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Several Metastable Alkaline Earth Feldspar Modifications*

DOV BAHAT
Israel Ceramic and Silicate Institute, Technion City, Haifa, Israel

Various metastable crystalline forms of alkaline earth feldspars were produced by the method of catalysed crystallisation of glass. Results obtained by differential thermal analysis and thermal expansion measurements suggest the existence of low-high displacive transformations in $SrAl_2Si_2O_8$ and $CaAl_2Si_2O_8$. The former is rapid and analogous to the one known in $BaAl_2Si_2O_8$ and the latter is rather sluggish.

1. Introduction

In this study various metastable alkaline earth feldspars were produced by catalysed crystallisation of glass [1, 2]. With the glass-ceramic technique, pure or nearly pure single metastable crystalline phases in pore-free bodies in any desired reasonable size were provided. This enabled thermal expansion measurements to supplement information on a new sluggish displacive transformation in a $SrAl_2Si_2O_8$ metastable phase, which was detected by the differential thermal analysis (DTA) technique, and to elucidate a new sluggish displacive transformation which was undetected by differential thermal analyses in a $CaAl_2Si_2O_8$ metastable phase.

A complementary study employing X-ray and infra-red techniques is being carried out at present on these metastable phases.

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 and strontium reagent carbonates. In addition, vanadium oxide (V_2O_5) and molybdenum oxide (MoO_3) were added to the batches as nucleating agents. The batch materials were weighed to an accuracy of 0.1 g and dry mixed. Batch mixtures of 600 g were melted at 1800°C in a gas-oxygen furnace 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 at 1000°C for 1 h. This was found to be sufficient for their conversion into glass ceramics.

The glass-ceramic specimens were examined by DTA at 12.5 and 25°C/min heating rates using alumina as the reference. Thermal expansion measurements of the glass-ceramic specimens were obtained on a differential dilatometer with reference to the expansion of alumina. Heating and cooling rates were 400°C/h with readings taken at intervals of 100°C.

A fine-grained glass-ceramic sample of hexagonal $CaAl_2Si_2O_8$ crystals was investigated by the scanning electron microscope technique. Glass-ceramic products were examined by standard methods of X-ray diffraction.

3. Results and Discussion

3.1. The $SrAl_2Si_2O_8$ Composition

There is a low-high displacive transformation in synthetic $BaAl_2Si_2O_8$ at about 300°C [3]. Takeuchi [4] has shown that this transformation involves a symmetry change with increasing temperature from twinned orthorhombic body-centred structure, which is pseudohexagonal, to a truly hexagonal structure. The difference in the two structures is confined to slight shifts of atoms other than barium, and the two X-ray powder patterns are similar. Both modifications are either metastable or unstable below 1590°C, and the hexagonal modification is stable from this temperature to the melting point [5].

The structure of hexagonal $SrAl_2Si_2O_8$ resembles hexagonal $BaAl_2Si_2O_8$ [6]. This displacive transformation of the type which occurs in $BaAl_2Si_2O_8$ might therefore be expected in $SrAl_2Si_2O_8$. A transformation was indeed indicated by differential thermal analysis (fig. 1) and thermal expansion measurements (fig. 2).

*This study was carried out while the author was an employee at Corning Glass Works.

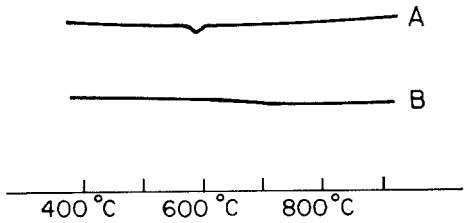

Figure 1 Differential thermal analysis curves. (A) A glass-ceramic of a high-symmetry strontium feldspar formed from a glass of the composition $SiO_2 = 30$, $Al_2O_3 = 45$, and SrO = 25 wt%, with 0.66% vanadium oxide (V_2O_5). (B) Glass-ceramic of high-symmetry calcium feldspar with traces of anorthite, formed from a glass of the composition $SiO_2 = 43.2$, $Al_2O_3 = 36.7$ and CaO = 20.1 wt% with an excess of 1% molybdenum oxide (MoO_3).

