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Covalent to ionic transition of $BiCl_3$ in LiCl-KCl eutectic melt

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Introduction

Structure and physical properties of polyvalent metal in molten alkali chloride solvent like LiCl-KCl eutectic are important information in the pyrochemical reprocessing of spent nuclear fuels[1]. It has been considered naturally that some important properties such as diffusion coefficient in the mixture are different from those in the pure melt.

We have obtained structural information on the structure of pure chloride melts like $LaCl_3$ and UCl_3 by X-ray diffraction[2] and XAFS[3] technique. In the present study, the structure of molten $BiCl_3$ and its mixtures in LiCl-KCl eutectic melt were investigated by using high-temperature XAFS technique.

Experimental

The Bi L_3-edge XAFS measurements of solid and molten $BiCl_3$ and molten $BiCl_3$ in LiCl-KCl eutectic were performed in transmission method at the BL27B station in the KEK-PF. The samples were sealed off in a quartz cell under reduced pressure. Details of the XAFS measurement of molten salts are described in ref.[4]. The XAFS data was analyzed by using WinXAS code[5].

Results and discussions

Fig.1 shows Fourier transform magnitude $|FT(k^3\chi(k)|$ of solid and molten $BiCl_3$, and molten 75% and 25%$BiCl_3$ in LiCl-KCl eutectic. Structural parameters from curve fitting analysis are listed in Table 1.

The parameters in solid state are close to the crystal structure data, in which Bi atom is surrounded by three Cl atoms with Bi-Cl distances; 2.468, 2.513 and 2.518Å. In molten state, the structural parameters did not change significantly from those in solid state. It suggests that molten $BiCl_3$ is a molecular liquid as reported by the neutron diffraction study[6]. The nearest Bi-Cl distance 2.48Å in molten $BiCl_3$ is almost the same as sum of covalent radii for Bi and Cl.

In molten 75%$BiCl_3$-LiCl-KCl eutectic, the parameters were still almost the same as those in solid and molten $BiCl_3$. On the other hand, the parameters drastically changed in molten 25%$BiCl_3$-LiCl-KCl eutectic. The 1st peak position is clearly shifted to longer distance (r=2.66Å) in the Fig.1. It is relatively close to sum of ionic radii for Bi and Cl. In addition, the coordination number increased from 3 to 4. It can bee seen that transition from covalent to ionic bonding occurred between 75% and 25%$BiCl_3$ concentration. This result concluded that polyvalent metal behavior is completely different between the pure melt and the mixture melts.

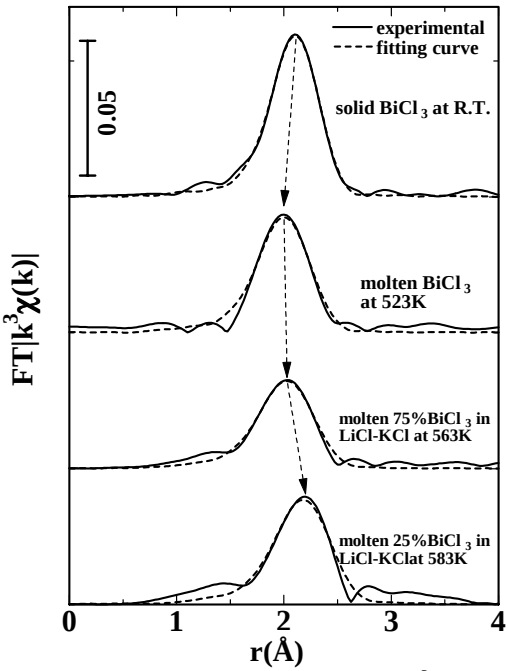

Fig.1 Fourier transform magnitude $|FT(k^3c(k)|$ of solid and molten $BiCl_3$, and molten 75% and 25%$BiCl_3$ in LiCl-KCl eutectic.

Table 1 Structural parameters of the nearest Bi-Cl

	N_{Cl}	$r_{Bi\text{-}Cl}$(Å)	$\sigma^2_{Bi\text{-}Cl}$(Å^2)
solid $BiCl_3$	3.0	2.54	0.0063
molten $BiCl_3$	3.3	2.48	0.0072
molten 75%$BiCl_3$	3.1	2.52	0.0100
molten 25%$BiCl_3$	4.1	2.66	0.0104

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