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The Mechanism of Nucleated Crystallisation of Glasses in Lithia-Alumina-Silica and Cordierite Systems

V. A. BLINOV
Miusskaya Sq-9, Moscow A-U7, USSR

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Two principal lines of investigation are discussed. In the first of these, in which glasses were crystallised under high pressure, it was shown that the low temperature α-forms of spodumene and eucryptite could be obtained. In further experiments the effects of substituting GeO_2 for SiO_2, Ga_2O_3 for Al_2O_3, MgO for Li_2O and TiO_2 for Al_2O_3 in Li_2O–Al_2O_3–SiO_2 glasses were studied. It was found possible to crystallise both α and β-forms of germanium and gallium containing spodumene and eucryptite. Infra-red absorption spectra, X-ray diffraction data and thermal expansion data are presented for the various crystal types. Based on the results of the investigation, it is suggested that nucleated crystallisation in the glasses may be due to the initial precipitation of a crystal phase which is isomorphous with the predominant crystal phase that is to be developed in the glass-ceramic, and that during the heat-treatment the crystals of the latter phase grow on the crystals of the primary phase.

1. Introduction

At present the problem of producing glass-ceramic materials by nucleated crystallisation is attracting the attention of a great number of scientists in various countries. Glass-ceramics are characterised by a fine-grained and uniform structure composed of tiny crystals and residual glass layers forming a bond between the crystals. These materials possess very interesting features and properties viz: high mechanical strength, high refractoriness, high chemical resistance and very low thermal expansion coefficient.

So far, there is no generally accepted viewpoint with regard to the mechanism of nucleated crystallisation of glass. The composition of crystallisation centres is still not clear. A number of scientists believe that particles of the catalyst are the centres of crystallisation i.e. rutile or another titanate in a crystalline state in titania nucleated glasses. At present, however, there is little or no experimental data supporting this point of view.

The objective of the present investigation was to study the mechanism of nucleated crystallisation of glasses in lithia-alumina-silica and cordierite systems.

At present, nucleated crystallisation of glass leading to the formation of homogeneous fine crystalline structure throughout the volume of the material is divided into two categories according to the mechanism of its action on the crystallisation process.

1. Nucleated crystallisation caused by the addition to glasses of metals possessing low solubility (copper, platinum, gold, and silver): these metals are capable of forming highly dispersed particles acting as nuclei at which the formation of the main crystalline phase takes place. Photosensitivity nucleated glass-ceramics fall in this category.
2. Nucleated crystallisation caused by chemical inhomogeneity of the glass structure with regions of submicroscope size (of order 100 Å); in this case one of the "submicrophases" crystallises more readily than the other.

For the controlled crystallisation of glasses in the lithia-alumina-silica and cordierite systems, TiO_2 is added as a nucleating agent and thus a great many nuclei are created in the base glass. Most scientists consider that glass-ceramics of this type fall into the second category.

As to the mechanism of nucleated crystallisation of glasses in the lithia-alumina-silica and cordierite systems the predominant point of view up to date is that the necessary precondition for the formation of nuclei in the glass-ceramic production is the separation of glass into two liquid phases.

There is a further possibility, however, which seems to have been overlooked. This is, that a crystalline compound is first precipitated which is isomorphous with the predominant crystal phase that is to be developed in the glass-ceramic. During appropriate heat-treatment, therefore, the predominant crystal phase grows on the crystals of the primary phase.

2. Experimental and Discussion

The mechanism of nucleated crystallisation was studied for glasses in the system Li_2O–Al_2O_3–SiO_2, in which SiO_2 was isomorphously substituted by GeO_2, Al_2O_3 was substituted by Ga_2O_3 and Li_2O by MgO. There is good reason to believe that by such substitutions glasses and glass-ceramics will be formed similar to those in the lithia-alumina-silica system.

Solid solutions formed in these systems were considered as β-quartz derivatives which are the result of substitution of some silicon ions in SiO_4 tetrahedra by aluminium ions. Because of substitution of SiO_4 groups by AlO_4 groups, silicate networks become alumosilicate ones. The AlO_4 group, however, introduces an additional negative charge into a structure unit, since Al^{3+} replacing Si^{4+} saturates only three but not four free oxygen valencies, in consequence of which one free negative charge remains. This requires the presence of one divalent ion (such as Mg^{2+}) per two AlO_4 groups or one monovalent ion (such as Li^+) per AlO_4 group to achieve electroneutrality.

