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Some Considerations on State of Fluorine Ion in Flux (Report II) †

Nobuya IWAMOTO *, Yukio MAKINO ** and Norimasa UMESAKI ***

Abstract

The behaviour of fluorine ion in several fluorogermanates was investigated with infrared absorption method. Densities and refractive indices of glasses in the $KF-GeO_2$ and $xCaF_2 \cdot (1-x)CaO \cdot SiO_2$ systems were also measured. With these results, total equivalent oxygen density and molar refractivity of CaF_2 were calculated in the latter system. It was suggested that alkaline fluoride has the same or a little stronger role as modifier in the glasses than alkaline oxide. Further, Ca-F interionic distance was calculated in the system $xCaF_2 \cdot (1-x)CaO \cdot SiO_2$ by empirical equation of Kordes and it was suggested that fluorine ion in this system has a tendency to become more compressed state with increasing x .

1. Introduction

As described in the previous report¹⁾ fluoride is generally added to flux for improving weldability based on many year's experience. However, the state analysis of fluorine ion in flux has not fully been performed despite the importance of fluoride addition. In the previous report¹⁾, the state of fluorine ion in several fluorosilicates was investigated with several spectroscopic methods, and it was suggested that it is difficult to accept the formation of Si-F bond in the system $xCaF_2 \cdot (1-x)CaO \cdot SiO_2$. However, it remains continuously questionable whether fluoride shows similar behaviour with another modifier oxides in the melt or not.

Binary fluorosilicate such as $CaF_2 \cdot SiO_2$ system is suitable in order to study the effect of fluoride addition. In general, however, it says that precipitation of crystalline materials takes easily place in a binary fluorosilicate. Accordingly, it is difficult to obtain an amorphous specimen necessitating to study the effect of fluoride addition. In this study, binary fluorogermanate such as $KF-GeO_2$ system was selected because the behaviour of germanium ion is similar to that of silicon ion in the melt and glassy state can easily be holded to room temperature when compared with fluorosilicate. Then, infrared absorption, density and refractive index measurements were carried out with several fluorogermanates. Further, density and refractive index were also measured with the specimens in

the system $xCaF_2 \cdot (1-x)CaO \cdot SiO_2$ and total equivalent oxygen density, molar refractivity of CaF_2 and Ca-F interionic distance were calculated with the use of Kordes's formula.

2. Experimental procedures

Each material used for the preparation of glasses was reagent grade alkaline fluoride (LiF, NaF, KF and RbF), CaF_2 , $CaCO_3$, GeO_2 and SiO_2 . The experimental conditions to make specimens and to do infrared absorption measurement were already described in the previous report¹⁾. Density measurement was performed with Archimedean method. As immersion liquid water or toluen was used. Refractive indices of specimens were measured with Abbe refractometer (Shimadzu Seisakusho Ltd., 3L type), using methylene iodide as the contact medium.

3. Infrared absorption study

The ionic size and ionic charge of germanium ion are very similar to those of silicon ion. The structure of germanate somewhat resembles to that of silicate. However, the ionic radius of germanium (0.53A) is very close to cation-anion ratio limit whether germanium ion can be occupied tetrahedral or octahedral site in the germanate. Octahedrally coordinated germanium ion is found in crystalline $2Na_2O \cdot 0.9GeO_2$ ²⁾ or tetragonal GeO_2 . On the

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other hand, it is well known that germanium ion occupies tetrahedral site in vitreous GeO_2 and hexagonal GeO_2 .

According to the previous study³⁾, tetrahedrally coordinated germanium ion shows the absorption peak at 878 cm^{-1} and octahedrally coordinated germanium ion shows the absorption peak at 688 cm^{-1} . Absorption peak in glassy GeO_2 shifts in lower wave number with the addition of alkaline oxide and this shift reaches to about 100 cm^{-1} . This can mainly be attributed to the formation of octahedrally coordinated germanium ion because the formation of non-bridging oxygen has only a small contribution to this shift as in the case of alkaline silicate⁴⁾. Assuming that the shift of alkaline germanate in infrared absorption spectrum is reduced to the formation of octahedrally coordinated germanium ion, the degree of the shift could be originated to the difference of modifying effect between alkaline-fluoride and -oxide in the melt.

