XAFS study of molten zinc dibromide

Yoshihiro Okamoto [a,*], Kazuko Fukushima [b], Yasuhiko Iwadate [c]

[a] *Japan Atomic Energy Research Institute, Shirakata-Shira, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan*
[b] *Department of Materials Technology, Chiba University, Yayoi-cho, Inage-ku, Chiba-shi, Chiba 263-8522, Japan*
[c] *Graduate School of Science and Technology, Chiba University, Yayoi-cho, Inage-ku, Chiba-shi, Chiba 263-8522, Japan*

Abstract

The local structure of molten $ZnBr_2$ was investigated by X-ray absorption fine structure measurements for both Zn and Br above their K-absorption edges at 723 K. The results show that a tetrahedral coordination $(ZnBr_4)^{2-}$ exists and most coordinates connect with the next ones through the Br^- ion. The two XAFS functions $k^3\chi(k)$ in the molten $ZnBr_2$ were reproduced by a combination of a molecular dynamics simulation and an ab initio mutiple scattering calculation of X-ray absorption spectrum.
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1. Introduction

We have studied the structure of molten halides by using the high-temperature XAFS technique [1]. Selectivity of the element and a high sensitivity to the nearest correlation in the XAFS are excellent characteristics that are not easily obtained by other experimental techniques. We observed a change of the nearest Y^{3+}–Cl^- correlation by XAFS of the Y K-edge in molten YCl_3-alkali chloride [2,3]. It was concluded that the structural stability of the octahedral coordination $(YCl_6)^{3-}$ increased by adding alkali chloride to the YCl_3. A similar result was obtained also for YBr_3–LiBr [3]. In the YBr_3 measurement, we obtained the Br

K-edge XAFS data in addition to the Y K-edge. It is very useful for understanding the local structure to get all the XAFS data of the constituent elements in the compound. In the present study, we obtained both Zn and Br XAFS data to investigate the local structure of molten $ZnBr_2$.

2. Experimental and MD simulation

Anhydrous $ZnBr_2$ samples were prepared by drying at 523 K for 24 h under reduced pressure to avoid moisture. The quartz cell [1,2] used consists of an upper receptacle, a melt path with 0.1 mm thickness (XAFS measurement part) and a bottom receptacle. The appearance of the cell is similar to an hourglass. The sample was at first set in the upper receptacle and sealed off under high vacuum. After melting, the melt penetrates the path. This can be checked by a change (decreasing) of

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* Corresponding author. Tel.: +81-29 282 5858; fax: +81-29 282 5922.
E-mail address: okamoto@molten.tokai.jaeri.go.jp (Y. Okamoto).

the transmitted X-ray intensity. The XAFS measurement was performed at the BL27B beamline in the Photon Factory of KEK, Tsukuba, Japan. Fixed time scans (1–3 s) were repeated in the energetic range of 9.15–10.75 keV for the Zn XAFS and 13.0–14.6 keV for the Br XAFS at 723 K (m.p. 667 K). The WinXAS ver.2.1 developed by Ressler [4] was used in the XAFS data analysis. The phase shift and the backscattering amplitude were evaluated by the ab initio multiple scattering calculation code FEFF7 [5] using the crystal structure of $ZnBr_2$.

In addition to the curve fitting analysis, we tried to reproduce the two XAFS functions of molten $ZnBr_2$ by a molecular dynamics (MD) simulation. The following Born–Mayer–Huggins type pair potential was used in the MD simulation

$$\phi_{ij}(r) = \frac{z_i z_j}{r} e^2 + A_{ij} b \exp\left[\frac{\sigma_i + \sigma_j - r}{\rho}\right], \qquad (1)$$

where z_i and σ_i are the electric charge number and the size parameter of ion i, respectively. A_{ij} is the Pauling factor defined from the number of electrons in the outer shell. The b is the constant 0.336×10^{-19} J and ρ is the softness parameter. The potential parameters were adjusted to reproduce the experimental XAFS functions. A basic cell containing 768 ions (256 Zn^{2+} ions and 512 Br^- ions) was used in the simulation. The temperature was controlled at 723 K by scaling the velocity in the NVT ensemble.