The hexagonal form of β-quartz is stable over the range 573° to 870° C and possesses slightly negative and very low birefringence (optical anisotropy). Isomorphous substitution of SiO_4 groups by AlO_4 groups leads to room temperature stabilisation of the β-quartz structure. Isomorphous substitution of SiO_4 by GeO_4 and AlO_4 by GaO_4 also leads to room temperature stabilisation of β-quartz.

It is interesting to note that among a very limited group of compounds, cordierite and eucryptite in the vitreous state possess a higher density and refractive index than in the crystalline one. Table I lists the values of the refractive indices of eucryptite, spodumene and cordierite. The second interesting feature is the fact that the thermal expansion coefficient of these materials is rather low and moreover, the expansion coefficient of eucryptite is negative.

TABLE I Refractive indices n_D and densities d of various crystals and glasses

	n_D	d
Eucryptite $Li_2O.Al_2O_3.2SiO_2$		
Low-temperature α-form	1.545	2.74
High-temperature β-form	1.522	2.36
Glass	1.541	2.42
Glass (compacted)	1.550	2.74
Spodumene $Li_2O.Al_2O_3.4SiO_2$		
Low-temperature α-form	1.670	3.16
High-temperature β-form	1.520	2.40
Glass	1.518	2.38
Glass (compacted)	1.59	2.77
Cordierite $2MgO.2Al_2O_3.5SiO_2$		
Low-temperature	1.546	2.62
High-temperature	1.526	2.58
Glass	1.550	2.64

There are two important points concerning the eucryptite and cordierite compositions. These are, first that the refractive indices are higher when the materials are in the vitreous state than in the crystalline state and secondly that the thermal expansion coefficients of the crystalline materials are low. We have attempted to achieve a better understanding concerning these questions by studying the crystallisation kinetics of glasses of the eucryptite and spodumene composition under high pressure and during production of low temperature phases of α-spodumene and α-eucryptite as well as by investigating the mechanism of nucleated crystallization of glasses in lithia-alumina-silica and cordierite systems.

By subjecting the glass of the spodumene and eucryptite composition to the action of ultra-high pressure of about 60 000 atm we have revealed structural changes in glass related to the change of Al-co-ordination number. With increasing pressure, holding time at a given temperature, and temperature (in appropriate ranges), a glass was obtained, the density and refractive index of which were higher than for the original glass. The calculation of the total molar refractivity (R) and refractivity of aluminium (R_{Al}) with the Lorentz-Lorentz equation has shown that aluminium in β-spodumene and β-eucryptite exists in a four-co-ordinated state [1]. Simultaneously it was shown that with increasing pressure the amount of Al in sixfold co-ordination in glass grew. Under elevated pressures of about 60 000 atm glasses of the spodumene and eucryptite composition were obtained in which all Al^{4+} ions exist in sixfold co-ordination (table I). On crystallisation of this glass under pressure for the first time we managed to synthesise a low-temperature or α-form of spodumene and α-form of eucryptite [2]. In the case when glass was crystallised using high pressure without preliminary change of Al-co-ordination number from four to six each time, a high-temperature β-spodumene and β-eucryptite was produced.

If the compacted glass i.e. glass which has undergone structural changes due to the change of Al-co-ordination number from four to six is reheated without applying pressure then the glass exhibits a tendency to convert to the initial state. In this case the change of Al from the sixfold co-ordination to the fourfold one is observed.

Figs. 1 and 2 show X-ray diffraction patterns and infrared spectra of synthesised α- and β-forms of spodumene, eucryptite and of samples of intermediate glass compositions

