (lines 4·74, 3·32, 2·72 Card No. 4–0273) and α-quartz (lines 4·28, 3·36 Card No. 5–0490) were formed in the crystallizing glass of G_1 (free of CaO). However, on the addition of CaO instead of B_2O_3 (i.e. G_2–G_5 Patterns II–V), the lithium metasilicate was increased, while the disilicate decreased, and various amounts of lithium borate phases, including lithium diborate, lithium tetraborate [$Li_2B_8O_{13}$] (lines 5·82, 4·48, 2·23 Card No. 11–537) and lithium pyroborate [α-$Li_4B_2O_5$] (lines 3·31, 3·22, 2·96 Card No. 18–719), were also crystallized, together with wollastonite [$CaSiO_3$] (lines 3·51, 3·31, 2·99 Card No. 29–372) and calcium borate [CaB_2O_5] (lines 5·82, 3·36, 3·03 Card No. 18–281). These are significantly related to the CaO/B_2O_3 and Li_2O/B_2O_3 ratios present in the glasses and the effect of thermal treatment. Table 1 exhibits a summary of the crystalline phases formed in the glasses.

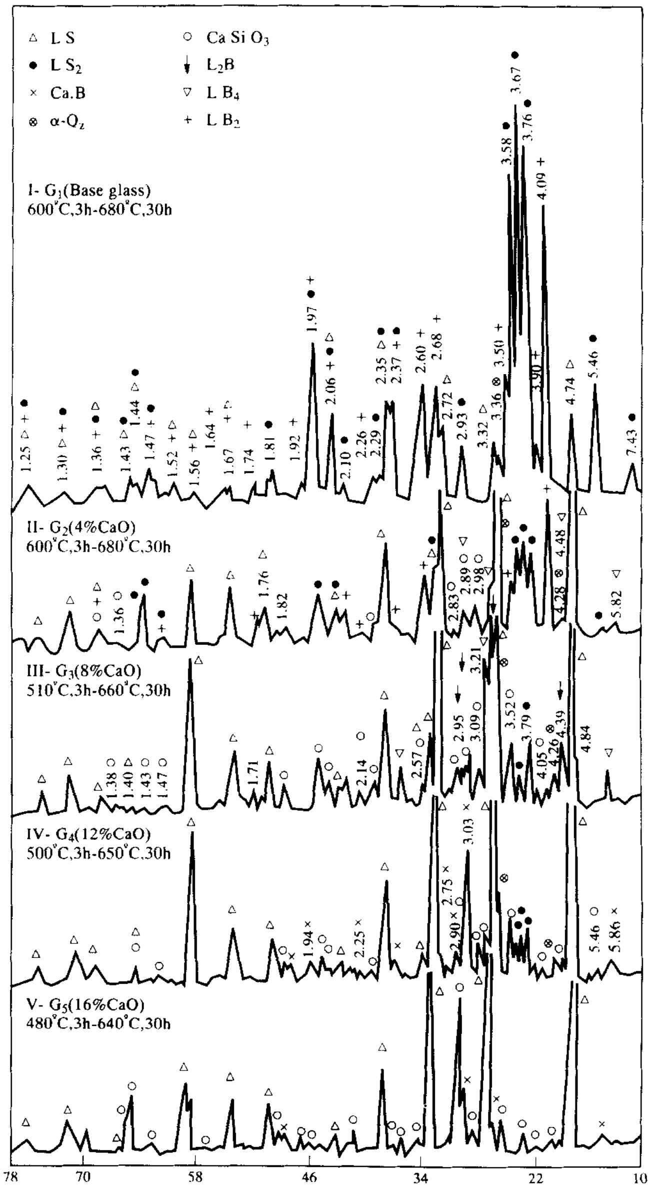

Fig. 6. XRD of crystallized glasses of various CaO/B_2O_3 replacements.

