EXAFS study of phase transitions in KIO_3

Kenichiro Yagi,[a]* Shunsuke Umezawa,[a] Hikaru Terauchi[a] and Hirofumi Kasatani[b]

[a]Advanced Research Center of Science and School of Science, Kwansei-Gakuin University, Sanda, Hyogo 669-1337 Japan, and [b]Department of Materials Science, Shizuoka Institute of Science and Technology, Fukuroi, Shizuoka 437-8555 Japan

The iodine K-edge EXAFS study of KIO_3 was performed to clarify local structural changes on the successive phase transitions. The pair-distribution function of three oxygen atoms in an oxygen octahedron is almost independent on temperature like a covalent bond, whereas that of the other three is gradually reduced with increasing temperature like an ionic bond. The result indicates that iodine and oxygen atoms exist as an IO_3^- molecule in a pseudo-perovskite-type structure. The anomalous behavior in the Debye-Waller factor for the latter pair-distribution function appears around 50 K, which is associated with the orientational glass transition.

Keywords: EXAFS; phase transition; KIO_3.

1. Introduction

Potassium iodate, KIO_3, is a ferroelectric material exhibiting non-linear optics. This compound undergoes five successive phase transitions at $T_{I,II} = 485$ K, $T_{II,III} = 345.5$ K, $T_{III,IV} \approx 258$ K, $T_{IV,V} \approx 113$ K and $T_{V,VI} \approx 33$ K (Herlach, 1961). The phase transitions at $T_{I,II}$ and $T_{II,III}$ are known as ferroelectric phase transitions accompanied with elastic anomaly. KIO_3 has a pseudo-perovskite-type structure, in which oxygen octahedra are largely distorted, and belongs to space groups of $R3c$ (rhombohedral phase I), Cm (monoclinic phase II) and $P1$ (triclinic phase III) (Hamid, 1973). The phase transitions have been well studied by means of dielectric and optical measurements, but the structural model has been still discussed because of a contradiction in the abundant experimental results (Crain, 1972). On the other hand, the phase transitions at $T_{III,IV}$, $T_{IV,V}$ and $T_{V,VI}$ are considered as orientational glass transitions. The anomalous behavior associated with the glass transition was observed in various physical properties, whereas there are few reports on structural properties for these transitions. In order to understand the mechanism of the phase transitions, we need to clarify structural changes on them. Recently, Maeda *et al.* (2000) have intensively studied the dielectric, elastic and piezoelectric properties of KIO_3, and reported the nature of orientational glass transitions at $T_{IV,V}$ and $T_{V,VI}$. We also have investigated the phase transitions using X-ray diffraction and EXAFS measurements to obtain additional structural information. In this paper, we report the results of iodine K-edge EXAFS measurements of KIO_3 in the temperature range from 10 K to 573 K, and discuss the phase transitions in KIO_3 from a structural point of view, in comparison with the result of X-ray diffraction measurements.

2. Experimental

The iodine K-edge EXAFS spectra ($E_0 = 33.169$ keV) of KIO_3 were measured at the beam line BL14A of Photon Factory (KEK, Japan) in the temperature range from 10 K to 573 K. The synchrotron radiation (2.5 GeV, 300 mA) was monochromatized by Si(553) double-crystals and detected using ionization chambers filled with Ar (I_0) and Kr (I) gases. Powder specimens of KIO_3 mixed with boron nitride were formed into a tablet. Closed-cycle He-gas refrigerator and electric heater were employed for the low- and high-temperature measurements, respectively. EXAFS spectra were measured in a heating process (2 K/min.) with equilibration time of 10 min. at given temperatures.

The programs of *FEFF7* and *UWXAFS3* were employed for the EXAFS analysis (Zabbinsky *et al.*, 1995, Stern *et al.*, 1995). The EXAFS spectra, $\chi(k)$, were extracted from absorption spectra using *AUTOBK* included in *UWXAFS3*. The radial structural function, $\phi(r)$, was obtained from the Fourier transform of k^3-weighted EXAFS spectra in the k-space from 3 $Å^{-1}$ to 14 $Å^{-1}$. The EXAFS parameters were estimated using *FEFFIT* included in *UWXAFS3* so that the observed spectra were fit to the calculated spectra in the r-space from 0 Å to 5 Å. The origin of photon energy was fixed at the value indicating maximum in the derivative of absorption spectra.