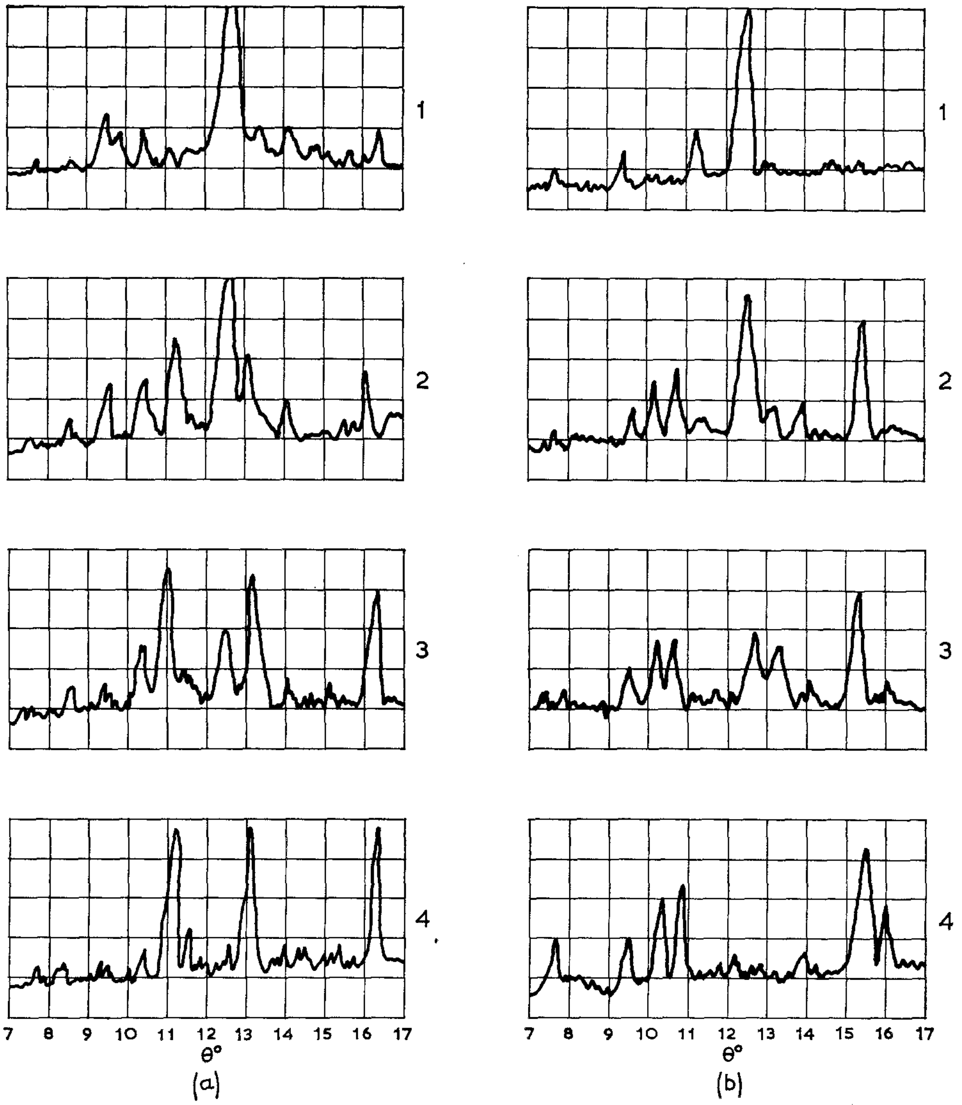

Figure 1 X-ray diffraction patterns of eucryptite (a) and spodumene (b). 1 β-form; 2 mixture β- and α-form; 3 mixture α- and β-form; 4 α-form.