Infrared absorption results are shown in Figs. 1, 2 and 3. From these results, it was suggested that KF is the same

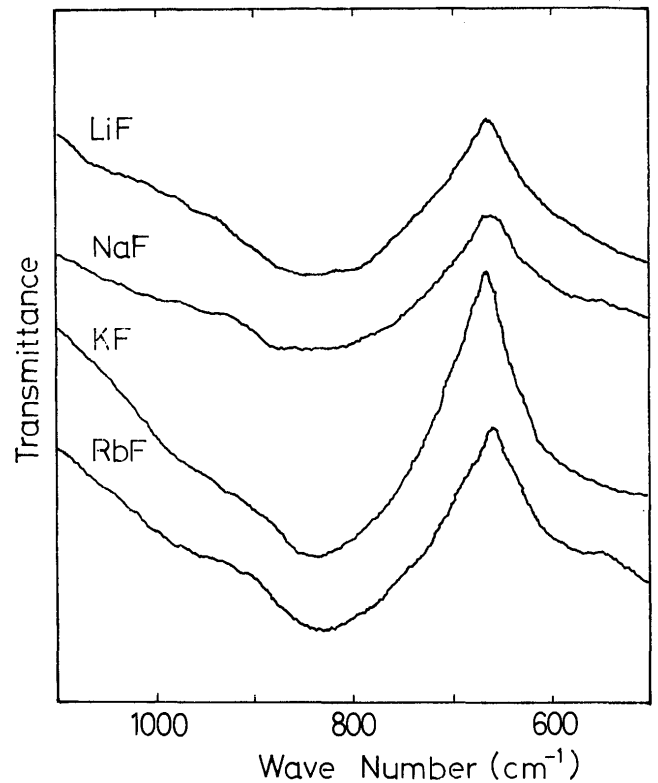


Fig. 2 Infrared absorption spectra of 0.2MF-0.8GeO₂ slags (M: Li, Na, K and Rb)

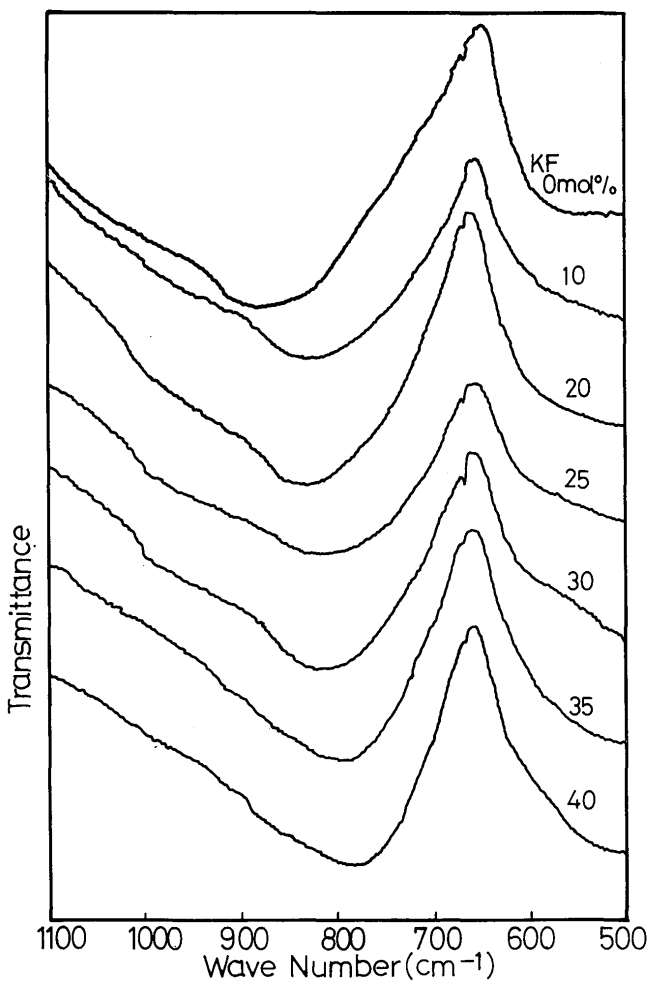


Fig. 1 Infrared absorption spectra of slags in the system KF-GeO₂

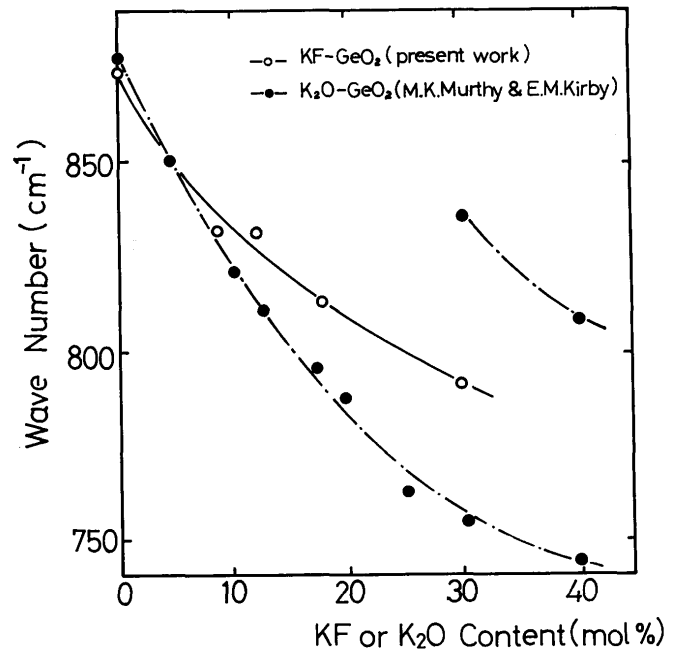


Fig. 3 Dependence of wave number shift in infrared absorption upon KF or K₂O content.

