CHARACTERISTIC DIFFUSION PHENOMENA OF FLUORINE
IN MOLTEN LiF-BeF₂ and NaF-BeF₂ SYSTEMS

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ABSTRACT
Self-diffusion coefficients of fluorine and cations in molten LiF-BeF₂ and NaF-BeF₂ systems were measured by the capillary reservoir technique. The characteristic diffusion phenomena of fluorine in these molten alkali fluoroberyllates are very similar to those of oxygen in molten CaO-SiO₂ and CaO-SiO₂-Al₂O₃ slag. The dynamical behavior of Li and F in molten Li₂BeF₄ was also analyzed by NMR technique.

INTRODUCTION
It has been reported that the alkali fluoroberyllate melt systems, RF-BeF₂ (R=Li, Na, K) are quite similar to the alkaline-earth silicate melt systems, R'O-SiO₂ (R'=Mg, Ca, Ba). Especially, the phase diagram of MgO-SiO₂ scaled down by the relation [(t°C+273°C)/2.88]+273 fit most of the diagram of LiF-BeF₂, as indicated by Thillo and Lehmann[1]. It was also recently found that the physical properties, such as viscosity, electrical conductivity, and molar volume, depend on simple quantitative relationships between molten alkali fluoroberyllate system and molten alkaline earth silicate system[2]. The results indicate that the statistical and dynamical properties of constituent ions in these molten states also have similar behavior.

Cantor et al.[3] showed in their viscosity study of molten LiF-BeF₂ that the viscosity decreases rapidly with an increase of LiF concentration, due to breaking of the fluorine bridges in a three-dimensional network of Be-F bonds, and estimated that the melt might lose its network character for a BeF₂ content smaller than 65mol%.

We have already reported the self-diffusion coefficients and their temperature dependence for F and Li in molten Li₂BeF₄ and LiBeF₃ and for F and Na in molten NaBeF₃ by the capillary reservoir technique[4-8], X-ray diffraction analysis of molten Na₂BeF₄ and NaBeF₃[9] and nuclear spin relaxa-
tation of $^{7}\text{Li}$ and $^{19}\text{F}$ in solid and molten Li$_2$BeF$_4$\cite{10}. In this report, all these data are summarized and compared with those in molten alkaline-earth silicates.

**EXPERIMENTALS**

The method of measurements of self-diffusion coefficients was described in detail elsewhere\cite{4-8}. The procedure of the experiment was carried out by the capillary reservoir technique.

**PREPARATION OF RADIOACTIVE OR STABLE TRACER**

The fluorine radioactive F-18 was prepared using JRR-3 (Japan Research Reactor-3). Highly purified Li$_2$CO$_3$ was used as a target material and the following reactions occurred to produce $^{18}\text{F}$. $^{6}\text{Li}(n,\alpha)^{3}\text{T}$ and $^{16}\text{O}(T,n)^{18}\text{F}$ \hspace{1cm} (1)

After irradiation, Li$_2$CO$_3$ powder was treated with aqueous hydrogen fluoride in a platinum crucible to produce the labelled Li$^{18}\text{F}$ deposit. On the other hand, the lithium stable $^{6}\text{Li}$ was prepared using Li$_2$CO$_3$ powder which a $^{6}\text{Li}/^{7}\text{Li}$ abundance ratio of 19 and then Li$_2$CO$_3$ was treated with aqueous hydrogen fluoride in the same way as above mentioned. $^{24}\text{Na}$ was made from NaF powder irradiated by thermal neutron for 1 min. in JRR-2.

**PREPARATION OF Li$_2$BeF$_4$, LiBeF$_3$ and NaBeF$_3$**

For the preparation of Li$_2$BeF$_4$, LiBeF$_3$ and NaBeF$_3$ in the diffusion cell, a mixture of BeF$_2$ and LiF or NaF was melted in a platinum container, treated with a HF+H$_2$ mixture at 600$^\circ\text{C}$ and then purged with He. The chemicals used were as follows: LiF and NaF prepared by Merck Co.(Germany), granulation of single crystal(1-4mm); BeF$_2$ prepared by Rare Metallic Co.(Japan) [known impurities(in ppm): K+Na,600; Ca,10; Al,20; Cr,30; Fe,10; Ni,10].

