Determination of the local structure in $Ba_{1-x}K_x BiO_3$ by x-ray-absorption spectroscopy

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The local structure around Bi atoms has been studied in $Ba_{1-x}K_x BiO_3$ (0.0 < x < 0.4) via x-rayabsorption spectroscopy. The structure is determined in terms of coordination numbers and interatomic distances around the Bi atoms between 300 and 13 K from Bi L_3 extended x-ray-absorption fine-structure data. The charges on Bi and O have been measured as a function of K doping using Bi L_3 , and O K-edge x-ray-absorption near-edge-structure spectroscopy. It was found that the ordered breathing-mode-type distortion in BaBiO₃ is replaced by a disordered distortion of the same type when K is substituted into the Ba site, which persists down to 13 K for x = 0.2 and disappears for the x = 0.4 composition. The overall Bi valence increases only slightly whereas O 2p orbitals are doped with holes with increasing K content. As the insulator-metal boundary is crossed for x = 0.35 these holes become delocalized, and contribute to the metallic behavior of the Ba_{0.6}K_{0.4}BiO₃ compound.

INTRODUCTION

The $Ba_{1-x}K_xBiO_3$ system has been extensively studied since it was discovered that the x = 0.4 composition becomes a superconductor at 30 K. $^{1-3}$ Neutron and x-ray diffraction experiments⁴⁻⁷ so far have given conclusive evidence for an ordered-type of breathing-mode distortion around the Bi atoms in the x = 0.0 compound. This distortion is completely suppressed⁸ for the x = 0.4 compound, which has cubic symmetry at room temperature and below. The semiconducting behavior of BaBiO₃ has been attributed to the breathing-mode lattice distortion, and the associated charge density wave (CDW).^{4,9} In terms of the Bi valence, this has been taken as evidence for charge disproportionation where the average valence of Bi⁴⁺ can locally be Bi³⁺ or Bi⁵⁺. Structural manifestation of this CDW is the presence of two distinct interatomic bond distances between Bi and O atoms. However, the structural studies so far has failed to observe a similar behavior for the x = 0.2 composition, with the exception of electron diffraction experiments, where an incommensurate structural modulation was observed.¹⁰

In this paper we will present evidence obtained from extended x-ray-absorption fine-structure (EXAFS) spec-

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troscopic data that the local structure around Bi remains intact as K is doped into the lattice of $Ba_{1-x}K_x BiO_3$ at x = 0.2. Two different Bi-O distances with equal proportion are maintained for x = 0.2 between 300 and 13 K. However, the ordered breathing-mode distortion is replaced by a disordered one, thus making it difficult to be observed by diffraction techniques.

The x-ray-absorption near-edge-structure (XANES) measurements of the Bi L_3 edge, as well as the O K edge indicate that potassium doping creates holes on the oxygen 2p orbitals, rather than on bismuth atoms. On crossing the insulator-metal transition, these localized 2p holes become itinerant, and contribute to the metallic, and subsequently, to the superconducting behavior of the Ba_{0.6}K_{0.4}BiO₃ compound.

EXPERIMENTAL

Samples of $Ba_{1-x}K_xBiO_3$ ($0 \le x \le 0.4$) were prepared by the melt method as described earlier.^{8,11} The x = 0.4sample is superconducting with a sharp transition at $T_c = 28$ K. Temperature dependent EXAFS studies have been carried out for BaBiO₃, Ba_{0.8}K_{0.2}BiO₃, and Ba_{0.6}K_{0.4}BiO₃ compositions between 13 and 300 K using a Displex refrigerator with a temperature control of ± 2 K. The Bi L_1 and L_3 -edge measurements were carried out at the CHESS facility at Cornell University, and at the X-18B beamline at NSLS. The energy resolution of the Si (220) monochromator was estimated to be 3 eV at 13419 eV. These measurements were done in the transmission mode, with Bi2O3 spectrum taken simultaneously as reference. Oxygen K-edge data were obtained at the Synchrotron Radiation Center, Stoughton, Wisconsin. A grating monochromator with 1200 lines/mm provided energy resolution better than 400 meV at 530 eV.

The data analysis was done in several steps. First, the PRIMEX (Ref. 12) package was used for background removal, and smooth line subtraction to obtain the oscillatory part of the EXAFS signal. Care was taken to remove the low frequency oscillations that may remain even after background removal. This data was then fitted using the EXCURV88 (Ref. 13) program, employing curved wave formalism. The theoretical phase shifts were refined along with Debye-Waller factors for $Ba_{0.6}K_{0.4}BiO_3$ at 13 K and at room temperature, since coordination numbers and the interatomic distances for this compound are well known.⁶ The same phase shifts were used to analyze the data for other compositions.