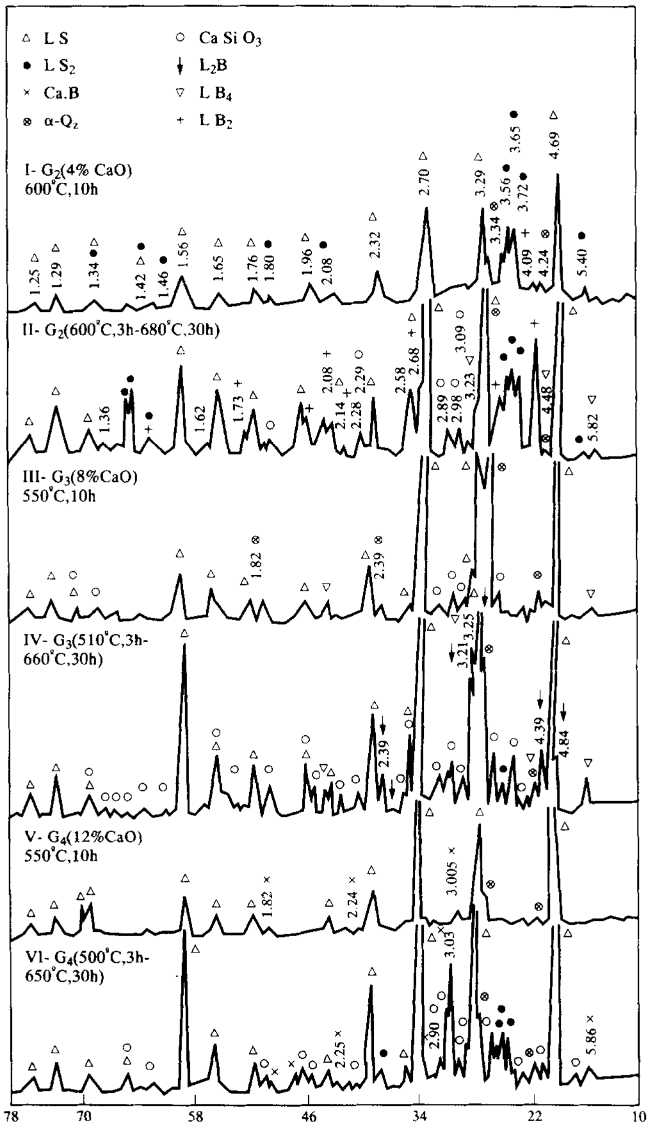

Fig. 7. XRD of some CaO/B_2O_3 glasses crystallized at different temperatures.

Table 1. Crystalline phases formed in the glasses

Glass no.	CaO% (mole%)	MgO% (mole%)	Heat treatment (°C/h)	Crystalline phases
Base	—	—	600/3:680/30	LS_2, LB_2, LS, α-Qz (m)
2	4	—	600/10	LS, LS_2, Qz (traces), LB_2 (trace)
2	4	—	600/3:680/30	LS, LB_2, LS_2, $CaSiO_3$, Qz, LB_4 (m)
3	8	—	550/10	LS, Qz, LB_4, LS_2 (traces), CaSiO (m)
3	8	—	510/3:660/30	LS, LB_4, L_2B, Qz, $CaSiO_3LS_2$ (m)
4	12	—	550/10	LS, α-Qz, $CaO.B_2O_3$ (m)
4	12	—	500/3:650/30	LS, $CaO.B_2O_3$, $CaSiO_3$, α-Qz, LB_4, LS_2 (m)
5	16	—	480/3:640/30	LS, $CaSiO_3$, $CaO.B_2O_3$
6	12	12	570/3:680/30	LS, Di, LB_2, α-Qz
7	16	12	540/3:660/30	LS, Di, LB_4, L_2B

LS_2 = lithium disilicate [$Li_2Si_2O_5$]; LB_2 = lithium diborate [$Li_2B_4O_7$]; LS = lithium metasilicate [Li_2SiO_3]; LB_4 = lithium tetraborate [$Li_2B_8O_{13}$]; L_2B = lithium pyroborate [α-$2Li_2O.B_2O_3$]; α-Qz = α-quartz; Di = diopside [$CaMgSi_2O_6$]; m = minor.

Detailed study of the effect of thermal treatment on the glasses, by the X-ray analysis (Fig. 7), indicated that glass 2 crystallized at 600°C for 10 h to give lithium metasilicate, lithium disilicate, α-quartz and traces of lithium diborate. However, heating at 680°C for 30 h, the crystallinity increased greatly and lithium tetraborate [$Li_2O{\cdot}4B_2O_3$] also crystallized (Patterns I & II). The crystallization of glass 3 at 550°C for 10 h led to the formation of predominant lithium metasilicate, α-quartz, lithium tetraborate [$Li_2O.4B_2O_3$], traces of lithium disilicate and wollastonite. On prolonged heating at 660°C for 30 h lithium pyroborate [α-$2Li_2O.B_2O_3$] was also formed (Patterns III & IV). Glass 4 crystallized at 550°C for 10 h to given lithium metasilicate together with α-quartz and a minor phase of calcium metaborate (Pattern V). However, at 650°C for 30 h the crystallinity was markedly increased with the appearance of calcium silicate (wollastonite) and a minor phase of lithium disilicate and lithium tetraborate (Pattern VI).

