Local structure of molten polyvalent metal chlorides

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Introduction

We have studied local structure of molten salt systems by high temperature XAFS technique[1]. It has been reported that many polyvalent metal halides have stable coordination like (MXn)m- (M=metal and X= halogen) in molten state. We describe the XAFS results of some molten polyvalent chlorides.

Experimental

The XAFS measurements of molten YCl₃(Y K-edge) at 1173K and molten 12%ZrCl₄(Zr K-edge) in LiCl-KCl eutectic at 723K were performed at BL27B station in the KEK-PF. The samples were sealed off in the quartz cell under reduced pressure(<10⁻⁵Torr).

Results and discussions

(1) Molten YCl₃ systems

The |FT| functions for the molten YCl₃ and mixtures with LiCl-KCl are shown in Fig.1. It has been reported[2] that YCl₃ has a 6-fold (YCl₆)³⁻ coordinate in molten state. The 1st Y³⁺-Cl⁻ peak in the |FT| increases by adding LiCl-KCl. It can be simply assigned to decreasing in the Debye-Waller factor, not to increasing in the coordination number, because the peak position does not change by the mixing. The 2nd peak was found around 3.7 Å only in the pure YCl₃. This is due to edge-sharing link(Y³⁺-Cl⁻-Y³⁺) of the coordinates. On the other hand, no significant peak was found over the 1st peak in the mixtures. Thus, the link is broken by adding Cl⁻ donor(LiCl-KCl). It can be expected that the coordinate is stabilized and move freely in the mixture melt.

(2) Molten 12%ZrCl₄ in LiCl-KCl eutectic

The |FT| functions for the 12%ZrCl₄ system is shown in Fig.2, together with that of solid ZrCl₄. The 1st peak in the melt is larger than that of the solid ZrCl₄. It is assigned to three distinct 1st Zr⁴⁺-Cl⁻ distances(2.307, 2.498 and 2.655Å) in the solid ZrCl₄[3] and single distance 2.51Å in the melt. The latter is close to sum of ionic radii r(Zr⁴⁺(VI))=0.72 Å and r(Cl⁻)=1.81 Å. Coordination number from the fitting was also 5.9±0.6. It suggests that the melt has a 6-fold (ZrCl₆)²⁻ coordinate.

References

[1] Y.Okamoto et al., To be submitted.

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