

Contribution of Al_2O_3 to Crystallization Characteristics of Some Lithia Manganese Calcia Magnesia Silicate Glasses

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Abstract

The effect of thermal treatment on the crystallization characteristics and phase composition of lithia aluminosilicate glasses with additional constituents of some divalent oxides were examined by DTA, X-ray analysis and microscopy.

On partial $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ replacement, lithia aluminosilicate (β -eucryptite and/or β -spodumene) solid solutions were formed at the expense of lithium silicate phases. The progress of β -eucryptite and/or β -spodumene crystallization was accelerated with the addition of Al_2O_3 instead of Li_2O . The stability field of β -eucryptite was shifted to higher temperature if the $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ ratio exceeded unity. In the presence of mixed divalent cations like Mn^{2+} , Ca^{2+} and/or Mg^{2+} , varieties of pyroxene solid solutions, Mn-containing phases and anorthite were crystallized.

The formation of various solid solution phases and their stoichiometric composition were greatly related to the $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ and/or the divalent oxide ratios in the glass as well as the conditions of thermal treatment.

Die Auswirkung einer Wärmebehandlung auf die Kristallisationscharakteristik und auf die Phasenzusammensetzung von Lithiumoxid–Aluminiumsilikat Gläsern mit zugegebenen zweiwertigen Oxiden wurde mittels DTA, Röntgendiffraktometrie und Mikroskopie untersucht. Bei einer teilweisen Substitution des Li_2O durch Al_2O_3 werden auf Kosten der Lithiumsilikat-Phase Lithiumoxid–Aluminosilikate (β -Eukryptit und β -Spodumen) gebildet. Die Kristallisation dieser Phasen wird durch die Zugabe von Al_2O_3 anstelle von Li_2O beschleunigt. Das Stabilitätsgebiet des β -Spodumen wird für Konzentrationsverhältnisse $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ oberhalb 1 zu höheren Temperaturen verschoben. Liegen Mischungen zweiwertiger Kationen, wie Mn^{2+} , Ca^{2+} und/oder Mg^{2+} oder feste Lösungen verschiedenartiger Pyr-

oxene vor, kristallisieren Mn-haltige Phasen und Anorthit aus. Die Bildung der verschiedenen festen Lösungen und ihre stöchiometrische Zusammensetzung werden hauptsächlich auf das $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ -Verhältnis und/oder auf das Mischungsverhältnis der dem Glas zugegebenen zweiwertigen Oxide und auf die Wärmebehandlung zurückgeführt.

Les auteurs ont examiné par DTA et RX l'effet du traitement thermique sur les caractéristiques de cristallisation et sur la composition de phase des verres en alumino-silicate de lithium, en présence d'additifs du type oxydes bivalents.

Lors d'une substitution partielle $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$, des solutions solides d'aluminosilicates de lithium (eucryptite β et/ou spodumène β) se sont formées au dépens des phases de silicate de lithium. La cristallisation de l'eucryptite β et/ou spodumène β est accélérée par l'addition d' Al_2O_3 . Le domaine de stabilité de l'eucryptite β est déplacé vers de plus hautes températures si le rapport $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ dépasse 1. En présence d'un mélange de cations bivalents comme Mn^{2+} , Ca^{2+} et/ou Mg^{2+} , des solutions solides de pyroxène, des phases contenant du Mn, et de l'anorthite cristallisent.

La formation des diverses solutions solides, ainsi que leur composition stoechiométrique, dépendent étroitement du rapport $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ et/ou du rapport des différents oxydes bivalents dans le verre, ainsi que des conditions de traitement thermique.

1 Introduction

In glass-ceramic formation the bulk chemical composition controls the glass formation and workability, as well as the tendency towards internal nucleation and crystallization in general. The phase composition, i.e. the type and proportion of

crystalline and amorphous phases, generally controls the physical and chemical properties of the resultant glass-ceramics.¹ The phase composition, of course, is controlled to a large extent by the bulk composition, but it is also a function of thermal history. Microstructure is generally the key to the mechanical properties. In the design of glass-ceramics, however, each of the three variables must be considered independently and carefully.²

Aluminosilicate glass-ceramics are of great commercial interest because they combine thermal stability and shock resistance with exceptional chemical durability. The resistance to thermal shock is based on the very low to moderate thermal coefficients found in many aluminosilicate framework structures, e.g. β -quartz ss, β -spodumene ss, cordierite and anorthite. Solid solution phases are easily formed in a great variety of aluminosilicate glasses containing Li^+ and Mg^{2+} ions.³⁻⁶ Al^{3+} together with Si^{4+} ions exhibit an essential contribution in the formation of the solid solution. Compositions crystallizing to form solid solution series are important to control the properties of the resultant materials.⁷

Crystallization of aluminosilicate glasses containing divalent oxides like Ca^{2+} and Mg^{2+} is of interest, and these glasses have been extensively studied. However, the crystallization characteristics of such glasses with addition of manganese have received little attention; this may be due to the experimental difficulties of its oxidation-reduction state. The present study is one in a series of investigations dealing with the crystallization of lithia MnO-silicate glasses,^{8,9} where the role of manganese in the formation of a variety of manganese silicate solid solutions has been discussed. Extension of the work is concerned with the study of the contribution of Al_2O_3 to the crystallization characteristics and phase composition produced in such glass systems. This may add further information on the behaviour of Al_2O_3 and manganese in glass-ceramic formation.