3. Results and discussion

3.1. XAFS of molten $ZnBr_2$

The Zn K-edge and the Br K-edge XAFS functions $k^3\chi(k)$ and the Fourier transform magnitudes of molten $ZnBr_2$ are shown in Fig. 1(a) and (b), respectively. The first shell $k^3\chi(k)$ functions were obtained by Fourier filtering in the range of $R = 1.4 - 2.7$ Å for the Zn|FT| and $R = 1.3 - 2.8$ Å for the Br |FT|. The filtered functions are shown in Fig. 2, together with the curve fitting results (open circle). The structural parameters obtained from the curve fitting are
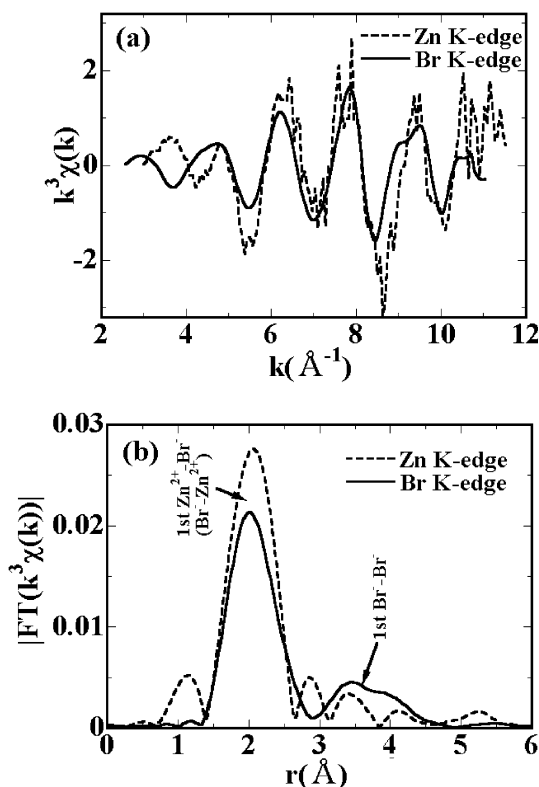

Fig. 1. (a) XAFS functions $k^3\chi(k)$ and (b) Fourier transform magnitudes |FT| of solid and molten $ZnBr_2$.

listed in Table 1, together with those obtained from the neutron diffraction (ND) data [6] and an XAFS analysis of the glass $ZnBr_2$ [7]. The nearest $Zn^{2+}–Br^-$ and $Br^-–Zn^{2+}$ distances were determined to be 2.46 and 2.45 Å, respectively. These are close to the values from the ND and the XAFS of the glass state. The coordination number of Br^- ions around Zr^{2+} is 3.9 ± 0.5. In the Br XAFS, the second peak was observed near 3.5–3.6 Å. It is assigned to the first $Br^-–Br^-$ correlation. The distance was estimated to be 3.9 Å from the phase shift value (0.3–0.4 Å), though a curve fitting was not performed. The ratio of the two distances $r(Br^-–Br^-)/r(Zn^{2+}-Br^-)$ was about 1.6. They show that a tetragonal coordinate $(ZnBr_4)^{2-}$ exists in the melts as well as in the molten $ZnCl_2$. The coordination number of Zn^{2+} ion around Br^- is 1.9 ± 0.5. This suggests that most Br^- ions are shared among two tetrahedra. This is taken as a
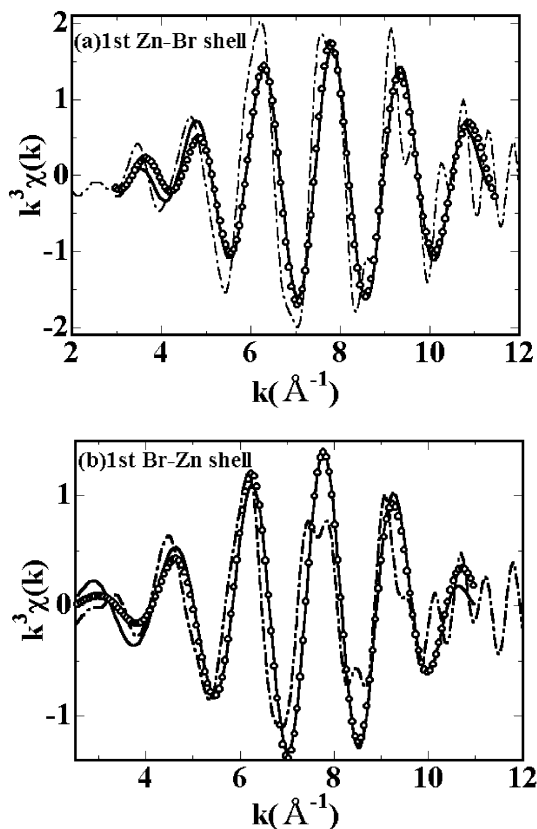
Fig. 2. The first shell $k^3\chi(k)$ functions (solid line: Fourier filtered functions, open circle: curve fitting results, a dot-dash line: MD+FEFF7 computation results).

proof of a network structure in the melt. Allen et al. [6] reported a prepeak in the ND patterns of molten $ZnBr_2$ and $ZnCl_2$, suggesting a medium-ranged structural order. The structure of molten $ZnBr_2$ resembles that of molten $ZnCl_2$.

