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# Self-Diffusion of Lithium in Molten LiBeF<sub>3</sub><sup>†</sup>

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## Abstract

The self-diffusion coefficients of lithium in molten LiBeF<sub>3</sub> have been measured with the capillary reservoir technique using <sup>6</sup>Li as a tracer. The self-diffusion coefficients D were calculated from the concentration profiles of <sup>6</sup>Li in a capillary obtained by an ion micro mass analyser. The result can be described with the Arrhenius equation,

$$D = 1.12 \times 10^{-2} \exp(-9310 \pm 3000/RT),$$

where D is expressed in cm<sup>2</sup>/sec, R in cal/mol-deg and T in degree Kelvin. The self-diffusion coefficients of lithium in molten LiBeF<sub>3</sub> are smaller than those in molten Li<sub>2</sub>BeF<sub>4</sub>. On the other hand, the activation energies are quite similar in molten Li<sub>2</sub>BeF<sub>4</sub> and LiBeF<sub>3</sub>. These results suggest that lithium ion diffuses through narrow space between the complex anions keeping electrical neutrality.

## 1. Introduction

Molten alkali fluoroberyllates, especially LiF-BeF<sub>2</sub> mixture system, are useful materials as solvent for fissile (UF<sub>4</sub>) and fertile (ThF<sub>4</sub>) materials in Molten Salt Breeder Reactor (MSBR) and as blanket medium of D-T nuclear fusion reactors.<sup>1,2)</sup> It has also been reported that the corresponding-state principle was established on molten alkali fluoroberyllates and alkaline-earth silicates and their physical properties in molten state, such as ionic packing densities (molar volumes), viscosity coefficients and equivalent conductivities had a simple quantitative relation between these two systems.<sup>3)</sup>

Molten BeF<sub>2</sub> with the network-type structure<sup>4)</sup> of tetrahedral BeF<sub>4</sub> is highly viscous and the breakdown of the network-type structure with addition of alkali fluorides is indicated by the analysis of viscosity,<sup>5)</sup> electrical conductance,<sup>6)</sup> thermal expansivity<sup>7)</sup> and enthalpy of mixing.<sup>8)</sup>

Our interest centers on how the diffusion behaviour of constituent ions, in particular the fluorine and lithium ions, in the molten LiF-BeF<sub>2</sub> system changes with composition of melts, because the diffusion coefficients give important informations to solve the dynamical structure of molten state and the chemical reaction process.

In previous papers,<sup>9~11)</sup> we presented self-diffusion coefficients and their temperature dependence for lithium in molten Li<sub>2</sub>BeF<sub>4</sub>, and for fluorine in molten Li<sub>2</sub>BeF<sub>4</sub> and LiBeF<sub>3</sub>. Their results for fluorine

showed the unusually high diffusion coefficients and activation energies, while those for lithium in molten LiBeF<sub>4</sub> were usually as low as cations in typical molten alkali halides.

In this paper, the self-diffusion coefficients of lithium in molten LiBeF<sub>3</sub> were investigated to get the more precise interpretation of ionic transport properties in molten mixtures of beryllium fluoride with alkali fluorides.

## 2. Experimental Procedures

All experimental procedures were almost the same as described in the previous paper.<sup>11)</sup> LiBeF<sub>3</sub> labelled with <sup>6</sup>Li (<sup>6</sup>Li/<sup>7</sup>Li abundance ratio=19) was used as filling into a Ni capillary of which the length was about 30 or 40 mm and the inner diameter was about 1 mm. After the diffusion run for about 50 minutes, the capillary was cut at intervals of about two millimeters. The concentrations of <sup>6</sup>Li and <sup>7</sup>Li at the surface of their sections were measured by ion micro mass analyser (HITACHI IMA-SS). The operational condition of ion micro mass analyser was as follows:

primary ion beam	:	Ar
ion beam energy	:	5 KeV
beam diameter	:	500 $\mu$ m

In order to avoid the electrical charging due to the insulating property of LiBeF<sub>3</sub>, electrons from a tungsten filament were showered onto the specimen,