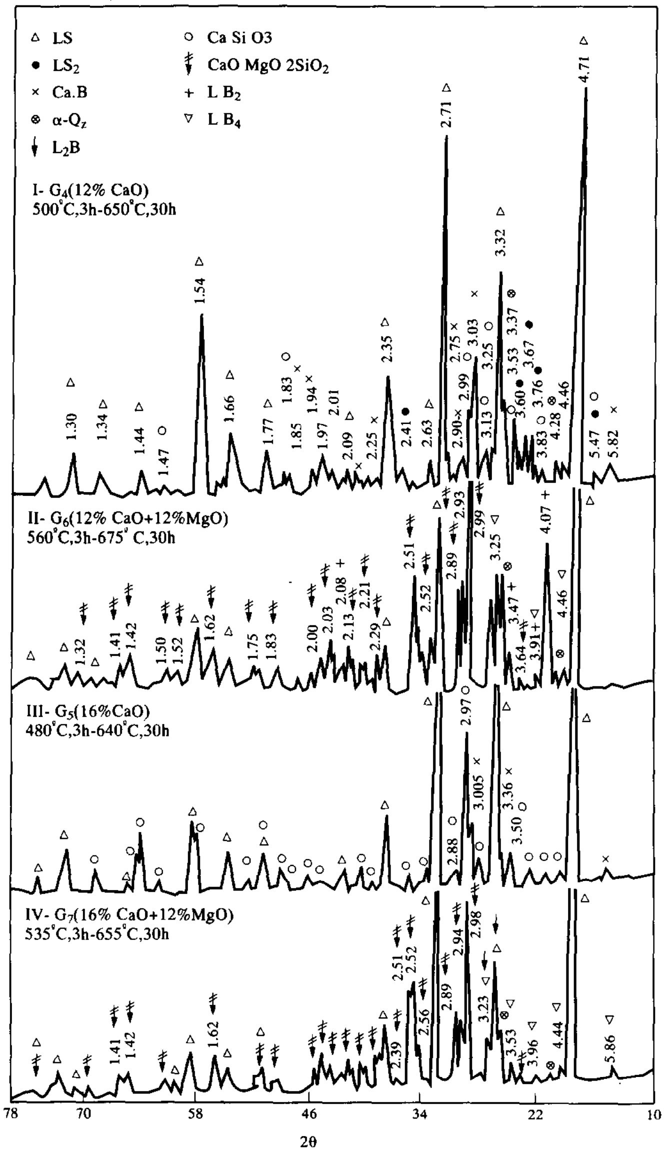

Fig. 8. XRD of crystallized glasses of various CaO/B_2O_3 and MgO/Li_2O replacements.

3.2.2 The combined effect of CaO/B_2O_3 and MgO/Li_2O replacements

The X-ray analysis (Fig. 8) revealed that glass 6 (with 12 mol% CaO+12 mol% MgO) was composed of lithium metasilicate together with diopside [$CaMgSi_2O_6$] (lines 3·21, 2·99, 289, 2·52, 2·51 Card No. 11–654), lithium diborate and a minor phase of α-quartz (Pattern I). However glass 7 (with 16 mol% CaO + 12 mol% MgO) crystallized into metasilicate, diopside with minor phases of lithium tetraborate [$Li_2O.4B_2O_3$] and lithium pyroborate [$Li_4B_2O_5$] (Pattern II).

4 DISCUSSION

4.1 Effect of CaO/B_2O_3 replacement

The addition of CaO instead of B_2O_3 in the present lithia–borosilicate glass decreases the temperature at which the crystallization begins. The DTA results give evidence that the crystallization of the glass was remarkably improved by CaO/B_2O_3 replacement. Both the endothermic dips and the onset of the crystallization exotherms were shifted to lower temperatures by adding CaO instead of B_2O_3, i.e. a lower energy is needed to induce crystallization in the glasses.

