The Phase Diagram (90 % SiO_2 + 10 % TiO_2)-CaF_2

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According to Ref. 1 the system SiO_2-TiO_2 has no compounds but a eutectic point at 1550° corresponding to a composition of 90 % SiO_2 + 10 % TiO_2 and a two-liquid area above 1780° and between the compositions 81 % SiO_2 + 19 % TiO_2 and 7 % SiO_2 + 93 % TiO_2.

The system SiO_2-CaF_2 has a eutectic point at 1240° corresponding to a composition of 47 % SiO_2 + 53 % CaF_2, a two-liquid area between 1290° and 1420° and the compositions 43 % SiO_2 + 57 % CaF_2 and 23 % SiO_2 + 77 % CaF_2.[2] In specimens cooled to room temperature a glassy phase was found, probably of a composition between 50 % SiO_2 + 50 % CaF_2 and 47 % SiO_2 + 53 % CaF_2. It was also suggested that two meta-stable phases, possibly of the compositions $SiO_2 \cdot CaF_2$ and $SiO_2 \cdot 2CaF_2$, may form in connection with the glassy phase.

According to Ref. 3 the system TiO_2-CaF_2 has a eutectic point at 1360° corresponding to a composition of 57 % TiO_2 + 43 % CaF_2 and a two-liquid area above a temperature of about 1365° and between the compositions 55 % TiO_2 + 45 % CaF_2 and 6 % TiO_2 + 94 % CaF_2.

The melting point of CaF_2 is 1418°.[4]

The phase diagram for the system (90 % SiO_2 + 10 % TiO_2)$-CaF_2$ 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 (90 % SiO_2 + 10 % TiO_2) to 100 % CaF_2 and by subsequent cooling of the samples in different ways, principally quenching in CCl_4 at room temperature. The experiments were performed in a specially constructed apparatus used in a series of phase diagram studies.[2,3] The raw materials used were of highest analytical purity. They were dried separately: CaF_2 at 800° and SiO_2 (quartz) and TiO_2 at 1200° (in order to prevent fluorine losses in the form of HF by reaction of CaF_2 with water vapor when heat treating the powder mixtures) before the grinding, weighing and mixing. The powders and the mixtures were always stored in desiccators with $Mg(ClO_4)_2$. 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 temperature was measured by a Pt−Pt 10 % Rh thermocouple and a "Leeds and Northrup Type K-3 Universal Potentiometer". 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 results are shown in Fig. 1.

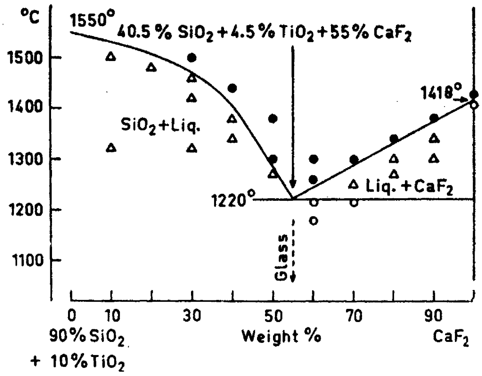

Fig. 1. The phase diagram (90 % SiO_2 + 10 % TiO_2)$-CaF_2$. ● fully melted samples; △ partly melted samples; ○ not melted samples.

The system has a eutectic point at 1220° corresponding to a composition of 40.5 % SiO_2 + 4.5 % TiO_2 + 55 % CaF_2. When fully melted samples of compositions ranging from 90 % SiO_2 + 10 % TiO_2 to 40.5 % SiO_2 + 4.5 % TiO_2 + 55 % CaF_2 (*i.e.* to the left of the eutectic) are cooled to room temperature, two phases are formed: SiO_2 (cristobalite and tridymite) and a glass-phase. When fully melted samples of compositions ranging from 40.5 % SiO_2 + 4.5 % TiO_2 + 55 % CaF_2 to 100 % CaF_2 (*i.e.* to the right of the eutectic), are cooled to room temperature two phases are also formed: CaF_2 and a glass-phase. The two crystalline phases SiO_2 and CaF_2 were never observed to form simultaneously in any one specimen, probably due to a very strong tendency towards glass formation as the remaining

