

The Phase Diagram (64 % SiO<sub>2</sub> + 36 % CaO)-CaF<sub>2</sub>

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Heat treatment, quenching, studying of the flow properties, microscopic appearance and X-ray powder photographs obtained with the help of a Guinier camera were used to construct the phase diagram for the system (64 % SiO<sub>2</sub> + 36 % CaO)-CaF<sub>2</sub>. There is a eutectic point at 1170° and a formation of a glass-phase. In part of the system the crystalline phase SiO<sub>2</sub>·2CaF<sub>2</sub> appears. The results of the present study were combined with literature data to construct the phase diagram SiO<sub>2</sub>-CaO-CaF<sub>2</sub>.

According to Ref. 1 the system SiO<sub>2</sub>-CaO has four compounds: CaO·SiO<sub>2</sub>,  $\frac{1}{3}$ CaO·2SiO<sub>2</sub>, 2CaO·SiO<sub>2</sub> and 3CaO·SiO<sub>2</sub> and a two-liquid area above 1705° and between the compositions 73 % SiO<sub>2</sub> + 27 % CaO and 99 % SiO<sub>2</sub> + 1 % CaO. The lowest eutectic point lies at 1436° corresponding to the composition 64 % SiO<sub>2</sub> + 36 % CaO.

The system CaO-CaF<sub>2</sub> has no compounds but a eutectic point at 1360° corresponding to a composition of 20 % CaO + 80 % CaF<sub>2</sub><sup>2</sup> (cf. also Refs. 3 and 4).

According to Ref. 5 the system CaO-CaF<sub>2</sub> has a two-liquid area between 1380° and 1485° and between the compositions 8 % CaO + 92 % CaF<sub>2</sub> and 0.5 % CaO + 99.5 % CaF<sub>2</sub>, but according to Ref. 2 there exists no such two-liquid area in the system CaO-CaF<sub>2</sub>.

The melting point of CaF<sub>2</sub> is 1418°.<sup>6</sup>

The system SiO<sub>2</sub>-CaF<sub>2</sub> has been studied in Ref. 7. Further details about this study will be given below. Heat treatment has been used at various temperatures in an atmosphere of pure dry argon, of powder mixtures of compositions ranging from 100 % SiO<sub>2</sub> to 100 % CaF<sub>2</sub> and subsequent cooling of the samples in different ways, usually quenching in CCl<sub>4</sub> at room temperature. The experiments were performed in a specially constructed apparatus used in a series of phase diagram studies (Refs. 8-10, 17, 18). The raw materials used were of highest analytical purity. They were dried separately: CaF<sub>2</sub> at 800° and SiO<sub>2</sub> (quartz) at 1200° (in order to prevent fluorine losses in the form of HF by reaction of CaF<sub>2</sub> 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  $\text{Mg}(\text{ClO}_4)_2$ . 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 flow properties of the sample at the experimental temperature were 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.

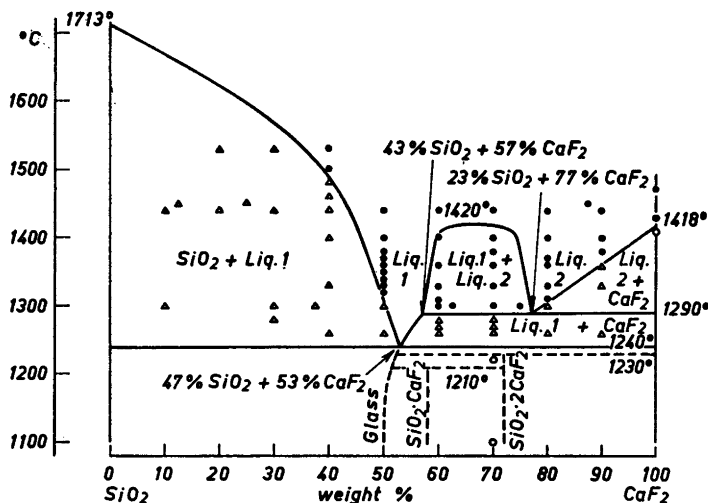


Fig. 1. The phase diagram  $\text{SiO}_2\text{--CaF}_2$ . ● fully melted samples,  $\Delta$  partly melted samples, ○ not melted samples.