3. Results and discussion

Figures 1 and 2 show the k^3-weighted iodine K-edge EXAFS spectra of KIO_3 and the Fourier transforms of them at 10 K, 100 K and 200 K. The observed spectra (closed circles) are well reproduced by the calculated ones (solid curves) using the perovskite-

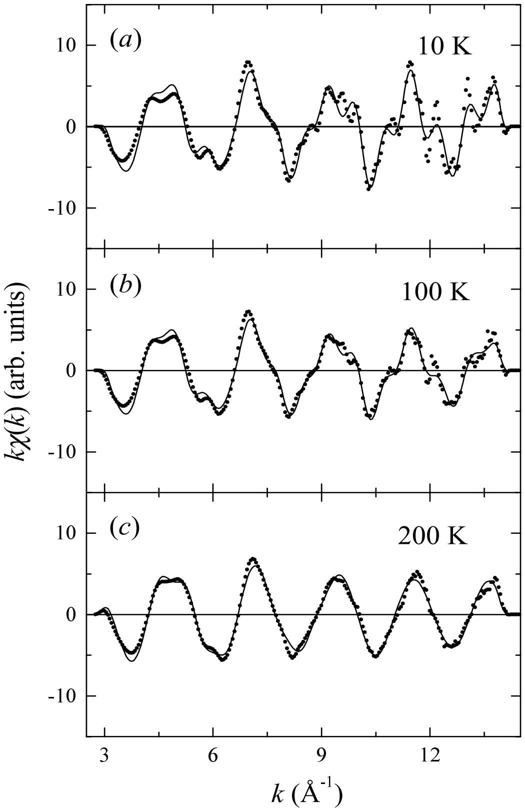

Figure 1
The k^3-weighted EXAFS spectra of KIO_3 at 10 K, 100 K and 200 K. The observed spectra (closed circles) were fit to the calculated ones (solid curves) using *FEFF7* and *UWXAFS3* programs.

type structure modified as follows. There are two kinds of bond length of about 1.8 Å and 2.7 Å between iodine and oxygen atoms, and the summation of the two length approximately corresponds to the lattice constant of a primitive rhombohedral unit cell. Three oxygen atoms in an oxygen octahedron are bonded to an iodine atom with the shorter distance. The fact implies that iodine and oxygen atoms exist as an IO_3^- molecule in the crystal, because the shorter distance corresponds to that in an IO_3^- molecule. Therefore, the other three oxygen atoms bonded with the longer distance should be contributed from the three neighboring IO_3^- molecules at a distance of the lattice constant. In addition, the third cumulant is employed for calculating the pair-distribution function (PDF) of iodine-potassium (I-K) around 3.3 Å and iodine-iodine (I-I) around 4.2 Å, instead of increasing the number of coordination shells. Actually, these PDFs consist of several coordination shells except for a cubic lattice, but it is difficult to separate them because of the slight distortion from the cubic lattice. Structural parameters for each coordination shell are listed in Table 1.

Table 1

EXAFS parameters, coordination number N, distance r, Debye-Waller factor σ^2 and third cumulant $\sigma(3)$, estimated using *FEFF7* and *UWXAFS3* programs.

Shells	N	Parameters	10 K	100 K	200 K
I-O(1)	3	r / Å	1.816(2)	1.815(2)	1.815(2)
		σ^2 / Å^2	0.001(1)	0.001(1)	0.001(1)
I-O(2)	3	r / Å	2.72(1)	2.74(2)	2.75(2)
		σ^2 / Å^2	0.006(2)	0.009(2)	0.010(3)
I-K	8	r / Å	3.98(4)	3.98(4)	3.94(6)
		σ^2 / Å^2	0.013(2)	0.016(2)	0.020(2)
		$\sigma(3)$ / Å^3	0.030(1)	0.027(1)	0.020(2)
I-I	6	r / Å	4.81(2)	4.83(2)	4.86(6)
		σ^2 / Å^2	0.005(1)	0.007(1)	0.011(2)
		$\sigma(3)$ / Å^3	0.002(1)	0.002(1)	0.003(1)
R factor			0.032	0.021	0.016