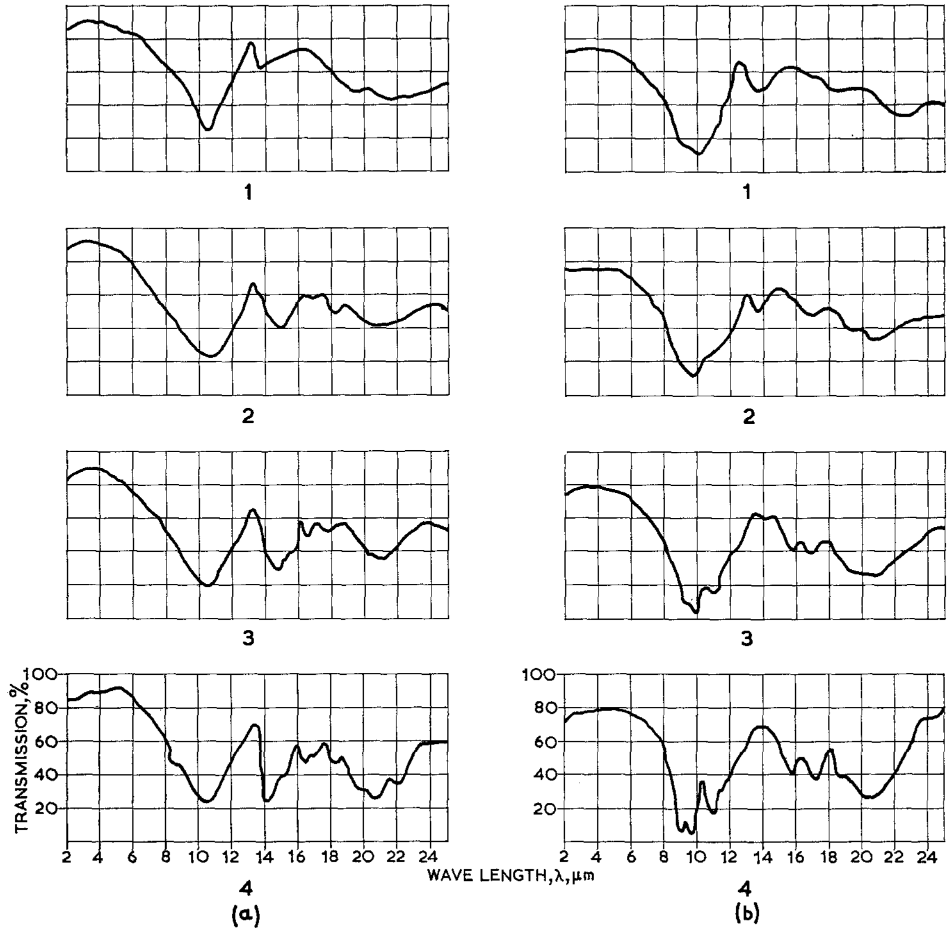

Figure 2 Infra-red spectra of eucryptite (a) and spodumene (b). 1 β-form; 2 mixture β- and α-form; 3 mixture α- and β-form; 4 α-form.

crystallised under various pressures in which a part of the aluminium is in a six-co-ordinated state and a part in a four-co-ordinated one.

Figs. 1 and 2 clearly show a steep change of Al-co-ordination from tetrahedral in the β-form of eucryptite and spodumene to octahedral in the α-form of eucryptite and spodumene.

The band of β-spodumene with a peak at 13.4 μm (745 cm^{-1}) is attributed to the vibration of tetrahedra (AlO_4); its disappearance indicates the variation of Al-co-ordination number from four to six. The bands of α-spodumene with peaks at 11 μm (910 cm^{-1}), 15.6 μm (640 cm^{-1}) and 17.1 μm (585 cm^{-1}) are assigned to the vibrations of octahedra (AlO_6); their existence indicates the change of Al-co-ordination number from four to six.

The foregoing results led to the conclusion that higher values of density and refractive index in glass of the eucryptite composition compared with the β-form of eucryptite could be accounted for by the fact that in glass of the eucryptite composition a part of the aluminium exists in sixfold co-ordination whereas in β-eucryptite all the aluminium exists in four-fold co-ordination.

In glass of the spodumene composition as well as in β-spodumene all the aluminium is in four-fold co-ordination, in consequence of which density and refractive index of the crystal are higher than those of the glass.

It is known that under the influence of high pressure, glass structure, temperature and kinetics of phase transformations as well as physical properties undergo marked changes. The effect of the additional parameter i.e. pressure, greatly complicates the interpretation of the results obtained. We attempted therefore to obtain glasses of the eucryptite and spodumene compositions where structural changes should be observed due to the change of Al-co-ordination from four to six without pressure. For this purpose the Li_2O–Al_2O_3–GeO_2 system was chosen. It was reasonable to assume that GeO_2 would favour the change of Al-co-ordination from four to six. We synthesised stoichiometric compositions of eucryptite and spodumene glasses where SiO_2 was substituted by an equimolar amount of GeO_2.

The attempts of some investigators to synthesise germanium-containing glass-ceramics with zero and negative thermal expansion coefficient were unsuccessful. The difficulty of such synthesis is accounted for by the fact that in synthesising germanate eucryptite, in addition to high-temperature or β-form (with low thermal expansion coefficient) a low-temperature or α-form of eucryptite (with high thermal expansion coefficient) is precipitated. We managed to synthesise separately α- and β-forms of eucryptite and to produce germanium-containing glass-ceramic material with zero and negative thermal expansion coefficient.

The synthesis of the high-temperature β-form of germanate eucryptite with a negative and zero thermal expansion coefficient once more supports the suggestion of obtaining germanate eucryptite which is isomorphous with silicate eucryptite. The thermal expansion coefficient of germanate eucryptite varies from -50×10^{-7} to $+80 \times 10^{-7}/°$ C. Moreover, glass-ceramic materials with zero expansion were synthesised.