It was reported[8] that CaO and MgO modify the properties of alkali-borosilicate glasses in a manner different from that observed with binary alkali-silicates. In all CaO-, as well as MgO-, containing glasses, opalisation after the cooling of molten glass was observed, whereas the basic glass showed no such tendency. The effect of modifying oxides on this property was found to be in the order CaO > MgO > BaO > ZnO.

In borate glass-containing calcium, the B^{3+} ions may exist as BO_3 triangles, or as BO_4 tetrahedra, as well as boroxol groups.[9] The Ca^{2+} cations may exist partly as bridges between the structural building units and partly enclosed within the available interstices. Nukulin *et al.* showed[7] that the oxides CaO or ZnO introduced into alkali-borosilicate glasses have a pronounced effect on their liquation capability. Glasses with addition of 0·25–0·5% CaO liquate much more rapidly. Experimental opacification of the CaO glass samples by thermal treatment at temperatures as low as 550°C was easily observed. The fact that even with a small addition of, for example, calcium, barium to the B_2O_3–SiO_2 miscibility gap occurred in which a separation into a SiO_2-rich and a borate phase, rich in the added cation, took place and also that segregation zones were present in the alkali-borosilicate glass system. The introduction of these cations into the B_2O_3–SiO_2 glasses reduces the melting temperature and viscosity promoting phase separation, which in the ternary calcium– or barium–borosilicate system is already present in the melt and which in the alkali-borosilicate system can be produced by tempering.[10]

Considering the above mentioned basis, the opacification property was easily developed in the heat-treated samples and consequently the crystallization of the glass becomes more apparent by the addition of CaO instead of B_2O_3.

Lithium disilicate was crystallized first as predominant phase together with lithium diborate from the base glass G_1. However, minor constituents of lithium metasilicate and α-quartz were crystallized as well. Crystallization of meta- and disilicate, and their ratios, depends on the temperature and duration of the process. Lithium disilicate is formed almost exclusively by low temperature treatment of glasses, while at higher temperature, lithium metasilicate appears.[11] However, Hench and others[12,13] revealed that a lithium metasilicate phase appears as a precursor to crystallization of the equilibrium lithium disilicate in the 33 mol% Li_2–SiO_2 glasses.

Theoretically, on the basis of the petrochemical calculation[14] of the present lithium–borosilicate glass composition into normative molecules, predominant lithium disilicate and lithium diborate only could be formed. The presence of B_2O_3 in the glass seemed to affect the ordering towards the metasilicate formation. Therefore, a remainder of Li-metasilicate and α-quartz in the crystalline base glass were encountered. Structurally, in both lithium and disilicate crystals, the Li^+ ions are tetrahedrally bonded with oxygen ions and are represented by triangles.[12] If alternate Li_2O groups at the interface between the crystals are removed from the metasilicate lattice, a small displacive shift will be sufficient to produce the disilicate lattice. Therefore, it seemed that the metasilicate phase was precipitated, metastably at lower temperature, by an ordering of extremely small regions in the glass containing randomly distributed $Li_2O.SiO_2$ chains. With additional heating or long duration Li_2O groups apparently diffuse out of the metasilicate crystallites, probably as ionic species, producing the complex layered disilicate structure from the SiO_2-rich matrix at the metasilicate interface.

The Raman spectra of the borosilicate glasses indicated[15] that below an alkali-to-boron ratio of 0·5 all, or nearly all, alkali ions are used to form primarily ring-type six-membered borate groups with one or two BO_4 groups that to a certain extent may be ordered to form a tetraborate or diborate group. At an alkali-to-boron ratio above 0·5 significant amounts of ring-type metaborate, pyroborate groups and orthoborate units are also formed as binary alkali borate glasses. At an alkali-to-boron ratio of about unity there seems to be an increase in the formation of ring-type metaborate groups for alkali-borosilicate glasses as the SiO_2 content increases.

In addition to the lithium silicate phases, varieties of the lithium borates, like lithium diborate, lithium tetraborate and lithium pyroborate, together with the Ca-bearing phases such as Ca-silicate and Ca-borate, were crystallized. The formation of these crystallized phase assemblages were greatly dependent on the glass oxide constituents, the ratios between them and the heat-treatment conditions.