**APPARATUS AND PROCEDURE**

A schematic diagram of the apparatus is shown in Fig.1. In this work some devices were adopted to avoid solidification of the melted tracer mixture in the capillaries before each diffusion run. After the tracer salt(C) in the Pt crucible(D) and non-tracer salt(E) in the Ni crucible(F) were melted under He atmosphere, the movable Ni rod with the capillaries was lowered into the Pt crucible. The capillaries were filled with the molten tracer salt by dipping their mouths into the salt under a vacuum and then feeding He gas slowly back in the apparatus. The capillaries were raised out of the molten tracer salt by means of the Ni rod and then submerged in the molten non-tracer salt after...
turning the stainless steel flange(I).

The capillaries which were 1mm inner diameter and 30-40mm length were made of Ni. The duration of diffusion run was in the range of 20-120 minutes. The maximum difference in temperature between the top and the bottom of the capillary was about 0.5°C.

After the diffusion run, the capillaries were lifted from the molten non-tracer salt and then removed. After cleaning the capillaries, they were cut by a saw at intervals of about 2mm. The concentration profiles of tracer $^{18}_F$ and $^{24}_Na$ or $^6_{Li}$ in the capillaries were measured with γ-ray spectrometer or ion micro mass analyser(HITACHI IMA-SS), respectively.

NUCLEAR MAGNETIC RESONANCE

Spin-lattice relaxation time $T_1$ was measured by pulse spectrometer controlled by a micro-processer. For $T_1$ values less than 0.1sec "180°-τ-90°" pulse technique was applied and the longer $T_1$ was measured by "(n·90°)-τ-90°" pulse technique. The 90° pulse length was about 15μs. For magnetization $M_z(t)$ the intensity of free induction decay(FID) signal following second 90° pulse were measured as a function of $τ$. The absolute $M_z(t)$ decay obeyed exponential law in all samples. In order to improve signal to noise ratio a digitalized signal averager was utilized. In all experiments a frequency of 10MHz or 20MHz was employed. Each sample was sealed in quartz sample tube with a length of 4cm and a diameter of 1cm. Temperature of the specimens was controlled up to 630°C with accuracy of ±2°C in an electrical furnace which was mounted between pole pieces of magnet. Temperature was measured by an Pt-Pt(13%Rh) thermocouple attached to the sample tube.

$T_1$ for $^7_{Li}$ and $^{19}_F$ has been determined using the relations $\frac{I}{I_0}$=1-exp(-τ/$T_1$) for relatively long $T_1$($T_1>0.1$sec).
or \( I = I_0 [1 - 2 \exp(-\tau/T)] \) for relatively short \( T_1 (T_1 < 0.1 \text{sec}) \).

**RESULTS AND DISCUSSION**

Typical concentration profiles of \(^{18}\text{F} \) and \(^{6}\text{Li} \) in capillaries are shown in Figs. 2 and 3. The salt was not contained within a few mm from the capillary mouth due to the volume contraction of the salt.

The diffusion coefficient \( D \) was calculated by applying the following equation to the observed concentration profiles,

\[
C_x = C_0 \text{erf} \left( \frac{x}{(D t)^{1/2}} \right),
\]

where \( C_0 \) is the initial concentration of the tracer and \( C_x \) the concentration of the tracer at distance \( x \) from the boundary after diffusion time \( t \).