2 Experimental

2.1 Glass composition and preparation

The selected glass compositions (Table 1) are based on the multicomponent system: $(23.12 - X)\text{Li}_2\text{O} - [13.28 - (Z + Y)]\text{MnO} - 63.6\text{SiO}_2$, where X is Al_2O_3 , which ranges from 0 to 13.87; Z is CaO ; Y is MgO ; and each of them ranged from 0 to 6.64. The batch compositions were prepared from purified silica sand, Analar grades of Li_2CO_3 , CaCO_3 , MgCO_3 and calcined Al_2O_3 , together with the highest purity of MnO_2 as a source of MnO . The glasses were made by fusing the starting material in fire clay crucibles in

Table 1. Chemical composition of the glasses

Glass number	Oxide (mol%)					
	Li_2O	MgO	CaO	MnO	Al_2O_3	SiO_2
1	23.12	6.64	—	6.64	—	63.6
2	17.34	6.64	—	6.64	5.78	63.6
3	11.56	6.64	—	6.64	11.56	63.6
4	9.25	6.64	—	6.64	13.87	63.6
5	23.12	—	3.32	9.96	—	63.6
6	9.25	—	3.32	9.96	13.87	63.6
7	9.25	3.32	3.32	6.64	13.87	63.6
8	11.56	—	6.64	6.64	11.56	63.6
9	11.56	3.32	6.64	3.32	11.56	63.6
10	11.56	6.64	3.32	3.32	11.56	63.6

a gas-fired furnace at 1400°C for 3 h, using the procedure detailed elsewhere.⁹

2.2 Differential thermal analysis

Differential thermal analysis (DTA) was performed on the annealed glasses to record their thermal behaviour. A recording apparatus of Shimadzu type DT-30 was used. The powdered glass sample (50 mg; passed through a 100-mesh sieve) was heated in the DTA apparatus against the same amount of Al_2O_3 standard. A uniform rate of heating of $10^\circ\text{C}/\text{min}$ and a sensitivity setting of $1.9685 \times 10^{-3} \mu\text{V}/\text{m}$ were maintained for all the runs.

2.3 Thermal treatment

Selected isotherms were used to investigate the progress of crystallization in the glasses using both single and consecutive heat-treatment regimes (i.e. double-stage schedule). In the former, the glass samples were heated at the required temperature in the 600 – 1000°C temperature range at 50°C intervals for 3.5 and sometimes 8 h; in the latter, the samples were first heated according to the DTA results at the endothermic peak temperature, which was followed by another treatment around the exothermic peak temperature of each glass for 3–8 h.

2.4 Material investigation

X-Ray diffraction technique, using Ni filter and Cu radiation, was used to detect and identify the crystalline phases and solid solutions formed in the thermally treated materials. An optical polarizing microscope was also used to follow the progress of crystallization and textural characteristics.

3 Results

3.1 Differential thermal analysis

The DTA traces of the glasses are exhibited in Fig. 1. Endothermic reactions in the temperature range 560 – 680°C were recorded. These endothermic effects may indicate the molecular rearrangement phenom-

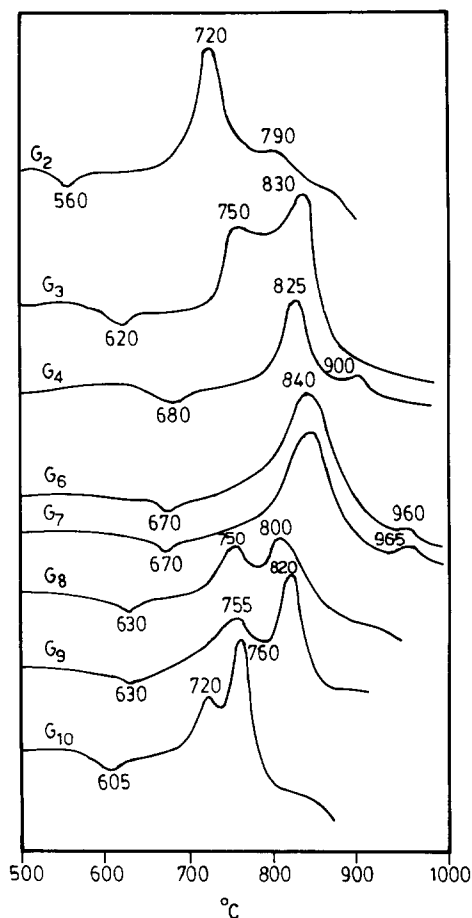


Fig. 1. DTA curves of the studied glasses.

enon preceding glass crystallization, i.e. precrystallization stage. This is followed by various exothermic effects with maxima in the temperature range 720–965°C, which indicate the crystallization reaction in the glasses.

3.2 Physical appearance of the glass-ceramics

Distinctly coloured glass-ceramic materials were produced by thermal treatment of the glasses. All the glasses turned deep brown in the bulk and had a brownish black, metallic sheen on the surface,

especially when MnO was greater than CaO and/or MgO. The presence of Al₂O₃ generally decreased the intensity of the colour. The interior of the material was marked by a pinkish colour and had a mild brown colour on the surface.

3.3 Crystallization process of the glasses

The progress of crystallization in the glasses, the type and proportions of the resulting crystalline phase assemblages were strongly dependent on the Al₂O₃/Li₂O ratio, the combined presence of one or more of the divalent cations (i.e. Mn²⁺, Ca²⁺ and/or Mg²⁺), as well as the heat-treatment effect.

3.3.1 Effect of various Al₂O₃/Li₂O replacements

These include glasses 2, 3 and 4, as well as glasses 5 and 6. In general, the substitution of Al₂O₃ for Li₂O in the glasses increases the temperature at which crystallization begins. The DTA traces of the glasses (Fig. 1, e.g. G₂, G₃ and G₄) indicated that both the endothermic dip and the onset of the crystallization exotherm were shifted to higher temperatures as the amount of Al₂O₃ was increased, i.e. a higher energy is needed to induce crystallization with addition of Al₂O₃ replacing Li₂O.

