Compositional Study and Properties Characterisation of Alkaline Earth Feldspar Glasses and Glass-Ceramics

DOV BAHAT
Research and Development Laboratories, Corning Glass Works, Corning, NY, USA

Received 31 March 1969

Fields in which metastable crystallisation of feldspars may occur as a result of heterogeneous nucleation were defined at 1000° C for the systems $BaO-Al_2O_3-SiO_2$, $SrO-Al_2O_3-SiO_2$, and $CaO-Al_2O_3-SiO_2$. The metastable fields of the above barium and calcium systems differ considerably from the respective primary liquidus fields of celsian and anorthite with the tendency for the stoichiometric compositions to be situated at the centre of the metastable region.

Various physical and dielectric properties of the glasses and glass-ceramics of the three systems are presented and compared. High linear thermal expansion, high electrical resistivity, and low loss tangent and dielectric constant characterise these glass-ceramics. One of them (No. 2, table I) has, in addition, high heat resistance and translucency at high temperatures.

1. Introduction

Polymorphism and stability relationships in the various alkaline earth feldspar compositions $CaAl_2Si_2O_8$, $SrAl_2Si_2O_8$, and $BaAl_2Si_2O_8$ have attracted extensive research in the last two decades. These minerals, apart from having a wide academic interest, are valuable to various materials science fields, mainly due to the high heat resistance and remarkable dielectric properties which some of them possess [1-3].

In recent years, with the development of glass-ceramics (ceramic materials formed through the controlled crystallisation of glass), considerable attention has been given to the various feldspar modifications as major and minor ingredients in various glass-ceramics [4]. Hexacelsian, for instance, is an important ingredient associated with $BaTiO_3$ in dielectric glass-ceramics [5]. Celsian and hexacelsian are also present in significant amounts in commercial tableware [6].

Ceramists who employ solid-state reaction methods may take advantage of information available in phase diagrams for reactions that reach equilibrium. However, the usefulness of phase diagrams for the glass-ceramic investigator is limited, since crystallisation from glass is often metastable, and equilibrium in many systems is not achieved.

In the present study, the $BaO-Al_2O_3-SiO_2$, $SrO-Al_2O_3-SiO_2$, and $CaO-Al_2O_3-SiO_2$ systems were investigated in the attempt to define the fields within which metastable crystallisation of feldspars occurs in glass, through heterogeneous nucleation by certain nucleating agents.

The thermodynamic significance of these metastable fields is limited, since their boundaries may vary with change in undercooling and nucleating agents. (Such variations are generally small – 2 to 3 wt % – in the phase diagram if undercooling is not too low.) In compositions near the boundaries which are RO-rich or are within the mullite primary, a minor amount of a secondary phase (0 to 20 wt %) may precipitate within the limits of the metastable field, and a feldspar may crystallise in minor amounts (0 to 20 wt %) outside the limits.

This data might help glass-ceramic investigators to anticipate feldspar heterogeneous nucleation from various compositions. It might also indicate the extent of the still unknown primary liquidus field of $SrAl_2Si_2O_8$. A correlation has been shown [7] between the chemical composition of the glass within the metastable field of $SrO.Al_2O_3.SiO_2$ and the type of polymorph that normally would grow from it.

Some chemical compositions of alkaline earth feldspar glasses and glass-ceramics and their physical and electrical properties are given (tables I, II, III) and evaluated.

2. Experimental Procedure

The glasses were prepared from Morgan Sand ($SiO_2 = 99.8\%$), T-61 aluminium oxide ($Al_2O_3 = 99.7\%$), and calcium, strontium, and barium reagent carbonates. In addition, standard quantities of nucleating agents were added to most batches, and these were as follows: to batches of the $CaO–Al_2O_3–SiO_2$ and $BaO–Al_2O_3–SiO_2$ systems, 1 % MoO_3 was added, and to batches of the $SrO–Al_2O_3–SiO_2$ system, 2% MoO_3 + 2% WO_3 were added. The batch materials were weighed to an accuracy of 0.1 g and dry mixed. Standard batch mixtures of 600 g were melted at 1800° C in a gas-oxygen furnace generally for 4 h in 20% Rh-80% Pt crucibles. Quenched patties were made from the melts by pouring them onto a cold cast-iron plate and annealing at 800° C for 1 h.

Portions of these patties were subjected to heat-treatments. A standard heat-treatment for most glasses was at 1000° C for 1 h. However, certain silica-rich glasses in the $SrO–Al_2O_3–SiO_2$ system were treated at higher temperatures and for longer durations (at temperatures higher than 1100° C for several days). Compositions were nominally made at intervals of 2 to 5 wt %.

