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Glass formation in the system $CaO–Al_2O_3–CaF_2$

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The formation of glass in the system $CaO–Al_2O_3–CaF_2$ has been investigated in sealed platinum capsules having about one atmosphere pressure of AlF_3 vapour. Transparent colourless glass could be obtained in the low-fluoride moderate-alumina region of the system (Al_2O_3 35 to 60%, CaF_2 0 to 20%). With the concentration of CaF_2 exceeding 20% considerable amount of quench crystals of CaF_2 appeared in the glass. Moderate-alumina low-lime melts containing more than 35% CaF_2 occur in an immiscibility zone. At the low-fluoride periphery of the liquid immiscibility zone a small zone of metastable liquid immiscibility has been found. The results of electron microscopic and infra-red spectroscopic studies of a few selected glasses have been analysed in combination with the molar refractivity data to reflect upon the co-ordination characteristics of aluminium in these glasses.

1. Introduction

Although during the last decade the system $CaO–Al_2O_3–CaF_2$ has been receiving considerable attention due to its multifarious technological importance, there is, however, little information available on the nature of glass formation in this system. The following is a preliminary and brief communication of our findings on this aspect of the above-mentioned ternary system.

2. Experimental

In connection with the phase equilibria studies of the system $CaO–Al_2O_3–CaF_2$ [1] it was revealed that its equilibrium relations in a closed fluorine-bearing atmosphere are sharply different from those in open atmospheres [2, 3]. In view of this and also in order to avoid any change of composition due to any direct loss of fluorine during heating, the glass formation was studied by quenching in sealed platinum capsules, the experimental set-up being the same as that of Gutt *et al* [2] and Zhmoidin and Chatterjee [3]. The capsules used in the quench experiments contained about 0.2 g of specimen and in the set-up used the time taken by a specimen to travel the distance from the hot zone of the furnace to the quenching medium did not exceed 0.3 sec. The equilibrium concentration of the reaction product CaO in the purely binary system $Al_2O_3–CaF_2$ as well as the development of p_{AlF_3} within the capsules were estimated thermodynamically. The details of this calculation are given in [3], where it has been shown that in the purely binary system $Al_2O_3–CaF_2$ p_{AlF_3} could be considerably high (1 atm at 1500K and 10 atm at 1800K), but in that case the equilibrium concentration of CaO should not exceed 10^{-3}%. But it is known that CaF_2 always contains some amount of dissolved oxygen and even when 99.9% pure CaF_2 is used, it is expected that CaO contained in it would be more than 10^{-3}%. If the initial CaO content is assumed to be 10^{-2}%, even then at 1800K p_{AlF_3} within the capsules does not exceed 0.6 atm. This indicates that under the present experimental conditions the total pressure within the capsules is expected to be equal to the atmospheric pressure or slightly more than that, due mainly to the thermal expansion of the atmosphere that remained inside after the sealing of the capsules. That the capsule pressure was very near to atmospheric pressure is corroborated by the swelling of the capsules made of sufficiently plastic platinum foils during heat-treatment, to less than their ultimate capacity and yet maintained a balance with the outer atmosphere. It is, therefore, obvious that the