The phases developed in glasses 2–4 over the investigated 700–1000°C temperature range, as identified by XRD (Table 2; Figs 2 and 3), were lithium-bearing phases Li₂Si₂O₅, Li₂SiO₃, β-eucryptite and β-spodumene ss, and manganese-bearing phases kanoite-(MnMg)₂Si₂O₆ and Mn-silicate ss. The XRD (Fig. 2) revealed that the lithium aluminium silicate solid solutions were formed at the expense of the lithium silicate phases, i.e. the increase of Al₂O₃ (at the expense of Li₂O) in the glass led to a corresponding increase of aluminosilicate and a decrease in lithium silicate formation.

The formation of β-eucryptite and/or β-spodumene ss phases was found to be dependent mainly on the crystallization parameters used and the Al₂O₃/

Table 2. The crystalline phases developed in the various Al₂O₃ glasses

Glass number	Al ₂ O ₃ /Li ₂ O ratio	Heat treatment (C/h)	Phases developed
1	—	500/3, 700/3	Li ₂ Si ₂ O ₅ , kanoite
2	0.33	700/3 560/3, 750/5 800/3 560/3, 850/8	β-eucryptite, Li ₂ SiO ₃ , Li ₂ Si ₂ O ₅ β-spodumene, β-eucryptite (m), Li ₂ SiO ₃ and Li ₂ Si ₂ O ₅ (m) β-spodumene, Li ₂ SiO ₃ , kanoite, Li ₂ Si ₂ O ₅ (m) β-spodumene, Li ₂ SiO ₃ , kanoite, Li ₂ Si ₂ O ₅ (m)
3	1	750/3 620/3, 800/3 620/3, 850/8	β-eucryptite β-eucryptite, β-spodumene, kanoite β-spodumene, kanoite
4	1.5	800/5 850/3 680/3, 900/3 680/3, 1000/8	β-eucryptite β-eucryptite, Mn-silicate ss β-eucryptite, β-spodumene, Mn-silicate ss β-spodumene, Mn-silicate ss

(m), Minor.

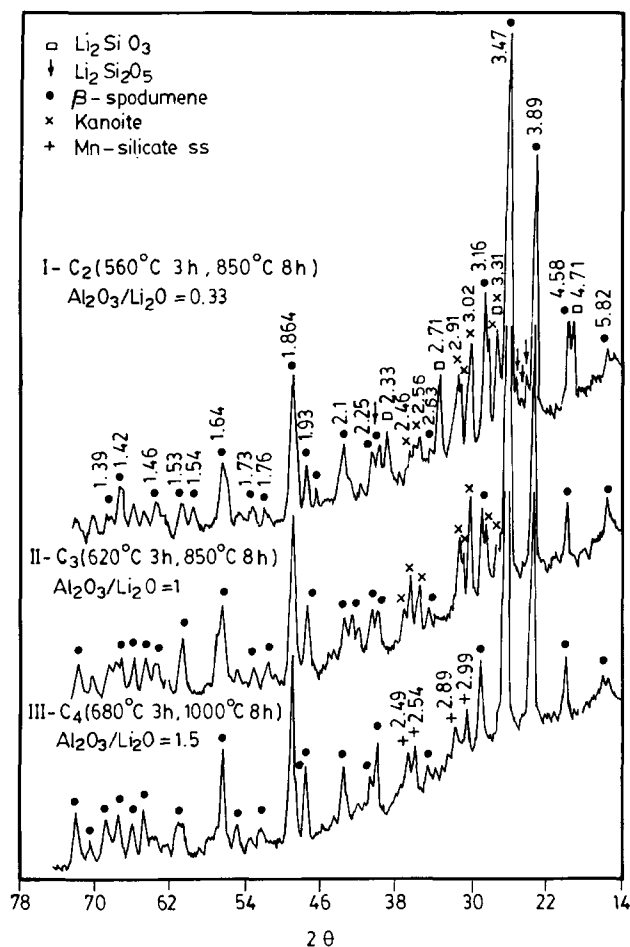


Fig. 2. XRD of crystallized glasses of various $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ ratios.

Li_2O ratio in the glass. Table 2 indicated that β -eucryptite was developed at 700°C in glass 2 (with $\text{Al}_2\text{O}_3/\text{Li}_2\text{O} < 1$) and its crystallization was shifted towards higher temperature, i.e. at 800°C in glass 3 and 850°C in glass 4, with higher $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ ratios,

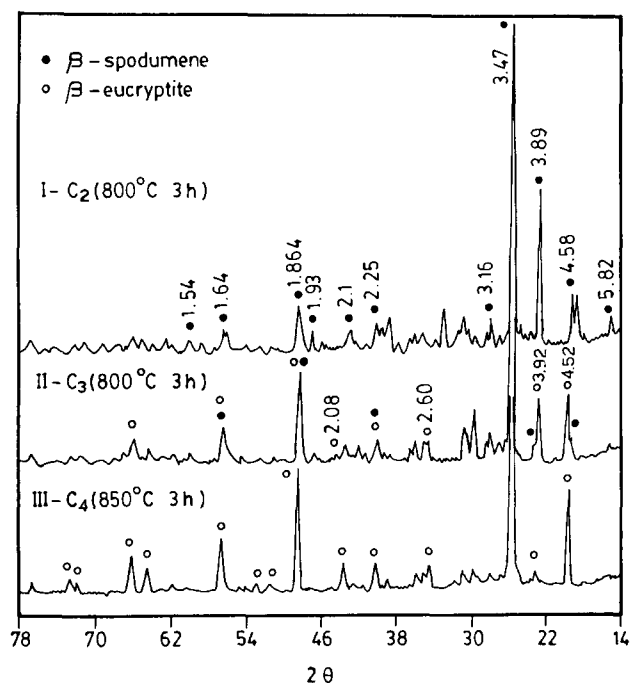


Fig. 3. XRD of glasses of various $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ ratios.

