J. Synchrotron Rad. (1999). **6**, 486–488

EXAFS studies of $KBr_{1-x}(NO2)_x$ mixed crystals

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EXAFS studies of $KBr_{1-x}(NO_2)_x$ mixed crystals ($x<0.4$) were performed to elucidate the local structure of their dipole glass. The local structure, especially the nearest bromine-potassium pair-distribution, is not affected by replacing bromine ions with nitrite ones even below the glass transition temperature. The mean-square displacement of the bromine-potassium pair-distribution obeys the Debye approximation, while that of average structure derived from previous X-ray diffraction studies deviates largely from the approximation. The results indicate that a cluster with only short-range ferroelectric correlation is induced by the short-range order of nitrite ions within the distorted or fluctuated lattice caused by their reorientational freezing.

Keywords: EXAFS; $KBr_{1-x}(NO_2)_x$; dipole glass.

1. Introduction

$KBr_{1-x}(NO_2)_x$ mixed crystals form a dipole glass associated with random reorientational freezing of nitrite ions below the glass transition temperature T_g. Successive phase transitions of KNO_2 are suppressed by replacing nitrite ions with bromine ones and the glassy state appears below the critical concentration x_c~0.5. In this region, the mixed crystals have NaCl-type structure and exhibit no anomalous behavior in lattice constants above and below T_g. Recent dielectric measurements of this compound showed the low-frequency dielectric dispersion around T_g as seen in other dipole glasses (Iwata *et al.*, 1998). Our previous X-ray diffraction measurements revealed the growth of diffuse scattering around the Brillouin-zone center of fcc lattice and the deviation of mean-square displacement of both potassium and bromine ions from the Debye approximation below T_g (Yagi *et al.*, 1997, 1998). These results indicate that the local distortion is induced by the reorientational freezing of nitrite ions. In this paper, we report results of EXAFS analysis to clarify the local structure of this compound.

2. Experimental

Powder crystals were prepared by grinding single crystals grown from the aqueous solution. The nitrite ion concentration was estimated by the mass ratio of crystals to silver bromide extracted from the sliver nitrate solution. The thickness of samples were adjusted by checking the magnitude of absorption edge ($\Delta\mu d$~1). EXAFS measurements were performed on conventional tube-type X-ray generator and two-axes diffractometer using an auto-focus bent monochromator (MosTec, Russia). The monochromator mounted at the center of diffractometer is made of a plate-like $SiO_2(24\bar{6}0)$ single crystal having its curvature automatically adjusted at each scattering angle. Thus, the divergent beam can be focused and monochromatized even on a conventional two-axes diffractometer. EXAFS spectra of Br-*K* edge (13.472 keV) were measured from room temperature down to 15 K using a closed-cycle He-gas refrigerator. The experimental energy resolution was less than 10 eV around the Br-*K* edge.

The EXAFS analysis was performed using packages of UWXAFS3 and FEFF7 (Zabinsky *et al.*, 1995). AUTOBK, ATOMS, FEFFIT and FEFF7 programs contained in these packages were used for separate portions of the analysis. The *k*-weighted EXAFS spectra were fit in the range of 3~12 Å^{-1} for *k*-space and 1.75~3.75 Å for *r*-space and Hanning window were used for Fourier transforms. Efforts were made to simplify the analysis because these mixed crystals locally exhibit site-dependent structure complicating local structure and resulting a large number of single and multiple scattering paths from central atom to its neighbors. We used the following simplifications. (1) All multiple scattering paths were neglected, (2) site occupancy was treated by only weighting a scaling factor of each path while correlations between mixed sites were neglected, and (3) parameters such as scaling factors were fixed to avoid the large correlations with other parameters. Fortunately, since our attention was focused on the behavior of nearest bromine-potassium pair-distribution, effects of mixed crystals do not directly influence them.

