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The effect of oxygen deficiency on the electronic and local structures of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ – $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$: an X-ray absorption study

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Abstract

The X-ray absorption spectroscopy (XAS) measurements at the Bi L_3 and Pb L_3 edges were made for Bi-based perovskite oxides: $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ ($x = 0, \delta \leq 0.2$; $x = 0.25, \delta \leq 0.15$; $x = 1, \delta \leq 0.4$) and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$ ($\delta \leq 0.2$). The oxygen reduction leads to larger changes in the Bi L_3 edge of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ ($x = 0.25, 1.0$) and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$ than in the Pb L_3 edge of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ ($x = 0, 0.25$). The extended X-ray absorption-fine structure (EXAFS) measurements indicate that the local structure around the Bi sites is more sensitive to the variation in oxygen stoichiometry than the local structure around the Pb sites. The single Pb–O bond length exhibits a certain dependence in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ ($x = 0, 0.25$) on the oxygen reduction. On the contrary, the separation between two different Bi–O bond lengths increases with δ in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ ($x = 0.25, 1$). Two Bi–O distances could be distinguished in a semiconducting $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{2.8}$. The local structure of oxygen deficient compounds was found to be essentially different from the crystalline structure refined from diffraction data.

The Bi valence states are discussed. The XAS data are in agreement with a $2\text{Bi}^{+4} \rightarrow \text{Bi}^{+3} + \text{Bi}^{+3}\underline{L}^2$ charge disproportionation model in BaPbBiO and BaKBiO , where \underline{L}^2 denotes the spread of two holes on 2p orbitals of six oxygen atoms surrounding the Bi ion.

Keywords: X-ray absorption spectroscopy (XAS); Local and electronic structures; Oxygen deficiency; Valence states of Bi ions; $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$

1. Introduction

Although the superconductivity in BaPbBiO and BaKBiO may be explained in the context of an electron–phonon coupling mechanism [1], several alternative approaches have been proposed [2–5]. All these alternative models are primarily based on charge fluctuation mechanisms. The charge disproportionation models and, in particular, the question of the valence state of Bi in BaPbBiO – BaKBiO have been actively discussed [6–18].

Claeson et al [10] and Boyce et al. [11] studied the Pb L_3 and Bi L_3 absorption edges for PbO , PbO_2 , BaPbBiO , BaBiO_3 , and Bi_2O_3 compounds. They found a strong similarity between the Bi L_3 and Pb L_3 edges in BaPbBiO and the same average edge position for Bi in BaPbBiO and BaBiO_3 . The authors have suggested a Bi^{+4} valence, though they mentioned that the Bi^{+5} standard is needed to confirm this suggestion. Later, Akhtar et al. [17] repeated

the measurements by Boyce et al. [11] using NaBiO_3 as a Bi^{+5} valence standard and concluded that the Bi valences is +4 or close to +4 in BaPbBiO – BaKBiO . Recently, we have reported the results of Pb(Bi) L_3 XANES studies of oxygen-deficient BaPbBiO and BaKBiO compounds [18]. It was found that in spite of the similarity in the Pb and Bi near-edge structures, the oxygen deficiency leads to larger changes in the Bi L_3 absorption edge than those of the Pb L_3 edge. A more detailed comparison study of the Bi and Pb L_3 XANES spectra with the varying oxygen content in BaPbBiO and BaKBiO to elucidate the charge disproportionation phenomenon in these compounds is the subject of our interest.

Another factor of primary importance is the local structure of the oxygen-deficient $\text{BaPbBiO}_{3-\delta}$ and $\text{BaKBiO}_{3-\delta}$. The local structure of the fully-oxygenated BaPbBiO and BaKBiO compounds has been investigated by several scientific groups [9–11,13–15]. However, no work has been published so far as far as we know, on the local structure study of oxygen-deficient perovskites.

In this paper we have studied the local environments of

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both the Pb and Bi atoms in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ ($x = 0, 0.25, 1$) and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$ as a function of oxygen deficiency, δ , using EXAFS spectroscopy.

2. Experiment

The $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x = 0, 0.25, 1$) ceramic samples were synthesised by the standard ceramic technology. The oxygen-rich $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ – $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ samples were then heated at 780°C and 400°C [19] respectively to prevent the evaporation of the metals for 6–8 h at a residual partial pressure of O_2 of 10^{-1} – 10^{-4} Torr. The oxygen losses were determined by thermogravimetry. The following oxygen-deficient samples were prepared: $\text{BaBiO}_{3-\delta}$ ($\delta = 0.05, 0.4$), $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{2.85}$, $\text{BaPbO}_{2.8}$, and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$ ($\delta = 0.02, 0.2$).