respectively. The XRD (Fig. 3) clearly indicated that β -spodumene was crystallized at 800°C in glass 2, both β -eucryptite and β -spodumene were formed in glass 3 at 800°C , while β -eucryptite was only detected at 850°C in glass 4. Irreversible transformation of the initially formed β -eucryptite ss into β -spodumene ss took place at about 750°C in G_2 , at 800°C in G_3 and at 900°C in G_4 . Manganese-containing pyroxene- $(\text{MnMg})_2\text{Si}_2\text{O}_6$ (kanoite) was developed in glasses 2 and 3, while manganese-metasilicate solid solution phase was mainly formed in glass 4.

Correlation between the crystal phases identified by XRD (Figs 2 and 3; Table 2) and DTA data (Fig. 1) suggests that the broad exothermic peak at 720°C in G_2 may be caused by simultaneous crystallization of β -eucryptite, β -spodumene and lithium silicate phases, while the small exothermic effect at 780°C may be attributed to further β -eucryptite, β -spodumene transformation and Mn-pyroxene crystallization. The exothermic effect recorded at 780°C by G_3 may correspond to β -eucryptite formation, and that at 840°C may arise from the β -eucryptite, β -spodumene transformation and Mn-pyroxene crystallization. The broad exothermic effect at 850°C given by G_4 may be attributed to the crystallization of β -eucryptite and Mn-silicate solid solution, while the β -eucryptite, β -spodumene transformation may be represented by the appearance of the small exothermic effect at 920°C .

For the effect of $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ in the CaO-containing glasses (G_5 – G_7), Table 3 and the XRD (Fig. 4) indicate that β -eucryptite was initially crystallized in glass 6 at 800°C and minor β -spodumene was crystallized as well at 900°C .

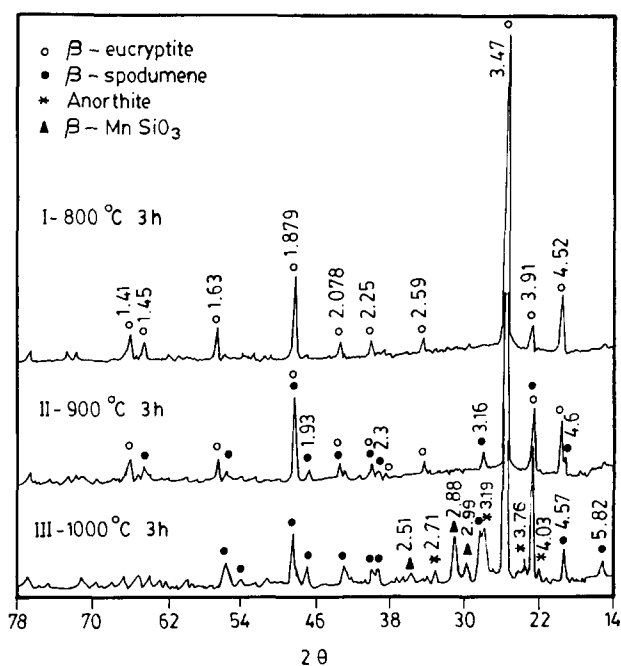
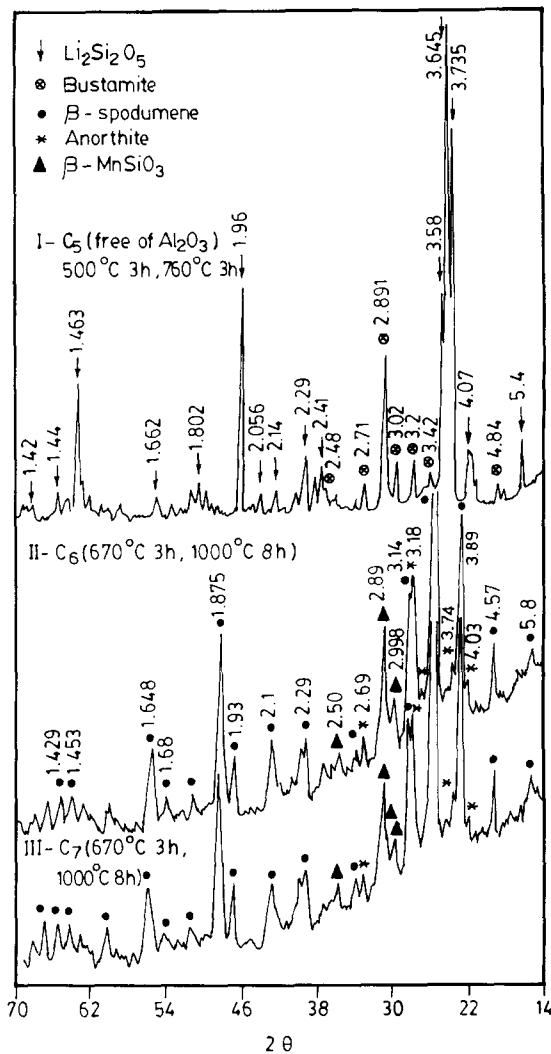
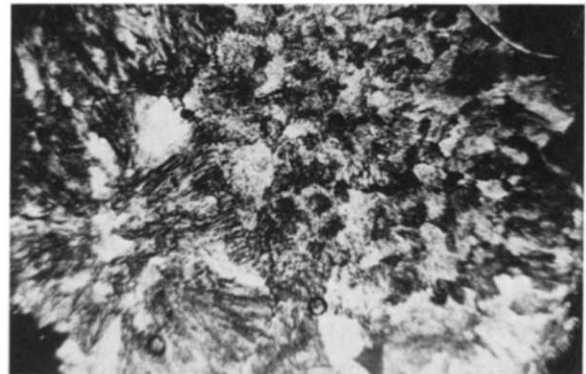
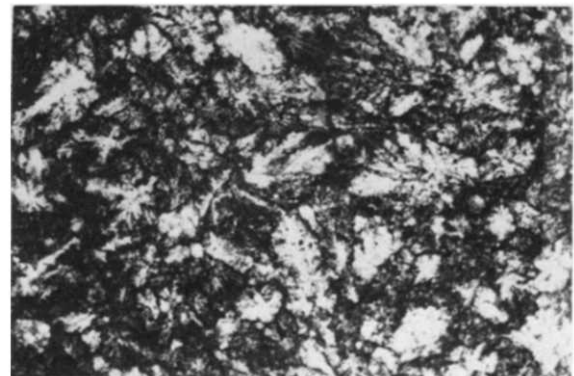