The diffusion coefficients are written in the form

\[
D = D_0 \exp \left( -\frac{E}{RT} \right),
\]

where \( E \) is the activation energy, \( R \) the gas constant and \( T \) the absolute temperature. The results as shown in Table 1 and Fig.4 were obtained by a least squares analysis from all experimental data.

| Table 1 Summary of self-diffusion coefficients \( D = D_0 \exp \left[ -E/RT \right] \) in molten \( \text{Li}_2\text{BeF}_4, \text{LiBeF}_3 \) and \( \text{NaBeF}_3 \) |
|---|---|---|
|   | \( D_0 \) (m\(^2\)s\(^{-1}\)) | \( E \) (KJ\cdot mol\(^{-1}\)) | Observed temperature range(°C) |
| \( \text{Li}_2\text{BeF}_4 \) | Li | 9.27x10\(^{-7}\) | 32.5±8.4 | 470-640 |
|   | F   | 6.61x10\(^{-1}\) | 128.1±14.2 | 510-650 |
| \( \text{LiBeF}_3 \) | Li | 1.12x10\(^{-6}\) | 38.7±12.5 | 440-560 |
|   | F   | 3.16x10\(^{-6}\) | 144.0±16.3 | 450-670 |
| \( \text{NaBeF}_3 \) | Na | 7.80x10\(^{-7}\) | 40.2±5.6 | 420-560 |
|   | F   | 4.93x10\(^{-4}\) | 79.6±6.5 | 440-600 |
Fig. 2 The distribution of $^{18}\text{F}$ in a capillary after a diffusion run.

Fig. 3 Distribution of $^6\text{Li}$ in a capillary after a diffusion run.
Fig. 4 Summary of the diffusion coefficients of fluorine and lithium or sodium in molten Li$_2$BeF$_4$, LiBeF$_3$ and NaBeF$_3$.

Fig. 5 Comparison of self-diffusion coefficient of various cations in molten salts and molten silicates under the reduced temperature scale $T/T_m$:

(a) KF (K); (b) NaCl (Na); (c) NaF (Na);
(d) NaF-AlF$_3$ (Na); (e) NaI (Na);
(f) KCl (K); (g) RbCl (Rb);
(h) CsCl (Cs); (i) LiCl (Li);
(j) FLINAK (Na); (k) FLINAK (K);
(l) FLINAK (Li);
(m) Na$_2$O-SiO$_2$ (23-77 mol%) (Na);
(n) CaO-SiO$_2$-Al$_2$O$_3$ (42-45-12 mol%) (Ca);
(o) CaO-SiO$_2$-Al$_2$O$_3$ (42-45-12 mol%) (Ca);
(p) CaO-SiO$_2$ (56-44 mol%) (Ca).
Figs. 5 and 6 show the results of self-diffusion coefficients in these molten alkali fluoroberyllates compared with those of cations and anions in molten alkali halides and molten silicates under the reduced temperature scale, $T/T_m$, where $T_m$ is the melting point. The diffusion coefficients and the activation energies of cations in molten Li$_2$BeF$_4$, LiBeF$_3$ and NaBeF$_3$ follow a similar pattern to those of cations in molten alkali halides. On the other hand, self-diffusion of fluorine in these molten alkali fluoroberyllates have unusually high diffusion coefficients and activation energies. The activation energies for self-diffusion coefficients of fluorine were larger than those for electrical conductivities[11] and viscosity coefficients [3].

It was reported from the analysis of X-ray diffraction [9,12] and the Raman spectrum measurements[13] that complex anions exist, such as BeF$_4^{2-}$ and Be$_2$F$_7^{2-}$ in molten Li$_2$BeF$_4$, LiBeF$_3$ and NaBeF$_3$. The fact that the magnitude of the diffusion coefficient measured in this work is unusually large can not be explained solely by mass transfer due to migration of the large fluoroberyllate anions.

Possible explanations for the large value of the fluorine diffusion coefficient could be the exchange of fluorine atoms between neighbouring beryllate units including the rotation of beryllate anions, or the fluorine diffusion by means of neutral ion pair, such as LiF, diffusion mechanism. The exchange mechanism involves the breaking of Be-F bonds and some steric difficulties with anion rotation, which can account for a high energy of activation for fluorine diffusion. In ion-pair diffusion,
on the other hand, the movement of fluorine with lithium involves breaking of Be-F bonds, because the content of free fluorine atoms in the melt seems small. This mechanism can also have a high activation energy.

