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Self-Diffusion of Fluorine in Molten LiBeF_3 [†]

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Abstract

The self-diffusion coefficients of fluorine in molten LiBeF_3 have been measured with the capillary reservoir technique using ^{18}F as tracer prepared in Japan Research Reactor-3. The result showed significantly large self-diffusion coefficient in spite of the large activation energy. This phenomena can be proved from the movement of fluoroberyllate anions, the exchange of fluorine ion with the neighbouring anions, and ion-pair diffusion.

1. Introduction

It is interesting to investigate the physical properties of molten LiF-BeF_2 system because of following objects:

1. The application of molten LiF-BeF_2 as solvent for fessile and fertile components in molten salt thermal breeder reactors and to the blanket medium of D-T nuclear fusion reactors.

It must be noticed in Oak Ridge National Laboratory that LiF-BeF_2 system is one of the molten salts. Especially, LiBeF_3 and Li_2BeF_4 molten salts are considered to be most suitable for the use to both reactors.

2. The investigations of molten silicates whose melting point is very high and the experiment is very difficult, so it will be useful to clarify silicate structure with utilizing the similarity of the structure of molten LiF-BeF_2 system.

For example, phase diagram of LiF-BeF_2 system is very similar to that of MgO-SiO_2 system.¹⁾ Therefore, it was thought that some relations will be hold between the physical properties of both systems. The following result that the viscosity²⁾ and electric conductivity³⁾ depend extremely on the quantity of LiF added to BeF_2 likewise in the case of alkaline oxide to silicate is a good example to prove each similarity about physical property. The fact can be supposed from the crystal similarity that BeF_2 take such a network structure of the tetrahedral unit as SiO_2 in silicate¹⁾.

In this paper, the authors show the self-diffusion coefficients of fluorine in molten LiBeF_3 measured with

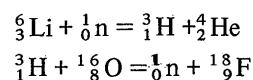
the capillary reservoir technique using ^{18}F as a tracer. The value gives directly important informations to solve the structure of molten salts. However, only a few self-diffusion measurements of fluorine in molten fluoride have been done by several investigators^{4~6)}. The difficulty of the measurement is caused by following reasons:

1. The difficulty of handling fluorine melts due to severe corrosion when used glass or ceramic as vessel.
2. The conveniently short half-life time of ^{18}F (109.7 min.).
3. The necessity of facilities such as nuclear reactor to produce radio isotope of ^{18}F .
4. The active radiation from tritium giving off at the time of ^{18}F production.

2. Experimental procedures

2-1 Preparation of Radioactive Tracer

Highly purified Li_2CO_3 powder (99.99%, 100mg) sealed in an evaluated quartz ampoule is irradiated in Japan Research Reactor-3 with a flux of $2 \times 10^{13} \text{ n/cm}^2/\text{s}$ for 20 to 60 minutes. The fluorine-18 is produced by the following reactions using thermal neutron:



After the irradiated Li_2CO_3 powder was treated with 48% hydrofluoric acid aqueous solution and dried, the labeled LiF was deposited. The caution should be payed to a great quantity production of tritium.

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2-2 Preparation of LiBeF_3

Commercial LiF (Morita Kagaku Kogyo Co.) and BeF_2 (Rare Metallic Co.) of analytical reagent grade were fully mixed, and was melted in a nickel container and treated with a HF-H_2 mixture at 700°C and then sparged with He .

2-3 Apparatus

Although intense activity of the experiment was wished, the diffusion from the capillary into salt bath was employed by considering the intensity of radio activity in the laboratory.

The capillary was made of Ni and had 1 mm inner diameter and 3 or 4 cm in length. Figure 1(a) shows the apparatus for filling the radioactive melt into a capillary. The cell which was placed in the furnace was composed of a fused silica tube and a stainless steel flange. A Ni tube (the bottom is closed) was connected to the center of the flange by an "O" ring seal which permitted the tube to move vertically. A thermocouple in the tube indicates the temperature of the radioactive LiBeF_3 which is melted in the platinum crucible placed on the bottom of the silica tube.

The diffusion cell is shown in Fig.1(b). Furnaces composed from four parts of nichrom resistance heat the non-active LiBeF_3 melt and capillary till they reach to desired temperature. A Ni tube connected to the flange was moved vertically and the temperature of the melt was measured by the same way as mentioned above.