Fig. 4. XRD of glass 6 crystallized at different temperatures.

Table 3. The crystalline phases developed in the glasses of various divalent ratios and 1.5Al₂O₃/Li₂O ratio

Glass number	Divalent oxide ratio, CaO/MgO/MnO			Heat treatment (C/h)	Phases developed
<i>Al₂O₃-free glass</i>					
5	1	---	3	500/3, 760/3	Li ₂ Si ₂ O ₅ , bustamite
<i>Al₂O₃ glasses</i>					
6	1	--	3	800/3	β -eucryptite
				670/3, 850/3	β -eucryptite
				900/3	β -eucryptite, β -spodumene
				670/3, 950/3	β -spodumene, β -MnSiO ₃ , anorthite, β -eucryptite
				1000/3 670/3, 1000/8	β -spodumene, anorthite, β -MnSiO ₃ β -spodumene, anorthite, β -MnSiO ₃
7	1	1	2	800/3	β -eucryptite
				850/3	β -eucryptite
				670/3, 900/3	β -eucryptite, β -spodumene (m)
				670/3, 950/3	β -spodumene, β -MnSiO ₃ , anorthite, β -eucryptite (m)
				1000/3 670/3, 1000/8	β -spodumene, β -MnSiO ₃ , anorthite β -spodumene, β -MnSiO ₃ , anorthite

(m), Minor.

**Fig. 5.** XRD of Al₂O₃ glasses with various divalent oxide ratios.**Fig. 6.** G₄ (680°C 3h-1000°C 8h). Fine prismatic growths of β -spodumene ss and tiny aggregates of Mn-silicate ss. CN (crossed nicols) $\times 100$.**Fig. 7.** G₆ (670°C 3h-1000°C 8h). Fine prismatic β -spodumene ss and interlocked growths of anorthite and β -MnSiO₃. CN $\times 100$.

However, at 1000°C the stable phases formed were β -spodumene ss, anorthite- $\text{CaAl}_2\text{Si}_2\text{O}_8$ and β - MnSiO_3 . The formation of these phases was confirmed by the XRD analysis of glass 6 crystallized at a two-stage heat treatment regime (Fig. 5, pattern II). These findings should be compared with those obtained from Al_2O_3 -free glass (G_5) treated at 800°C, where lithium disilicate and bustamite phase ($\text{Ca}_{0.25}\text{Mn}_{0.75}$) $_3\text{Si}_3\text{O}_9$ were formed (Fig. 5, pattern I). A broad exothermic peak with a maximum at 850°C and a small exothermic effect at 960°C were recorded on the DTA trace of glass 6. The first peak may arise from the β -eucryptite- β -spodumene formation, while the second peak may be due to the formation of anorthite and β - MnSiO_3 phases. Two-stage heat treatments of the above-mentioned glasses, according to the DTA data, did not affect the type of the crystallizing phases, but the crystallinity and the bulk nucleation were enhanced, and in most cases fine-grained microstructures were developed (e.g. Figs 6 and 7).

3.3.2 Effect of various divalent oxides

The study of the effect of MgO/MnO replacement in high Al_2O_3 glasses (i.e. $\text{Al}_2\text{O}_3/\text{Li}_2\text{O} > 1$) could be followed by comparing the crystallization behaviour of glass 6 with that of glass 7. Both glasses developed volume crystallization to an almost holocrystalline mass without deformation using the same thermal treatment of the double-stage regime. The XRD (Fig. 5, patterns II and III) reveal that glass 7 crystallized, as did glass 6, into β -spodumene ss, anorthite and β - MnSiO_3 . The DTA trace of glass 7 was largely identical to that of glass 6 (Fig. 1).