Fig. 7 shows the temperature dependence of spin-lattice relaxation time $T_1$ of $^{19}\text{F}$ and $^7\text{Li}$ in molten Li$_2$BeF$_4$[10]. $T_1$ of $^{19}\text{F}$ had minimum and $T_1$ at frequency of 20MHz was longer than that at frequency of 10MHz at temperatures below $T_1$ minimum. However, both values of $T_1$ approached to the same at temperatures above $T_1$ minimum. $T_1$ of $^7\text{Li}$ had also minimum and the minimum temperature of $^7\text{Li}$ was a little higher than that of $^{19}\text{F}$.

The magnetic impurities such as Ni$^{2+}$ and Fe$^{2+}$ in the sample will have important effect upon the relaxation time and resonance absorption spectra. The concentration of magnetic impurity was estimated by the analysis of magnetic susceptibility measured at temperatures below 4.2°K. The concentration of magnetic impurity used in the measurements of NMR was about 2.9ppm calculated in terms of Fe$^{2+}$ ion.

Fig. 8 shows the resonance absorption spectra of $^{19}\text{F}$ and $^7\text{Li}$ in solid and molten Li$_2$BeF$_4$[10]. The frequency was 10MHz. The remarkable result was the line width of resonance absorption spectrum of $^{19}\text{F}$ at 435°C(solid) is nearly equal to that at 550°C(liquid).

![Fig. 7 Temperature dependence of $T_1$ of $^7\text{Li}$ and $^{19}\text{F}$ in molten Li$_2$BeF$_4$.](image-url)
As there is mainly $\text{BeF}_4^{2-}$ and $\text{Li}^+$ ions in molten $\text{Li}_2\text{BeF}_4$, the following relaxation mechanisms will be considered as the relaxation of $^{19}\text{F}$.

1. Rotation of $\text{BeF}_4^{2-}$ ion.
2. Migration of $\text{BeF}_4^{2-}$ ion.
3. Interaction between $\text{F}^-$ and $\text{Li}^+$ ions.
4. Dissociation of F atom from $\text{BeF}_4^{2-}$ ion and diffusion of fluorine.

The contribution of these four mechanisms to $T_1$ are shown precisely in Ref.[10] and the essential equations and results will be presented in this paper.

1. Relaxation due to the rotation of $\text{BeF}_4^{2-}$ ion.

There are two models, diffusion model and kinetic model. In diffusion model, the relaxation time of rotation $\tau_2$ is much shorter than periodic time of rotation $T_0 (\tau_2 < T_0)$ and $T_1$ is expressed by the following equation,

$$\frac{1}{T_1} \text{rot.diff} = \frac{2}{5} (\gamma - 1) \frac{h}{\gamma} r_{\text{F-F}}^2 I_F (I_F + 1) x \frac{\tau_2}{1 + \omega^2 \tau_2^2} + 4 \tau_2 / (1 + 4 \omega^2 \tau_2^2).$$

On the other hand, $T_1$ in kinetic model ($\tau_2 > T_0$) is expressed by the following equation,

$$\frac{1}{T_1} \text{rot.kin} = \frac{1}{5} \left( \frac{1}{T_1} \right) \text{rot.diff}.$$ 

In these equations, $I_F$ is the quantum number of F nuclear spin ($I = 1/2$), $\gamma$ the number of F atoms in $\text{BeF}_4^{2-}$ ion (=4), $\gamma_F$ the gyromagnetic ratio of F nuclei and $r_{\text{F-F}}$ the atomic distance of F-F pair.

The diffusion coefficient $D'$ of rotation of complex ion is expressed by Stokes relation with a viscosity $\eta$.