or somewhat stronger modifier than K₂O and similar results would be found in other alkaline fluorides. A little difference between KF and K₂O appears to correlate with bridging behaviour of anion. The difference among various

fluorides was not remarkably detected in the degree of the shift near 850 cm^{-1} .

4. Total equivalent oxygen density and molar refractivity

Total equivalent oxygen density and molar refractivity can be connected with the difference of slag structure as explained in the previous report¹⁾. The former is related to the packing behaviour of ions in slag and the latter to the polarization of ions. The results in the system $x\text{CaF}_2 \cdot (1-x)\text{CaO} \cdot \text{SiO}_2$ are shown in Figs. 4 and 5. Both density and refractive index linearly decreased

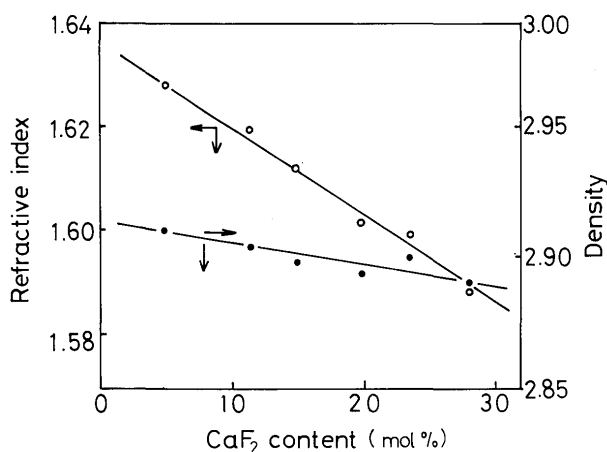


Fig. 4 Dependence of density and refractive index upon CaF_2 content in system $x\text{CaF}_2 \cdot \text{SiO}_2$

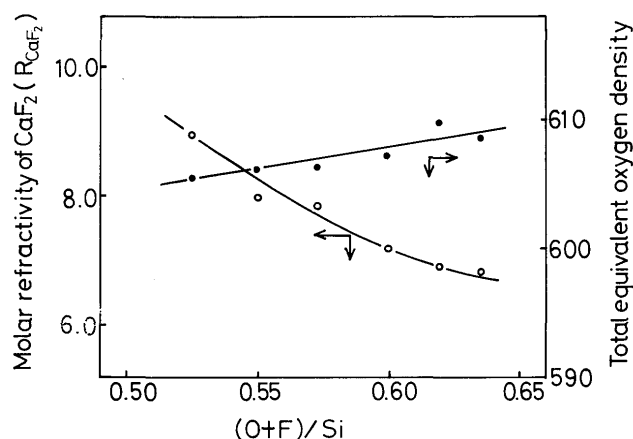


Fig. 5 Calculated values of molar refractivity of CaF_2 and total equivalent oxygen density in the system $x\text{CaF}_2 \cdot (1-x)\text{CaO} \cdot \text{SiO}_2$

with increasing x and it seems to correspond to simple exchange of fluorine ion for oxygen. Same phenomena were appeared in the results of total equivalent oxygen density and molar refractivity. In opposed to the fairly success in the state analysis of aluminium in slag⁵⁾, it can be realized that these physical properties could not be so sensitive to discuss the state of fluorine ion in slag.

Density and refractive index results in the system KF-GeO_2 are shown in Fig. 6. The maxima were shown in