The XAS data were recorded on the EXAFS line of VEPP-3 at the Siberian Synchrotron Radiation Centre (SSRC), Budker Institute of Nuclear Physics (Novosibirsk, Russia). The storage ring was operated at an energy of 2.0 GeV and a current of 60–120 mA. The synchrotron radiation was monochromatised by a Si (111) double crystal. The energy resolution for a 0.2 mm slit was estimated to be ~ 2 –3 eV at 13 keV. The XAS data were taken at the Pb L_3 (13.035 keV) and Bi L_3 (13.418 keV) edges in the transmission mode at room temperature. The EXAFS spectra for the $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$ were also recorded at 80 K.

3. The near edge structure

3.1. Experimental results

First, we introduced a response function for the electronic structure at the Bi and Pb L_3 edges, taking into account the amount of oxygen vacancies. The normalised function to δ value may be written as:

$$\eta^{\text{Exp}}(E) = \{ \text{XANES}_{\text{norm}}(E) - \text{XANES}_{\text{vac}}(E) \} / \delta.$$

Here $\text{XANES}_{\text{norm}}(E)$ and $\text{XANES}_{\text{vac}}(E)$ denote the experimental XANES spectra for the oxygen-rich ($\delta \equiv 0$) and the oxygen-deficient samples, respectively. The both $\text{XANES}(E)$ functions correspond to the samples having the equal composition of x .

To compare the Bi L_3 and Pb L_3 XANES spectra, the energy scale of the Pb L_3 edge was made coincident with the energy scale of the Bi L_3 edge at the maxima of the first derivatives (see Fig. 1). The main changes of the $\eta^{\text{Exp}}(E)$ function occurred for the B and C features. The C feature exhibited a similar behaviour for all compounds. Variations of the B feature increase, while going from a metal phase ($\text{BaPbO}_{3-\delta}$ ($\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$), $\delta \leq 0.2$) to a semiconductor one ($\text{BaBiO}_{3-\delta}$).

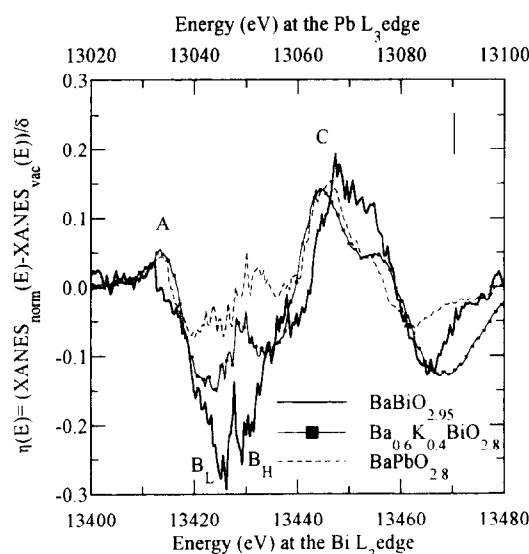


Fig. 1. The response functions normalised to the value of the oxygen deficiency, δ , of experimental spectra: for $\text{BaBiO}_{2.95}$ ($\delta = 0.05$), $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{2.8}$ ($\delta = 0.2$) at the Bi L_3 edge; and on the Pb L_3 edge for $\text{BaPbO}_{2.8}$ ($\delta = 0.2$). The energy scale of the Pb L_3 edge was made coincident with the energy scale of the Bi L_3 edge at the maxima of the first derivatives. The error in the relative energy position is ± 0.5 eV. The vertical bars denote the errors in the normalised spectra.

Thus, the Bi L_3 and the Pb L_3 edges exhibit a different behaviour with oxygen deficiency. We suppose that the Bi valence cannot be the same as the Pb valence (i.e. +4), as it was proposed by earlier studies [10,11,17]. Indeed, there are differences, for example, between the fine structure of the Bi L_3 edge in $\text{BaBiO}_{3-\delta}$ and the fine structure of the Pb L_3 edge in $\text{BaPbO}_{3-\delta}$ for the oxygen-deficient samples. It may be shown that some differences between the fine structure of the Bi L_3 edge and the fine structure of the Pb L_3 edge in BaPbBiO exist also for the oxygen-rich samples [20], although their scale is smaller than that of the oxygen-deficient samples. An increase in δ makes these differences more pronounced. The difference between the hybridisation of the Bi and O atoms and the hybridisation of the Pb and O atoms is supposed to be a possible reason of the different behaviour of the Bi L_3 and the Pb L_3 edges as the oxygen deficiency varies.

