

Lattice softening in superconducting compositions of Ba(K)BiO₃

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Temperature dependent x-ray absorption spectra investigation were measured for Ba_{1-x}K_xBiO₃ (Bi L₃-edge) with $x = 0.0, 0.25, 0.4, 0.5$ and for BaPbO₃ (Pb L₃-edge). It was found that at low temperatures the Debye-Waller factor of the square diagonal Bi-Bi bond has the maximum value near the insulator-metal phase transition for the compound with $x = 0.25$ and $x = 0.4$. Temperature dependence of the Debye-Waller factor of Bi-Bi bond strongly differs from the Einstein model curve that well describes the harmonic systems (for example BaPbO₃). This behavior is consistent with the strong anharmonicity of the Bi-O shell due to the double-well vibration potential reported by us earlier. Presented results point to the essential lattice softening of the superconducting compositions, which is important for the understanding of superconductivity mechanism in perovskite type oxides. **Keywords:** local distortions; Debye-Waller

factor; perovskite.

1. Introduction

The crystal lattice structures of copper oxide high temperature superconductors (HTSC) and bismuth-based oxides such as Ba_{1-x}K_xBiO₃ (BKBO) and BaPb_{1-x}Bi_xO₃ (BPBO) have some important common characteristics. Both oxide classes have perovskite-like lattices with CuO_n ($n=4, 5, 6$) or Bi(Pb)O₆ complexes joined at the common oxygen ions. In bismuthates, the intersection of the octahedral complexes in the three crystallographic directions determines their three-dimensional cubic structure. The CuO_n complexes are joined in CuO₂ planes, which produces the two-dimensional structure of copper-oxides.

Because of the strong hybridization of covalent Bi(Pb)6s, Cu3d – O2p_σ bonds, the above mentioned complexes are the most tightly bound items of the perovskite-like structure. Therefore such important peculiarities of perovskite structure as the lattice instability with respect to the soft tilting mode of CuO_n or BiO₆ complexes (see for review (Plakida, 1995)) and highly anisotropic thermal factors of oxygen ions vibration (Wignacourt *et al.*, 1988; Kwei *et al.*, 1989) are inherent to the both classes of superconducting oxides and cause anharmonic vibrations of oxygen atoms.

The layered structure of the copper-based perovskites, the presence of several non-equivalent copper positions, and there being a number of different Cu-O bonds complicate the local structure analysis. At the same time, the simplicity of the cubic three-dimensional structure, the simpler electronic structure of $s - p$ valence band of BPBO-BKBO systems in comparison with $d - p$ band of cuprates and lack of charge reservoirs and of magnetic ions makes the interpretation of the local sensitive experimental data easier to a great extent.

The local structure of the superconducting alloys Ba_{1-x}K_xO₃ with $x > 0.37$ dramatically differs from the average one. The integral methods (x-ray and neutron scattering) showed a simple cubic structure for these compounds (Pei *et al.*, 1990) while the Raman scattering pointed out the local deviations from a simple cubic symmetry (Anshukova *et al.*, 1990), EXAFS studies showed the existence of the local oxygen octahedra tilting up to 4° – 5° (Yacoby *et al.*, 1997), XPS spectra found the strong splitting of the Bi 4f spectral lines which pointed on the existence of two different Bi valence states in the superconducting compositions (Qvarford *et al.*, 1996).

Our recent EXAFS - studies of the nearest oxygen environment of Bi in BKBO evidenced that oxygen ions vibrate in the double-well potential and their vibration are correlated with the charge carriers transfer due to the existence of the two different electronic structures of the octahedral complexes BiO₆ and BiL²O₆ (here, L² denotes the hole pair in the antibonding Bi6sO2p_σ* orbital of the octahedral complex) (Menushenkov *et al.*, 1998; Menushenkov & Klementev, 2000). The local lattice instabilities observed as the double-well potential of oxygen ion vibrations move around the lattice in correlation with the local carrier pairs movement and should influence on the lattice dynamics in the Bi-Bi sub-lattice.

It is the purpose of the paper to study the behavior of the Bi-Bi sub-lattice of BKBO system at the different K-doping levels and temperatures which was not investigated in previous works (Menushenkov *et al.*, 1998; Menushenkov & Klementev, 2000). We study here the Bi-Bi shell along the square diagonal of BiO₂ plane which has no multiple scattering input into EXAFS signal and is treated well in the single scattering approximation.