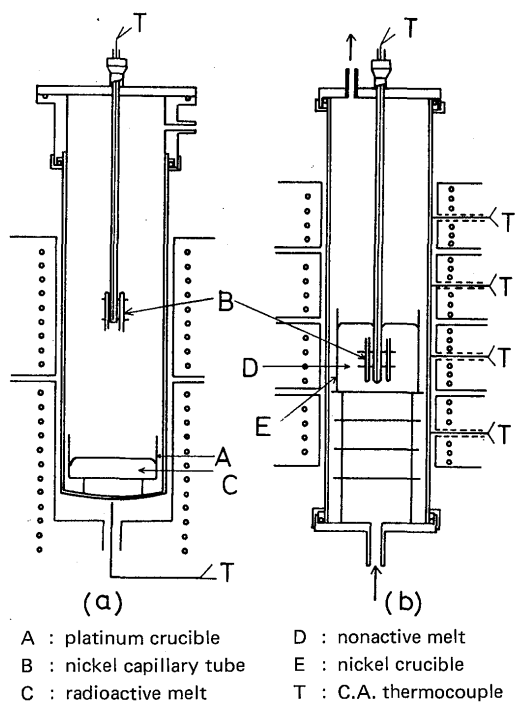


Fig. 1(a) Cell for filling a radioactive salt into capillaries.

Fig. 1(b) Cell for diffusion run.

2-4 Experimental Procedures

The LiF powder labeled with ^{18}F was mixed and melted together with non-radioactive LiBeF_3 in platinum vessel in the filling cell. Seven~ten capillaries whose mouths faced down were wound with Ni wire to be held at the lower end of the tube. The cell was evacuated and then the capillaries were held just above the melt. After they were heated enough, the capillaries were filled with active salt by dipping their mouths in the melt under vacuum and then feeding argon slowly into the cell. They were then raised out from the melt and were taken out from the cell after cooling.

The outside of each capillary was carefully polished with abrasive paper and washed with acetone. Then the radioactivity of ^{18}F in each capillary was measured by γ -ray spectrometer with NaI(Tl) detector. After performed the radioactivity counting, the capillaries were set in the diffusion cell. The cell was evacuated and then filled with argon.

This furnace consists of four nichrom resistances adjusted with each temperature controller. As the capillaries were slowly brought down, the temperature of them increased gradually. Notice was paid not to overheat the salt in the capillaries abruptly.

The capillaries were submerged in the reservoir melt to allow diffusion from 20 to 120 minutes due to the temperature of the melt. After the diffusion run, the capillaries were slowly lifted out of the melt and then removed from the cell. After cleaning the outside of the capillaries, their γ -ray activities were measured.

3. Results

The γ -ray spectrum of the labelled LiBeF_3 is shown in Fig.2. The intense peak at 0.51 MeV is due to ^{18}F . The weak peaks at 1.39 and 2.75 MeV are considered to be due to the impurity Na in the Li_2CO_3 . Figure 3 shows the relation between γ -ray intensity from ^{18}F and measurement time. It shows that the half-life time of ^{18}F is about 110 minutes.

Diffusion coefficients were calculated by comparing the total activity in the capillary before and after the diffusion run. The well-known solution of a suitable diffusion equation for the present work was used.

$$\frac{\pi}{8} \frac{C_{av}}{C_0} = \sum_n \frac{1}{(2n+1)^2} \exp(-(2n+1)^2 \pi^2 D t / 4L^2)$$

, where C_0 is the initial concentration of ^{18}F , C_{av} its residual concentration, D the self-diffusion coefficient, L the length of the capillary, and t the duration time. In \sum_n , the value up to 6 as n were used.

Figure 4 shows the diffusion coefficient of fluorine in LiBeF_3 (solid line) and compared with that in Li_2BeF_4

investigated by T. Ohmichi, H. Ohno and K. Furukawa.⁴⁾ The effect of volume change of the salt from the molten state to the solid state were excluded from diffusion coefficients obtained in this study.

The diffusion coefficient can be written with the following form

$$D = D_0 \exp\left(-\frac{E_d(F)}{RT}\right)$$

, where $E_d(F)$ is the activation energy of fluorine diffusion, R the gas constant, and T the absolute temperature. By using the least square method to arrange all experimental data, the following result for LiBeF_3 was obtained:

$$E_d(F) = 34.5 \pm 5.0 \text{ Kcal/mole}$$

$$\log D_0 = 4.5 \pm 1.0 \text{ cm}^2/\text{sec}$$

The authors should reconsider that the diffusion coefficient shows very large value in spite of showing the large activation energy.

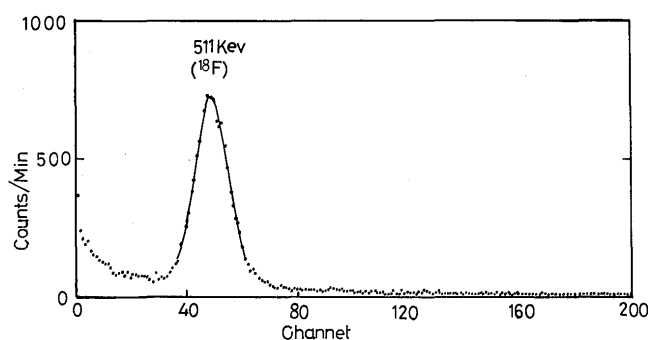


Fig. 2 γ -ray spectrum of LiBeF_3 labelled with ^{18}F .

