EXAFS OF THE SUPERCONDUCTING OXIDE $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$

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The two-valence state $\text{Bi}^{3+}$ and $\text{Bi}^{5+}$ of Bi in the semiconductor $\text{BaBiO}_3$ and in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x = 0, 0.25, 0.6$ and $1$) system has been determined from the EXAFS spectra above the $L_{\text{III}}$-edges of Ba, Pb and Bi. Peaks in the radial distribution function up to $5\,\text{Å}$ from the absorber have been identified through a model calculation using theoretical amplitudes and phase shifts and the interatomic distances from neutron diffraction measurements. We found indication of local disorder in the Pb–Bi sublattice for the mixed compound.

1. INTRODUCTION

SINCE THE DISCOVERY of the superconductivity in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system [1] the question concerning the valence state of Bi in this compound has taken on great importance. Solid solutions $\text{BaPbO}_3$–$\text{BaBiO}_3$ have a distorted perovskite-type structure at room temperature which varies from orthorhombic–tetragonal–orthorhombic–monoclinic as a function of increasing $x$ and superconductivity is confined to the tetragonal phase [2].

For many years the question of the oxidation state of Bi in $\text{BaBiO}_3$ [3–5] was unresolved. Lately, independent neutron diffraction studies by Thornton and Jacobson [6] and Cox and Sleight [7] showed that the unit cell of $\text{BaBiO}_3$ is monoclinic and contains four formula units, Fig. 1(a). A striking feature of this structure is that Bi ions occupy two quite distinct sites with average nearest-neighbor oxygens at 2.28 and 2.12 Å, which is consistent with the valence configuration $\text{Ba}_2\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_6$ [7]. The corresponding plot of the thermal ellipsoids of $\text{BaBiO}_3$ is shown in Fig. 1(b). Concerning the mixed compounds $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($x \neq 0, 1$), the valence state configuration of Bi is still an open problem as well as the degree of order of the bismuth–lead sublattices. These issues are relevant to understand the electronic structure [8] and the mechanism of the superconductivity in this material [9, 10].

![Fig. 1. (a) Double unit cell of the monoclinic distorted perovskite-type structure of $\text{BaBiO}_3$ at $T = 300$ K. (b) ORTEP thermal ellipsoids of $\text{BaBiO}_3$ at 419 K showing one octant of the face-centered cell (from [7]).](image-url)
From the analysis of the EXAFS spectra above the L_{III} edges of Ba, Pb and Bi we demonstrate that: (1) oxygen occupies average different positions around Bi which gives clear support to the double valence of Bi in the mixed compound, (2) around each absorber there is no indication of a strong lattice disorder in BaBiOs and BaPbO_{3} at least up to 5 Å. However, we find evidence of some disorder in the further (∼4.4 Å) Pb–Bi shell in BaPb_{1-x}Bi_{x}O_{3} (x = 0.25 and 0.6).

2. EXPERIMENTAL

The compounds BaPb_{1-x}Bi_{x}O_{3} with x = 0, 0.25, 0.6 and 1 were prepared in Moscow Engineering Physics Institute by using the conventional ceramic technology [12]. The temperature dependence of the resistivity $\rho(T)$ showed superconducting properties ($T_{c} \approx 13$ K) for x = 0.25, typical semiconducting behaviour for x = 0.6 and 1 and semimetallic behaviour for BaPbO_{3}. Powders suitable for EXAFS measurements were prepared by mixing BaPb_{1-x}Bi_{x}O_{3} with a small amount of HBO_{3}. The effective thickness d of the samples was chosen from the condition $1 \leq \mu d \leq 3$, where $\mu$ is the atomic absorption coefficient above the interesting core edge. The source of soft X-rays was the storage ring Adone operated at 1.5 GeV and 50 mA. The X-rays were monochromatized by a Si(2 2 0) channel-cut single crystal at about 17 m from the tangent point. Further experimental details have been reported elsewhere [13]. EXAFS spectra were collected above the $L_{III}$-edges of Ba (5247 eV), Pb (13,035 eV) and Bi (13,418 eV). The experimental region scanned — typically 10 Å^{-1} from each edge — was limited by the occurrence of the Ba $L_{III}$-edge for Ba, of the Bi $L_{III}$-edge for Pb and by the maximum photon energy available (14,500 eV) for Bi. These boundaries set a limit to the
3. RESULTS AND DISCUSSION