To clarify the reasons for the different behaviour of the Pb(Bi) L_3 edges as a function of oxygen deficiency, the single-electron multiple scattering calculations of the Bi(Pb) L_3 XANES spectra were carried out. Details of the calculations may be found in Ref. [21]. Here we give only the main results:

- 1) The experimental and calculated $\eta(E)$ functions for $\text{BaPbO}_{3-\delta}$ are in satisfactory agreement, while it should be noted there is a poor agreement of these functions for $\text{BaBiO}_{3-\delta}$.
- 2) According to the single electron MS calculations, the

small variations in $\eta^{\text{Calc}}(E)$ are suggested while going from $\text{BaPbO}_{3-\delta}$ to $\text{BaBiO}_{3-\delta}$. However, the experimental $\eta^{\text{Exp}}(E)$ functions are essentially different in $\text{BaPbO}_{3-\delta}$ and in $\text{BaBiO}_{3-\delta}$ (Fig. 1).

Thus, the different behaviour of the Pb L_3 and Bi L_3 edges versus the δ , that was observed experimentally, was not predicted by our single-electron calculations. At least two reasons may be proposed to explain this discrepancy: (i) there are strong distortions of the oxygen octahedra in the $\text{BaBiO}_{3-\delta}$ ($\delta > 0$), such that more than two sets of Bi–O distances occur upon oxygen reduction and (ii) the Bi L_3 XANES cannot be described adequately in the single-electron approximation, in contrast to the $\text{BaPbO}_{3-\delta}$ case.

In our opinion, an EXAFS study of the local structure vs. the oxygen deficiency, δ , is able to clarify the former of two reasons.

4. EXAFS results

4.1. EXAFS of unreduced samples ($\delta = 0$)

The EXAFS results concerning the non-reduced samples are in good agreement with previous reports [9–11,13–15]. A single Pb–O distance ($r = 2.16 \pm 0.01 \text{ \AA}$) was derived for the BaPb_2O_3 . Two separate Bi–O distances ($r_1 = 2.29 \pm 0.02 \text{ \AA}$, $r_2 = 2.12 \pm 0.02 \text{ \AA}$, $\Delta r \sim 0.17 \text{ \AA}$) were obtained for the BaBiO_3 . It should be emphasised that *two* Bi–O distances ($r_1 = 2.17 \pm 0.02 \text{ \AA}$, $r_2 = 2.10 \pm 0.02 \text{ \AA}$, $\Delta r \sim 0.07 \text{ \AA}$) exist in the $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ superconductor at 80 K.

4.2. EXAFS of oxygen-deficient samples

The Pb–O oxygen shell for $\text{BaPbO}_{3-\delta}$ ($\delta = 0.2$) was analysed assuming either one or two Pb–O distances. The $\chi(k) \cdot k^2$ function was fitted to a model function in k -space from 3 to 16 \AA^{-1} . A single Pb–O distance rather than two different distances was formed in $\text{BaPbO}_{3-\delta}$ ($\delta \leq 0.2$).

In the $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$ compound the oxygen reduction gives rise to a separation of the Bi–O distances ($\Delta r = r_{\text{Bi(1)-O(1)}} - r_{\text{Bi(2)-O(2)}}$) from $\Delta r = 0.07 \pm 0.02 \text{ \AA}$ at $\delta = 0.0$ to $\Delta r = 0.13 \pm 0.02 \text{ \AA}$ at $\delta = 0.15$.

A similar effect was observed for $\text{BaBiO}_{3-\delta}$ with a small amount of oxygen vacancies. The Δr was increased from 0.17 \AA at $\delta = 0.0$ to $\Delta r = 0.19 \text{ \AA}$ at $\delta = 0.05$. A good two-sphere fit was obtained. A partial amorphism of the $\text{BaBiO}_{3-\delta}$ was observed for a large value of δ ($\delta \geq 0.4$). Thus, the *two* sphere fit was found to be good at a small value of δ (at least at $\delta \leq 0.05$). On the contrary, more than two sets of Bi–O distances may exist, according to EXAFS data, at a higher oxygen deficiency ($\delta \geq 0.4$).

The $\chi(k) \cdot k^3$ functions of the Bi–O shell for $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$ ($\delta = 0, 0.2, 0.2$) are shown in Fig. 2.