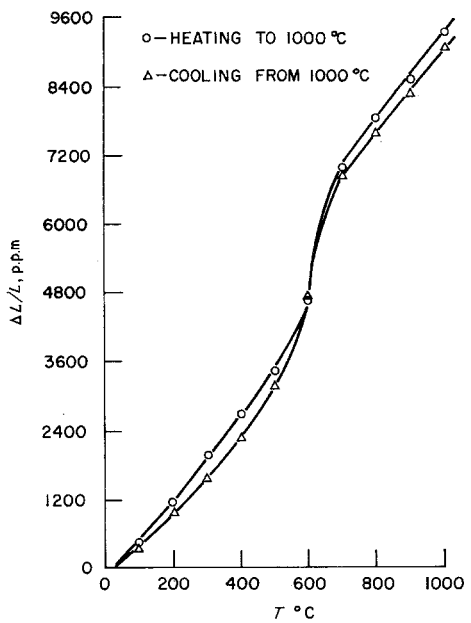

Figure 2 Expansion curves of strontium hexagonal feldspar glass-ceramics (identical to the sample description in fig. 1A), showing a displacive transformation around 600° C.

The glass had the composition $SiO_2 = 30$, $Al_2O_3 = 45$ and SrO = 25 wt% with 0.66% V_2O_5 added. The DTA peak of glass-ceramic was at 590° C. In the glass-ceramic, oxides in excess of the amount required for crystallisation remained as glass.

The expansion curves (fig. 2) suggest the existence of low-high displacive transformation in $SrAl_2Si_2O_8$. One phase is metastable below the transformation temperature and unstable above it, and the other is unstable below the transformation temperature and metastable above it. The hexagonal $SrAl_2Si_2O_8$ and $CaAl_2Si_2O_8$ and the orthorhombic $CaAl_2Si_2O_8$ (see below) do not have any fields of stability (at normal atmospheric pressure).

3.2. The $CaAl_2Si_2O_8$ Composition

Davis and Tuttle [7] discovered and described two crystalline modifications of $CaAl_2Si_2O_8$ which were obtained by a devitrifications process in glass. These phases were hexagonal and orthorhombic. The hexagonal modification resembles the hexagonal $BaAl_2Si_2O_8$ phase, but actually it is considerably deformed from hexagonal to trigonal symmetry [8]. The orthorhombic modifications of the calcium and barium systems [4] have no resemblance. The two calcium feldspar modifications occur together at room temperature. Davis and Tuttle [7] did not observe low-high displacive transformation of the calcium hexagonal form up to 1200° C. Takeuchi and Donnay [8] considered that the lack of such transformation is due to the high deformation of the hexagonal $CaAl_2Si_2O_8$ form.

In the present study, a glass of the $CaAl_2Si_2O_8$ stoichiometric composition ($SiO_2 = 43.2$, $Al_2O_3 = 36.7$ and CaO = 20.1 wt%) with an excess of 1% MoO_3 was produced. The glass was heated at 1000° C for 60 min. and a fine-grained (grain size of about 10 μm) glass-ceramic was

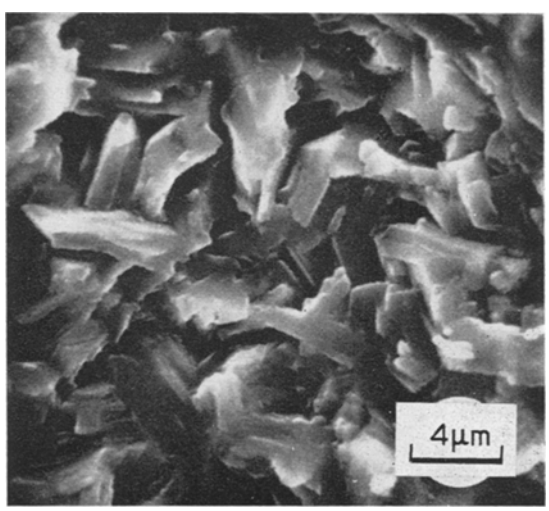

Figure 3 A scanning electron micrograph showing fine-grained hexagonal $CaAl_2Si_2O_8$ crystals (identical to the sample described in fig. 1B). Traces of anorthite found by X-ray diffraction cannot positively be identified in the micrograph.