The effect of MgO/MnO replacement could be seen by studying the crystallization characteristic of glass 8 as compared with that of glass 9 ($\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ ratio = 1). The crystallization of the glasses proceeded without great difficulty through the entire volume on heating over 700–850°C, resulting in a

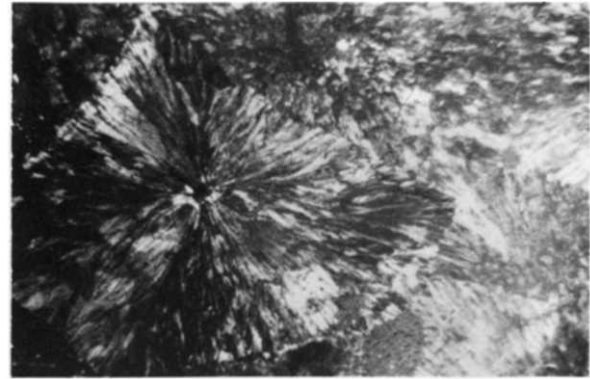


Fig. 8. G_8 (630°C 3 h–850°C 8 h). Radial fine fibrous growths of β -spodumene ss and bustamite. CN \times 100.

holocrystalline mass at 850°C (e.g. Fig. 8). The XRD data (Fig. 9; Table 4) reveal that the β -eucryptite and bustamite- $(\text{CaMn})_3\text{Si}_3\text{O}_9$ were developed at 750°C in glass 8, while β -spodumene was formed together with β -eucryptite on heating the glass at 800°C. At 850°C β -spodumene and bustamite only were detected (Fig. 9, pattern I). For glass 9, β -eucryptite with minor amounts of β -spodumene and bustamite were formed at 750°C, while at 850°C β -spodumene and a Mn-containing phase of d-spacing lines nearly identical to that of the schefferite phase were developed (Fig. 9, pattern II). Therefore, the exothermic effects given by glasses 8 and 9 (Fig. 1) at about 750°C may correspond to the formation of the lithia aluminosilicate and bustamite phases, and that recorded at 800°C by G_8 may be caused by β -eucryptite- β -spodumene transformation, while that produced at 820°C by G_9 may be due to the schefferite and further β -spodumene crystallization.

Correlation between the XRD data of crystallization products of glasses 9 and 10 (Fig. 9, patterns II and III; Table 4) may exhibit the effect of CaO/MgO replacement. Glass 10 developed Mn-pyroxene solid solution phase of diopsidic type and β -eucryptite at 720°C, while at 760°C β -spodumene was crystallized

Table 4. Crystalline phases developed in the glasses of various divalent ratios and unity of $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ ratio

Glass number	Divalent oxide ratio, CaO/MgO/MnO			Heat treatment (°C/h)	Phases developed
8	1	—	1	630/3, 750/3 630/3, 800/3 630/3, 850/8	β -eucryptite, bustamite β -spodumene, bustamite, β -eucryptite (m) β -spodumene, bustamite
9	2	1	1	700/3 630/3, 750/5 800/3 630/3, 850/8	β -eucryptite, bustamite β -eucryptite, β -spodumene, bustamite β -spodumene, β -eucryptite, bustamite β -spodumene, schefferite
10	1	2	1	610/3, 720/5 610/3, 760/5 610/3, 800/8 610/3, 850/8	β -eucryptite, β -spodumene β -spodumene, Mn-diopside, β -eucryptite (m) β -spodumene, Mn-diopside β -spodumene, Mn-diopside

(m), Minor.

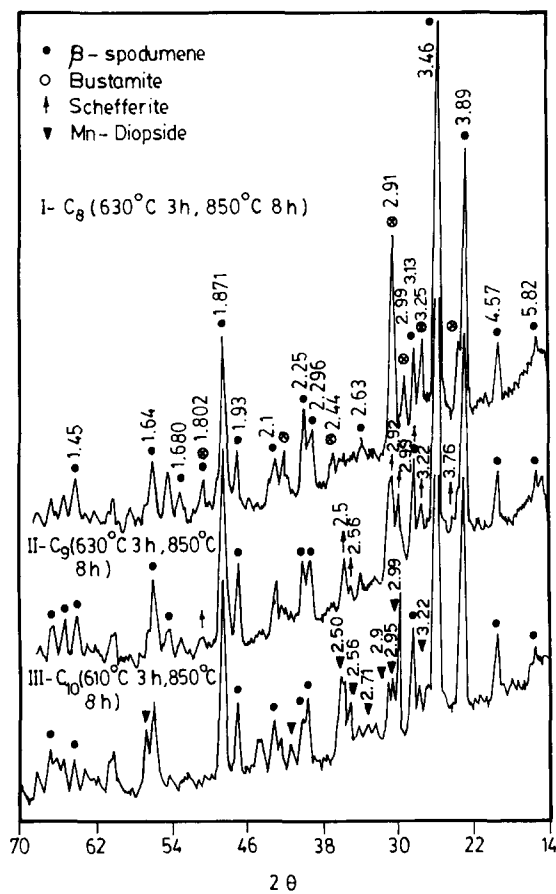


Fig. 9. XRD of crystallized glasses of equal Al_2O_3 content and various divalent oxide ratios.

as well. Therefore, two exothermic effects at 720 and 760°C were recorded on the DTA trace of glass 10.

4 Discussion

It is generally accepted¹⁰ that, in the lithia silica glass, the Li^+ ions having a high electrostatic field tend to form regions of high alkali composition in their attempt to screen themselves, preferentially with non-bridging polarizable O^{2-} ions. The ease to the crystallization of the lithia glass is achieved generally by a two-phase separation resulting from the incompatibility of Li_2O with SiO_2 . In the present work, although there is no direct evidence for phase separation, there is a slight positive indication which may support phase separation. In contrast to the colourless Al_2O_3 -containing glasses, glasses of G_1 and G_5 (free of Al_2O_3) showed a weak opacity by heating at low temperature ($\leq 450^\circ\text{C}$); however, no crystallinity could be detected by X-ray analysis. This may be due to the phase separation phenomena.