Similar results were obtained by isomorphous substitution of Al_2O_3 by Ga_2O_3 in the system Li_2O–Ga_2O_3–SiO_2. α- and β-forms of gallium eucryptite and spodumene were formed by glass crystallisation in the systems Li_2O–Ga_2O_3–$2SiO_2$ and Li_2O–Ga_2O_3–$4SiO_2$.

Figs. 3, 4 and 5 present the X-ray diffraction patterns and infra-red spectra of the α- and β-forms of silicate and gallium spodumene and eucryptite.

Since the ionic radii Si^{4+} (0.39 Å) and Ge^{4+} (0.44 Å) and Al^{3+} (0.57 Å) and Ga^{3+} (0.62 Å) are close, the precipitated crystalline compounds of the α- and β-forms of silicate, germanate, and gallium eucryptite and spodumene differ only slightly in their interplanar crystal spacings from each other. The X-ray diffraction patterns of synthesised compounds clearly show the analogy between synthesised silicate, germanate, and gallium forms.

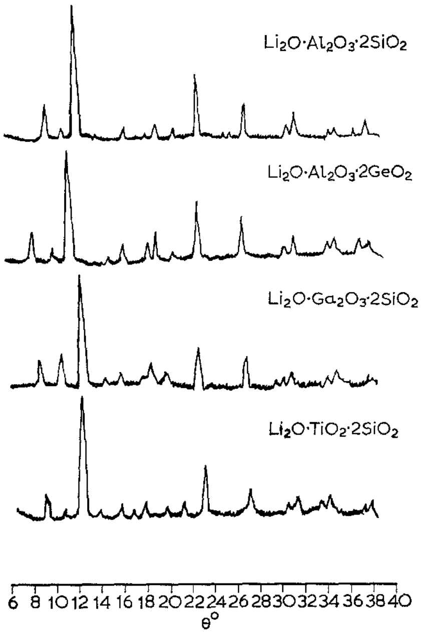

Figure 3 X-ray diffraction patterns of $Li_2O.Al_2O_3.2SiO_2$, $Li_2O.Al_2O_3.2GeO_2$, $Li_2O·Ga_2O_3.2SiO_2$, $Li_2O.TiO_2.2SiO_2$ (β-form).

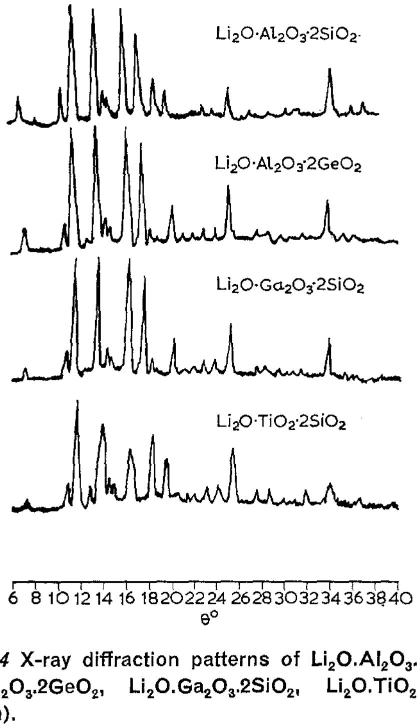

Figure 4 X-ray diffraction patterns of $Li_2O.Al_2O_3.2SiO_2$, $Li_2O.Al_2O_3.2GeO_2$, $Li_2O.Ga_2O_3.2SiO_2$, $Li_2O.TiO_2.2SiO_2$ (α-form).

Infra-red spectra of silicate, germanate, and gallium-containing glasses show considerable differences. In the silicate eucryptite and