2. Experimental and data analysis

We have measured the ceramic samples of BaPbO₃ and BKBO with $x = 0, 0.25, 0.4, 0.5$ synthesized as described in (Anshukova *et al.*, 1990). The materials were examined by x-ray powder diffraction for phase purity. The samples were controlled using transport and susceptibility measurements. BaBiO₃ and the compositions of BKBO with $x = 0.25$ showed semiconductor-like behavior, while compounds with $x = 0.4$ and 0.5 showed typical metallic $\rho(T)$ dependence and superconducting properties with $T_c \simeq 30$ K and $T_c \simeq 16$ K, respectively. The samples of BaPbO₃ were metallic but not superconducting at all temperatures.

For the XAS measurements, a crushed fine powder was precipitated onto a micropore substrate. The thicknesses of the samples were about two absorption lengths at the chosen absorption edge.

The x-ray absorption spectra were collected at D-21 line of DCI (LURE, Orsay, France) synchrotron operated at the energy 1.85 GeV and the average current ~ 250 mA of positron beam at the L₃ edges of Bi (13040.6 eV) and Pb (13426 eV). The energy resolution of the double-crystal Si [311] monochromator at 13 keV was about 2–3 eV. The low-temperature measurements were carried out using a liquid-helium circulation-type cryostat with a temperature control of ± 1 K.

The background in the experimental spectra was removed as described in (Newville *et al.*, 1993), taking care to remove the low frequency oscillations. The EXAFS-functions $\chi(k)k^2$ obtained from absorption spectra were Fourier transformed in the range of wavenumber k from 1.5 to 16.5 Å⁻¹, using Kaiser-Bessel windowing function (see Fig. 1).

The model EXAFS-function was constructed as

$$\chi(k) = NF(k) \sin[2kR + \phi(k)] \exp(-2k^2\sigma^2)/(kR^2) \quad (1)$$

and fitted to Fourier-filtered experimental $\chi(k)$, where k is the photoelectron wave number, N , R , and σ^2 are the coordination number, length, and Debye-Waller (DW) factor of Bi-Bi bond, correspondingly. The phase shift $\phi(k)$ and scattering amplitude $F(k)$ were calculated, using FEFF code.

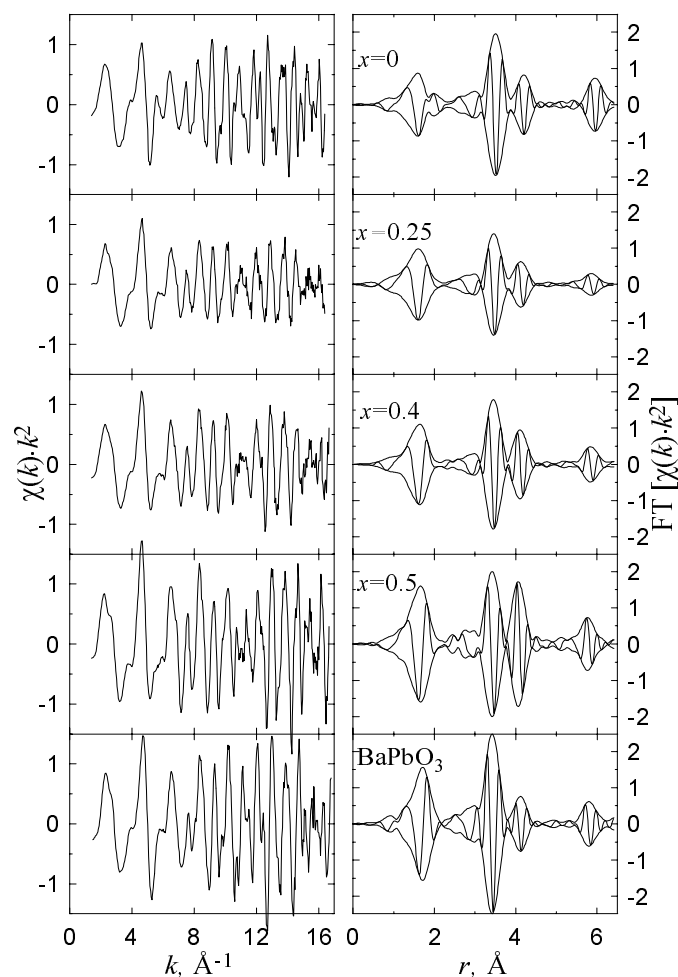


Figure 1
Experimental EXAFS $\chi(k)k^2$ (left) and its Fourier transform magnitude and imaginary part (right) for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($x = 0, 0.25, 0.4, 0.5$) and BaPbO_3 at 7 K.