Thermal treatment of glass 2 of low CaO/B_2O_3 ratio (0·17) at 600°C for 10 h led to the formation of lithium silicates together with minor phases of lithium diborate and α-quartz. However, at 680°C for a longer duration (30 h) the crystallization of lithium diborate increased and both Ca-silicate (wollastonite) and lithium tetraborate were developed, as proved by X-ray analysis (Fig. 6). It seems, therefore, that both Li-silicate and Li-diborate were initially formed at low temperature in the glass, with the remaining B_2O_3 and SiO_2 together with CaO in the glass matrix. For prolonged heating at high temperature, a redistribution of the elements seemed to take place and the residual of silica can combine with CaO to form $CaSiO_3$, while the remaining boric can combine with Li-diborate to form the tetraborate as follows:

$$CaO + SiO_2 \rightarrow CaSiO_3$$
$$Li_2B_4O_7 + 2B_2O_3 \rightarrow Li_2B_8O_{13} \text{ (tetraborate)}$$

On increasing the CaO/B_2O_3 replacement up to a CaO/B_2O_3 ratio 0·4, i.e. G_3, lithium metasilicate, lithium tetraborate, α-quartz, Ca-silicate, and lithium pyroborate, with a minor phase of lithium disilicate, were crystallized. No lithium tetraborate was detected and the lithium pyroborate [$Li_4B_2O_5$] was developed only at temperatures as high as 650°C for long duration. The crystallization of lithium tetraborate was increased by long duration heat treatment (i.e. 660°C for 30 h). It seems that, at temperatures as low as 550°C, the glass may contain some remaining B_2O_3 in the glassy matrix. It is suggested, therefore, that for prolonged heating at 660°C the remaining B_2O_3 can react with some of the lithium metasilicate to form the pyroborate phase and silica, which crystallized as α-quartz, as follows.

$$2Li_2SiO_3 + B_2O_3 \rightarrow Li_4B_2O_5 + 2SiO_2$$

Sastry and Hummel[16] showed that the compound $Li_2O.4B_2O_3$ exists and melts incongruently at 635° ± 10°C. A glass containing 89% B_2O_3 (i.e. situated in the region between $Li_2O.3B_2O_3$ and $Li_2O.4B_2O_3$) crystallized to $Li_2O.4B_2O_3$ and $Li_2O.2B_2O_3$ when heated at 500°C for one week. They also concluded that the compound $2Li_2O.B_2O_3$ existed in two polymorphic forms (i.e. low form α-$2Li_2O.B_2O_3$ and high form β-$2Li_2O.B_2O_3$) in the temperature range between 600 and 650°C. The high temperature form appeared first and then converted to the equilibrium low form.

Further crystallization of $Li_2O.4B_2O_3$ by thermal treatment, as indicated by X-ray analyses, gives evidence that the glass may contain residual B_2O_3 and Li_2O in the glass matrix, which is favourable on prolonged heating for the formation of lithium pyroborate.

On further addition of CaO instead of B_2O_3, i.e. G_4 (with CaO/B_2O_3 ratio = 0·75), predominant lithium metasilicate α-quartz, with a minor phase of calcium borate, were formed at low temperature (550°C), while at higher temperature for long duration (650°C, 30 h) the crystallization of Ca-borate increased and Ca-silicate (wollastonite), lithium tetraborate and lithium dislicate were also crystallized. This means that some of CaO, B_2O_3 and SiO_2 are still remaining in the glassy matrix at low temperature of heat treatment. Theoretically, on the basis of petrochemical calculation,[14] there is a residual free silica and boron after the formation of lithium silicate, Ca-silicate and Ca-borate phases. Therefore, at higher temperature it seems that a co-reaction can take place between these remaining elements, resulting in the formation of the above mentioned phases as indicated by the schematic equations.

$$CaO + SiO_2 \rightarrow CaSiO_3$$
$$Li_2SiO_3 + 4B_2O_3 \rightarrow Li_2B_8O_{13} + SiO_2$$
$$Li_2SiO_3 + SiO_2 \rightarrow Li_2Si_2O_5$$

The CaO content of glass 4 was sufficient to combine with silica and B_2O_3 to form the Ca-metasilicate and Ca-borate phases.