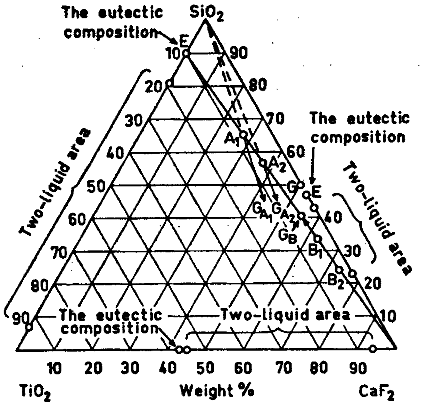

Fig. 2. The formation of glasses in the system $SiO_2-TiO_2-CaF_2$ SiO_2-TiO_2 according to Ref. 1; SiO_2-CaF_2 according to Ref. 2; TiO_2-CaF_2 according to Ref. 3.

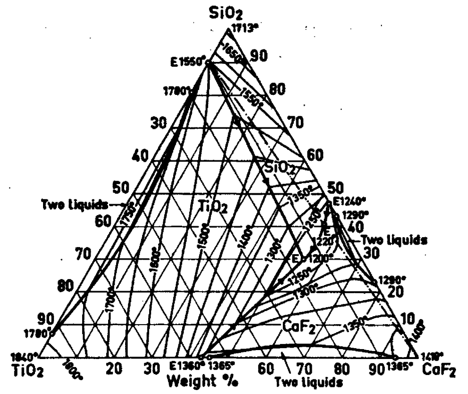

Fig. 3. Tentative phase diagram for $SiO_2-TiO_2-CaF_2$ SiO_2-TiO_2 according to Ref. 1; SiO_2-CaF_2 according to Ref. 2; TiO_2-CaF_2 according to Ref. 3; (90 % SiO_2 + 10 % TiO_2)$-CaF_2$ according to this investigation.

liquid phase in a sample approaches the eutectic composition (or temperature).

All samples examined in this study were situated along the section indicated by a full line in Fig. 2. The glass formed after cooling of the fully melted samples of composition with more than 55 % CaF_2 (for instance B_1 or B_2) has formed after a precipitation of CaF_2. As a consequence, its composition, G_B, lies in the section as demonstrated by the arrow B_2, B_1-G_B. An estimate by quantitative microscopy seemed to indicate that the composition of the glass G_B in these samples is rather independent of the initial composition of the sample and is approximately 40.5 % SiO_2 + 4.5 % TiO_2 + 55 % CaF_2, which is the composition of the eutectic in the section mentioned.

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 demonstrated by the arrows A_1-G_{A1} an A_2-G_{A2} in Fig. 2, the composition of this glass will thus be situated outside the section and contain more TiO_2 than the glass G_B. The exact composition of the glass is now depending on the initial composition of the sample.

All the glasses thus found in the present study of the ternary system $SiO_2-TiO_2-CaF_2$ have SiO_2-contents similar to that of the glass G formed in the binary system SiO_2-CaF_2 according to Ref. 2, *i.e.* in the region 40–50 % SiO_2.

The shape of the liquidus surface of CaF_2 (Fig. 1) in the region 55–80 % CaF_2 seems to indicate that the two-liquid area in the binary system SiO_2-CaF_2 (Ref. 2) does not extend far into the ternary system $SiO_2-TiO_2-CaF_2$.

Neither of the two meta-stable phases, $SiO_2 \cdot CaF_2$ and $SiO_2 \cdot 2CaF_2$, proposed in Ref. 2, seems to form in samples on the section examined in the present study.

In combining the results of the present work with those of Refs. 1, 2, and 3, an attempt was made to construct the ternary phase diagram for the system $SiO_2-TiO_2-CaF_2$ (Fig. 3). Nothing is known about the extension of the three two-liquid areas of the binary systems into the ternary system. Thus their extensions were drawn tentatively in Fig. 3.

The position of the ternary eutectic point is also unknown and it was placed at 30 % SiO_2 + 10 % TiO_2 + 60 % CaF_2 and 1200° rather arbitrarily.

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