When Al_2O_3 is added to the lithia silica glass, the non-bridging oxygens originally associated with the Li^+ ions increase the coordination numbers of Al^{3+} ions from three- to four-fold coordination. The Li^+ ions deprived of their polarizable oxygens are no

longer capable of developing a two-phase separation, and thus the glass loses its ability to crystallize uniformly.¹⁰ On the other hand, the replacement of Li_2O by Al_2O_3 causes an increase in the viscosity of the resultant glasses, which is increased by the addition of more Al_2O_3 instead of Li_2O in the glass composition. This seems to hinder the diffusion of the different ions and ionic complexes, and consequently decreases the rate of crystal growth; therefore, the sluggish crystallization nature of high Al_2O_3 -containing glasses is expected.

The occurrence of the various phases developed was a function of the $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ ratios, the proportion of the divalent oxides present in the glass and the heat treatment applied. Li_2O exhibits a very great affinity to combine with Al_2O_3 and SiO_2 in order to form aluminosilicate. Theoretically, on the basis of the petrochemical method,¹¹ the recalculation of the chemical composition of the glasses into normative (stoichiometric) mineral molecules indicates that when Al_2O_3 is added it first combines with equivalent amounts of Li_2O and SiO_2 to form lithium aluminium silicate (β -eucryptite or β -spodumene). If there is an excess of Li_2O over Al_2O_3 (as in the case of G_2), the excess can then combine with silica to form lithium silicate phases. The formation of β -spodumene and/or β -eucryptite takes place at the expense of the lithium silicate phase. This means that at low $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ replacement (i.e. $\text{Li}_2\text{O} > \text{Al}_2\text{O}_3$) the lithium silicate crystallizes together with the lithium aluminosilicate phases. However, at $\text{Al}_2\text{O}_3 \geq 1$ no lithium silicate phases are detected, since the amount of Li_2O is either just enough or insufficient to combine with Al_2O_3 to form lithium aluminosilicate.

Table 5 shows that a lithium silicate phase was found to be formed in Al_2O_3 -containing glasses only when the molar ratio of $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ was greater than unity (G_2). The lithium silicate phase in this glass was calculated as $\text{Li}_2\text{Si}_2\text{O}_5$ molecules. However, the XRD revealed the formation of lithium metasilicate (Li_2SiO_3) together with the lithium disilicate. This may be attributed to the great tendency of β -spodumene formed in G_2 to form a solid solution with silica.^{1,2,5} The residual glass is then relatively poor in silica, and it is easier to separate the metasilicate than the disilicate.

The β -quartz ss are metastable hexagonal crystalline phases which form near the stoichiometric end-member composition, LiAlSiO_4 . This phase is stable and is often referred to as the β -eucryptite phase; β -spodumene is tetragonal and exhibits a stuffed derivative structure of the silica polymorph keatite. Its composition is $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$, where n varies from 4 to 10. Considerable replacement of magnesium for lithium is permitted in its structure ($\text{Mg}^{2+} \rightarrow 2\text{Li}^+$), although less than that which is

Table 5. Normative calculation of samples 1, 2 and 3

Glass number	$\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ ratio	% of normative molecule			
		$\text{LiAlSi}_2\text{O}_6$	$\text{Li}_2\text{Si}_2\text{O}_5$	$(\text{MnMg})_2\text{Si}_2\text{O}_6$	SiO_2
1	—	—	75.11	21.52	3.37
2	3	37.57	37.57	21.54	3.32
3	1	75.13	—	21.56	3.31

allowed in the metastable β -quartz precursor. β -Spodumene always forms from the pre-existing metastable solid solution during glass-ceramic heat treatment.¹

In the present work, the crystallization of β -eucryptite ss and β -spodumene ss was essentially a function of the crystallization parameters used and, to some extent, of the composition of base glass. Thus, the lithium aluminosilicate phase developed in the low temperature range (700–850°C) was a metastable β -quartz structure phase, wherein the Si^{4+} were replaced by Al^{3+} in pairs with Li^+ ions, and this phase recrystallized entirely into the stable β -spodumene ss above 800–900°C, depending on the glass composition. This agrees reasonably well with the literature.^{1,2,5,12,13} The preferential formation of such metastable β -eucryptite ss at low temperature, even from glasses of stoichiometric spodumene composition, may be explained¹⁴ as the surmounting of the lower energy barrier consistent with the closer symmetry of its hexagonal structure to the isotropic spherically symmetrical glass structure.

In the high Al_2O_3 -containing glass, i.e. where $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ molar ratio exceeds unity (G_4 , G_6 and G_7), crystallization began at lower temperatures, up to 850–900°C, with the formation of β -eucryptite ss, which transforms at higher temperature into the stable β -spodumene. Concurrent deposition of β - MnSiO_3 , Mn solid solutions or anorthite- $(\text{CaAl}_2\text{Si}_2\text{O}_8)$ was detected, in most cases as a function of the content of the divalent oxides present in the glass.

Although glass 4 has $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ greater than unity (1.5) and MgO/MnO ratio equal to unity, no Mn-bearing phase other than Mn-metasilicate solid solution was crystallized, while the expected normative Mn-containing pyroxene, i.e. kanoite- $(\text{MnMg})_2\text{Si}_2\text{O}_6$, was not detected. β -Spodumene ss occurred as the only Al-bearing phase among the crystallization of this glass. The excess of Al_2O_3 over that required for spodumene formation seems to be incorporated in the β -spodumene lattice, where it is supposed that a solid solution of Al^{3+} and Li^+ in such β -quartz-like structures is formed during crystallization with presumably Si^{4+} ions statistically substituted by Al^{3+} in pairs with Li^+ and probably with the other suitable Mg^{2+} ions.^{5,6} If there is an excess of Mg^{2+} ions, it can combine with

Mn^{2+} and silica to form the Mn-metasilicate-like phase, i.e. $(\text{MnMg})\text{SiO}_3$, rather than the expected kanoite phase, $(\text{MnMg})_2\text{Si}_2\text{O}_6$. The displacement of the major characteristic lines of this metasilicate solid solution towards higher 2θ values may support the suggestion that some of the Mg^{2+} ions were incorporated in the manganese metasilicate structure. No displacement was observed in the position of the main characteristic lines of the other phases formed in glass 4.