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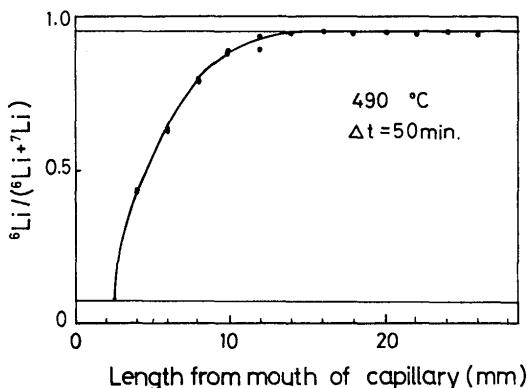
It was assumed that the ratio of  ${}^6\text{Li}^+/({}^6\text{Li}^+ + {}^7\text{Li}^+)$  gave the concentration profile of  ${}^6\text{Li}$  in a capillary because the values obtained of  ${}^6\text{Li}^+/({}^6\text{Li}^+ + {}^7\text{Li}^+)$  accorded with the natural abundance (0.074) and enriched abundance (0.95) at the mouth of the capillary and the nondiffused portion, respectively.

### 3. Results

The typical concentration profile of  ${}^6\text{Li}$  in a capillary is shown in **Fig. 1**. Diffusion coefficient  $D$  was calculated by the following equation,

$$C_x = C_0 \operatorname{erf} [x/(Dt)^{1/2}], \quad (1)$$

where  $C_0$  is the initial concentration of  ${}^6\text{Li}$  and  $C_x$  the concentration of  ${}^6\text{Li}$  at distance  $x$  from the boundary after diffusion time  $t$ .

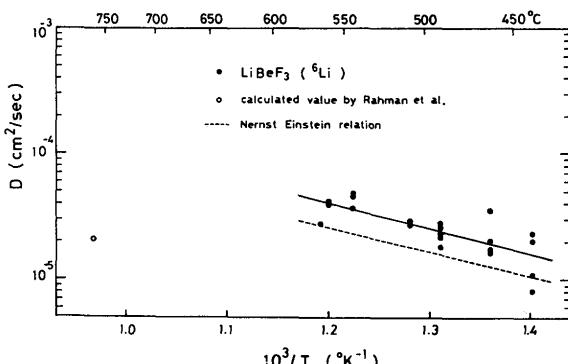


**Fig. 1** Distribution of  ${}^6\text{Li}$  in a capillary after a diffusion run  $\text{LiBeF}_3$ , temperature:  $490^\circ\text{C}$ , diffusion time: 50 min., capillary length: 30 mm

The results of the experiments (solid circle) in molten  $\text{LiBeF}_3$  are given in **Fig. 2**. The diffusion coefficients of lithium are written in the form

$$D = D_0 \exp [-E_D(\text{Li})/RT], \quad (2)$$

where  $E_D(\text{Li})$  is the activation energy of lithium diffusion,  $R$  the gas constant, and  $T$  the absolute



**Fig. 2** Diffusion coefficients of lithium (solid line) in  $\text{LiBeF}_3$  melt and a calculated value at  $1035^\circ\text{K}$  (open circle) by Rahman et al.<sup>12)</sup> Dashed line shows diffusion coefficient calculated from electrical conductivity.

temperature. The following result was obtained by least squares from all experimental data,

$$D = 1.12 \times 10^{-2} \exp (-9310 \pm 3000/RT) \quad (3)$$

The open circle in **Fig. 2** shows the diffusion coefficient of lithium in molten  $\text{LiBeF}_3$  calculated from molecular dynamics by Rahman et al.<sup>12)</sup>

The dashed line in **Fig. 2** shows the diffusion coefficient obtained from the electrical conductance of molten  $\text{LiBeF}_3$  using Nernst-Einstein relation,<sup>13)</sup>

$$D = \sigma KT/(Ze)^2 n, \quad (4)$$

where  $\sigma$  is electrical conductance,  $K$  Boltzmann constant,  $Z$  charge number of diffusion ion,  $e$  electron charge,  $n$  number of ions per unit volume,  $T$  absolute temperature. The values of  $\sigma$  was after Robbins et al.<sup>6)</sup>