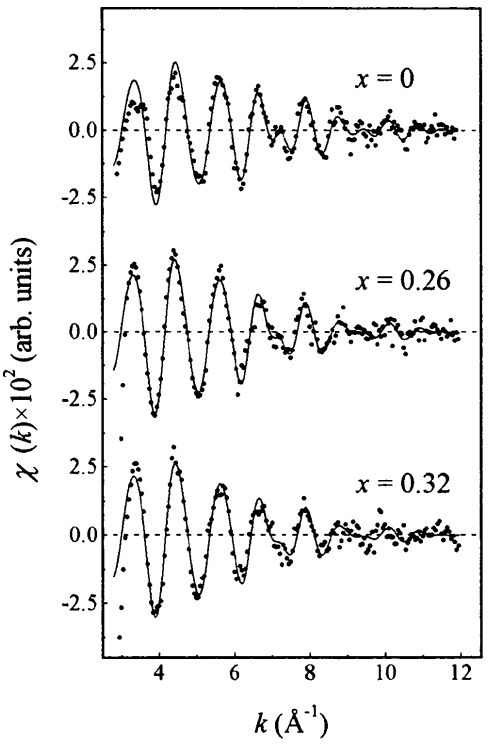

Figure 1
Br-*K* edge EXAFS spectra of $KBr_{1-x}(NO_2)_x$ mixed crystals for various concentration. Closed circles represent observed spectra and solid curves is calculated using programs of FEFF7 and FEFFIT.

3. Results and discussion

Br-*K* edge EXAFS spectra of $KBr_{1-x}(NO_2)_x$ powders, having x=0, 0.26 and 0.32, at 15 K, and their Fourier transforms are shown in Figs. 1 and 2, respectively. The observed spectra (closed circles) match closely with spectra calculated using programs of FEFF7 and FEFFIT (solid curves). The obtained EXAFS parameters are listed in Table 1. The bromine-potassium and bromine-bromine/nitrite pair-distribution appears around 2.9 Å and 4.3 Å, respectively. Atomic positions of nitrite ions were derived from X-ray diffraction measurements (Yagi *et al*, 1998) and were fixed during the analysis, because nitrite ions are dynamically or statically disordered among several equivalent positions and the scattering amplitude for them is much smaller than that of bromine ions. While the bromine-bromine/nitrite pair-distribution is reduced by replacing bromine ions with nitrite ones, the bromine-potassium pair-distribution exhibits no structural changes for all concentrations even below T_g (~120 K for x=0.26, ~140 K for x=0.32). This result conflicts with the large increase of mean-square displacement of bromine and potassium ions revealed from X-ray diffraction measurements.

The temperature dependence of EXAFS spectra was also measured to determine the relationship between local and average structures. Unfortunately, we failed to obtain accurate values of the Br-K ionic distance, especially at high temperatures, because of large errors caused by the correlation with other parameters despite taking into account the third cumulant. The temperature dependence of XAFS mean-square displacement of the bromine-potassium pair-distribution is shown in Fig. 3(a), where it is compared with that derived from X-ray diffraction measurements (closed squares). The X-ray diffraction mean-square displacement of a single crystal having x=0.36 was determined by the general X-ray structure analysis (Yagi *et al.*, 1998). The XAFS mean-square displacement for all concentrations shows the same behavior with increasing temperature and is reproduced by the Debye approximation (solid curve) with the Debye temperature θ_D=210 K, while the X-ray diffraction mean-square displacement deviates largely from the approximation below T_g that the reorientation of nitrite ions freezes. The relationship between XAFS and X-ray diffraction mean-square displacement is

Table 1
EXAFS parameters obtained using FEFF7 and FEFFIT.

Fixed parameters				
Real part of energy shift, E_0 (eV)	0.0			
Imaginary part of energy shift, E_i	7.0 (eV)			
Scaling factor, S_0^2	2.5 (x=0), 3.0 (x=0.26, 0.32)			
Variable parameters, ionic distance r and mean-square displacement σ^2 of bromine-potassium pair-distribution, and discrepancy factor R				
x	T(K)	r(Å)	σ^2(Å^2)	R(%)
0	15	3.293	.0114	0.7
	100	3.308	.0142	6.0
	200	3.316	.0186	14.2
0.26	15	3.293	.0114	0.7
	100	3.279	.0148	0.6
	200	3.322	.0213	7.9
0.32	15	3.281	.0119	3.0
	100	3.282	.0157	5.2
	200	3.242	.0243	10.8

