Debye-Waller Factor Low Temperature Anomalies in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$

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Abstract. Temperature dependent x-ray absorption investigations have been made on the Bi L_3 edge in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ with $x=0.0, 0.75, 1.0$. Essentially abnormal behaviour of the Debye-Waller factor σ^2 of Bi-O bonds was observed at low temperatures for BaBiO_3 and $\text{BaPb}_{0.25}\text{Bi}_{0.75}\text{O}_3$ in contrast to Einstein model. It was found that the Debye-Waller factors of both Bi-O bonds increase with temperature decreasing from ~ 90 K along with abnormal increasing of Bi-O and Bi-Ba distances. At the same time Pb-O, Pb-Ba bonds of BaPbO_3 show normal behaviour with temperature. The nature of the anomalies is discussed in the frame of the dynamic fluctuation of the oxygen octahedra rotation mode that may give a new look to understanding of HTSC phenomenon in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$.

1. INTRODUCTION

Despite the superconductivity in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ (BPB) was discovered considerably earlier [1] than in cuprates [2], there is no generally accepted description of the mechanism of superconductivity in these alloys so far. Moreover, it is not clear if the pairing mechanism is the same in the similar compounds of BPB and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKB) [3].

There is considerable controversy concerning phase diagram of superconducting BPB alloys ($0 < x < 0.35$) and for both BPB end members: BaBiO_3 and BaPbO_3 (see, e.g. [4]). In the diffraction studies [5,6] an essential anisotropy in the thermal vibration of oxygen atoms (oblate along the Bi-O-Bi bonds) for both BPB and BKB systems was observed. Heald *et al.* [7] (XAS study) found some peculiarities of the BKB local structure at low temperatures: two different temperature dependencies of the Debye-Waller (DW) factor σ^2 were obtained for two Bi-O bonds in BaBiO_3 , for the superconducting compound ($\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$) the σ^2 temperature behaviour showed a significant deviation from the Einstein model. Besides, an abnormal increase of the both Bi-O distances with the temperature decrease was observed in a pure and slightly potassium doped BaBiO_3 [8].

All these uncertainties seem to arise from the complexity of the BPB and BKB structures due to two unequal Bi positions. Here we present an EXAFS- study of the local structure anomalies for the BPB compounds which are more pronounced at low temperatures and discuss their nature in the frame of perovskite structure peculiarities.

2. EXPERIMENT AND EXAFS DATA REDUCTION

The samples of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ with $x=0, 0.75$, and 1 were prepared by heating mixtures of oxides and carbonates (BaCO_3 , Pb_3O_4 , and Bi_2O_3) in air at $800 - 1000^\circ\text{C}$. The powder samples were three times annealed and then slowly cooled and ground. All the samples had a pure phase, which was examined by x-ray diffraction. For the EXAFS measurements the fine powder was uniformly deposited on polytetrafluoroethylene membrane. Their thickness was about 2 absorption lengths.

The x-ray absorption measurements were performed on D21 beam line of the DCI storage ring LURE (France) at the Bi and Pb L_3 edges using a Si(111) double-crystal monochromator. The storage ring was operated at 1.85 GeV positron beam energy and 300 mA maximum current. The energy resolution was ~ 3 eV at 13 keV. The low temperature measurements were carried out with a liquid helium circulation cryostat. The temperature was regulated by a helium flow and measured with a carbon probe with the accuracy about 1 K.

The XAFS function $\chi(k)$ was filtered by Fourier technique. Near neighbour distance R , the DW factor σ^2 , and the number of the neighbours N related to the sphere obtained were determined by fitting as:

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

The phase shift $\phi(k)$ and the scattering amplitude $F(k)$ were calculated using the FEFF-5 code.

The closeness of L_3 Pb (13.035 keV) and Bi (14.418 keV) edges complicates the quantitative analysis of the mixed compounds ($x \neq 0, 1$). The Pb background presents noticeably above the Bi L_3 edge and should be subtracted. A possible way of solving this problem is to construct a model using the data between the Pb and Bi L_3 edges [9] and to prolong it over the Bi L_3 edge. Here we used the subtraction of the $\chi(k)$ of the BaPbO_3 experimental spectra (Pb L_3 edge) taken at the same temperature. In this case the subtracted spectrum contains information about *all* the coordination shells (in contrary to the subtraction of the model $\chi(k)$ that contains 2 or 3 shells only). At the same time there is some difference between the local environment of Pb in the mixed compounds and in the BaPbO_3 and for the $x=0.75$ compound this difference is not negligible. Nevertheless, the Pb

absorption is three times as small as the Bi one and some shortage of accuracy in such a small Pb background is not so important.

