

The Phase Diagram (95 % SiO₂ + 5 % Al₂O₃)-CaF₂

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According to Refs. 1 and 2 the system SiO₂-CaF₂ has a eutectic point at 1240°C corresponding to a composition of 47 % SiO₂ + 53 % CaF₂ and a two-liquid area between 1290°C and 1420°C and the compositions 43 % SiO₂ + 57 % CaF₂ and 23 % SiO₂ + 77 % CaF₂. In specimens cooled to room temperature a glassy phase was found, probably of a composition between 50 % SiO₂ + 50 % CaF₂ and 47 % SiO₂ + 53 % CaF₂. It was also suggested that two metastable phases, possibly of the compositions SiO₂ · CaF₂ and SiO₂ · 2CaF₂, may form in connection with the glassy phase.

The melting point of CaF₂ is 1418°C,³ of SiO₂ 1713°C,⁴ and of Al₂O₃ 2040°C.⁵

The system SiO₂-Al₂O₃ has one compound, mullite. The eutectic point between SiO₂ and mullite has been determined by several authors (Refs. 6-9), the results varying between 1530°C and 1670°C and 95 % SiO₂ + 5 % Al₂O₃ and 90 % SiO₂ + 10 % Al₂O₃. The most reliable determination seems to be the one by Aramaki and Roy,⁶ yielding the result 1595°C and 94 % SiO₂ + 6 % Al₂O₃.

According to Ref. 10 the system Al₂O₃-CaF₂ has no compounds and no solid solutions but a eutectic point at 1290°C and at a composition of 9 % Al₂O₃ + 91 % CaF₂. This is, however, not in agreement neither with the results obtained by Pascal¹¹ who found solid solutions between Al₂O₃ and CaF₂ but no compounds, nor with those of Günther and Perlit¹² who found two compounds: 5Al₂O₃ · CaF₂ and Al₂O₃ · CaF₂.

The phase diagram for the system (95 % SiO₂ + 5 % Al₂O₃)-CaF₂ has now been studied by heat treatment at various temperatures in an atmosphere of pure dry argon, of powder mixtures of compositions ranging from 100 % of (95 % SiO₂ + 5 % Al₂O₃) to 100 % CaF₂ and subsequent cooling of the samples in different ways, usually quenching in CCl₄ at room temperature. The experiments were performed in a specially constructed apparatus used in

a series of phase diagram studies (Refs. 1, 2, 13-15). The raw materials used were of highest analytical purity. They were dried separately: CaF₂ at 800°, SiO₂ (quartz) at 1200°, and Al₂O₃ (α) at 1200° (in order to prevent fluorine losses in the form of HF by reaction of CaF₂ with water vapor when heat treating the powder mixtures) before the grinding, weighing and mixing. The powders and mixtures were always stored in desiccators with Mg(ClO₄)₂. Each sample was placed in a small Pt envelope and suspended in the hot zone of a vertical Pt 40 % Rh-wound furnace for a period of 60-120 min.

The flow properties of the sample at the experimental temperature was estimated from the shape of the sample after quenching. One half of each sample was prepared for microscopic examination and the other half was used for obtaining X-ray powder photographs with a Guinier camera. The flow property, the microstructure and the phase analysis were all combined for estimating the position of the liquidus.

The position of all samples will be found in Fig. 1 together with the phase diagram. The system has a eutectic point at 1220° corresponding to a composition of 42.8 % SiO₂ + 2.2 % Al₂O₃ + 55 % CaF₂. When fully melted samples of compositions ranging from 95 % SiO₂ + 5 % Al₂O₃ to 42.8 % SiO₂ + 2.2 % Al₂O₃ + 55 % CaF₂ (*i.e.* to the left of the eutectic) were cooled to room temperature, two phases were formed: SiO₂ (cristobalite and tridymite) and a glass-phase. When fully melted samples of compositions ranging from 42.8 % SiO₂ + 2.2 % Al₂O₃ + 55 % CaF₂