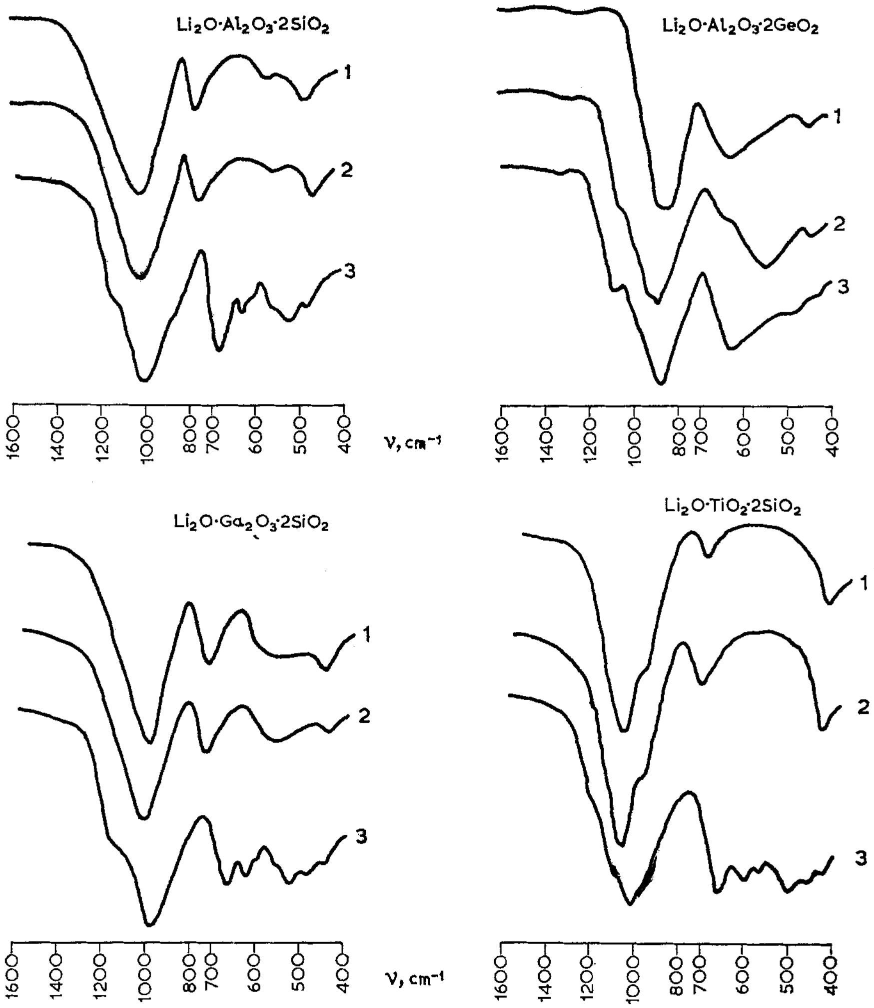

Figure 5 Infra-red spectra of $Li_2O.Al_2O_3.2SiO_2$, $Li_2O.Al_2O_3.2GeO_2$, $Li_2O.Ga_2O_3.2SiO_2$, $Li_2O.TiO_2.2SiO_2$ (1 glass; 2 β-form 3 α-form).

spodumene glasses almost all of the aluminium ions are in fourfold co-ordination; in gallium-containing glasses a part of the gallium ions is in fourfold and a part in sixfold co-ordination whereas glasses of the germanate composition contain Al^{3+} in sixfold co-ordination. As in the original germanate glass Al^{3+} is in sixfold co-ordination, on crystallisation the low-temperature form of α-eucryptite which contains Al^{3+} in sixfold co-ordination will be precipitated as the main crystalline phase. By changing the heat treatment schedule it is quite possible to precipitate separately both α- and β-eucryptite and α- and β-spodumene.

In addition to the X-ray diffraction patterns of the synthesised compounds their low thermal expansion coefficients gave further evidence of the isomorphic substitution in the glass and glass-ceramic compositions.

Interesting results have been achieved during the substitution of Al_2O_3 by TiO_2 in the system Li_2O–TiO_2–SiO_2. Similarly these compositions as well as germanium undergo the isomorphic substitution of SiO_2. The X-ray diffraction patterns and infra-red spectra of synthesised α- and β-titanate, eucryptite and spodumene are illustrated in figs. 3, 4 and 5. The X-ray diffraction patterns of the samples of the composition Li_2O. $TiO_2.2SiO_2$ and $Li_2O.TiO_2.4SiO_2$ given in figs. 3 and 4 indicate a good correlation between