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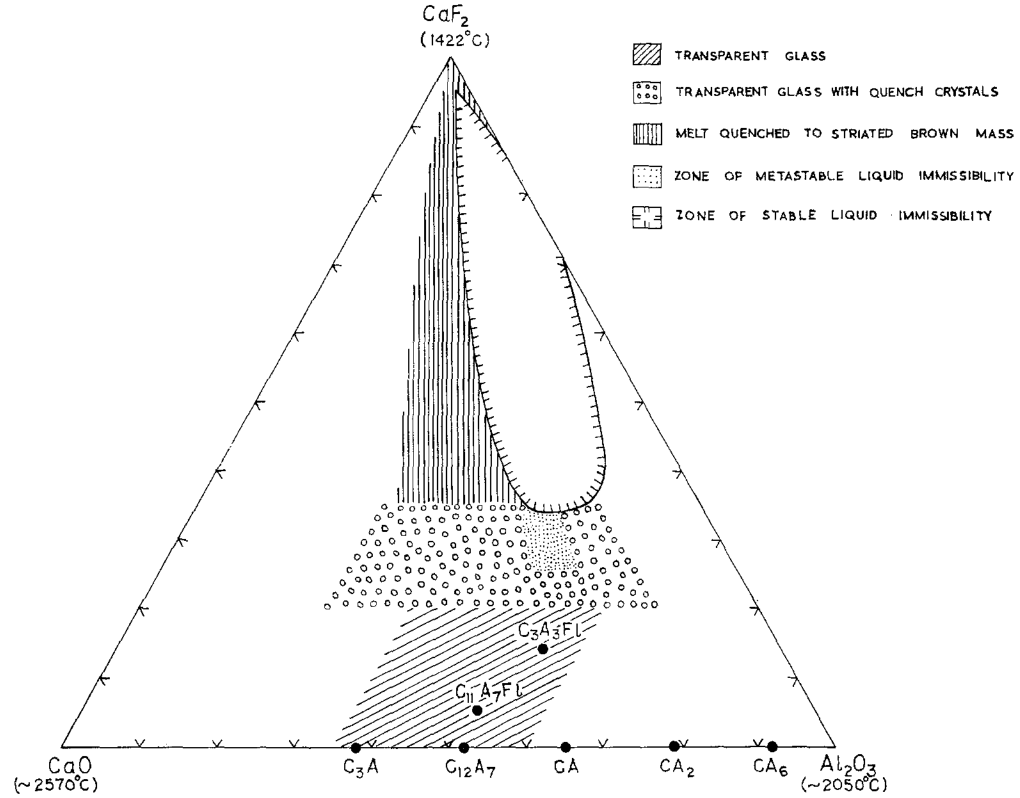

Figure 1 Glass formation in the system CaO–Al_2O_3–CaF_2.

glasses investigated here, were obtained from melts that were in equilibrium with AlF_3 vapours in the capsules, the pressure of which was almost atmospheric.

The nature of formation of glasses was studied individually in the following joins; Al_2O_3–CaF_2; CA_2*–CaF_2 CA–CaF_2, $C_{12}A_7$–CaF_2, C_3A–CaF_2, CaO–$C_{11}A_7Fl$, C_3A–$C_{11}A_7Fl$, $C_{11}A_7Fl$–C_3A_3Fl, CA_2–C_3A_3Fl,CaO–CaF_2 and CaO–Al_2O_3 (Fig. 1). A transverse join CaO–(30% Al_2O_3 + 70% CaF_2) was also investigated.

3. Results and discussion

3.1. Optical and electron microscopic studies

On the basis of the optical and electron microscopic studies of products quenched from their melts in the temperature interval 1425 to 1600° C the ternary diagram CaO–Al_2O_3–CaF_2 could be schematically divided into certain zones as shown in Fig. 1. It is evident from the diagram that clear transparent glass could be obtained in the moderate-alumina region (35 to 60% Al_2O_3 approximately) up to 20% CaF_2. Above this level of fluoride concentration, quench crystals of CaF_2 are observed in glass, often forming minute star-shaped inclusions (Fig. 2). Beyond 35% CaF_2 level the dimension and frequency of quench crystals increase to such an extent that under an optical microscope the quenched melt looks like a brown striated mass (Fig. 3). In the high fluoride high-alumina region there is a wide zone of liquid immiscibility where one of the two co-existing glasses contains less proportions of quench inclusions (Fig. 4).

Of special interest is the small zone of metastable liquid immiscibility (Fig. 1). Here one often finds two transparent glasses – one colourless and the other with a brownish tinge with a detectable difference of refractive indices. But this co-existence of two glasses is not always reproducible, when only a feebly opalescent glass is obtained. The opalescence is due to the presence of a second glass phase which is

*CaO = C, Al_2O_3 = A, CaF_2 = Fl.