3. GENERAL RESULTS

For the BaPbO_3 ($x=0$) and BaBiO_3 ($x=1$), the EXAFS data were obtained by the Fourier transform (FT) over the range $3\text{--}14 \text{ \AA}^{-1}$ in k -space. The back Fourier transform was done using square windows $1.0\text{--}2.1 \text{ \AA}$ for Pb-O and Bi-O shells and $2.5\text{--}4.0 \text{ \AA}$ for the Pb(Bi)-Ba shell. For $x=0.75$ compound, the k -range of FT's at the Pb L_3 edge is limited by $9.6 \text{ \AA}^{-1}$, where the Bi L_3 edge begins. This limitation broadens the peaks of the FT and, hence, produces some uncertainties in the amplitudes and the DW factors. Data from the Bi L_3 fine structure were extracted after the subtracting the oscillating background from the Pb L_3 edge. For this procedure we used the Pb L_3 XAFS from BaPbO_3 measured at the same temperatures. The Pb L_3 XAFS was transformed back to the energy scale ($E=E_0 - \hbar^2 k^2 / 2m_e$) and renormalised to the step height at the Pb L_3 edge: $\mu(E) = \chi(E)\mu_0(E) + \mu_0(E)$. This spectrum reproduces completely the area between the Pb and Bi L_3 edges. After the subtraction we obtain the EXAFS spectrum that is relatively free of the Pb L_3 edge contribution. Then, using the forward and back FT, we have got partial spheres of the oxygen and barium for all the compounds. To get numerical results we performed non-linear least-square fit in the k space. The Pb(Bi)-O and Pb(Bi)-Ba distances are summarised in Table I with an error of $\sim 0.01 \text{ \AA}$.

For the Pb first neighbour environment we have found that there is only one Pb-O distance for both $x=0$ and $x=0.75$ compounds. The thermal expansion caused an ordinary increasing the Pb-O and Pb-Ba distances as well as an increasing the DW factor of Pb-O bond (see Table I).

For undoped BaBiO_3 (see Table I) we have determined two Bi-O distances separated by $0.15 \text{ \AA}$ at 300 K and by $0.18 \text{ \AA}$ at 7 K . The difference between the two Bi-O bond lengths agrees with other XAFS studies and data of neutron diffraction [7-10].

Table 1. The results of EXAFS analysis (r , $\text{\AA}$; σ^2 , $10^{-3} \text{ \AA}^2$).

BaPbO₃

T, K	r(Pb-O)	σ^2 (Pb-O)	r(Pb-Ba)	σ^2 (Pb-Ba)
7	2.15	0.76	3.76	3.1
30	2.16	0.93	3.76	3.5
80	2.16	1.04	3.76	3.9
90	2.17	1.20	3.76	3.9
100	2.17	1.42	3.77	4.0
250	2.18	1.44	3.77	8.1

BaBiO₃

T, K	r(Bi-O) _{1/2}	σ^2 (Bi-O) _{1/2}	Δr	$\langle \sigma^2 \rangle$	r(Bi-Ba)	σ^2 (Bi-Ba)
7	2.15, 2.34	2.3, 4.8	0.19	2.24	3.83	2.9
30	2.14, 2.32	2.0, 4.3	0.18	2.23	3.82	3.1
55	2.13, 2.31	0.7, 2.0	0.18	2.22	3.81	3.7
90	2.14, 2.30	0.6, 2.4	0.16	2.22	3.81	3.9
250	2.14, 2.29	3.0, 6.0	0.15	2.22	3.80	7.0

BaPb_{0.25}Bi_{0.75}O₃

T, K	r(Bi-O) _{1/2}	Δr	$\langle \sigma^2 \rangle$	r(Pb-O)	r(Bi-Ba)	r(Pb-Ba)
7	2.14, 2.29	0.15	2.21	2.21	3.81	3.80
30	2.13, 2.28	0.15	2.21	2.19	3.81	3.79
55	2.12, 2.26	0.14	2.19	2.19	3.80	3.78
250	2.12, 2.25	0.13	2.18	2.18	3.79	3.77

We observed an abnormal temperature dependence of the Bi-O bond DW factors for compounds with $x=1.0$, 0.75 at temperature range $7\text{--}90 \text{ K}$. As can be seen from Fig.1 and Table. I, the DW factors of both Bi-O bonds increase with the temperature decreasing. From the Einstein model's point of view, which should fit well the temperature dependence of harmonic systems, this tendency is absolutely abnormal.