The position of all samples will be found in Fig. 1 together with the phase diagram. The stable system has a eutectic point at 1240° corresponding to a composition of 47 %  $\text{SiO}_2$  + 53 %  $\text{CaF}_2$  and a two-liquid area between 1290° and 1420° and the compositions 43 %  $\text{SiO}_2$  + 57 %  $\text{CaF}_2$  and 23 %  $\text{SiO}_2$  + 77 %  $\text{CaF}_2$ . When fully melted samples of compositions ranging from 100 %  $\text{SiO}_2$  to 47 %  $\text{SiO}_2$  + 53 %  $\text{CaF}_2$  (*i.e.* to the left of the eutectic) were cooled to room temperature, two phases were formed:  $\text{SiO}_2$  (cristobalite and tridymite) and a glass-phase. When fully melted samples of compositions ranging from 47 %  $\text{SiO}_2$  + 53 %  $\text{CaF}_2$  to 100 %  $\text{CaF}_2$  (*i.e.* to the right of the eutectic), were cooled to room temperature, there were always formed  $\text{CaF}_2$  and a glass-phase. Furthermore one or two more phases were formed depending on the initial composition of the samples. These phases were suggested to correspond to the ideal compositions  $\text{SiO}_2 \cdot \text{CaF}_2$  and  $\text{SiO}_2 \cdot 2\text{CaF}_2$ . It was also suggested that they do not belong to the stable equilibrium phase diagram  $\text{SiO}_2\text{--CaF}_2$  but can only form in a supercooled liquid phase. The dashed lines

in Fig. 1 are tentative and illustrate the possible meta-stable equilibrium between these two phases and the supercooled liquid.

An estimate by quantitative microscopy seemed to indicate that the composition of the glass in all samples was rather independent of the initial composition of the melted sample and was approximately the same as the eutectic. Furthermore the quantitative microscopy seemed to indicate that the composition of the two unknown crystalline phases appearing in samples to the right of the eutectic were approximately  $\text{SiO}_2\cdot\text{CaF}_2$  and  $\text{SiO}_2\cdot 2\text{CaF}_2$ . Measuring of their  $d$ -values with the help of the Guinier method and  $\text{CuK}\alpha$  radiation and with  $\text{CaF}_2$  as an internal standard gave the results collected in Table 1.

Table 1.  $d$ -Values of  $\text{SiO}_2\cdot\text{CaF}_2$  and  $\text{SiO}_2\cdot 2\text{CaF}_2$ .

Lattice distances $d$ in Å units	Relative intensities *	Lattice distances $d$ in Å units	Relative intensities *
$\text{SiO}_2\cdot\text{CaF}_2$		$\text{SiO}_2\cdot 2\text{CaF}_2$	
8.58	VW	2.549	VW
6.96	W	2.527	VVW
4.232	W	2.495	VVW
3.619	W	(2.472	VVW)
3.465	VVW	2.453	VVW
3.117	W	2.304	VW
2.829	W	2.288	VW
2.610	VVW	(2.087	VVW)
2.512	W	2.061	VW
2.225	VW	2.048	VVW
2.025	W	2.016	VW
1.950	VW	1.994	VVW
1.857	VVW	1.986	VVW
1.750	VVW	1.883	W
		1.833	VW
		1.823	VW
		1.811	VVW
		1.786	VVW
		(1.770	VVW)
		1.732	W
		1.693	VVW
		(1.612	VVW)
		(1.600	VVW)
		1.583	VW
		1.574	VW
		(1.550	VVW)
		(1.538	VVW)
		1.490	VW
		1.447	VVW
		1.335	VVW
		1.220	VVW
		1.168	VVW
$\text{SiO}_2\cdot 2\text{CaF}_2$			
7.37	VW		
7.14	VW		
5.29	VW		
5.16	VW		
3.682	VW		
(3.543	VVW)		
(3.442	VVW)		
(3.356	VVW)		
3.227	WM		
3.067	M		
2.944	W		
2.933	W		
2.898	W		
2.870	WM		
2.569	VW		

\* M medium, WM weak medium, W weak, VW very weak, VVW very very weak.