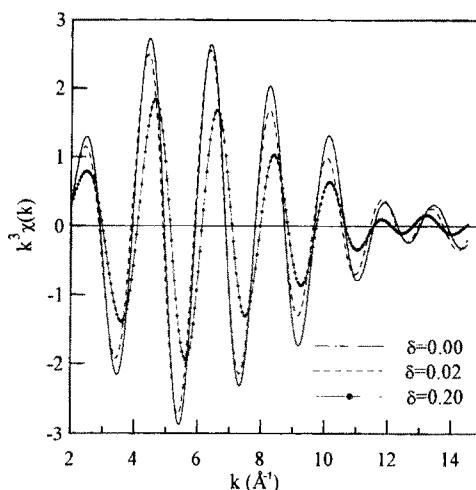


Fig. 2. The X-ray absorption fine structure from the Bi–O shell in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$ as a function of oxygen deficiency, δ . The Fourier transform range was $2\text{--}14.7 \text{ \AA}^{-1}$, square window. The back Fourier transform range in r -space was $1\text{--}2 \text{ \AA}$.

Small changes were found in $\chi(k) \cdot k^3$ at $\delta \sim 0.02$. Fitting over the range $k = [3\text{--}14] \text{ \AA}^{-1}$ gives a single distance $r = 2.14 \pm 0.01 \text{ \AA}$, as for the case of the non-reduced sample. Another result was observed first at $\delta \sim 0.2$. The beating at $k \sim 12 \text{ \AA}^{-1}$ and the abnormal phase changes at $k = 10\text{--}13 \text{ \AA}^{-1}$ imply that *two* distinct Bi–O distances must be formed. The two-sphere fitting results in $r_{\text{Bi(1)-O}} = 2.19 \pm 0.02 \text{ \AA}$, $r_{\text{Bi(2)-O}} = 2.12 \pm 0.02 \text{ \AA}$.

The Bi–O distances vs. the concentration of Pb(K) in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$) have been reported earlier by Boyce et al. [15]. The new EXAFS data allow us to extend this dependence on the oxygen deficient samples. The $\mathcal{R}(x, \delta)$ function describes the Bi–O bond lengths as a function of x, δ compositions in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$ (Fig. 3). The area of two (and more) Bi–O distances is hatched in the (x, δ) plane. A precise definition of its boundaries is the subject of a refinement in further studies.

5. Discussion

To summarise, the different dependence of the Bi L_3 and Pb L_3 near-edge structures on δ has been observed in $\text{BaPbBiO}_{3-\delta}$ and $\text{BaKBiO}_{3-\delta}$. The EXAFS data indicate that the local structure around the Bi sites is more sensitive to the varying oxygen stoichiometry than the local structure around the Pb sites. These peculiarities are perhaps due to the difference between the hybridisation of the Pb and O ions, on the one hand, and the hybridisation of the Bi and O ions, on the other.

It was found that the Pb–O bond exhibits no charge

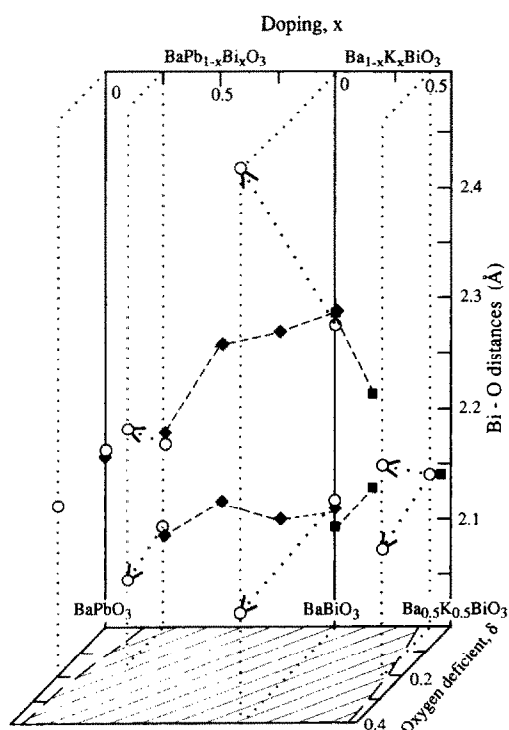


Fig. 3. The dependence of the Bi–O distances in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$ on the Pb(K) doping, x , and oxygen deficiency, δ , (the $\mathcal{M}(x, \delta)$ function). The Pb–O distance in $\text{BaPbO}_{3-\delta}$ is also shown as a function of δ . The EXAFS results presented (open circles) are given in combination with the data from Ref. [15] (diamonds) and from Ref. [13] (squares). Both the diamonds and squares are in the $\delta=0$ plane. In order to not overload the figure, we omitted the points corresponding to $\delta=0.05$ in $\text{BaBiO}_{3-\delta}$ and $\delta=0.02$ in $\text{Ba}_{0.6}\text{K}_{0.4}\text{O}_{3-\delta}$. Variations of the Bi–O distances with δ are schematically shown by arrows. Note that the single Bi–O distance was found in the superconducting $\text{Ba}_{0.8}\text{K}_{0.2}\text{BiO}_{3-\delta}$ ($\delta=0.02$).