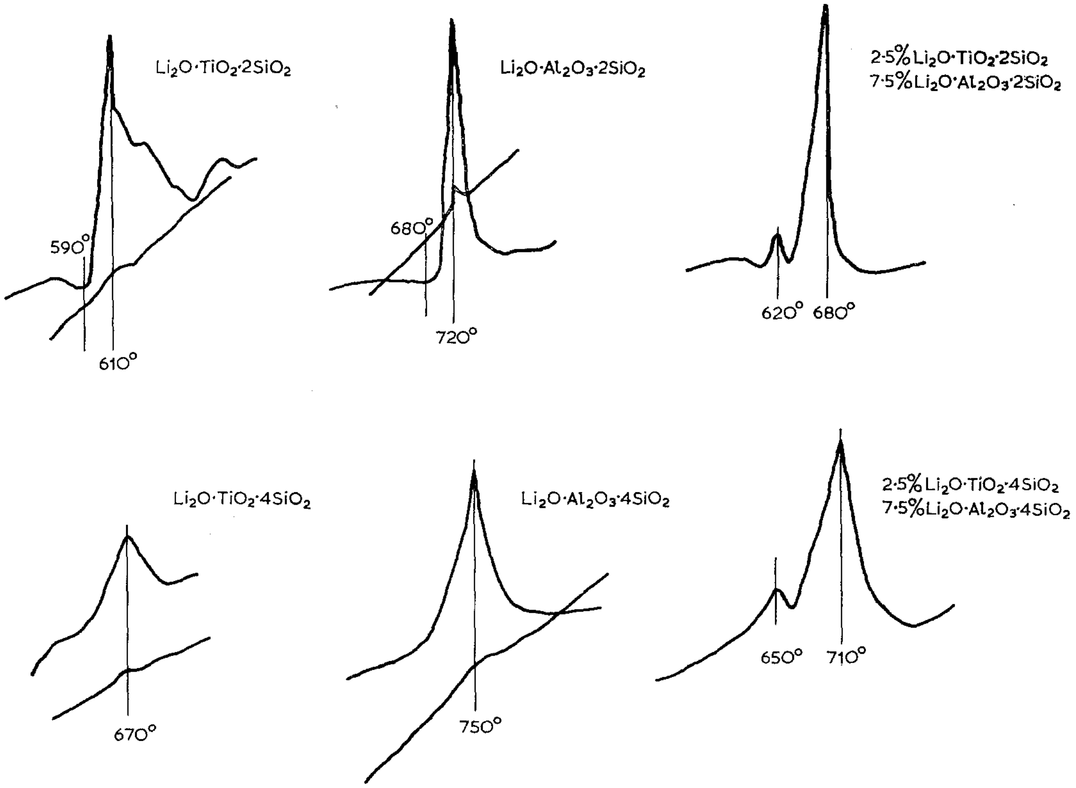

Figure 6 Differential thermal analysis curve of $Li_2O.TiO_2.2SiO_2$, $Li_2O.Al_2O_3.2SiO_2$, 2.5% $Li_2O.TiO_2.2SiO_2$, 7.5% $Li_2O.Al_2O_3$. $2SiO_2$, $Li_2O.TiO_2.4SiO_2$; $Li_2O.Al_2O_3.4SiO_2$, 2.5% $Li_2O.TiO_2.4SiO_2$, 7.5% $Li_2O.Al_2O_3.4SiO_2$.

interplanar crystal spacings for these compositions and for those containing silicate eucryptite and spodumene. We have also produced the titanate eucryptite with zero and negative thermal expansion coefficients.

Differential thermal analysis of glass of the composition $Li_2O.TiO_2.2SiO_2$ indicated that the crystalline phase $Li_2O.TiO_2.2SiO_2$ is developed at 600° C which is 90° C lower than the crystallisation temperature of glass of the eucryptite composition $Li_2O.Al_2O_3.2SiO_2$.

Differential thermal analysis of glass of the composition $Li_2O.TiO_2.4SiO_2$ revealed that the crystalline phase is developed at 650° C whereas the crystalline phase of glass of the spodumene composition is developed at a temperature 70° C higher. Two exothermic peaks were revealed on the thermogram of the mixture of two glasses (25% $Li_2O.TiO_2.2SiO_2$ and 75% $Li_2O.Al_2O_3$. $2SiO_2$) as well as of the fused glass. The first peak corresponds to the development of the first precipitated crystalline phase $Li_2O.TiO_2.2SiO_2$ and the second one corresponds to the development of the second phase Li_2O. $Al_2O_3.2SiO_2$ which is isomorphous with the first one and grows on it (fig. 6).

The foregoing results suggest that in glass of the eucryptite composition with TiO_2 as a nucleating agent for volume crystallisation, a primary crystalline phase is identified which is a compound isomorphous with the main crystalline phase and is precipitated at a temperature 90° C lower than the crystallisation temperature of the main crystalline phase.