The phase diagram for the system (64 %  $\text{SiO}_2$  + 36 %  $\text{CaO}$ )— $\text{CaF}_2$  has now been studied by the same method and apparatus that was used in the study of  $\text{SiO}_2\text{—CaF}_2$  described above. (The raw material  $\text{CaCO}_3$ , precipitated, was of highest analytical purity and was dried at  $200^\circ$ ).

The position of the liquidus in the system (64 %  $\text{SiO}_2$  + 36 %  $\text{CaO}$ )— $\text{CaF}_2$  thus found is shown in Fig. 2. The system has a eutectic point at  $1170^\circ$  corre-

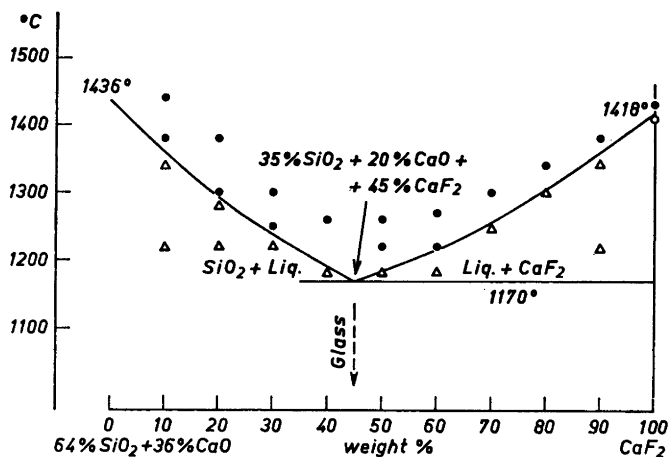


Fig. 2. The phase diagram (64 %  $\text{SiO}_2$  + 36 %  $\text{CaO}$ )— $\text{CaF}_2$ . ● fully melted samples, Δ partly melted samples, ○ not melted samples.

sponding to a composition of 35 %  $\text{SiO}_2$  + 20 %  $\text{CaO}$  + 45 %  $\text{CaF}_2$ . When fully melted samples of compositions ranging from 64 %  $\text{SiO}_2$  + 36 %  $\text{CaO}$  to 35 %  $\text{SiO}_2$  + 20 %  $\text{CaO}$  + 45 %  $\text{CaF}_2$  (*i.e.* to the left of the eutectic) are cooled to room temperature, two phases are formed:  $\text{SiO}_2$  (cristobalite, tridymite and quartz) and a glass-phase. When fully melted samples of compositions ranging from 35 %  $\text{SiO}_2$  + 20 %  $\text{CaO}$  + 45 %  $\text{CaF}_2$  to 100 %  $\text{CaF}_2$  (*i.e.* to the right of the eutectic) are cooled to room temperature, there are formed three phases:  $\text{CaF}_2$ , a glass-phase and a crystalline phase whose  $d$ -values are identical with those of  $\text{SiO}_2 \cdot 2\text{CaF}_2$  mentioned above.

The precipitation of  $\text{SiO}_2 \cdot 2\text{CaF}_2$  is supposed to take place, in resemblance to the system  $\text{SiO}_2\text{—CaF}_2$ , after the precipitation of  $\text{CaF}_2$  (see point B in Fig. 3).