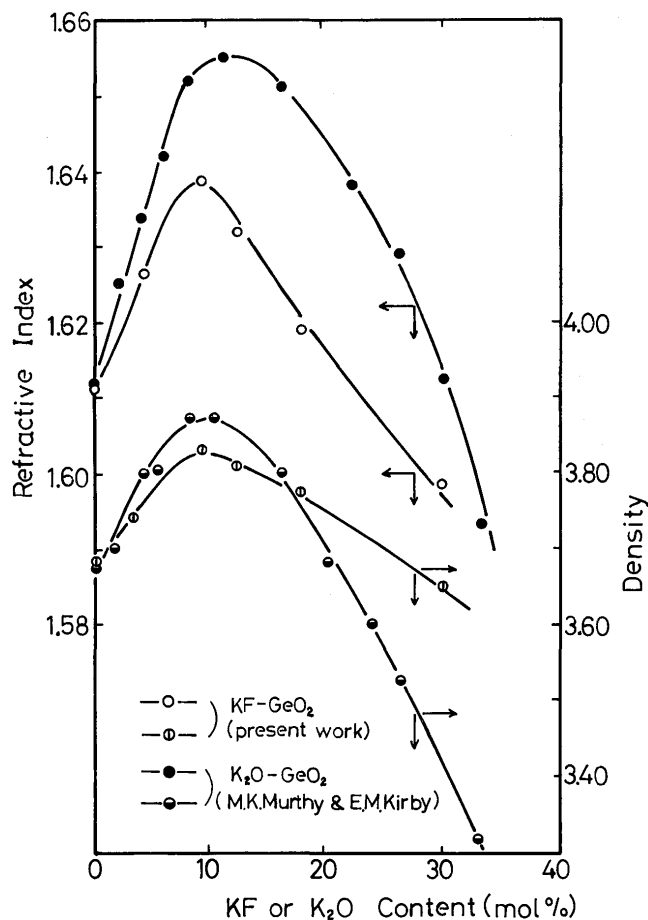


Fig. 6 Dependence of refractive index and density upon KF or K_2O content in the $\text{GeO}_2\text{-KF}$ and $\text{GeO}_2\text{-K}_2\text{O}$ systems

this system as well as in the case of alkaligermanates^{6),7)}. These maxima can be attributed to the formation of GeO_6 group, hence the position of the maximum can become a measure of the modifying strength in the melt because the formation of GeO_6 group corresponds to network destruction. According to this consideration, it is suggested that the strength of KF as modifier is the same or a little larger than that of K_2O . It is expected that the relation between another alkaline-fluoride and -oxide will show the similar result as in the case of potassium. Total equivalent oxygen density and molar refractivity in the system KF-GeO_6 were not calculated because the characteristics of these physical properties was not attributed to the state of fluorine ion but the change of the coordination of germanium ion.

5. Calculation of interionic distance

Interionic distance in an amorphous state is generally determined from radial distribution function calculation

by X-ray measurement. However, interionic distance in inorganic glass can be more easily calculated by use of following Kordes's empirical equation:^{8),9)}

$$\left(\frac{R}{0.603}\right)^{2/9} = k \cdot r \cdot z / n - 1$$

- R = ionic refractivity per Avogadro ion based on Lorentz-Lorenz formula
 k = a constant with the value of unity for noble ion
 r = ionic radius
 z = valence of ion
 n = Born repulsion exponent with the value of 7.1 for neon type ion.

Ionic refractivity of fluorine ion was calculated from molar refractivity of CaF₂ on the assumption that ionic refractivity of calcium ion is unchangeable. The calculated values of Ca-F interionic distance are shown in Fig. 7.

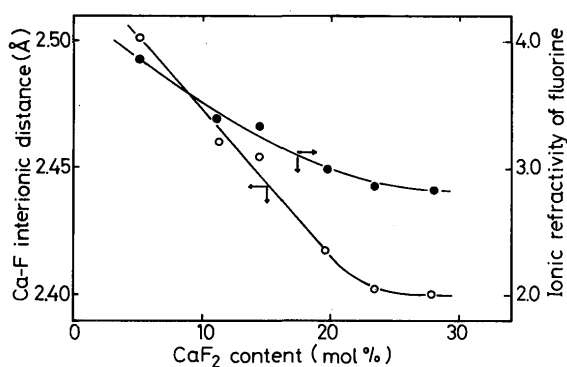


Fig. 7 Ionic refractivity of fluorine ion and Ca-F interionic distance calculated from Kordes's formula

Considerably larger values were obtained in compared with the sum of each Pauling's ionic radius. Therefore, it would be reasonable to interpret that fluorine ion in slag exists in somewhat released state and becomes more released with decreasing CaF₂ content.

6. Summary

In order to compare the behaviour of alkaline fluoride with that of alkaline oxide, infrared absorption measurement was performed in several alkaline fluorogermanates. Assuming that the shift near 850 cm⁻¹ is attributed to the occurrence of octahedrally coordinated germanium ion, the behaviour of KF as modifier could be compared with that of K₂O from the degree of the shift. From these results, it was suggested that the strength of KF as modifier is the same or a little larger than K₂O. No difference among various alkaline fluorides was detected in the degree of the shift near 850 cm⁻¹. In the dependence of refractive index or density upon KF content the similar results were obtained as infrared absorption measurement. In the xCaF₂·(1-x)CaO·SiO₂ system, nearly perfect substitution of fluorine ion with oxygen ion could be suggested from the calculation of total equivalent oxygen density and molar refractivity of CaF₂. Further, the calculated values of Ca-F interionic distance suggested that fluorine ion in this system takes more released state with decreasing CaF₂ content.

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