At higher CaO/B_2O_3 replacement (i.e. CaO/B_2O_3 ratio = 1·33), only lithium metasilicate, calcium metasilicate and calcium metaborate were formed and no other Li-bearing phases were encountered. It should be mentioned that the addition of CaO at the expense of B_2O_3 favoured the formation of both Ca-metasilicate, Ca-metaborate, and led to a decrease in the lithium disilicate phase which totally disappeared by replacing 16% of B_2O_3 with CaO. This may be ascribed to the variation of the ratio of the glass oxide constituents, i.e. CaO/B_2O_3, Li_2O/B_2O_3 and CaO/B_2O_3 present in the glass and the heat-treatment effect.

4.2 Combined effect of CaO/B_2O_3 and MgO/Li_2O replacements

The addition of MgO, instead of Li_2O, in the CaO-containing glasses increased the temperature at which crystallization started. The DTA results clearly indicated that both the temperature of the nucleation endotherm and the crystallization temperature exotherm were increased by the addition of MgO in replacing Li_2O. Li_2O was a good glass modifier and has a beneficial effect in lowering the temperature of the glass to convert it into glass-ceramic. It can be housed in the glass structure in the interstitial position which increases the number of groups between the (SiO_4) chain, i.e. decrease the (SiO_4) chain.[17] Unlike Li_2O, MgO can form in the glass structure as MgO_4 group forming tetrahedral coordination because of the large amounts of oxygen available from the lithia present. This may account for the increase in the coherency of the glass structure, which results in a compact structure.[17] The MgO/Li_2O replacement causes the glass structure to stiffen, increasing the viscosity of the glass which hinders the diffusion of different ions. Therefore, the tendency of the glass–crystalline conversion becomes more difficult by addition of MgO instead of Li_2O.

The addition of MgO, in replacing Li_2O, in CaO-containing glasses (i.e. G_6 and G_7) led to the formation of a pyroxene phase of diopsidic-type. Thus, during the crystallization of the glasses it was assumed that CaO can combine with the equivalent amount of MgO, together with the proper amount of SiO_2, to form the pyroxene phase in both glass 6 and 7 as follows:

$$CaO + MgO + 2SiO_2 \rightarrow CaMgSi_2O_6 \text{ (diopside)}$$

No other phases containing calcium, like Ca-borate or silicate, were formed in either glass.

Pyroxene consists of a group of minerals of variable composition which crystallizes fairly readily. They are closely related in crystallographic and other physical properties, as well as in chemical composition.[18] A wide variety of ionic substitution occurs in the members of the pyroxene group and there is a solid solution between the group component, e.g. diopside [$CaMgSi_2O_6$] and wollastonite [$CaSiO_3$].

The CaO/MgO ratio in glass 6 equals unity, while the CaO in glass 7 is greater than that needed to combine with MgO (CaO/MgO = 1·33) to form diopside. It is assumed, therefore, that the CaO (after diopside formation) can combine with silica to form Ca-silicate (wollastonite) [$CaSiO_3$], which is accommodated in the diopside structure to form a pyroxene solid solution.[19]

A lithium diborate phase [$Li_2B_4O_7$] was formed among the crystallization products of glass 6 (with Li_2O/B_2O_3 ratio = 1·33). At higher Li_2O/B_2O_3 ratios (i.e. 1·77, G_7), both lithium tetraborate [$Li_2B_8O_{13}$] and lithium pyroborate [$Li_4B_2O_5$] were crystallized. Therefore, it seems that at the higher Li_2O/B_2O_3 ratio (e.g. G_7) the excess Li_2O reacts with the component of the diborate phase to yield lithium tetraborate and pyroborate phases according to the following equation:

$$3Li_2B_4O_7 + 2Li_2O \rightarrow 2Li_4B_2O_5 + Li_2B_8O_{13}$$

The crystallization of these phases, in glasses of various B_2O_3 content (i.e. G_6 and G_7) may support that their formation is greatly related to the Li_2O/B_2O_3 ratio present in the glass.

5 CONCLUSIONS

The crystallization characteristics of lithia–calcia–magnesia-borosilicate glasses were studied, in particular the nature and sequence of formation of crystalline phases and the tendency towards crystallization.

Calcium oxide has a pronounced effect on the liquation capability and opacification of lithium borosilicate glasses. It accelerates the crystallization tendency of the glasses. MgO, however, when added instead of Li_2O, has no such effect and a relatively higher temperature was needed to induce crystallization. In all cases, glass-ceramic materials of intense microcrystalline structure could be successfully obtained.