Fig. 8 Resonance absorption spectra of $^{19}\text{F}$ and $^7\text{Li}$

S: solid; L: liquid
\[ D' = \frac{kT}{8\pi a^3} \eta. \]  
(6)

The relaxation time \( \tau_2 \) will be calculated using the relation \( \tau_2 = (6D')^{-1} \) and the observed viscosity \( \eta = 5.94 \times 10^{-4} \exp(38.4/RT) \) poise[3]. \( \tau_2 \) at 530°C was roughly estimated to be \( 1.7 \times 10^{-10} \) s.

On the other hand, eq. (4) is expressed using parameter \( r_{F-F} = 2.56 \AA \) as follows.

\[
\left( \frac{1}{T_1} \right)_{\text{rot}} = 1.7 \times 10^9 \left[ \tau_2 / (1 + \omega^2 \tau_2^2) + 4 \tau_2 / (1 + 4 \omega^2 \tau_2^2) \right] s^{-1}.
\]  
(7)

This equation has maximum at \( \omega \tau_2 = 0.64 \). The estimated relaxation time by Stokes relation \( \tau_2 = 1.7 \times 10^{-10} \) s show \( \omega \tau_2 = 1.02 \times 10^{-2} \) which is much smaller than unity and cannot explain the observed \( T_1 \) minimum at 530°C.

The contribution of rotation of \( \text{BeF}_4^{2-} \) ion to \( T_1 \) will be estimated to be 1.4 s\(^{-1}\) by eq. (7) and \( \omega \tau_2 = 0.07 \times 10^{-2} \), which is much smaller than the observed value \( (1/T_1)_{\text{exp}} = 200 \) s\(^{-1}\). Then the contribution of rotation to \( T_1 \) will be small.

(2) Relaxation due to the migration of \( \text{BeF}_4^{2-} \) ion.

\( T_1 \) due to the migration of complex ion will be expressed by

\[
\left( \frac{1}{T_1} \right)_{\text{diff}} = 3/2 \gamma^4 N^2 I(I+1) \left[ 8\pi / 15 J(\omega) + 32\pi / 15 J(2\omega) \right]
\]  
(8)

and

\[
J(\omega) = (N/\pi d^2) \int [J_{3/2}(u)]^2 u du / (u^4 + \omega^2 u^2),
\]  
(9)

where \( D \) is the diffusion coefficient of migration of complex ion, \( N \) the spin density, \( d \) the diameter of complex ion and \( J_{3/2} \) Bessel function. The integration in eq. (9) has maximum value 0.133 at \( \omega = 0 \) and decreases monotonically. Then \( (1/T_1)_{\text{diff}} \) has no maximum.

The diffusion coefficient \( D \) of migration of complex ion is roughly estimated by Stokes relation \( D = kT/6\pi a \eta \) and \( D = 1 \times 10^{-10} \) m\(^2\)/s at 530°C. Then using \( N = 7 \times 10^{30} / \text{m}^3 \) and \( D = 1 \times 10^{-10} \) m\(^2\)/s(530°C), the contribution of migration of \( \text{BeF}_4^{2-} \) ion to \( T_1 \) is estimated to be \( (1/T_1)_{\text{diff}} = 0.3 \), which is also much smaller than the observed value.

(3) Relaxation due to interaction between \( \text{Li}^+ \) and \( F^- \)

\( T_1 \) will be expressed essentially by eq. (8) with different parameters such as \( I = 3/2, D = a^2/6 \tau, d = r_{F-F} - r_T, N = \text{spin density of Li}, \) and \( \gamma^4 = \gamma_F^2 \gamma_L^2 \). Using \( r_{F-F} = 1.85 \AA, N = 3.5 \times 10^{30} / \text{m}^3 \) and \( D_{Li} = 9.27 \times 10^{-7} \exp(-32.5/RT) \), we get \( (1/T_1)_{\text{F-Li}} = 1.5 \times 10^{-3} \), which is also much smaller than the observed value.
Dissociation of F atom from BeF$_2^-$ ion and diffusion of fluorine

The behavior of T$_1$ is attributed to the dissociation of F from complex ions and the long distance diffusion of F ions in the liquid by the following mechanisms.