RESULTS

The advantage of EXAFS spectroscopy over x rays or neutron diffraction lies in the fact that it does not require long-range order. As a local probe, it is very useful in studying the coordination number, interatomic distances,

and lattice dynamics of a particular system, when a chemically similar compound of known structure exists. In the present case, the structure of $Ba_{0.6}K_{0.4}BiO_3$ is well known. The fits shown in Fig. 1 are based on the phase shifts derived from this standard compound and transferred to the rest of the series. The results presented in Fig. 1 are obtained by first Fourier transforming χk^3 data, and filtering out the contribution from the higher shells, fitting the filtered spectrum in k space using EXCURV88, and finally backtransforming into r space without any further truncation. For the first nearest neighbor of Bi in a $Ba_{1-x}K_xBiO_3$, a two-shell fit was necessary for x = 0 and x = 0.2 with Bi-O distances at room temperature of 2.29-2.11 Å and 2.24-2.09 Å, respectively. The contribution of each shell to the total radial distribution function is shown in Fig. 2. An equal atomic proportion of each shell was necessary for a reasonable fit for both compounds, while a single shell Bi-O distance of 2.14 was sufficient for the Ba_{0.6}K_{0.4}BiO₃ compound. The complete results at various temperatures are tabulated in Table I. The Debye-Waller factors representing the mean-square atomic displacements around Bi atoms, calculated from the temperature dependent experiments, are also given in Table I, and they are in reasonable agreement with the previous experiments.¹⁴ Note that for BaBiO₃ the Bi-O distances were found to increase by 0.03 Å at low temperature. This may be due to a structural phase transformation at low temperature observed by Pei et al.⁶ The important aspect of this work is that in the $Ba_{0.8}K_{0.2}BiO_3$ compound two separate Bi-O distances are observed with the equal population.



FIG. 1. $k^{3}\chi(k)$ EXAFS (top) and its Fourier transform magnitude (bottom) for (a) Ba_{0.6}K_{0.4}BiO₃ at 13 K, (b) Ba_{0.8}K_{0.2}BiO₃ at 13 K, (c) BaBiO₃ at 32 K, for the first Bi-O near-neighbor shell. The solid lines (-----) correspond to the experiment and the dashed lines (--) to the theoretical fit. Note that the magnitude of Fourier transform of cubic Ba_{0.6}K_{0.4}BiO₃ is twice that of orthorhombic Ba_{0.8}K_{0.2}BiO₃ and of monoclinic BaBiO₃.



FIG. 2. Breakdown of Fourier transform magnitude (a) for the short (Bi-O)₂ and (b) for the long (Bi-O)₁ distances for $Ba_{0.8}K_{0.2}BiO_3$ at 13 K, (c) for the short (Bi-O)₂, and (d) for the long (Bi-O)₁ distances for BaBiO₃ at 32 K. The solid lines (_____) correspond to the experimental and the dashed lines (_____) to the theoretical fit.

Therefore, this provides evidence for the existence of a local breathing-mode distortion. Such a distortion has also been observed in Pb-doped BaBi_{0.25}Pb_{0.75}O₃.¹⁵ This distortion has not been observed by neutron diffraction⁶ possibly because the coherence length of the distortion is smaller than would be detected by diffraction technique.

The question of charge balance in K-doped BaBiO₃ can be addressed from different points of view. Since Bi has $6s^{2}6p^{3}$ atomic configuration it can be stabilized either in 3+ or in 5+ valence free ion state. However, this is a too simplistic point of view. In solids, a more realistic configuration would be $6s^{2-\delta} 6p^{\delta}$ for 3+ Bi, and $6s^{\epsilon}6p^{\sigma}$ for 5+ configuration. The coefficients δ , ϵ , and σ would depend on the type of ligand, as well as the near-neighbor distances.

XANES spectroscopy can be used to measure the charge on Bi as a function of K doping in $Ba_{1-x}K_xBiO_3$. We have measured the Bi L_3 -edge XANES for Bi₂O₃, and for $Ba_{1-x}K_xBiO_3$ for x = 0.0, 0.1, 0.2, 0.3, and 0.4. The results are shown in Fig. 3(a). Two reference spectra of Bi_2O_3 , and $KBiO_3$ containing nominally 3 + and 5 +Bi, respectively, are also included in Fig. 3. The L_3 -edge absorption corresponds to $2p_{3/2}$ to 6s or 6d transition in Bi. When compared to Bi_2O_3 , there is a shift of about 2 eV to higher energy in the general position of absorption edge for the entire $Ba_{1-x}K_xBiO_3$ series. With respect to K doping, however, there are small but systematic changes. These changes are highlighted by subtracting the Bi_2O_3 spectrum from the others, and they are shown in Fig. 3(b). The peak appearing at about -8 eV (with respect to the 13 419-eV absorption edge) can be attributed to a $2p_{3/2}$ to 6s transition which increases as the net

TABLE I. Interatomic distances and coordination number around Bi atoms in $Ba_{1-x}K_x BiO_3$ for x = 0.0, 0.2, and 0.4 as obtained from Bi L_3 -edge EXAFS data as a function of temperature. r_x —from this work; r_n —from neutron data (Ref. 6), N = coordination number around Bi central atom.