Figure 1. Temperature dependences of the DW factors σ^2 for the oxygen subshells in BaBiO_3 with the longer bond length ($\blacktriangle$) and with the shorter one ($\square$). The solid lines are the Einstein model fits.

Figure 2. First (oxygen) shell at Bi L_3 edge for BaBiO_3 at different temperatures: 7, 90, 250K.

To illustrate the reality of our results we present in Fig.2 the isolated first shell of $k^2 \chi(k)$ for BaBiO_3 at three temperatures: 7 K, 93 K and 250 K. One can see that the beating at 93 K is stronger not only than at 250 K but also than at 7 K, which indicates that at 93 K the contributions of the both Bi-O shells are almost equal so that their interference in the EXAFS spectra has a maximum effect near this temperature. In the case of the ordinary $\sigma^2(T)$ dependence for the both Bi-O bonds the strongest beat would be observed at the lowest temperature.

The anomalies in behaviour of DW factors are accompanied by an abnormal increasing of Bi-O, Bi-Ba distances with temperature decreasing from 90K to 7K for both $x=1$ and $x=0.75$ samples. It is in agreement with results of Salem-Sugui, Jr *et al.* [8] and with the negative linear thermal coefficient of expansion found by Anshukova *et al.* [11].

With the temperature decreasing, the difference between two Bi-O bond lengths increases from 0.15 Å (250 K) to 0.18 Å (7 K) due to the increase of the longer Bi-O bond length (2.29 Å (250 K) - 2.34 Å (7 K)). At the same time the shorter Bi-O bond length does not practically change (see Table I).

4. DISCUSSION

It is worth to notice, that the DW factors increasing with a temperature fall is very unusual phenomena. Previously the same behaviour was observed in the mixed valence $\text{Sm}_{0.7}\text{Y}_{0.3}\text{S}$ and was connected with softening of optics phonons [12]. We suppose that the anomalies in BaBiO_3 arise from the asymmetry of the dynamic fluctuation of the oxygen octahedra rotation (tilting) mode. Tilting vibration displacements produce the additional fluctuation of Bi-O lengths with rotation mode frequency. Thus, the values of the DW factor σ^2 of Bi-O bonds extracted from the EXAFS spectra should contain at least two parts: σ_b^2 and σ_r^2 , - from the breathing and rotation modes respectively. At high temperatures ($T > 90\text{K}$) the value of σ_r^2 is negligible in comparison with σ_b^2 and the temperature dependencies of the DW factor σ^2 are in the agreement with the Einstein model.

With temperature decreasing, the static tilting angle grows [4,7], which increases both the long Bi-O distance and the contribution from the tilting fluctuations into σ^2 value (see Tab. 1 and Fig. 1). Besides, it is known [13], that the fluctuation of the tilting displacement becomes remarkable on cooling. Thus, from our viewpoint the anomalous behaviour of the DW- factors for monoclinic distorted BaBiO_3 arise from the rotation part σ_r^2 in the total $\sigma^2(T)$ temperature dependence (see Fig.1). Apparently, owing to the essential difference in the Bi-O bond lengths, the fluctuation asymmetry of the tilting mode is considerable and leads to a negative thermal expansion coefficient [11]. It was observed as the Bi-Ba bond length growth for both the BaBiO_3 and $\text{BaPb}_{0.25}\text{Bi}_{0.75}\text{O}_3$ compounds in our experiments (see Table I).

In contrast to monoclinic distorted BaBiO_3 , the other BPB end member BaPbO_3 has a weak lattice distortion. All Pb-O bonds have the same strength. The oxygen octahedra around the Pb atoms are equivalent. That is why the Pb-O bond length and its DW factor show an ordinary growth with temperature, unlike those in BaBiO_3 and $\text{BaPb}_{0.25}\text{Bi}_{0.75}\text{O}_3$.

In the superconducting BPB compound with $x=0.25$ our previous results also showed an ordinary increase of Bi-O and Bi-Ba bond lengths with temperature. Probably it is connected with a less distorted structure compared with BaBiO_3 due to a small bismuth content [4].

A possible connection of the rotation mode fluctuation with superconductivity in BKB, BPB systems was noticed in a number of works [13,14]. The rotation type vibration mode of oxygen octahedra plays the main role in the anharmonic model for high- T_c superconductors by Plakida *et al.* [14]. That is why it is necessary to carry out more accurate investigations of local structure in the superconducting phases $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($0 < x < 0.35$) and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($0.37 < x < 0.5$) at low temperature. Such a study is under way (see preliminary results in Ref.[15]) and will be published later.

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