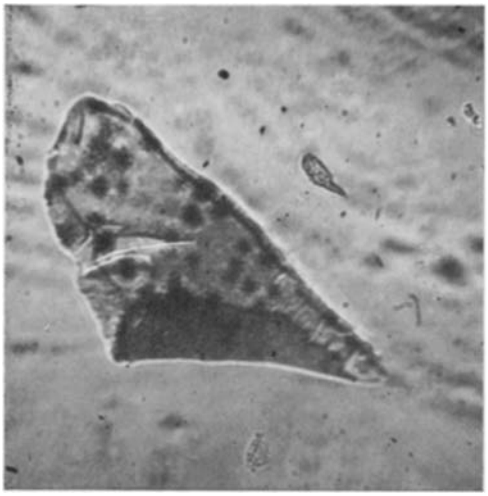

Figure 2 Star-shaped inclusions of CaF_2 crystals in glass (without crossed nicols) (× 160).

Figure 3 Appearance of glass compositions with more than 35% CaF_2 after quenching (without crossed nicols) (× 160).

revealed only by electron microscopy after low temperature annealing of these glasses.

3.2. Characterization of the zone of low-fluoride and moderate-alumina transparent glasses

Since the zone of transparent glasses (Fig. 1) is more important from the point of view of material development, it was investigated in greater details.

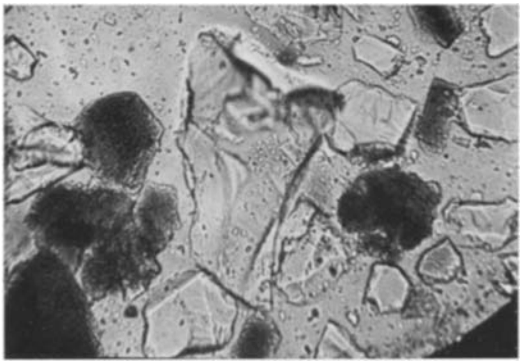

Figure 4 Co-existing glasses (without crossed nicols) (× 160).

Glasses obtained from the compositions $C_{12}A_7$, CA 95% + CaF_2 5%, $C_{11}A_7Fl$ and C_3A_3Fl were subjected to infra-red spectroscopic studies. The second composition was so chosen as the pure CA could not be quenched to a clear glass. The infra-red spectra of these glasses are shown in Fig. 5 and the major absorption bands are given in Table I. Although the spectra are not fully explained, it is evident from Fig. 5 and Table I that the infra-red spectra of the glasses under consideration are characterized by the medium-intensity bands due to the stretching

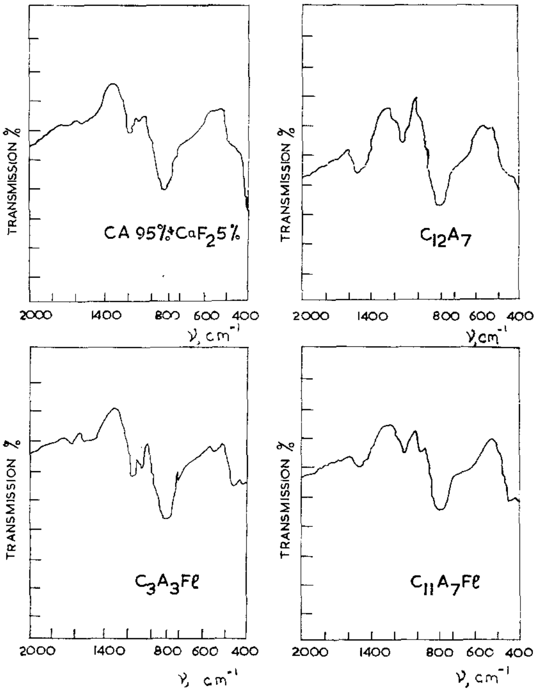

Figure 5 Infra-red spectra of calcium aluminate and aluminofluoride glasses.

TABLE I Absorption bands of infra-red spectra of some glasses

Absorption band (cm^{-1})	$C_{12}A_7$	CA 95% + CaF_2 5%	$C_{11}A_7Fl$	C_3A_3Fl	Explanation
420	—	—	—	VW	Bending motion of condensed AlO_4
470	—	—	W	W	
790-900	M	M	M	M	Stretching vibration of condensed AlO_4
960	—	—	—	—	Not deciphered
1020	—	VW	—	VW	
1110	W	W	W	W	Not deciphered
1500	W	—	W	W	

vibration and low-intensity bands due to the bending motion of condensed AlO_4 groups. The absorption bands characterizing the stretching vibrations of isolated AlO_4, AlO_5 and condensed AlO_6 – that are noticed in the corresponding crystalline phases [4] – are conspicuously absent in these glasses. The addition and increase of fluoride concentration do not cause any appreciable change in the spectra and fluorine, therefore, is expected to enter into the anionic complexes by partial isomorphous replacement of oxygen. This, however, does not preclude the possibility of discrete fluorine ions being present.