In exchange model of fluorine atoms between neighbouring beryllate units including rotation of beryllate anions, the diffusion distance with one step will be at most 6Å. Using the relation $D=\langle a^2 \rangle /6\tau$ and the observed diffusion coefficient $D=2\times10^{-9}$m$^2$/s at 530°C, the estimated correlation time $\tau$ is $2\times10^{-11}$s which is much smaller than the observed $\tau=3\times10^{-8}$s and is comparable with that of the rotation of the molecule. This is not reasonable.

On the other hand, in dissociation and long distance diffusion model of fluorine, the relaxation time will be expressed by the following equation.

$$\frac{1}{T_1} = 8\pi/15\cdot\gamma^4 N/3\tau[(2(1+(\omega\tau/2)^2)+\tau)/(1+\omega^2\tau^2)]$$

Equation (10) has maximum at $\omega\tau=1.41 (\tau=2.25\times10^{-8}$s at $\omega=6.28\times10^7$s$^{-1}$) and we get $1/T_1_{\text{max}}=50$, which is much larger than the former three relaxation mechanisms. Then root mean square (RMS) distance $\langle \ell^2 \rangle$ of one step of fluorine diffusion, which is the distance between dissociation of F from a complex ion, diffusion in the liquid and trap at F vacancy of another complex ion, is roughly estimated by relation $\langle \ell^2 \rangle = 6\tau D$. At 530°C, the observed value of $\tau$ and D were $2.25\times10^{-8}$s and $2\times10^{-9}$m$^2$/s, respectively and $\langle \ell^2 \rangle \approx 100$Å was obtained.

The results of NMR indicate that the dissociation of F from complex ions and the long distance diffusion of F ions has largest contribution to the diffusion in molten Li$_2$BeF$_4$ and T$_1$ of this mechanism is in good agreement with the experimental value. The solid curves in Fig.9 are the theoretical ones with

$$\frac{1}{\tau}=2\times10^{15}\exp(-103.7/RT), \quad (11)$$

and

$$\frac{1}{T_1}=S[1/(1+\omega^2\tau^2)+4\tau/(1+4\omega^2\tau^2)]. \quad (12)$$

S was determined to fit the theoretical curve to the observed one at 640°C and $\omega=2\pi\times10^7$s$^{-1}$. The theoretical equation indicates good agreement with temperature and frequency dependency of the observed T$_1$. The activation energy 103.7KJ/mol is also in good agreement with that of self-diffusion of fluorine with tracer method, 128KJ/mol, as shown in Table 1.
Fig. 9 Temperature dependence of \(1/T_1\) of \(^{19}\text{F}\) in molten \(\text{Li}_2\text{BeF}_4\). The solid curves are the theoretical one with \(1/\tau=2\times10^{15}\exp(-103.7/RT)\).

CONCLUSION

(1) Characteristic diffusion of fluorine in molten alkali fluoroberyllates could be explained by the diffusion mechanism with dissociation of F from complex anion and long distance diffusion.

(2) The results of self-diffusion of fluorine in molten \(\text{Li}_2\text{BeF}_4,\text{LiBeF}_3\) and \(\text{NaBeF}_3\) are qualitatively similar to those of oxygen in molten \(\text{CaO-SiO}_2\) and \(\text{CaO-SiO}_2-\text{Al}_2\text{O}_3\) slag[14,15]. X-ray diffraction analysis of molten \(\text{NaBeF}_3\) [9] and \(\text{CaSiO}_3\) [16] also indicates the similarity of the structures. Thus, the research on molten alkali fluoroberyllates will contribute to the analysis of statistical and dynamical behaviors of constituent ions in molten alkaline-earth silicates which is relatively difficult because of high temperature.

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