Here, we focus on the temperature dependencies of the Bi-Bi bond length and of the Debye-Waller (DW) factors σ^2 corresponding to the square diagonal Bi-Bi shell which manifests itself as the peak around 6 Å in Fig. 1(right).

3. Results and discussion

The main results are presented in Fig. 2(a), (b). From this picture it is clear, that the square diagonal Bi-Bi distances slightly change with temperature. In the same time the temperature dependence of the Debye-Waller factors of Bi-Bi bonds are not trivial. For the metallic, but not superconducting compound BaPbO_3 the Pb-Pb vibrations are simple harmonic, i.e. the Debye-Waller factor temperature dependence is in accordance with the Einstein model [the squares in Fig. 2(b)]. This behavior is in full agreement with the observed harmonic behavior of the nearest Pb-O shell in BaPbO_3 (Menushenkov & Klementev, 2000).

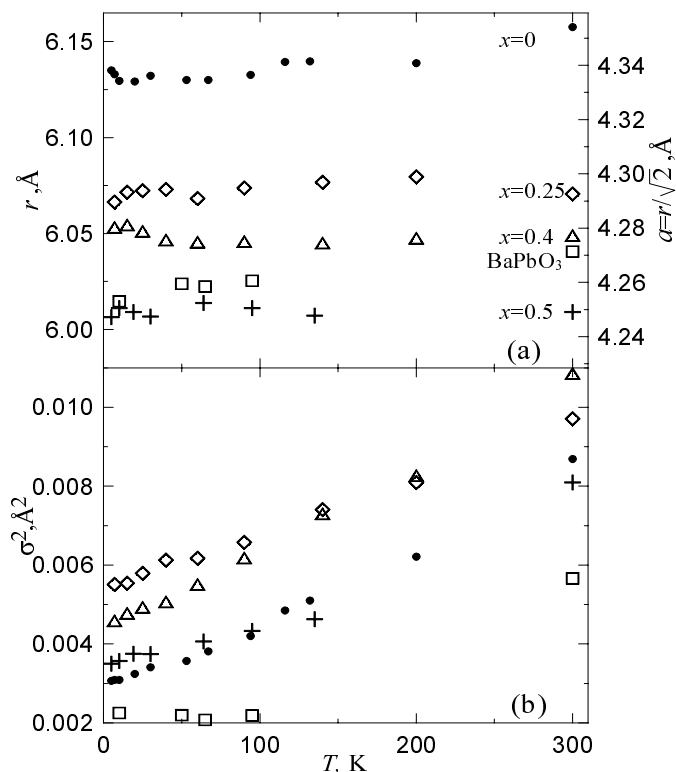


Figure 2
Temperature dependence of the square diagonal Bi-Bi distances a) and Debye-Waller factor values b) for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($x = 0, 0.25, 0.4, 0.5$) and BaPbO_3 .

For the insulating BaBiO_3 so as for the K-doped compounds with $x = 0.25, 0.4, 0.5$ the character of the Debye-Waller factor temperature dependence essentially differs from the harmonic Einstein model. They begin quickly increase with temperature at low temperatures. For example for BKBO with $x = 0.4$ the temperature dependence of the Debye-Waller factor is close to linear [the triangles in Fig. 2(b)]. Such a behavior can not be explained from the point of view of the conventional lattice vibrations. However it finds fully explanation in the frame of our model of the relationship between the local crystal and the local electronic structures of the Bi-based perovskites (Menushenkov & Klementev, 2000; Kagan *et al.*, 2000).

The model includes the following key positions:

1. The parent compound BaBiO_3 represents a system with the initially preformed local electron and hole pairs spatially and energetically localized inside the octahedral complexes BiO_6 and BiL_2O_6 . The BiL_2O_6 octahedra have stiff (quasi-molecular) Bi-O bonds and the smaller radius, and BiO_6 octahedra represent non-stable molecules with filled antibonding orbitals and the larger radius. Because the sum of the nearest octahedron radii exceeds the lattice parameter a , the octahedral system is tilted around [110] axis, producing a monoclinic distortion of BaBiO_3 as a combination of the static breathing and tilting distortions.

2. The conductivity of BaBiO_3 occurs only at the local pair transfer due to the dynamic exchange $\text{BiL}_2\text{O}_6 \leftrightarrow \text{BiO}_6$. The localization energy of a pair determines the transport activation gap E_a . The binding energy of a pair E_b becomes apparent as the optical gap.