Although the infra-red spectra show that aluminium in these glasses is present in a network of four-fold co-ordination, the refractive index data give a different picture (Table II). It is evident that in the transition from the crystalline to the glass phase there is a persistent increase of refractive indices. This is obviously indicative of the increase of co-ordination number of aluminium which is possibly effected by the transition of a part of aluminium from the condensed anionic complexes to purely cationic state. Similar increases are known in the refractive index of caesium halides with the increase from six- to eight-fold co-ordination [5]. However, it may be mentioned here that the vibration frequency of condensed octahedra of Al—O is in the range 540 to 560 cm^{-1}. But since our infra-red spectra studies do not contain any band in that range and since the increase of refractive index during glass transformation is persistent, one is led to conclude that a certain amount of aluminium in these glasses is present, like calcium, in the isolated cationic holes. The vibration frequency in that case is probably so low that it did not appear in the range of spectra studied here. The possible transition of aluminium from the four- to six-fold co-ordination in the melts of the system $CaO–Al_2O_3$ has also been indicated by Zhmoidin [6].

The molar refractivity of a compound as calculated with the Lorentz-Lorenz equation often provides an additional evidence about the

TABLE II Refractive index and molar refractivity of crystalline and glass phases

Composition	Refractive index		Density (g cm^{-3})		Molar refractivity of Al_2O_3 (cm^3 mol^{-1})	
	Crystalline	Glass	Crystalline	Glass*	Crystalline	Glass
$C_{12}A_7$	1.608	1.67	2.69	3.69	12.8	7.2
$C_{11}A_7Fl$	1.602	1.66	2.70	3.67	12.7	7.6
CA 95% + CaF_2 5%	1.655†‡	1.66	2.98†	3.73	11.9†	9.1
C_3A_3Fl	1.623‡	1.63	2.96	3.68	12.1	8.1

*Computed values.
†The values are for pure CA composition.
‡Average value.

co-ordination of certain cations. Safford and Silverman [7] evaluated the contribution of Al_2O_3 to the total molar refractivity when the aluminium ions occupy either four- or six-fold co-ordination sites, the reported values being 12.3 and 10.5 $cm^3 mol^{-1}$ respectively.

In the present study the total molar refractivities of $C_{12}A_7$, $C_{11}A_7$ Fl, CA(CA 95% and CaF_2 5% for glass) and C_3A_3Fl were calculated from the densities and refractive indices listed in Table II using the Lorentz-Lorentz equation. The molar refractivity of the Al_2O_3 for each compound was determined by subtracting the molar refractivity contribution of the CaO and CaF_2 from the total molar refractivity of each compound. The values of 7.5 and 6.5 $cm^3 mol^{-1}$ were used for the molar refractivity of CaO and CaF_2.

It is evident from Table II that the molar refractivity of alumina in all the compositions under study in the crystalline state is quite close to the value given by Safford and Silverman [7] for four-fold co-ordination of aluminium whereas in the glassy state the values have considerable deviation from the value suggested for either four- or six-fold co-ordination of aluminium. Although the values in the glassy state are comparatively closer to the six-fold co-ordination of aluminium, still the deviation is strong enough to indicate significant departure from regular six-fold co-ordination characteristics of aluminium, thereby indirectly confirming the suggested hypothesis of the presence of some aluminium in cationic holes.

4. Conclusion

In the system $CaO-Al_2O_3-CaF_2$, clear transparent glass could be obtained in the low-fluoride moderate-alumina region from the melts that are in equilibrium with AlF_3 vapours. Aluminium is present in these glasses mainly as a tetrahedral network and partly in the cationic holes. Flourine takes part in the Al—O network by anionic isomorphism of oxygen without, however, causing any appreciable change in the infra-red spectra.

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