Figure 3 shows the absolute part of the Fourier transforms of the k^3-weighted iodine K-edge EXAFS spectra of KIO_3 at various temperatures. The PDF of iodine-oxygen with the shorter bond (I-O(1)) is almost independent on the temperature, while that of iodine-oxygen with longer bond (I-O(2)), as well as I-K and I-I, is strongly reduced with increasing temperature. Figure 4 shows the temperature dependence of the Debye-Waller (DW) factor estimated from each PDF. The DW factor for the PDF of I-O(1) is almost fixed at about 0.001 Å^2, indicating the strong bond like a covalent bond in an IO_3^- molecule. On the other hand, the DW factor for the other PDFs monotonically increase due to the thermal vibration as expected from the Debye approximation. The result implies that iodine and oxygen atoms exist as an IO_3^- molecule even at high temperatures, and that the spatial correlation between IO_3^- molecules becomes weak with increasing temperature. This is also supported by the fact that the distance

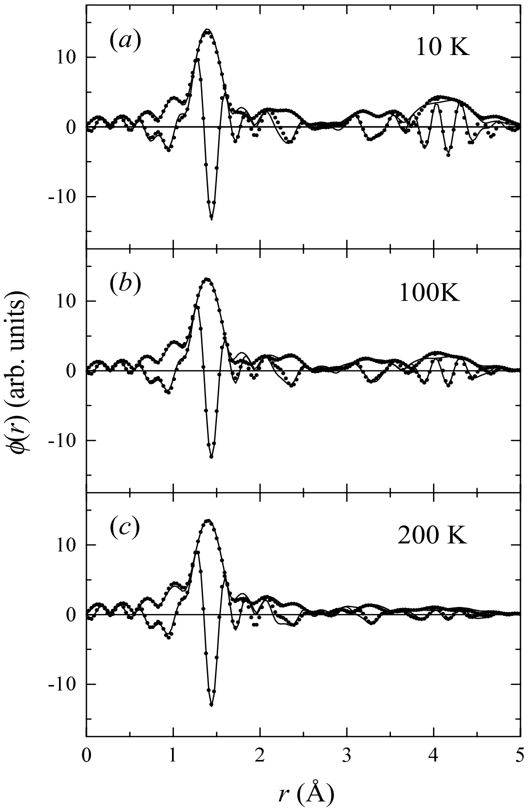

Figure 2

The Fourier transforms of k^3-weighted EXAFS spectra of KIO_3 at 10 K, 100 K and 200 K. The observed spectra (closed circles) were fit to the calculated ones (solid curves) using *FEFF7* and *UWXAFS3* programs.

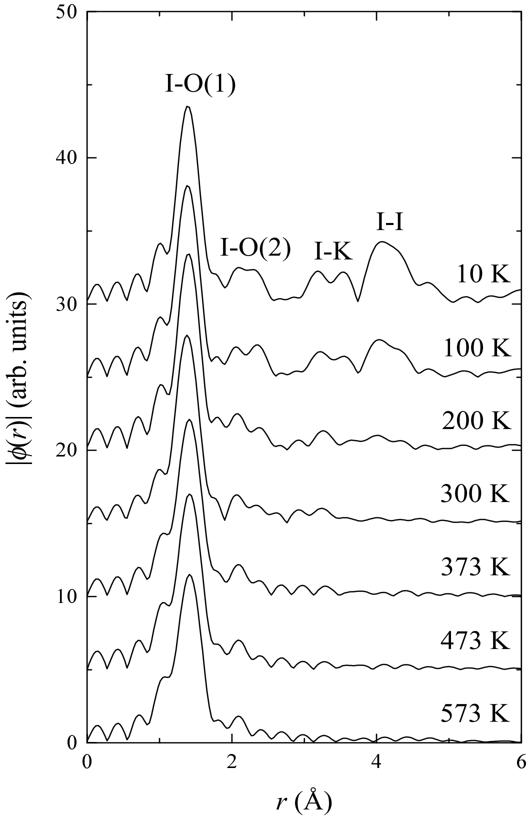

Figure 3

The Fourier transforms of k^3-weighted EXAFS spectra of KIO_3 at various temperatures. The I-O(1) and I-O(2) indicate the iodine-oxygen pair-distribution with the shorter and longer bond, respectively.