The accommodation of Al^{3+} and Mg^{2+} in the β -spodumene-like structure crystallized in glasses of a high Al_2O_3 content could be evidenced by investigation of the XRD of G_6 and G_7 . Glass 6 (free of MgO) has MnO/CaO ratio equal to 3, and glass 7 has $\text{MnO}/\text{CaO}/\text{MgO}$ of the ratio 1:1:2; however, both the glasses were crystallized into β -eucryptite, β -spodumene, β - MnSiO_3 and anorthite- $(\text{CaAl}_2\text{Si}_2\text{O}_8)$. It is suggested, therefore, that the Mg^{2+} ions present in glass 7 could be combined with Al^{3+} in the β -spodumene structure. No displacement was observed in the main characteristic lines of the β - MnSiO_3 phase detected by X-ray of glasses 6 and 7, indicating the inclusion of Mg^{2+} ions in the β -spodumene structure.^{5,12–15}

The present investigation also revealed that, when Li_2O , CaO and MnO are present together in aluminosilicate, the phase distribution can be calculated, assuming that Li_2O combines with an equivalent amount of Al_2O_3 and SiO_2 to form lithia aluminosilicate. If $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ in the glass exceeds unity, the excess Al_2O_3 combines with CaO to form anorthite- $\text{CaAl}_2\text{Si}_2\text{O}_8$. The great tendency for the formation of lithium aluminosilicate, rather than Ca-aluminosilicate, under normal conditions of heating was explained on the basis¹⁶ of the higher effect of the field strength of the Li^+ ion compared with the Ca^{2+} ion. Mn^{2+} can react with silica to form Mn-silicate, while the Mn-aluminosilicate-like cordierite phase, $\text{Mn}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, was not favoured in the present glasses, since the latter phase needs a mother glass of a high silica content rather than that needed for the formation of the lithia aluminosilicate solid solution phases.

On the other hand, in the glass of $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ ratio equal to unity, on changing the proportion of the divalent oxide (e.g. $G_{8–10}$), the Li_2O in these glasses is in just sufficient amounts to combine with

Al_2O_3 to form β -spodumene ($\text{LiAlSi}_2\text{O}_6$) together with one or another of Mn-, Ca- and/or Mg-containing phase, depending upon their relative proportions in the glass. At a CaO/MnO ratio of unity the bustamite phase of the probable formula $(\text{Ca}_{0.5}\text{Mn}_{0.5})\text{Si}_2\text{O}_6$ was formed, while in the presence of mixing of the three divalent oxides (i.e. Ca^{2+} , Mg^{2+} and Mn^{2+}) metasilicates of these divalent ions were assumed to be formed, i.e. CaSiO_3 , MgSiO_3 and MnSiO_3 , which go into solid solution to form a pyroxene solid solution series. The bulk composition of the solid solution was greatly dependent on the ratios of divalent present in the glass.

In the case of glass 9 in which the divalent mole ratio is 2CaO/1MnO/1MgO, Mn-pyroxene solid solution was formed, where Mn^{2+} replaced Mg^{2+} to form a schefferite phase of the probable formula $(\text{Ca}^{2+})(\text{Mn}_{0.5}\text{Mg}_{0.5})\text{Si}_2\text{O}_6$.⁹ However, in the case of glass 10 in which the divalent mole ratio present in the glass is 1CaO/1MnO/2MgO, the pyroxene solid solution phase with the d-spacing lines closely similar to those of diopside could be formed, assuming that a Mg-rich diopside- $\text{CaMgSi}_2\text{O}_6$ can be formed and the MnO can be accommodated in the diopside structure, giving rise to a pyroxene solid solution of the probable formula $(\text{Ca}_{0.5}\text{Mn}_{0.5})(\text{Mg})\text{Si}_2\text{O}_6$.⁹

The present results revealed also that the appreciable formation of manganese silicate phases like β - $\text{Mn}^{2+}\text{SiO}_3$, kanoite- $(\text{Mn}^{2+}\text{Mg})_2\text{Si}_2\text{O}_6$, diopside- $\text{Ca}(\text{Mn}^{2+}\text{Mg})\text{Si}_2\text{O}_6$ and bustamite- $(\text{CaMn}^{2+})_3\text{Si}_3\text{O}_9$ in their stability field under the heat treatment applied may indicate the prevalence of the manganous divalent state rather than the manganic trivalent state.

5 Conclusion

Coloured glass-ceramic materials can be successfully prepared by controlled crystallization of certain lithium manganese calcia magnesium aluminosilicate glasses. The crystallization of β -eucryptite and/or β -spodumene solid solution in such glasses is mainly sensitive to the $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ ratio in the glass, and to heat treatment. The concentration of Al_2O_3 influenced the nature of the crystalline phases, especially those crystallized in the glasses of $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ ratio greater than unity. In

this case, lithia aluminosilicate solid solution phases prefer to accommodate Mg^{2+} in their lattice rather than either Ca^{2+} or Mn^{2+} ions. Therefore, on addition of CaO, a calcia aluminosilicate $\text{CaAl}_2\text{Si}_2\text{O}_8$ phase could be formed, while in the presence of Mn^{2+} varieties of Mn-containing pyroxene and/or Mn-silicate solid solution were detected.

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