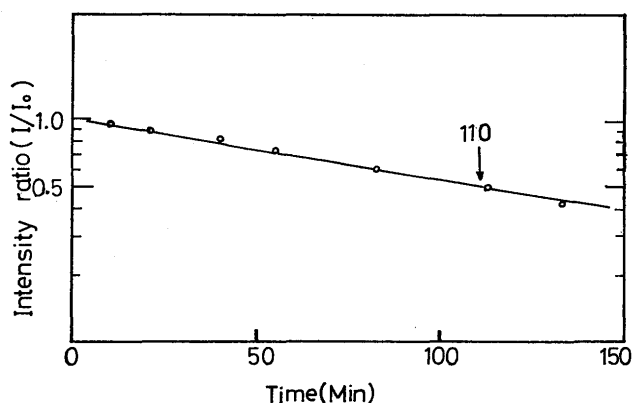


Fig. 3 γ -ray distribution curve of ^{18}F .

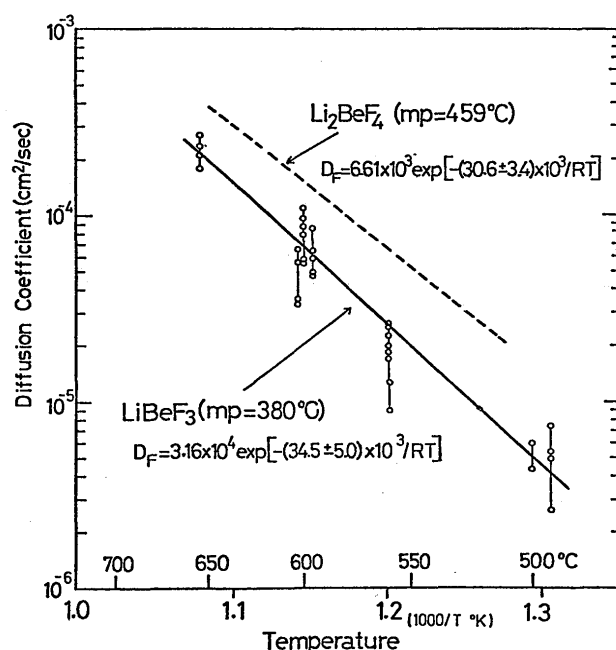


Fig. 4 Self-diffusion coefficients of fluorine in LiBeF_3 (solid line) and Li_2BeF_4 (dashed line).

4. Discussions

The typical melt such as ZnCl_2 having structure from three dimensional network has generally large activation energy of 14~18 Kcal/mole at the vicinity of the melting point. Exclusive of molten oxide systems, at about 100°C higher than the melting point the activation energy decreases and becomes as large as that of other molten salt systems.⁷⁾ It is considered to be due to breaking of the chloride bridges in a three-dimensional network of Zn-Cl bonds.

It is difficult to explain these results for fluorine diffusion behaviour with a simple model because of the unusual combination of relatively larger diffusion coefficient and higher activation energy. It is, however, interesting that the results for fluorine diffusion are quite similar to those for oxygen diffusion in a molten lime-silica-alumina slag.⁸⁾ The diffusion coefficient for oxygen is about ten times as large as those for metallic cations (calcium and aluminum) and the activation energy for diffusion (80 Kcal/mole)⁹⁾ and electrical conductivity (42 Kcal/mole).¹⁰⁾ In molten LiBeF_3 , the activation energy for fluorine diffusion (34.5 Kcal/mole) is also higher than those determined by viscosity (15 kcal/mole)²⁾ and electrical conductivity (8 Kcal/mole).³⁾ These facts might closely relate some extraordinary behaviours in fluorine diffusion and in oxide.

According to Cantor, Ward and Moynihan²⁾, molten LiF-BeF₂ might lose the three dimensional network of Be-F bonds when BeF₂ content is lower than 65 mole%. If it is so, the LiBeF₃ melt is considered to have no network structure. However, the existence of larger ions such as Be₂F₇³⁻ could not be always denied from the measurements of Raman scattering^{11,12)} and X-ray diffraction.¹³⁾

The fact that the magnitude of the diffusion coefficient obtained in this work is extraordinarily large cannot be explained solely by mass transfer due to migration of the large fluoroberyllate anions such as BeF₄⁴⁻ and Be₂F₇³⁻.

The large value of fluorine diffusion coefficient might be explained by following mechanism: 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. As the former involves some state difficulties to anion rotation and both mechanisms necessitate the breaking of Be-F bonds, these might show large activation energy.

In order to obtain the more precise value of self-diffusion coefficient and to do a reasonable clarification of the diffusion mechanism in a LiF-BeF₂ melt, we are in progress to measure the diffusion coefficient of fluorine and cations in this LiF-BeF₂ system.

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