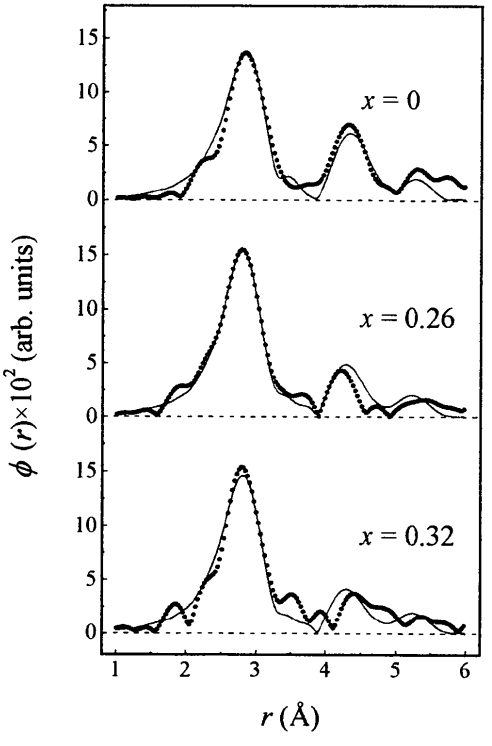

Figure 2
Fourier transforms of the spectra shown in Fig.1. The bromine-potassium and bromine-bromine/nitrite pair-distribution appears around 2.9 Å and 4.3 Å, respectively.

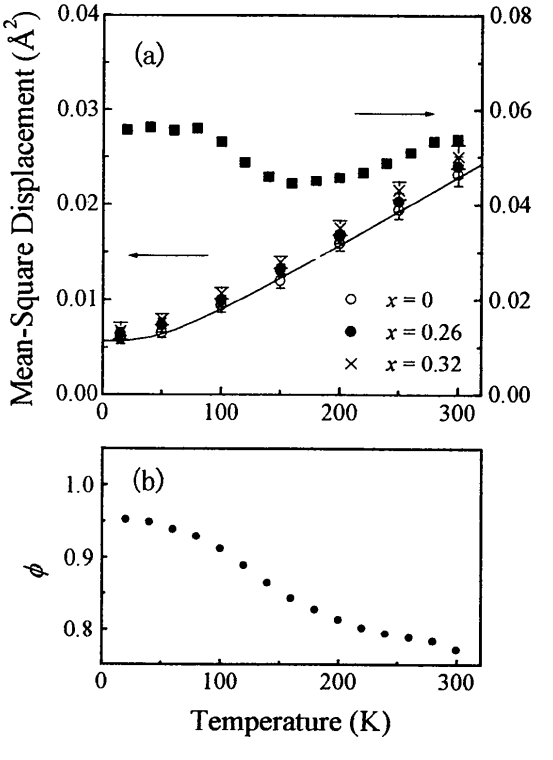

Figure 3
(a) Temperature dependence of the XAFS mean-square displacement of bromine-potassium pair-distribution in comparison with the X-ray diffraction mean-square displacement of potassium ions (closed square). The solid curve is fit to the Debye approximation (θ_D=210 K). (b) Temperature dependence of the correlation parameter ϕ obtained using eq. (1).

given by the following equation (Booth *et al.* 1995),

$$\sigma_{KBr}^2 = \sigma_K^2 + \sigma_{Br}^2 - 2\sigma_K^2\sigma_{Br}^2, \quad (1)$$

where σ_{KBr}^2 is the XAFS correlated mean-square displacement of potassium-bromine pair-distribution, σ_K^2 and σ_{Br}^2 are the X-ray diffraction uncorrelated mean-square displacement of potassium and bromine ions, respectively. The correlation parameter ϕ obtained by this relation is shown in Fig. 3(b) as a function of temperature. The value of ϕ gradually increases below about 200 K and approaches to 1, indicating the highly correlated fluctuation or distortion such as a long wavelength acoustic phonon. We infer from our results that the distorted or fluctuated lattice caused by the reorientational freezing of nitrite ions exhibits an apparent increase of the X-ray diffraction mean-square displacement. However, the local structure is still as rigid as that of pure potassium bromide even below T_g because of the highly correlated fluctuation or distortion that seems to be caused by the ferroelectric short-range order of nitrite ions revealed from X-ray diffraction measurements.

In summary, we measured Br-*K* edge EXAFS spectra of $KBr_{1-x}(NO_2)_x$ powders to elucidate the local structure of their dipole glass. The bromine-potassium pair-distribution is not affected by replacing bromine ions with nitrite ones and the mean-square displacement obeys the Debye approximation even below T_g. The conflict with the result of X-ray diffraction measurements suggests that a cluster with only short-range ferroelectric correlation is induced by the short-range order of nitrite ions within the distorted or fluctuated lattice caused by the reorientational freezing of nitrite ions. Finally, these EXAFS measurements in our laboratory were performed using a new technical device, 'auto-focus bent monochromator'. Higher-quality EXAFS measurements should help resolve some of the outstanding questions in regard to this work.

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(*Received 10 August 1998; accepted 18 January 1999*)