disproportionation and the Pb valency is +4 [10,11,15,17,18]. At the same time, questions related to charge disproportionation in Bi–O complexes and, in particular, of the Bi valence, are matters of active discussion [6–18].

One can find two approaches related to the Bi ion disproportionation:



where Δ is a small positive value.

The former is based on the results derived by Cox and Sleight [6] who determined the crystal structure of BaBiO_3 using neutron diffraction. They have shown that Bi occupies two distinctive sites with different bond lengths and suggested the $\text{Ba}_2(\text{Bi}^{+3}\text{Bi}^{+5})\text{O}_6$ valency disproportiona-

tion. These results were supported by X-ray absorption studies [12,16]. However, XPS results [8] do not give any appreciable amount of charge transfer. The L_3 XANES studies of Claeson [10], Boyce [11], Ahktar [15] could find no Bi disproportionation and concluded that the Bi valence is +4 or close to +4. However, according to model (2), some localised magnetic moment should be on the Bi ions, even if one takes into account the covalence of the Bi–O bond. No magnetic ordering was observed in BaPbBiO , BaKBiO in muon spin rotation experiments [22].

Thus, there are experimental data against both the $2\text{Bi}^{+4} \rightarrow \text{Bi}^{+3} + \text{Bi}^{+5}$ and the $2\text{Bi}^{+4} \rightarrow \text{Bi}^{+4+\Delta} + \text{Bi}^{+4-\Delta}$ models.

Recently, the following Bi disproportionation model has been proposed by Ignatov [20]:



where \underline{L}^2 denotes two holes on the O 2p orbitals. These holes spread *dynamically* around six oxygen atoms, surrounding the Bi ion.

It should be noted that the idea of holes on the O 2p orbital in BaPbBiO and BaKBiO is not new. The charge density ordering of holes on the oxygen sites was first proposed by Mattheiss and Hamann [23] for BaPbBiO . They have shown that the energy E_s needed to put a hole on the Bi 6s orbital, is over 2 eV higher than the energy E_p needed to put a hole on the O 2p one. Direct experimental evidence of the O 2p holes was obtained by Salem-Sugui et al. [14] from the oxygen K-edge measurements on BaKBiO .

The detailed description of the disproportion model (3) required a many-body approach which is beyond the scope of the present paper and will be published elsewhere. Here we would like to illustrate that the experimental XAS data are in agreement with model (3).

The presence of holes on the oxygen 2p orbitals must lead to a decrease in its activation energy,

$$E_a \propto E_{\text{Coul}} \sim \sum_i \frac{Z_{\text{ef}}^o \cdot Z_{\text{ef}}^i}{R_i},$$

since the effective charge on the oxygen atom with holes is less than the effective charge on the usual oxygen atom. Here Z_{ef}^o , Z_{ef}^i are the effective charges on the oxygen atom and the i th surrounding atom, respectively; R_i is the interatomic distance.

Thus, in the frame of model (3), the oxygen atoms must release predominantly from $\text{Bi}^{+3}\underline{L}^2\text{--O}_6$ complexes and, hence, destroy the electronic and local structure of these complexes. This simple consequence from model (3) is in good agreement with XAS experimental results. The XAS is a *locally sensitive* spectroscopy, it probes the local electronic and crystal structures within 4–5 Å around the absorption atoms of a definite type. The more pronounced variations in the XANES and EXAFS spectra at the L_3 Bi edge than those at the L_3 Pb edge indicate that the main

changes in oxygen reduction take place in the electronic and local structures of Bi–O complexes.

Model (3) explains the poor agreement between the calculated and the experimental Bi L_3 edges of $\text{BaBiO}_{3-\delta}$, while the calculated and the experimental Pb L_3 Pb edges of $\text{BaPbO}_{3-\delta}$ are in good agreement. We suppose that these discrepancies are due to the limitation of the single-electron description of the Bi L_3 edge spectrum. A many-body description of $\text{Bi}^{+3}\underline{L}^2$ complexes and, hence, the electronic structure, including Bi L_3 XANES, of BaPbBiO and BaKBiO is necessary.