3.2. XAFS simulation by using MD output and FEFF7

In the previous section, a curve fitting procedure was used to obtain the structural parameters. Recently, Filipponi [8] indicated that this is not appropriate for the XAFS analysis of liquids. We considered that the curve fitting should not be applied to obtain the nearest Zn^{2+}–Zn^{2+} and the Br^-–Br^- correlations. The partial correlation functions $G_{ij}(r)$ from the MD simulation of molten $ZnBr_2$ are shown in Fig. 3. As for the Zn^{2+}–Br^- (B^-–Zn^{2+}) correlation, the first correlation can be regarded as an independent peak. On the other hand, the first peaks of the Zn^{2+}–Zn^{2+} and the Br^-–Br^- correlations are not isolated. A boundary between the first and the second coordination shells is not clear in the two partial $G_{ij}(r)$s.

We proposed an XAFS simulation procedure of the FEFF computations in which the MD output is directly used as the input data. Atomic arrangement data is usually obtained as the output
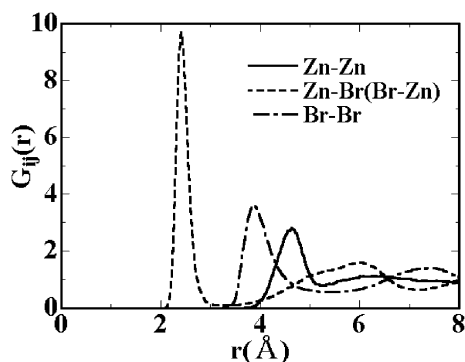
Table 1
Structural parameters: interionic distance, r_{ij}, coordination number, N_{ij}, and Debye–Waller factor, σ_{ij}^2, in molten $ZnBr_2$ obtained by curve fitting and MD simulation

	r_{ij} (Å)	N_{ij}	σ_{ij}^2 (Å^2)	Residual[a]
$Zn^{2+} - Br^-$				
XAFS+Curve fitting	2.46 ± 0.03	3.9 ± 0.5	0.0097 ± 0.0006	14.15
MD	2.44	4.1		
Allen et al. [6][b]				
	2.42 ± 0.01	3.9 ± 0.1		
$Br^- - Zn^{2+}$				
XAFS + Curve fitting	2.45 ± 0.01	1.9 ± 0.4	0.0113 ± 0.0009	29.52
MD	2.44	2.1		
Kadono et al. [7][c]	2.425	2.0	0.069	
$Br^- - Br^-$				
MD	3.98			
Allen et al. [6][b]	4.08 ± 0.03			

[a] Residual is defined as $\sum_{i=1}^{N} \left| k^3\chi_{exp}(k) - k^3\chi_{cal}(k) \right| / \sum_{i=1}^{N} \left| k^3\chi_{exp}(k) \right|$.
[b] ND data at 693 K.
[c] Br K-edge XAFS data of glass $ZnBr_2$.

Fig. 3. Partial correlation functions, $G_{ij}(r)$, in the molten ZnBr$_2$ obtained by the MD simulation.

information in the MD simulation, and is one of the basic input data in the FEFF computation. The XAFS function without fluctuation elements (Debye–Waller factors) can be calculated with the FEFF computation using the single arrangement data. The XAFS function is obtained by averaging the FEFF computations. We confirmed that an average of the FEFF computations for more than 1000 computations gave a converged value for the XAFS function. The 2500 FEFF computations obtained from 1000 MD steps data were used to obtain the Zn and the Br XAFS functions. The pair potential parameters optimized by the XAFS simulation are shown in Table 2. The calculated XAFS functions are shown as a dot-dash line in Fig. 2. In this MD simulation, we confirmed that the main complex species are tetrahedral $(ZrBr_4)^{2-}$ coordinates and that most of them are connected

with the next tetrahedra as suggested in the previous section. The structural parameters from the MD simulation are listed in the Table 1. These are in good agreement with the ND results.

4. Conclusion

XAFS measurements of both the Zn and the Br K edges were performed to examine the local structure of molten ZnBr$_2$. It is concluded that $(ZnBr_4)^{2-}$ tetrahedra exist in the molten state and these are connected through the Br$^-$ ions. The local structure is close to that of molten ZnCl$_2$. The XAFS functions were reproduced by a combination of the MD simulation and the FEFF7 computations. We proposed pair potential parameters from the MD simulation that give a good agreement with the experimental XAFS data.

Table 2
Parameters in the pair potential

	Zn^{2+}	Br$^-$
z_i	+2.0	−1.0
σ_i (Å)	0.90	1.95
ρ (Å)	0.34	
A_{Zn-Zn}	1.400	
A_{Zn-Br}	1.075	
A_{Br-Br}	0.750	

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