### 4. Discussions

Molten  $\text{BeF}_2$  has network-type structure in which tetrahedral  $\text{BeF}_4$  units are bridged at corners.<sup>4)</sup> The addition of  $\text{LiF}$  to molten  $\text{BeF}_2$  indicates the breakdown of the network-type structure of  $\text{BeF}_2$ <sup>5)</sup> and it is expected to exist independent anions, such as  $\text{BeF}_4^{2-}$  and  $\text{Be}_2\text{F}_7^{3-}$  in molten  $\text{Li}_2\text{BeF}_4$  and  $\text{LiBeF}_3$ .<sup>4,14,15)</sup> Unusually high diffusion coefficients and activation energy of fluorine in molten  $\text{LiF-BeF}_2$  mixture seem to be attributed to the movement accompanying both the rotation of large fluoroberyllate complex anions and the exchange of fluorine between neighbouring anions,<sup>9,10)</sup> as shown in **Fig. 3**. On the other hand, the comparison of the self-diffusion coefficients of lithium in molten  $\text{Li}_2\text{BeF}_4$  and  $\text{LiBeF}_3$  with those of cations in molten alkali halides and molten silicates under the reduced temperature scale (Fig. 3 in ref. (11)) shows the self-diffusion coefficients and the activation energy of lithium in molten  $\text{Li}_2\text{BeF}_4$  have the similar behaviour to those of cations in molten alkali halides.

In molten  $\text{LiBeF}_3$ , the activation energy of lithium has nearly equal value to that in molten  $\text{Li}_2\text{BeF}_4$ . But the self-diffusion coefficients of lithium in molten  $\text{LiBeF}_3$  are about one third smaller than those in molten  $\text{Li}_2\text{BeF}_4$ . This will be due to smaller probability of exchange between the neighbouring lithium keeping electrical neutrality because of the small amount of lithium contained in molten  $\text{LiBeF}_3$  or the large jumping distance of lithium because of larger complex anions comparing with  $\text{Li}_2\text{BeF}_4$  system. If the activation process is regarded as the movement of lithium through a narrow space between the complex anions, it seems reasonable that the both activation

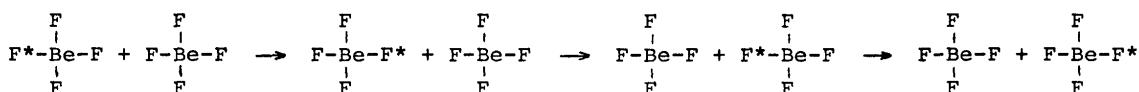


Fig. 3 Schematic diffusion process of fluorine in molten Li<sub>2</sub>BeF<sub>4</sub> and LiBeF<sub>3</sub>. Asterisk expresses a tracer ion of fluorine.

energies on Li<sub>2</sub>BeF<sub>4</sub> and LiBeF<sub>3</sub> show approximately equal value. These phenomena consist with the result of the electrical mobility of lithium in molten LiF-BeF<sub>2</sub>.<sup>16)</sup> Dotted line in Fig. 2 shows the diffusion coefficient of lithium calculated by equation (4) with the electrical conductance in molten LiBeF<sub>3</sub>. The observed diffusion coefficients of lithium are larger than those of calculated one in this molten salts, and the differences are much larger than those in typical molten alkali halides, such as NaCl<sup>17)</sup> and NaF.<sup>18)</sup>

It is noticed in Fig. 2 that the self-diffusion coefficient of lithium in molten LiBeF<sub>3</sub> calculated using molecular dynamic method by Rahman et al.<sup>12)</sup> does not agree with our self-diffusion coefficient extrapolated at 762°C. The observed self-diffusion coefficients of fluorine were not consistent with their calculated one, too. This will be due to that the molecular dynamics calculation of them is not so enough to reflect the exact diffusion mechanism of various elements in molten LiBeF<sub>3</sub> because the model used in the calculation is too small (32 molecules of LiBeF<sub>3</sub>) and the periodic boundary condition restricts too much the movement of constituent atoms and ions, especially the rotation of large complex anions such as BeF<sub>4</sub><sup>2-</sup> and Be<sub>2</sub>F<sub>7</sub><sup>3-</sup> which exist stably in the melt.

In previous papers,<sup>9,10)</sup> it was reported that the behaviour of oxygen in molten lime-silica-alumina slag<sup>19,20)</sup> is qualitatively similar to those of fluorine in molten Li<sub>2</sub>BeF<sub>4</sub><sup>9)</sup> and LiBeF<sub>3</sub>.<sup>10)</sup> In order to discuss more precisely the relation of self-diffusion behaviour of various constituent ions of molten fluoroberyllates and molten silicates, it will be necessary to obtain the self-diffusion coefficients of Be in LiF-BeF<sub>2</sub> mixture, Na, F and Be in NaF-BeF<sub>2</sub> mixture and Mg, Si and O in MgO-SiO<sub>2</sub> system.

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