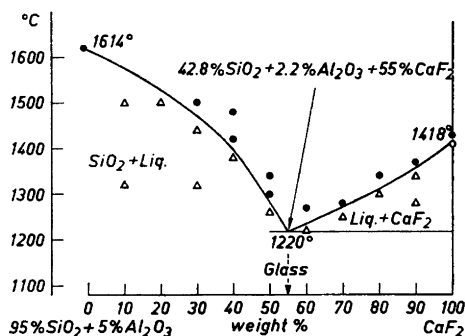


Fig. 1. The phase diagram (95 % SiO₂ + 5 % Al₂O₃)-CaF₂; ● fully melted samples, △ partly melted samples, ○ not melted samples.

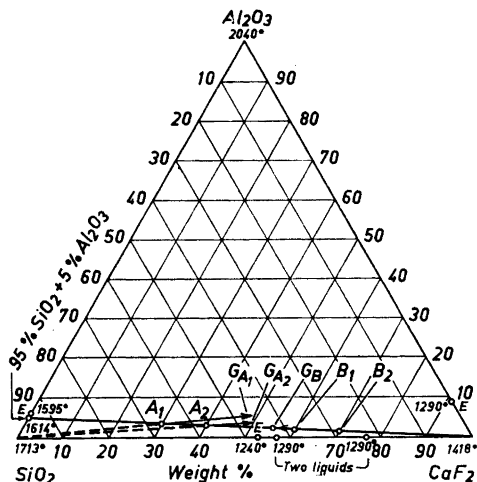


Fig. 2. The formation of glasses in the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2$: $\text{SiO}_2\text{-Al}_2\text{O}_3$ according to Ref. 6, $\text{Al}_2\text{O}_3\text{-CaF}_2$ according to Ref. 10, $\text{SiO}_2\text{-CaF}_2$ according to Refs. 1 and 2, (95 % $\text{SiO}_2 + 5\% \text{Al}_2\text{O}_3$)- CaF_2 according to this investigation.

to 100 % CaF_2 (*i.e.* to the right of the eutectic), were cooled to room temperature, there were always formed CaF_2 and a glass-phase.

When fully melted samples of compositions between 42.8 % $\text{SiO}_2 + 2.2\% \text{Al}_2\text{O}_3 + 55\% \text{CaF}_2$ and 100 % CaF_2 (for instance B_1 or B_2 in Fig. 2) are cooled to room temperature, the glass-phase is supposed to form in the following way. When the precipitation of CaF_2 from the melt is taking place, the composition of the melt approaches that of point G_B in the section (95 % $\text{SiO}_2 + 5\% \text{Al}_2\text{O}_3$)- CaF_2 , *i.e.* the eutectic composition, and the glassy phase that forms on cooling may have about the same composition independent of the initial composition of the melted sample. On the other hand, in the samples on the other side of the eutectic, *i.e.* with less than 55 % CaF_2 , the formation of glass is preceded by a precipitation of SiO_2 . As a consequence the composition of this glass is situated outside the section (95 % $\text{SiO}_2 + 5\% \text{Al}_2\text{O}_3$)- CaF_2 and it contains more Al_2O_3 than the glass G_B . The exact composition of this glass is dependent on the initial composition of the melted sample. The formation of such glasses is demonstrated