All the products which resulted from the heat-treatments were routinely examined by X-ray diffraction. The same applied to glasses which crystallised on cooling.

Wet chemical analyses were carried out on glasses No. 1 and 4 and glass-ceramic No. 2 (table I). Thermal expansion measurements of glasses and glass-ceramics were obtained on a differential dilatometer with reference to the expansion of alumina in the range of 25 to 1000° C. Electrical properties were measured using gold electrodes with a Beckman ultrohmeter.

3. Results and Discussion

3.1. Compositional Study

In figs. 1 to 3 the metastable fields of crystallisation of feldspar glass-ceramics are shown for the barium, strontium, and calcium aluminosilicate systems, respectively. Compositions within the fields surrounded by solid lines in these three systems form glasses which upon heating can be nucleated by small amounts of nucleating agents and produce crystals which are either solely feldspars or have feldspars as the dominant and primary phase. In the barium system, hexacelsian is the only feldspar that crystallises, whereas in the strontium and calcium systems both high-symmetry and low-symmetry feldspars may be obtained [7]. Only the low-symmetry calcium and strontium feldspars crystallise here in their stability fields. In figs. 1 and 2, the vertically lined areas indicate glasses of low viscosity and high mobility of cations which may be readily nucleated and crystallised to glass-ceramics on cooling unless they are rapidly quenched. Compositions outside the solid lines in the various figures may be generally described as follows:

(i) In the barium system, compositions richer in SiO_2 and poorer in Al_2O_3 form stable glasses (nucleation of these glasses is impossible or difficult). Glasses of compositions richer in Al_2O_3 and poorer in SiO_2 readily crystallise on cooling to oxides; they do not form feldspar glass-ceramics. Compositions poorer in BaO within the primary field of mullite form glass-ceramics dominated by mullite. Compositions rich in BaO form glass-ceramics in which feldspar may be a minor phase.

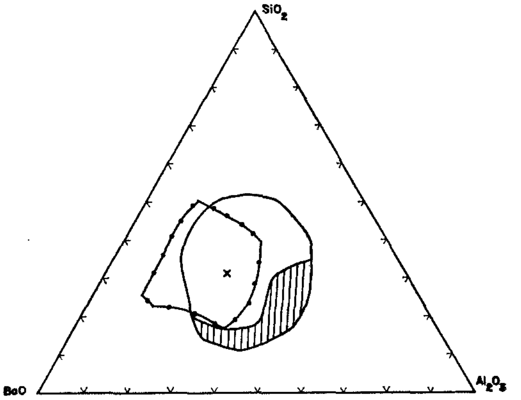

Figure 1 A comparison between the primary field of $BaAl_2Si_2O_8$ (dash-dot) line and the metastable crystallisation field of hexacelsian at 1000° C when nucleated by molybdenum oxide (solid line). The area marked by vertical lines indicates glasses which crystallised on cooling unless rapidly quenched. In figs. 1 to 3 the x mark shows the locations of the corresponding feldspar stoichiometries.

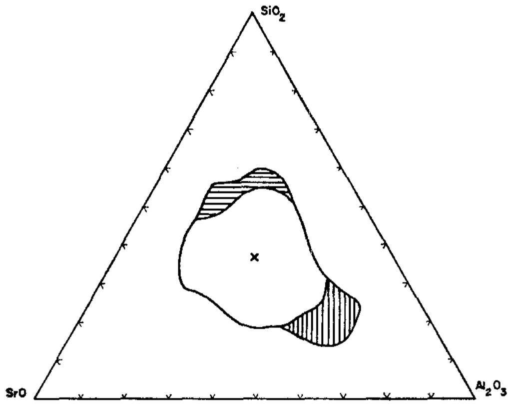

Figure 2 Metastable crystallisation field of various polymorphs of $SrAl_2Si_2O_8$ at 1000° C when nucleated by molybdenum and tungsten oxides. The area marked by vertical lines indicates glasses which crystallised on cooling unless rapidly quenched. The area marked by horizontal lines indicates glasses which had to be severely heat-treated before crystallisation occurred.