The measured EXAFS spectra above the $L_{III}$-edge of Ba and the corresponding radial distribution functions $F(R)$ for BaPb$_{1-x}$Bi$_x$O$_3$ ($x = 0, 0.25$ and 1) are shown in Figs. 2(a) and 2(b), respectively. To identify the peaks in $F(R)$ we resorted to a model $\chi(k)$ built with amplitudes and phase shifts from Teo and Lee tabulations [14] and interatomic distances from neutron diffraction data [6, 7, 15] for the model compounds BaPbO$_3$ and BaBiO$_3$. For BaPbO$_3$ the simulated spectrum shows that the first peak arises from O atoms, the second from Pb and the third is due to the superposition...
of Ba and Pb shells. The doublet at 2.95 and 3.75 Å is due to the shape of the backscattering amplitude characteristic of the heavy elements [11] and therefore is referred to as a single Ba-Pb distance. Similarly, a single Ba-Bi(Pb) distance is found in BaBiO₃ and BaPb₀.₇₅Bi₀.₂₅O₃. In BaBiO₃ the nearest-neighbor oxygen shell consists of three peaks, which is consistent with the existence of three (or more) inequivalent sites for the oxygen ions in accordance with the two-valence model by Cox and Sleight [4] for Ba₂Bi⁴⁺Bi⁵⁺O₆.

Additional information is obtained from the analysis of the L_{III}-edges of Pb and Bi, shown in Fig. 3 for compounds with x = 0, 0.25, 0.6 and 1. The identification of the FT peaks was made from simulation which showed that the four main peaks in the BaPbO₃ radial distribution function arise from O, Ba, superposition of Ba and Pb, and Pb. The weak structure marked (†) is due to the limited k-region of the FT and to the use of a Hanning window function. Using a Gaussian window such a peak disappears but, as usual, the overall resolution worsens.

In both BaPbO₃ and BaBiO₃ radial distribution functions the fourth peak, which corresponds to the Pb-Bi subshell, is sharp. The substitution of Bi for Pb [see Fig. 3(b) x = 0.25] leads to the disappearance of this peak. The same result takes place when Pb substitutes Bi in BaBiO₃ [see Fig. 3(b) x = 0.6]. This fact is taken as indicative of some disorder in the Pb-Bi sublattice for the mixed compounds.

The FT of the BaBiO₃ spectrum clearly shows the oxygen peak split into two shells. According to the simulation, the separation of these shells ΔR = 0.2 Å is in good agreement with Cox and Sleight [4] neutron diffraction data. This splitting is additional evidence of the two-valence state of Bi in BaBiO₃.

For BaPb₀.₄Bi₀.₆O₃ the first oxygen shell around Bi is unresolved and the corresponding peak of F(R) occurs at a lower distance than the Pb-O peak in BaPb₀.₇₅Bi₀.₂₅O₃. However, the nearly coincidence of the Bi-Ba and Pb-Ba peaks in both these spectra shows that the difference between the phase shifts of Bi and Pb absorbers is negligible. Thus the average distances of the oxygen ions are actually different around Pb and Bi.

Lead enters the lattice substitutionally to bismuth, in Pb⁴⁺ valence state, as suggested by the fact that the positions of the Pb-O peak coincide in both BaPbO₃ and BaPb₀.₇₅Bi₀.₂₅O₃ spectra. Apparently the Bi⁴⁺(Bi⁵⁺)-O bond lengths are modified by Pb so that the oxygen doublet, exhibited by BaBiO₃, reduces to a single peak at an intermediate distance which differs from the Pb-O distance. This result could indirectly support a double valence state for bismuth in mixed compounds.

4. CONCLUSIONS

We have shown that a detailed analysis of the EXAFS spectra of BaPb₁₋ₓBiₓO₃ above the L_{III}-edges of Ba, Pb and Bi gives new additional evidence of two-valence state of Bi in BaBiO₃ and in the mixed compounds. It was also found that some disorder exists in the local environment of Pb-Bi sublattices which can, in principle, create local fluctuations of the density of states. This may be important for understanding the mechanism of conductivity and superconductivity in this system.

Further information is contained in the analysis of the X-ray absorption near edge structure (XANES) which will be presented in a separate paper. 

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REFERENCES