When fully melted samples of compositions between 35 %  $\text{SiO}_2$  + 20 %  $\text{CaO}$  + 45 %  $\text{CaF}_2$  and 100 %  $\text{CaF}_2$  (for instance  $B_1$  or  $B_2$ ) are cooled to room temperature, the glass-phase is supposed to form in the following way (see Fig. 3). First  $\text{CaF}_2$  is precipitated from the melt. As a consequence the composition of the melt ( $B_1$  and  $B_2$ ) approaches that of point B ( $\sim 48$  %  $\text{CaF}_2$ ) in the section (64 %  $\text{SiO}_2$  + 36 %  $\text{CaO}$ )— $\text{CaF}_2$ . Then a precipitation of  $\text{SiO}_2 \cdot 2\text{CaF}_2$  is taking place and as a consequence of this the glass finally formed ( $G_B$ ) will have a composition outside the section. This glass 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,

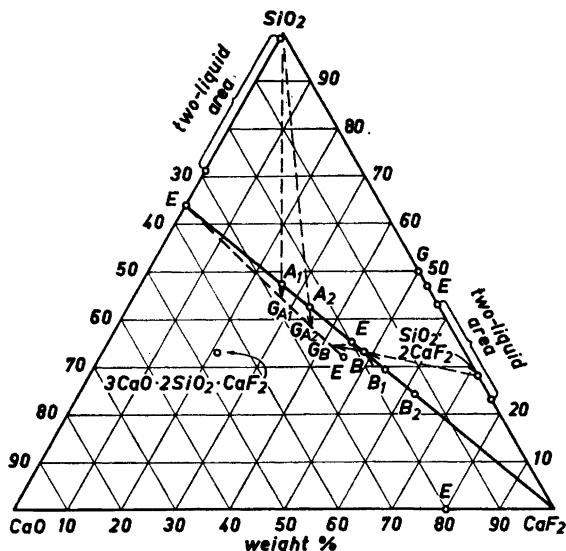


Fig. 3. The formation of glasses in the system  $\text{SiO}_2$ - $\text{CaO}$ - $\text{CaF}_2$ .  $\text{SiO}_2$ - $\text{CaO}$  according to Ref. 1,  $\text{CaO}$ - $\text{CaF}_2$  according to Ref. 2,  $\text{SiO}_2$ - $\text{CaF}_2$  according to Ref. 7, (64 %  $\text{SiO}_2$  + 36 %  $\text{CaO}$ )- $\text{CaF}_2$  according to this investigation.

*i.e.* with less than 45 %  $\text{CaF}_2$ , the formation of glass is preceded by a precipitation of  $\text{SiO}_2$ . As a consequence the composition of this glass is also situated outside the section (64 %  $\text{SiO}_2$  + 36 %  $\text{CaO}$ )- $\text{CaF}_2$ . The exact composition of this glass is dependent on the initial composition of the melted sample. The formation of such glasses is demonstrated in Fig. 3 ( $G_{A1}$  and  $G_{A2}$ ). An estimate by quantitative microscopy seemed to indicate that the  $\text{SiO}_2$  content of all these glasses ( $G_B$ ,  $G_{A1}$ , and  $G_{A2}$ ) approximately lies in the region 35–50 %.

The shape of the liquidus surface of  $\text{CaF}_2$  (Fig. 2) in the region 45–80 %  $\text{CaF}_2$  seems to indicate that the two-liquid area in the binary system (Ref. 7) does not extend far into the ternary system  $\text{SiO}_2$ - $\text{CaO}$ - $\text{CaF}_2$ .

Fig. 3 also shows the position of the compound cuspidine,  $3\text{CaO}\cdot 2\text{SiO}_2\cdot \text{CaF}_2$ . This compound was found by Brisi<sup>11</sup> (and McCaughey *et al.*<sup>12</sup>) in the system  $\text{CaF}_2$ - $\text{CaO}\cdot \text{SiO}_2$ - $2\text{CaO}\cdot \text{SiO}_2$ , but it was not found by Mukerji<sup>2</sup> and Bååk<sup>13</sup> and not in the present work.