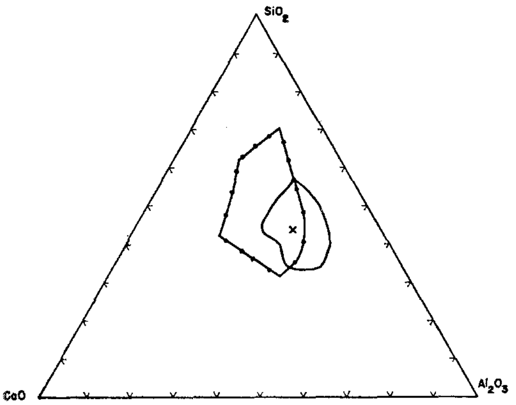

Figure 3 A comparison between the primary field of $CaAl_2Si_2O_8$ (dash-dot line) and the metastable crystallisation field of various polymorphs of $CaAl_2Si_2O_8$ at 1000° C when nucleated by molybdenum oxide (solid line).

(ii) The field of strontium feldspar glass-ceramics generally resembles its barium counterpart in extent, though it is somewhat richer in SiO_2 than the latter, and can take more alumina, i.e. the glass-forming region of the $SrO–Al_2O_3–SiO_2$ system is larger than that of the $BaO–Al_2O_3–SiO_2$ system around the main ternary stoichiometry. In the $SrO–Al_2O_3–SiO_2$ system, similar to $BaO–Al_2O_3–SiO_2$, compositions rich in strontium which lie outside the solid line form glass-ceramics dominated by phases other than feldspar, but feldspar may be present as well. The horizontally lined area defines a region of viscous glasses which require an intense heat-treatment in order to form feldspars.

(iii) The field of calcium feldspar glass-ceramics is different from the other two; it is much smaller. Glasses which are outside the solid line in fig. 3 normally do not readily nucleate to glass-ceramics (with the exception of mullite glass-ceramics), and their products are not feldspar phases.

The metastable fields of feldspar crystallisation in the $BaO–Al_2O_3–SiO_2$ and $CaO–Al_2O_3–SiO_2$ systems differ considerably from their respective primary fields [8, 9]. In the $BaO–Al_2O_3–SiO_2$ system, the metastable field differs from the primary field mainly by being extended towards the $SiO_2–Al_2O_3$– and $BaO–Al_2O_3$ binaries, and by being withdrawn from the BaO-rich region. In the $CaO–Al_2O_3–SiO_2$ system, the metastable field is considerably smaller than the respective primary field. It is generally shifted somewhat towards the $SiO_2–Al_2O_3$ binary in relation to the primary field. No published data on the primary field of strontium feldspar to compare with the related metastable field is yet available. It seems likely, however, that the $SrO_2–Al_2O_3–2SiO_2$ primary field should resemble more the $BaO–Al_2O_3–2SiO_2$ primary field than that of $CaO–Al_2O_3–SiO_2$, and probably be larger than the former. Furthermore, it would be shifted more to the centre of the $SrO–Al_2O_3–SiO_2$ triangle. Note that in the three systems there is a tendency for the stoichiometric compositions to be situated at the centre of the metastable fields.

3.2. Properties Characterisation

3.2.1. Chemical Compositions

Chemical compositions of eight glasses and glass-ceramics are given in table I. Of these, three are glasses having the stoichiometric compositions of barium, strontium, and calcium feldspars (No. 1, 4, and 7). The other five are glass-ceramics which were made of glasses which deviated to various extents from the stoichiometric compositions of the three feldspars.

3.2.2. Physical Properties

Some of the physical properties of these glasses and glass-ceramics are given in table II. The information on the glass-ceramics is supplemented with the corresponding heat-treatments which caused the formation of the glass-ceramics.

TABLE I Chemical compositions of glasses and glass-ceramics of $RO-Al_2O_3-SiO_2$ systems

	1	2	3	4	5	6	7	8
SiO_2	31.83	34.82	48	36.6	30	30	43.2	45
Al_2O_3	26.6 ± 0.1	24.7 ± 0.1	17	31.6 ± 0.1	45	40	36.7	30
BaO	40.6 ± 0.1	38.3 ± 0.06	35					
SrO		0.08		31.1 ± 0.5	25	30		
CaO		0.13					20.1	25
Fe_2O_3		0.70						
K_2O		0.80						
Na_2O		0.28						
MgO		0.16						
$RhCl_3$			+ 0.5					
V_2O_5					+ 0.66			
MoO_3								+ 1.0
$IrCl_4$						+ 0.16		

Nos. 1, 2, and 4 are chemical analyses. Other results are calculated from batch materials.