PaPiO	$(\text{Bi-O})_1$ N=2			$(\text{Bi-O})_2$ $N = 3$		
$\frac{\text{DaBIO}_3}{T (\text{K})}$	r_x (Å)	r_n (Å)	$2\sigma_x^2$ (Å ²)	r_x (Å)	r_n (Å)	$2\sigma_x^2$ (Å ²)
295	2.29(1)	2.283	0.017(1)	2.11(1)	2.117	0.008(1)
175	2.29		0.014	2.11		0.007
50	2.29		0.009	2.11		0.006
32	2.30		0.008	2.12		0.005
13	2.33		0.008	2.15		0.004
$Ba_{0.8}K_{0.2}BiO_3$						
295	2.25(1)	2.169	0.014(1)	2.09(1)	2.169	0.008(1)
100	2.25		0.013	2.10		0.007
13	2.24		0.009	2.09		0.006
$Ba_{0.6}K_{0.4}BiO_3$		N = 6				
295	2.140 ^a		0.013(1)			
175			0.011			
100			0.008			
50			0.008			
32			0.009			
22			0.008			
13			0.009			

^aThis distance was kept constant to generate phase shifts which were then used throughout the rest of the fits.



FIG. 3. The effect of K addition to $Ba_{1-x}K_xBiO_3$ monitored by Bi L_3 -edge XANES. (a) The main absorption edge position remains fixed as K doping is increased. (b) To highlight the effect of K doping, the Bi₂O₃ XANES spectrum is subtracted from each other spectra. The changes are small but consistent. See text for further comments.

positive charge on Bi increases. Another prominent change is the peak appearing at 22 eV which seems to be the signature of 5+ Bi compounds. The lack of shift in the overall position of the absorption edge in the $Ba_{1-x}K_xBiO_3$ series in Fig. 4 implies that the charge compensation for K doping must come from somewhere else. Bi is indirectly affected via hybridization of 6s and 6p levels with that of O 2p levels. This hybridization can be monitored by measuring Bi L_1 -edge XANES.¹⁶ Therefore, we suggest that the charge disproportionation should not be taken as a rigid Bi³⁺-Bi⁵⁺ separation, but rather a subtle balance between O and Bi atoms.

In the case of the Bi—O bond, it is found that O is always deficient in 2p occupancy, i.e., there are holes in the 2p orbitals as evidenced by O K-edge XANES data given in Fig. 4. The O K-edge spectra is normalized as follows: first, a linear background is fitted to the preedge region between 510 and 520 eV, and the resulting background is subtracted. Then, as suggested by Kuiper *et al.*,¹⁷ we have integrated the area under the absorption spectra between 515 and 545 eV, and normalized spectra with respect to the area. We observe that the first peak intensity increases for K = 0.2, and then decreases for K = 0.4. We would like to avoid any quantitative interpretation of



FIG. 4. The O K-edge XANES for BaBiO₃, Ba_{0.8}K_{0.2}BiO₃, and Ba_{0.6}K_{0.4}BiO₃. The peak at 526 eV is well isolated, and indicates the existence of O 2p-type holes in the undoped as well as in the doped compounds.

the data based on peak heights. The peak at 525 eV in the O K-edge data can be taken as evidence of holes with an O 2p character. Electronic structure calculations predict that for pure BaBiO₃ that the energy required to put a hole in the Bi 6s state of Bi^{3+} is 2 eV higher than to put a hole in p level.^{9,18} Qualitatively, one can see that the intensity of the peak at 525 eV increases as K is substituted into Ba sites in BaBiO₃. As the K content increases this first peak intensity decreases. Note that the insulatormetal transition boundary is crossed at about x = 0.35,⁶ and the system becomes cubic, with one unique Bi-O distance of 2.14 Å, instead of two different distances of 2.25 and 2.09 Å, as shown in Table I. There is no sudden change in Bi valence associated with this phase transition, as we do not observe any change in the Bi L3 edge absorption spectra shown in Fig. 3. Therefore, we interpret this change in intensity of the first peak at 525 eV as evidence for the holes on the O 2p levels spread in energy space, and become bandlike, in $Ba_{0.6}K_{0.4}BiO_3$.

CONCLUSIONS

The effect of K doping on the atomic and electronic structures of $Ba_{1-x}K_xBiO_3$ for 0.0 < x < 0.4 has been studied by x-ray absorption spectroscopy. The Bi L_3 -edge EXAFS results indicated that the ordered breathing-mode-type distortion in x = 0.0 composition is replaced by a disordered distortion of the same type in x = 0.2 which is related to its nonmetallic behavior. The charge compensation for K doping is accomplished by creating holes in the oxygen 2p levels. These holes then become bandlike as the structure becomes cubic, and the breathing-mode distortion disappears when the K content is increased beyond x = 0.35.

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