Finally, let us discuss briefly the most general modifications of the local crystalline structures in BaPbBiO and BaKBiO upon oxygen reduction.

It is well known that in BaPbBiO and BaKBiO the charge ordering is closely related to the distortions of the local structure [11,14,15]. In the BaPbBiO and BaKBiO alloys the carriers are supposed to be partly localised, partly itinerant. Extra carriers supplied by Pb(K) doping modify the charge distribution and the bond length. The separation of the Bi–O distances ($\Delta r = r_{\text{Bi}(1)-\text{O}} - r_{\text{Bi}(2)-\text{O}}$) in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x > 0.25$) and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, ($x < 0.4$), determined from EXAFS, was found to decrease with increasing of Pb(K) doping [15]. The localisation of an extra charge due to the oxygen vacancies [24] should bring an opposite effect, so that an increase of Δr value should be observed with oxygen reduction. Our EXAFS data did show an increase of such a separation in $\text{BaBiO}_{3-\delta}$ ($\delta = 0.05, 0.4$) and in $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{2.85}$ (Fig. 3).

Two Bi–O distances rather than the single one were found in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{2.8}$. This result is different from the X-ray diffraction studies of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$ by Ueki et al. [25] and Idemoto et al. [19]. Both works reported a cubic symmetry with increasing the oxygen deficiency, δ , even for the δ value causing the superconductivity suppression. The Bi–O bond lengths were found not to be split [19,25]. The strong local distortions of crystalline structure were obtained also for $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{2.85}$ and $\text{BaBiO}_{2.6}$. EXAFS data pointed out that the symmetry of the unit cell in these compounds seems to be non-cubic. A possible reason for such a discrepancy is the different sensitivities of X-ray diffraction and X-ray absorption spectroscopy to the variations in the local structure. Oxygen vacancies are expected to bring about a mainly *local disorder*. The displacement of the atoms surrounding an oxygen vacancy from their primary crystallographic position may be ordered over a *short range* and, hence, might not appear in long-range order experiments.

From our EXAFS experiments, we cannot conclude whether the Bi–O distance distortions are static or dynamic. A temperature-dependent study should be done. It may be noted that if static distortions dominate in the semiconducting $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$, the EXAFS results in combination with X-ray diffraction data [19,25–27] might point out a *local phase separation*

in these compounds. In this connection, the cluster model is supposed to be the most suitable to describe the electronic and local structures of the oxygen-deficient $\text{BaPbBiO}_{3-\delta}$ and $\text{BaKBiO}_{3-\delta}$ compounds.

6. Conclusion

We have studied the electronic and local structures of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ ($x = 0, 0.25, 1$) and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{3-\delta}$ as a function of oxygen deficiency, δ , by means of X-ray absorption measurements at the Pb L_3 and Bi L_3 edges.

The XAS results indicate that the electronic and local structures around the Bi sites are more sensitive to the oxygen stoichiometry variation than those around the Pb sites. This means that oxygen vacancies leave the Bi–O complexes more easily than the Pb–O ones. We suggest that the difference between the hybridisation of the Bi and O atoms and that of the Pb and O atoms is due to the observed peculiarities. The experimental data may be reasonably explained assuming a charge disproportionation scheme $2\text{Bi}^{+4} \rightarrow \text{Bi}^{+3} + \text{Bi}^{+3}\underline{L}^2$ in BaPbBiO and BaKBiO , where \underline{L}^2 denotes the spread of two holes on 2p orbitals of six oxygen atoms, surrounding the Bi ion.

The local structure of oxygen deficient compounds has been found to be essentially different from the crystalline structure refined from diffraction data. The oxygen reduction leads to an increase of Bi–O distance separation in $\text{BaBiO}_{3-\delta}$ and $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_{3-\delta}$. Two distances ($r_{\text{Bi}(1)-\text{O}} = 2.19 \pm 0.02 \text{ \AA}$ and $r_{\text{Bi}(2)-\text{O}} = 2.12 \pm 0.02 \text{ \AA}$) were found in a semiconducting $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_{2.8}$. The oxygen vacancies are expected to bring about a mainly *local disorder*. The displacement of the atoms surrounding oxygen vacancy from their primary crystallographic position may be ordered over a *short range* and, hence, might not appear in long-range order experiments.

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