The crystallization process was investigated as a function of temperature, thermal history and glass-oxide constituents. Lithium silicates and varieties of lithium borate phases together with Ca-metasilicate and metaborate or Ca–Mg-silicate were developed. The sequence of crystalline phase formations was sensitive to all three of the latter additions.

REFERENCES

1. BEAL, G. H., Design of glass-ceramics. *Review of Solid State Science*, **3**(3,4) (1989) 333–54.
2. CHUANGTION C., BOCHANG, WA., AIDONY, J. & GUIMING, Y., *China Science Section B*. Optical properties and growth of a new type of SHC crystal B. BaB_2O_4 (1984) 588–604.
3. TULLER, H. L., BUTTON, D. P. & UHLMANN, D. R., Fast ion transport in oxide glasses. *J. Non-Cryst. Solids*, **40**(1–3) (1980) 93–118.
4. BUTTON, D. P., MOON, P. K., TULLER, H. L. & UHLMANN, D. R., Structure–transport relationship in oxide glasses, fast ion transport in alkali borosilicate glasses. *Glastech. Ber.*, **56K** (1983) 856.
5. TATSUMISAGO, M., YONEDA, K., MACHIDA, N. & MINAMI, T., Ionic conductivity of rapidly quenched glasses with high concentration of lithium ions. *J. Non-Cryst. Solids*, **95/96** (1987) 857–64.
6. AYDIN GOKTA, A., NEILSON, G. F. & WEINBERG, M. C., Crystallization of lithium borate glasses. *J. Mater. Sci.*, **27** (1992) 24–8.
7. NIKULIN, V. KH., VIKTOROVA, O. S., PRUSAKOVA, L. M., AINETDINOVA, R. I. & MESHCHERYAKOVA, M. G., Effect of liquidation on the properties of low-alkali-borosilicate glasses. *Glass and Ceramics*, **48** (1991) 145–50.
8. YAMAMOTO, J., Effect of CaO and MgO on the glasses of the system $Na_2O–B_2O_3–SiO_2$. *J. Ceram. Ass. Japan*, **61**(688) (1953) 495.
9. KROGH-MOE, J., Interpretation of IR spectra of boron oxide and alkali borate glasses. *Phys. Chem. Glasses*, **6**(2) (1965) 46–54.
10. VOGEL, W., The structure of the opalescent sodium-borosilicate glasses. In *Structure and Crystallization of Glasses*. Pergamon Press, Oxford, 1971, pp. 71–3.
11. KALININA, A. M., FILIPOVICH, V. N., KOLESOVA, V. A. & BONDER, I. A., Crystallization products of lithium silicate glasses. In *The Structure of Glass*, Vol. 3. Consultants Bureau, New York, USA, 1965, pp. 53–64.
12. HENCH, L. L., FREIMAN, S. W. & KINSER, D. L., The early stages of crystallization in $Li_2O{\cdot}2SiO_2$ glass. *Phys. Chem. Glasses*, **12**(2) (1971) 58.
13. KINSER, D. L. & HENCH, L. L., Effect of metastable precipitate on the electrical properties of an $Li_2O.SiO_2$ glass. *J. Am. Ceram. Soc.*, **51**(7) (1968) 378–82.
14. BARTH, T. F., *Theoretical Petrology*, 2nd edn. Wiley, New York, 1962.
15. KONIJNEDIJK, W. L., The structure of borosilicate glasses, Philips Research Supplement No. 1. Thesis, Eindhoven University of Technology, 1975.
16. SASTRY, B. S. R. & HUMMEL, F. A., Studies in lithium oxide systems; 1, $Li_2O.B_2O_3–B_2O_3$. *J. Am. Ceram. Soc.*, **41**(1) (1958) 7–17.
17. SCHOLZE, H., *Glass (Nature, Structure and Properties)*. Springer-Verlag, NY, 1990.
18. DEER, W. A., HOWIE, R. A. & ZUSSMAN, J., *Rock Forming Minerals, Vol. 2, A Chain Silicates*. Longman, London, 1962.
19. SALAMA, S. N., Glass-ceramics containing some varieties of Mn-solid solution phases. *Mater. Chem. Phys.*, **28** (1991) 237–57.