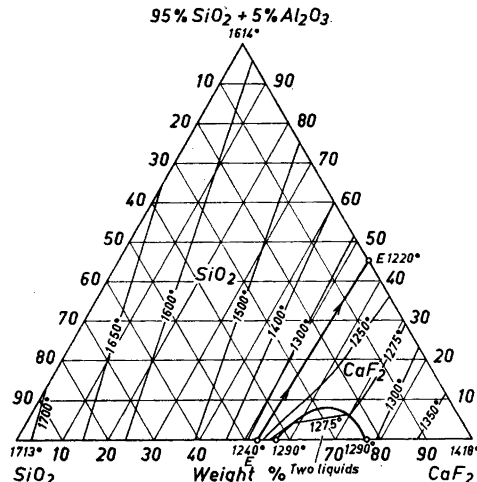


Fig. 3. Tentative phase diagram for the system $\text{SiO}_2\text{-(95\% SiO}_2 + 5\% \text{Al}_2\text{O}_3)\text{-CaF}_2$: SiO_2 (95 % $\text{SiO}_2 + 5\% \text{Al}_2\text{O}_3$) according to Ref. 6, $\text{SiO}_2\text{-CaF}_2$ according to Refs. 1 and 2, (95 % $\text{SiO}_2 + 5\% \text{Al}_2\text{O}_3$)- CaF_2 according to this investigation.

in Fig. 2 (G_{A1} and G_{A2}). An estimate by quantitative microscopy seemed to indicate that the SiO_2 content of all these glasses (G_B , G_{A1} , and G_{A2}) approximately lies in the region 40–50 %.

In combining the results of the present work with those of Refs. 1, 2, and 6 an attempt has been made to construct the ternary phase diagram for the system $\text{SiO}_2\text{-(95\% SiO}_2 + 5\% \text{Al}_2\text{O}_3)\text{-CaF}_2$ (Fig. 3). Nothing is known about the extension of the two-liquid area of the system $\text{SiO}_2\text{-CaF}_2$ into the ternary system. Thus its extension was drawn tentatively in Fig. 3. The ternary phase diagram $\text{SiO}_2\text{-(95\% SiO}_2 + 5\% \text{Al}_2\text{O}_3)\text{-CaF}_2$ in Fig. 3 shows the boundary between the primary crystallization fields for SiO_2 and CaF_2 and the liquidus isotherms.

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Received November 12, 1965.

Mass Spectra of two Deuterated Isothiocyanates

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In a previous paper¹ the mass spectral fragmentation of about forty isothiocyanates was studied and tentative identifications of some of the observed ions were presented. In the present note evidence

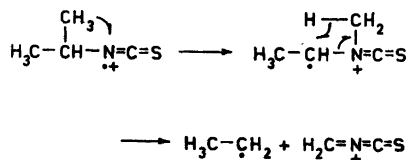
* Part LIV of a series of papers on isothiocyanates. Part LIII: *Acta Chem. Scand.* **19** (1965) 1989.

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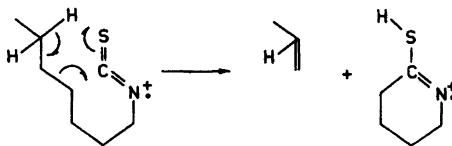
based on deuteration experiments is adduced to substantiate some of the previous suggestions.

The two α -branched alkyl compounds studied, 2-propyl and 2-butyl isothiocyanate, both exhibited a peak at m/e 72, attributable to the ion CH_2NCS^+ , possibly formed by an intramolecular rearrangement involving the transfer of a methyl group:



In order to test this possibility 2-*d*-2-propyl isothiocyanate was prepared from 2-*d*-2-propylamine, which, in turn, was obtained by reduction of acetoxime with lithium aluminium deuteride. The mass spectrum of the α -deuterated isothiocyanate exhibited a very strong molecular ion peak (m/e 102), the expected signal at m/e 87 ($M-15$), and, most significantly, a peak at m/e 72 of about the same relative intensity as the m/e 72 signal in the non-deuterated species, indicating that the α -carbon atom does not contribute to the formation of the CH_2NCS^+ -ion. Hence, the previously suggested migration of a methyl group, followed by breakage of the original α -bond, appears to be correct.*

In the series of straight-chain isothiocyanates a strong peak at m/e 115 was consistently observed in all species containing six or more carbon atoms in the side chain. Tentatively the following rearrangement was proposed,¹ where the required deviation from linearity of the functional group in the molecular ion could be brought about by 'unpairing' of π -electrons from one of the double bonds.



* Until recently alkyl migrations in the mass spectrometer have been considered to be relatively rare (cf. Ref. 2). Lately, however, several such cases have been encountered.^{3,4}