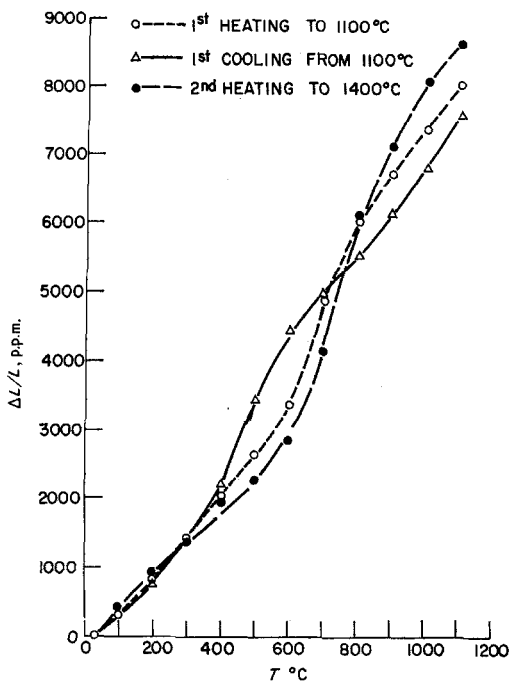

Figure 4 Expansion curves of hexagonal calcium and traces of triclinic feldspar glass-ceramics (identical to the sample described in fig. 1B), showing a sizeable hysteresis in a sluggish displacive transformation in the 400 to 800° C range.

produced (fig. 3). X-ray tests indicated that the glass-ceramic consisted of a mixture of a bulk hexagonal and traces of triclinic (anorthite) phases.

The expansion curves of this glass-ceramic material showed that in the 600 to 800°C temperature range there was an increase in the expansion rate; and, due to a sizeable hysteresis, an increase in the contraction rate occurred on cooling in the range 400 to 600°C (fig. 4). Such a combination of expansion curves suggests a displacive transformation analogous to the one which occurs in $SrAl_2Si_2O_8$ and $BaAl_2Si_2O_8$. This transformation is, however, sluggish, and five thermograms of the same glass-ceramic showed no signs of heat effects in the range of 400 to 800°C (fig. 1). It is well known [9] that the magnitude of the DTA peaks depends on the various instrumental and sample parameters. Gruver has shown for instance [10], that by increasing the sensitivity of the differential recorder by twenty-five times, the tridymite transformations at 117 and 163°C could be seen in a mixture of 40% tridymite, 30% cristobalite, and 30% quartz. In this mixture only the more pronounced cristobalite transformation at 270°C and the quartz transformation at 573°C had been seen before an increase in the sensitivity was accomplished. It is quite possible that low sensitivity of the differential recorder prevented the detection of the unpronounced transformation of the hexagonal $CaAl_2Si_2O_8$ phase in the present and previous studies.

A glass-ceramic material of the pure orthorhombic modification was nucleated in a glass about 4% richer in silica and poorer in alumina than the stoichiometric composition of anorthite (SiO_2 = 47.5, Al_2O_3 = 31.5, and CaO = 19.7 wt %, and excess of 1% MoO_3). This material was found to have a uniform linear expansion over the temperature range 25 to 1000°C. The estimated coefficient is $70 \times 10^{-7}°C^{-1}$.

Triclinic strontium and calcium feldspar glass-ceramics may be crystallised in significant amounts only from compositions that deviate from the $RAl_2Si_2O_8$ stoichiometries, and hexagonal strontium and calcium feldspars do crystallise from the respective stoichiometries. This suggests that nucleation of the more stable alkaline earth feldspar phase is generally easier from compositions that deviate from the $RAl_2Si_2O_8$ stoichiometry, and nucleation of stoichiometric compositions is more likely to produce phases with lower stabilities.

On the basis of this observation and the preference of the orthorhombic $CaAl_2Si_2O_8$ to crystallise from a composition off the stoichiometry, it is considered that within their metastable fields, the orthorhombic calcium feldspar is more stable than the hexagonal modification.

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References

1. S. D. STOOKEY and R. D. MAURER, "Progress in Ceramic Science", **2** (Pergamon Press, New York, 1961) 77.
2. D. BAHAT, *J. Mater. Sci.* **4** (1969) 855.
3. M. YOSHIKI and K. MATSUMOTO, *J. Amer. Ceram. Soc.* **34** (1951) 283.
4. Y. TAKEUCHI, *Mineral J.* **2** (1958) 311.
5. H. C. LIN and W. R. FOSTER, *Amer. Mineral.* **53** (1968) 134.

6. C. A. SORRELL, *ibid* **47** (1962) 291.
7. G. L. DAVIS and D. F. TUTTLE, *Amer. J. Sci. Bowen* **107** (1952) 107.
8. Y. TAKEUCHI and G. DONNAY, *Acta Cryst.* **12** (1959) 465.
9. W. WM. WENDLANDT, "Thermal Methods of Analysis" (Interscience Publishers, a division of John Wiley & Sons, New York, 1964).
10. R. M. GRUVER, *J. Amer. Ceram. Soc.* **31** (1948) 323.

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