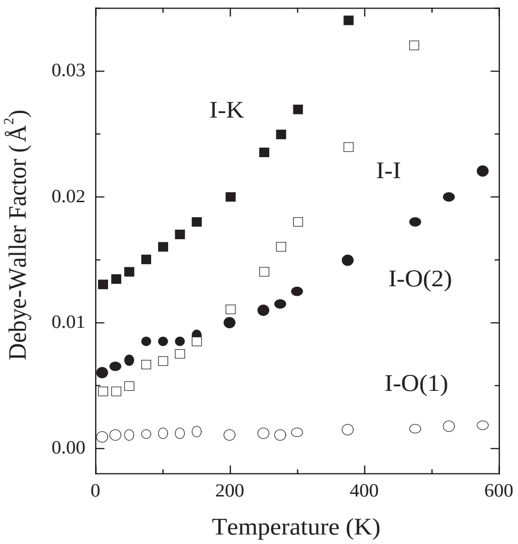

Figure 4
The temperature dependence of the Debye-Waller factor estimated from each pair-distribution function. The I-O(1) and I-O(2) indicate a pair of iodine and oxygen atoms with the shorter and longer bond, respectively.

for the PDF of I-O(1) is fixed at the value corresponding to the bond length between iodine and oxygen atoms in an IO_3^- molecule, while the distance for the other PDFs depends on temperature as shown in Table 1.

In addition, one should notice that the anomalous behavior appears in the DW factor for the PDFs of I-O(2) and I-I around 50 K that is near the phase transition temperature, $T_{V,VI} \approx$ 33 K. The phase transition at $T_{V,VI}$ is considered as a glass transition whose transition temperature is diffused over the wide temperature range. Therefore, the anomaly in the DW factor should be contributed from the glass transition at $T_{V,VI}$, associated with the reorientational freezing of IO_3^- molecules revealed from the dielectric measurements (Maeda *et al.*, 2000). The reorientational freezing of IO_3^- molecules is expected to increase the spatial correlation between the neighboring IO_3^- molecules, which causes the decrease in the DW factor. On the other hand, there appears no anomalous behavior in the DW factor expect for the glass transition at $T_{V,VI}$. The DW factor seems to be not so sensitive to the slight distortion of lattice, because the PDFs of I-I and I-K are strongly reduced by the fluctuation of IO_3^- molecules with increasing temperature. Recently, we revealed from the results of X-ray diffraction measurements of KIO_3 single crystals that the slight distortion of lattice in the (111) plane of primitive rhombohedral unit cell is accompanied with the phase transitions at $T_{I,II}$ and $T_{II,III}$. The expansion of lattice along the $\langle 111 \rangle$, that is characterized by the glass transition, was also observed below about $T_{V,VI}$. However, any structural changes could not be observed at $T_{III,IV}$ and $T_{IV,V}$ in X-ray diffraction measurements as well as EXAFS ones, despite the anomalous behavior in various physical properties. The phase transitions at $T_{III,IV}$ and $T_{IV,V}$ might be associated with the nature of structural domains that is generally independent on the atomic arrangement. However, we fail to explain the phase transitions at $T_{III,IV}$ and $T_{IV,V}$ from the results of EXAFS measurements, therefore we have proceeded further investigations especially on the nature of structural domains for these transtions.

4. Conclusion

We performed the iodine *K*-edge EXAFS study of KIO_3 to clarify the structural changes on the phase transitions. The PDF of I-O(1) is almost independent on temperature, whereas the PDFs of I-O(2), I-K and I-I increase monotonically with increasing temperature as expected from the Debye approximation. The anomalous behavior in the Debye-Waller factor for PDF of I-O(2) and I-I appears around 50 K, which is associated with the glass transition. It is suggested from the results that iodine and oxygen atoms exist as an IO_3^- molecule even at high temperatures, and that reorientation of IO_3^- molecules freezes with some short-range order that increases the spatial correlation between them below about 50 K.

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