The coefficients of thermal expansion of the glasses (Nos. 1, 4, and 7) are nearly identical. This indicates that the thermal expansion is independent of the specific alkaline earth species present and is primarily a factor of the tetrahedral network. The thermal expansion of the various glass-ceramics varies, and it is a function of the thermal expansion of the feldspar modification, the effect of the displacive transformation [10, 11], and the expansion of the residual glass in each glass-ceramic.

The linear expansion of the hexagonal barium feldspar glass-ceramic (No. 2, table II) is 80 × 10^{-7}/° C. This glass-ceramic is nearly fully crystalline with only traces of glass. Here the hexagonal feldspar has a rapid volume change at 300° C due to a displacive transformation [10]. Glass-ceramic No. 3 has a lower expansion (74 × 10^{-7}/° C) which is due to the presence of low-expansion silica-rich residual glass and also due to the sluggishness of the displacive transformation of the hexagonal feldspar in this matrix.

Glass-ceramic No. 5 has a very high expansion (92 × 10^{-7}/° C). In this material there is a very pronounced displacive transformation [11] which is accompanied by a large volume change in the strontium hexagonal feldspar. Glass-ceramic No. 6, on the other hand, has a sluggish displacive transformation and a lower expansion (75 × 10^{-7}/° C).

Glass-ceramic No. 8 has a still lower expansion (71 × 10^{-7}/° C), due to the presence of traces of anorthite in addition to the hexagonal calcium feldspar. There is also a very sluggish displacive transformation of the hexagonal feldspar [11].

TABLE II Physical properties of glasses and glass-ceramics of $RO-Al_2O_3-SiO_2$ systems

	Heat-treatment of glass-ceramics	Visual description	Crystal phases	25-1000° C exp. coeff. × 10^{-7}/° C	Heat resistance ° C
1	—	clear glass	—	65	
2	1000° C × 40 min	translucent green-brown glass-ceramic	hexacelsian	80	1680
3	1000° C × 60 min 1100° C × 60 min	slightly translucent grey glass-ceramic	hexacelsian	74	1250
4	—	clear glass	—	63	
5	1000° C × 60 min	bluish-green glass-ceramic	hexagonal strontium feldspar	92 92	
6	1050° C × 40 min	translucent light grey glass-ceramic	hexagonal strontium feldspar	75	1100
7	—	clear glass	—	65	
8	1000° C × 40 min	grey-white glass-ceramic	hexagonal calcium feldspar and traces of anorthite	71	

Glass-ceramics Nos. 2 and 6 have high translucency even when the grain size of the feldspar is high (1 to 10 μm). This can be attributed to a high optical isotropy of the material, which must depend on a low birefringence of the hexagonal feldspars, since the orientation of the crystals is completely random. The refractive index of the ordinary ray of the barium hexagonal feldspar is 1.573 [10]. The refractive index of the extraordinary ray has not been determined. It is assumed, however, that there must be very little birefringence.

For glass-ceramics Nos. 2, 3, and 6, the maximum temperatures of service at which translucency is maintained are given in table II. Glass-ceramics Nos. 2 and 3 sag above 1680 and 1250° C respectively, due to the presence of residual glass. In glass-ceramic No. 6, the hexagonal modification of strontium feldspar transforms fairly rapidly (within an hour) to the triclinic modification at 1350° C. The transformation rate decreases as the temperature decreases, and at 1100° C the hexagonal form is persistent. No. 2 has perhaps the highest heat

TABLE III Dielectric properties of glasses and glass-ceramics of RO-Al_2O_3-SiO_2 systems