In glass of the spodumene composition with TiO_2 as a nucleating agent the compound Li_2O. $TiO_2.2SiO_2$ is a primary crystalline phase isomorphous with spodumene which is developed at a temperature 70° C lower than the temperature of formation of the main crystalline phase of β-spodumene.

It is suggested that these crystalline phases, $Li_2O.TiO_2.2SiO_2$ for eucryptite, $Li_2O.TiO_2$. $4SiO_2$ for spodumene, and $2MgO.2TiO_2.5SiO_2$ for cordierite glasses are nucleus phases. The main crystalline phase isomorphous with the first formed crystalline one grows on these precipitated crystalline phases.

3. Conclusions

The following conclusions may be drawn from the data presented in this paper.

Nucleated crystallisation in glasses of lithia-alumina-silica and cordierite composition is due to the initially spontaneous precipitation of compounds with structures which are isomorphous with the main crystalline phase observed at the higher temperature.

In contrast to the way in which metallic additions promote nucleated crystallisation these compounds dissolve in glasses and upon heat treatment at lower temperatures they are initially formed and behave as nucleating agents for the main phase.

Microseparation in lithium- and cordierite-containing glasses occurs, as in photosensitive glasses but is not dominant in nucleated crystallisation of these glasses.

References

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Letter

Hedvall Effect and Synthesis of Zircon

The synthesis of zircon, from the constituent oxides ZrO_2 and SiO_2, has been the subject of many investigations [1-8]. The most comprehensive study probably was that of Curtis and Sowman [7] who showed that the lowest temperature at which zircon can be synthesised from ZrO_2 and SiO_2 is approximately 1315° C and the rate of synthesis increases rapidly as the temperature is increased from 1425 to 1535° C.

Hedvall [9] has shown that a material undergoing a polymorphic transformation or decomposition is in a very reactive state and consequently the rate of reaction is greatest at the transformation or decomposition temperature. Zirconia undergoes a reconstructive, disruptive transformation from monoclinic to tetragonal symmetry at 1170° C, at which temperature the synthesis of zircon from ZrO_2 and SiO_2 may be expected to take place at an enhanced rate. The purpose of this investigation is to verify the Hedvall effect in the synthesis of zircon from ZrO_2 and SiO_2.

Monoclinic zirconia, obtained from the Bhabha Atomic Research Center, Bombay (having the impurities: 200 ppm Hf, 150 ppm Fe, 275 ppm Mg, 150 ppm Ti) and quartz powder, SiO_2 99.9% from Pennsylvania Glass Sand Corporation (with impurities : 230 ppm Fe_2O_3, 90 ppm TiO_2 and 900 ppm Al_2O_3) were employed in the present investigation. An equimolecular mixture of ZrO_2 and SiO_2, thoroughly mixed in a glass mortar, was used in the experiments. Using a Temp-Pres Research furnace mounted on a General Electric XRD-6 X-ray diffractometer, the mixture was heated at 1155, 1170 1200, 1300 and 1400° C for varying periods of time. Filtered CuK_α radiation was used and the range $20° < 2\theta < 45°$ was scanned. At the end of each temperature run, the furnace was cooled and the room temperature X-ray pattern recorded. A fresh sample was used for each temperature run.

By plotting the intensity of the $(11\bar{1})$ line (at 2θ: 28.3°) of monoclinic zirconia and of the (101) line (at 2θ : 29.7°) of the tetragonal phase versus temperature, the monoclinic to tetragonal transformation was seen to start at 1130° C and to be completed at about 1200° C.

The role of temperature and time on the rate of formation of zircon from ZrO_2 and SiO_2 is brought out clearly in fig. 1, where the intensity of the (200) line of zircon (which occurs at 2θ : 27°) is plotted as a function of temperature with time as a parameter. The amount of zircon formed goes through a maximum at 1200° C. This marked peak in the 1170 to 1200° C region is attributed to the high reactivity of ZrO_2 at the monoclinic-tetragonal phase transformation in this range. As the temperature is increased beyond 1300° C, the amount of zircon formed increases due to the increased thermal energy. Further, cristobalite formation from quartz via a transitional phase with a disordered structure [11], becomes significant at 1300°C and beyond. This transformation contributes to the enhanced formation of zircon at temperatures beyond 1300° C. Preliminary studies indicate a decrease of quartz and increase of cristobalite at 1300° C. Detailed studies of this are under way.