In combining the results of the present work with those of Refs. 1 and 7 an attempt has been made to construct the ternary phase diagram for the system  $\text{SiO}_2$ -(64 %  $\text{SiO}_2$  + 36 %  $\text{CaO}$ )- $\text{CaF}_2$  (Fig. 4). Nothing is known about the extension of the two two-liquid areas of the binary systems into the ternary system. (The results of Refs. 14 and 15 are contradictory to those of Ref. 7 and to the present work). Thus their extensions were drawn tentatively in Fig. 4. The ternary phase diagram  $\text{SiO}_2$ -(64 %  $\text{SiO}_2$  + 36 %  $\text{CaO}$ )- $\text{CaF}_2$  in Fig. 4 shows the boundary between the primary crystallization fields for  $\text{SiO}_2$  and  $\text{CaF}_2$  and the liquidus isotherms.



In combining the results of the present work, dealing with the system  $\text{SiO}_2$ —(64 %  $\text{SiO}_2$  + 36 %  $\text{CaO}$ )— $\text{CaF}_2$ , with those of Ref. 2, dealing with the system  $\text{CaO}\cdot\text{SiO}_2$ — $\text{CaO}$ — $\text{CaF}_2$  based on Refs. 2, 4, 13 and 16, an attempt has been made to construct the ternary phase diagram for the complete system  $\text{SiO}_2$ — $\text{CaO}$ — $\text{CaF}_2$  (Fig. 5). As distinguished from Ref. 2 the phase diagram  $\text{SiO}_2$ — $\text{CaO}$ — $\text{CaF}_2$  in Fig. 5 has excluded the large two-liquid field which has been replaced by two tentative two-liquid fields. Furthermore Fig. 5 shows the primary phase boundary between the  $\text{SiO}_2$ - and  $\text{CaF}_2$ -fields, the ternary eutectic point at  $\sim 1160^\circ$  between the  $\text{SiO}_2$ -,  $\text{CaF}_2$ - and  $\text{CaO}\cdot\text{SiO}_2$ -fields and the liquidus isotherms in the whole region  $\text{SiO}_2$ — $\text{CaO}\cdot\text{SiO}_2$ — $\text{CaF}_2$ .

## REFERENCES

1. Phillips, B. and Muan, A. *J. Am. Ceram. Soc.* **42** (1959) 414.
2. Mukerji, J. *J. Am. Ceram. Soc.* **48** (1965) 210.
3. Budnikov, P. P. and Tresvyatskii, S. G. *Dokl. Akad. Nauk. SSSR* **89** (1953) 481.
4. Eitel, W. *Zement* **27** (1938) 469.
5. Bååk, T. *Acta Chem. Scand.* **8** (1954) 1727.
6. Kelley, K. K. *U. S. Bur. Mines Bull.* **584** (1960).
7. Hillert, L. *Acta Chem. Scand.* **18** (1964) 2411.
8. Hillert, L. *Acta Chem. Scand.* **19** (1965) 1516.
9. Hillert, L. *Acta Chem. Scand.* **19** (1965) 1774.
10. Hillert, L. *Acta Chem. Scand.* **19** (1965) 1986.
11. Brisi, C. *J. Am. Ceram. Soc.* **40** (1957) 174.
12. McCaughey, W. J., Kautz, K. and Wells, R. G. *Am. Mineralogist* **33** (1948) 200.
13. Bååk, T. *Physical Chemistry of Steelmaking*, John Wiley and Sons, New York 1958, p. 84.
14. Olshanskii, Y. I. *Dokl. Akad. Nauk. SSSR* **114** (1957) 1246.
15. Ershova, Z. P. and Olshanskii, Y. I. *Geokhimiya* **2** (1958) 144.
16. Oelsen, W. and Maetz, H. *Mitt. Kaiser Wilhelm Inst. Eisenforsch. Düsseldorf* **23** (1941) 195.
17. Hillert, L. *Acta Chem. Scand.* **19** (1965) 2436.
18. Hillert, L. *Acta Chem. Scand.* **20** (1966). *In press.*

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