	Dielectric constant °C			Loss tangent °C			Vol. resistance log ohm/cm °C	
		temp	DC		temp	LT	temp	log ρ
1	100 c/s	25	9.46	100 c/s	25	0.0012	347.0	14.21
		298.2	9.75		298.2	0.0015	394.7	13.06
		498.7	10.23		498.7	0.034	444.7	12.09
	10 Kc/s	25	9.43	10 Kc/s	25	0.0014	498.7	11.21
		298.2	9.71		298.2	0.0014		
		498.7	9.98		498.7	0.0040		
2	100 c/s	25	9.25	100 c/s	25	0.00005	303.5	14.13
		303.5	9.61		303.5	0.0041	350.8	13.13
		404.9	9.93		404.9	0.020	404.9	11.96
	10 Kc/s	25	9.22	10 Kc/s	25	0.00009	503.3	10.35
		303.5	9.54		303.5	0.0019		
		404.9	9.71		404.9	0.0042		
3	100 c/s	25	6.89	100 c/s	25	0.0011	190	13.73
		293	7.86		293	0.074	203	11.58
		393	—		393	—	393	9.88
	10 Kc/s	25	6.88	10 Kc/s	25	0.0008	494	8.66
		293	7.17		293	0.013		
		393	7.57		393	0.051		
4	100 c/s	25	8.40	100 c/s	25	0.0017	354.7	14.17
		306.1	8.75		306.1	0.0021	405.1	13.15
		509.0	9.17		509.0	0.031	454.0	12.23
	10 Kc/s	25	8.36	10 Kc/s	25	0.0018	509.0	11.49
		306.1	8.70		306.1	0.0021		
		509.0	8.99		509.0	0.0070		
5	100 c/s	25	8.15	100 c/s	25	0.14	278	12.44
		278	8.58		278	0.08	344	11.09
		381	—		381	0.39	381	10.35
	10 Kc/s	25	7.47	10 Kc/s	25	0.008	431	9.52
		278	7.77		278	0.013	500	8.76
		381	8.58		381	0.09		
6	100 c/s	25	7.80	100 c/s	25	0.00078	307	14.63
		307	7.95		307	0.0017	350	13.58
		398	8.05		398	0.0095	398	12.47
	10 Kc/s	25	7.78	10 Kc/s	25	0.0097	502	10.69
		307	8.02		307	0.0011		
		398	8.11					
7	100 c/s	25	7.17	100 c/s	25	0.0013	347	14.52
		295	7.45		295	0.0021	395	13.29
		497	7.96		497	0.036	448	12.16
	10 Kc/s	25	7.14	10 Kc/s	25	0.0016	497	11.31
		295	7.41		295	0.0019		
		497	7.71		497	0.0058		
8	100 c/s	25	7.42	100 c/s	25	0.0021	204	15.09
		100	7.64		100	0.0020	306	12.51
		306	8.43		306	0.012	407	10.55
	10 Kc/s	25	7.37	10 Kc/s	25	0.0021	520	9.16
		100	7.60		100	0.0021		
		306	8.34		306	0.0020		

resistance of translucent glass-ceramics so far produced.

3.2.3. Dielectric Properties

Volume resistivity is high in these glasses, due to the presence of immobile alkaline earth cations (table III). It does not vary much between the glasses of the various feldspar stoichiometries (Nos. 1, 4, and 7). It is lowered somewhat in the glass-ceramics, due to contamination. In spite of considerable contamination in glass-ceramic No. 2 (table I), volume resistivity is still considerably higher than in fused silica [12].

The loss tangent in these glasses and glass-ceramics is low. The loss tangent in glass-ceramic No. 2 is particularly low; it is considerably lower than the loss tangent of Corning Code 9606 glass-ceramic [13].

The dielectric constants are generally low. They decrease with the decrease of the divalent ionic radius. Glass-ceramics do not differ much from the corresponding glasses. Type No. 3 has a particularly low dielectric constant.

Acknowledgement

The author is indebted to members of Technical Staffs Services, to Dr G. H. Beall, who critically read the manuscript, and to Mr W. F. Lynch for his technical assistance.

References

1. G. S. BOGDANOVA, E. M. ORLOVA, and L. S. ZEVIN, *State Glass Research Institute* (translation from Russian 1965) 1816.
2. H. C. LIN and W. R. FOSTER, *Amer. Min.* **53** (1968) 134.
3. R. M. BARRER and P. J. COEN, *Trans. Faraday. Soc.* **59** (1963) 2376.
4. S. D. STOOKEY, US Patent 2,920,971 (to Corning Glass Works, 1960).
5. A. HERCZOG, *J. Amer. Ceram. Soc.* **47** (1964) 107.
6. D. A. DUKE, J. E. MEGLES JR, J. F. MACDOWELL, and H. F. BOPP, *ibid* **51** (1968) 98.
7. D. BAHAT, *J. Materials Sci.* **4** (1969) 847.
8. N. A. TOROPOV, F. YA. GALAKOV, and I. A. BONDAR, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **5** (1964) 756.
9. E. F. OSBORN and A. MUAN, Phase Equilibrium Diagrams of Oxide Systems, Plate 1 (1960).
10. M. YOSHIKI and K. MATSUMOTO, *J. Amer. Ceram. Soc.* **34** (1951) 283.
11. D. BAHAT, in preparation.
12. J. K. DAVIS, *Elect. Engin.* (1958) 29.
13. "Materials Handbook", sixth edition (Radome Department Technical Products Division, Corning Glass Works, 1963).