3. The two types of carriers are present in the metallic phase of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x > 0.37$: the itinerant electrons from the infinite $\text{BiL}^2\text{O}_6 - \cdots - \text{BiL}^2\text{O}_6$ Fermi-cluster (fermions) and the delocalized local electron pairs from the BiO_6 complexes (bosons). The former produce the Fermi-liquid state and are responsible for the insulator-metal transition observed at $x \approx 0.37$. The latter provide the superconductivity at $T < T_c$ due to the free moving of the local electron pairs in the process of the dynamic exchange $\text{BiL}^2\text{O}_6 \leftrightarrow \text{BiO}_6$. The both Fermi and Bose subsystems are spatially separated in these compounds since belong to the different clusters.

4. The pairing mechanism in the bismuthates is more probably of the electronic than of the phonon-mediated origin. However the lattice plays an important role in superfluid providing the phase coherence of the local pair moving. It is the phase coherence destruction that limits the critical temperature in BKBO-BPBO systems.

In according with the above model all the octahedral complexes PbL^2O_6 in the metallic BaPbO_3 are equivalent and oxygen ion vibrations are simple harmonic. The conventional harmonic vibrations of the nearest Pb-O shell do not effect on the Pb sub-lattice dynamics, so we observe the normal Einstein-like Debye-Waller factor temperature dependence [the squares in Fig. 2(b)].

In the parent compound BaBiO_3 there is an alternating system of the different octahedral complexes BiO_6 and BiL^2O_6 and oxygen ions vibrate in the double-well potential. These unharmonic oscillations influence on the Bi-sub-lattice dynamics: the absolute values of the Debye-Waller factors increase and the character of their temperature dependence changes [the closed circles in Fig. 2(b)]. However the existence of the visible static tilting (up to 11°) of the oxygen octahedra in BaBiO_3 diminishes the effect of the double-well potential influence: oxygen ions vibrates between two nearest Bi ions, but slightly aside the Bi-Bi line. Substitution of each two potassium atoms for two barium atoms introduces a hole pair and converts a larger octahedron to a smaller one. This destroys the strict alternating sequence of octahedra and results in appearance of neighboring small octahedra, which contracts the lattice [Fig. 2(a)]. Therefore, $\sigma^2 = \sigma_1^2 + \sigma_2^2$, where σ_1 is the mean-square displacement from ordinary phonons, σ_2 is caused by the local disorder. The share of oxygen atoms belonging to two small octahedra is equal to x . It is easy to show that $\sigma_2^2 = \delta^2(1-x)x$, where δ is the difference between radii of the larger and the smaller octahedra or between positions of double-well potential minima and may have as static so dynamic behavior. Since δ depends on x , the maximum of σ^2 falls not on $x = 0.5$. In Ref. (Menushenkov & Klementev, 2000) we found δ 's at $T = 7\text{K}$: 0.18 \AA ($x=0.25$), 0.17 \AA ($x=0.4$), 0.13 \AA ($x=0.5$). From these values one can find that the maximum of σ^2 falls on $x \approx 0.25$, just as we have found from EXAFS analysis [Fig. 2(b)]. However, this compound is not superconductive because the percolation threshold is not achieved. Among superconducting compounds the Debye-Waller factor of Bi-Bi bond has the maximum value at low temperatures for the compound with $x = 0.4$ which has the highest $T_c \sim 30\text{K}$. Fur-

ther increasing of the potassium concentration leads to diminishing of the Debye-Waller factor values. The lattice stiffness increases which reflects the decreasing of the critical temperature to $T_c = 16\text{K}$ for $x = 0.5$ compound. This facts are in the full agreement with the above model since the K-doping decreases the number of centers where the oxygen ions vibrates in the double-well potential and increases the lattice stiffness due to the increasing the number of the stiff BiL^2O_6 octahedra.

4. Conclusion

The presented EXAFS investigation of Bi-Bi sub-lattice of BKBO system pointed out that the existence of the double-well vibration potential in the Bi-O shell essentially influences on the Bi sub-lattice dynamics. It leads to the unusual temperature dependence of the Bi-Bi Debye-Waller factors. The lattice has the most softness near the insulator-metal transition where the critical temperature in the superconducting range has maximum value. The above results evidence in favor of the model of the relationship between the local crystal and the local electronic structures of the Bi-based perovskites proposed by us earlier.

We acknowledge the LURE Program Committee for providing beamtime. The work is supported by Russian Foundation for Basic Researches (Grant No. 99-02-17343) and Program "Superconductivity" (Grant No. 99010).

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