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## X-ray absorption near-edge studies of $\text{BaBiO}_3$ , $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ systems

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**Abstract.** The valence state of Bi in pure and doped (Pb, K)  $\text{BaBiO}_3$  has been determined by x-ray absorption near-edge structure (XANES) spectroscopy. In all materials the Bi valence is found to be close to IV. A disproportionation of Bi(IV) into Bi(III) and Bi(V) is not indicated by analysis of the XANES data. The valence state of Pb is also found to be IV in  $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ .

### 1. Introduction

Since the discovery by Sleight *et al* (1975), that Pb-doped  $\text{BaBiO}_3$  shows superconductivity up to 13 K, and the subsequent observation of superconductivity up to 30 K in K-doped  $\text{BaBiO}_3$  (Cava *et al* 1988, Hinks *et al* 1988), the valence state of Bi in  $\text{BaBiO}_3$  has remained in dispute. The crystal structure of  $\text{BaBiO}_3$  was determined by Cox and Sleight (1976, 1979) using powder neutron diffraction. They showed that Bi occupies two distinctive sites, having bond lengths of  $\text{Bi}(1)\text{--O} = 2.28 \text{ \AA}$  and  $\text{Bi}(2)\text{--O} = 2.12 \text{ \AA}$ . This suggests valence disproportionation, that is, Bi(1) corresponds to Bi(III) and Bi(2) to Bi(V). These results were supported by neutron diffraction studies (Thornton and Jacobson 1978) and x-ray absorption studies (Balzarotti *et al* 1984, Kulkarni *et al* 1990, Flavell *et al* 1992). However, analysis of the neutron diffraction data of Chaillout *et al* (1985, 1988) indicated that the Bi–O bond lengths do not differ by more than 0.01  $\text{ \AA}$ ; and these authors proposed that Bi in  $\text{BaBiO}_3$  has a valence state of IV. The results were supported by x-ray photoelectron spectroscopy (Wertheim *et al* 1982), and band structure calculations (Mattheiss and Hamann 1983).

Zhang and Catlow (1991) predicted from computer simulation studies that the charge disproportionation energy for Bi is very high, suggesting that in  $\text{BiBaO}_3$  the valence state of Bi is IV. X-ray absorption studies of Claeson *et al* (1989) and Boyce *et al* (1990) also supported this valence state. However, these latter results are inconclusive as no comparison was made with compounds containing Bi(V). In addition no previous studies have collected XANES data on K-doped compounds. XANES has been used in past to study the valence state of Cu in high- $T_c$  cuprates, (Alp *et al* 1987, Tranquada *et al* 1987). In the present study we employ XANES spectroscopy to investigate both Bi and Pb in  $\text{BaBiO}_3$ ,  $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$  and  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  systems, in order to determine their valence state in the pure and doped material.

### 2. Sample preparation

$\text{BaBiO}_3$  powders were prepared from  $\text{BaCO}_3$  and  $\text{Bi}_2\text{O}_3$  taken in appropriate amounts and

then mixed and ground in acetone and heated at 800 °C in air for one day. Following cooling to room temperature, they were reground and again heated under the same conditions (Chaillout *et al* 1988).

Powders of  $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$  (where  $x = 0.75$  and  $0.70$ ), were prepared from  $\text{Bi}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{PbO}_2$  which were mixed and ground for 30 minutes in acetone, and then heated at a temperature of 800 °C for one day. After the first heat treatment, the sample was reground and fired at 850 °C for one day. Following the approach of Khan *et al* (1977) the samples were reground for a third time and heated at 930 °C for one day.

Samples of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  (where  $x = 0.4$  and  $0.5$ ) were prepared by mixing the appropriate amounts of  $\text{BaO}$ ,  $\text{K}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$  in acetone. The mixture was placed in an alumina crucible and heated under flowing nitrogen at 700 °C for one hour. It was then cooled to room temperature, while still in flowing nitrogen, after which the atmosphere was changed to oxygen with heating at 425 °C for one hour followed by slowly cooling to room temperature. After one heat treatment in the presence of nitrogen and oxygen, the material was reground and again heated under the same conditions (Hinks *et al* 1988, 1989). In order to obtain a uniform material we used several cycles of regrinding and refiring, using a nitrogen–oxygen firing sequence. Finally, x-ray diffraction was carried out for each sample to verify that a single-phase material had been prepared.

### 3. XANES spectroscopy

X-ray absorption edges contain a variety of information on the chemical state and the local structure of the absorbing atom. On the higher energy side of an absorption edge fine structure is observed due to backscattering of the emitted photoelectrons. Two regions are distinguished: the extended x-ray absorption fine structure (EXAFS) typically covers an energy range up to hundreds of eV above the edge, and yields information on the radial distribution of atoms surrounding the central atom (Lee and Pendry 1975, Stern *et al* 1975). However, within 50 eV of an absorption edge, the spectrum is interpreted in terms of the appropriate components of the local density of states, which should be sensitive to the valence state of the atom. In this near edge region (XANES) absorption modulations are strong due to multiple scattering (Durham *et al* 1982, Bianconi 1983). XANES has been successfully employed to determine the valence states in mixed valence compounds (see, for example, Belli *et al* 1980, Martin *et al* 1980, Launois *et al* 1980, Bianconi 1981, Davoli *et al* 1983). A direct comparison of the absorption edges for atoms of interest with known model compounds gives information on the electronic charges of atoms in different systems.

### 4. XANES data and discussion

The XANES experiments were performed at the SERC Daresbury Laboratory, UK using station 9.2 of the Synchrotron Radiation Source (SRS). The SRS ran at 2 GeV with a typical beam current of 150 mA. All XANES spectra reported in this study were taken in transmission mode and at room temperature. Data were collected for Bi and Pb edges for a variety of systems as detailed below.

In the present study the model compounds used were  $\text{Bi}_2\text{O}_3$  and  $\text{NaBiO}_3$  for Bi(III) and Bi(V) and  $\text{PbO}$  and  $\text{PbO}_2$  for Pb(II) and Pb(IV) respectively. Figure 1 shows normalized spectra of the Bi  $L_{III}$  edges of  $\text{Bi}_2\text{O}_3$ ,  $\text{BaBiO}_3$ ,  $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$  and  $\text{NaBiO}_3$ ; and in figure 2 we compare the K-doped materials with the model compounds. From these figures we note that the Bi edge in  $\text{Bi}_2\text{O}_3$  is different from that for pure and doped  $\text{BaBiO}_3$  at the edge position; similarly,  $\text{NaBiO}_3$  has a pre-edge feature which is absent in all other spectra;

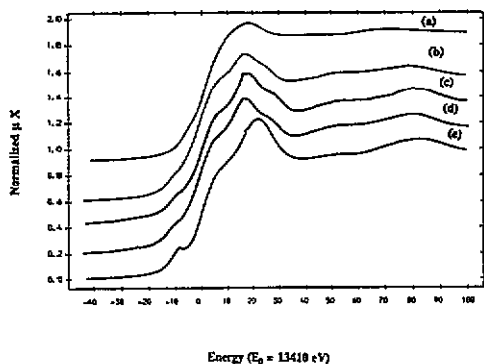


Figure 1. The x-ray absorption at the Bi  $L_{III}$  edges of (a)  $Bi_2O_3$ , (b)  $BaBiO_3$ , (c)  $BaBi_{0.25}Pb_{0.75}O_3$ , (d)  $BaBi_{0.3}Pb_{0.7}O_3$  and (e)  $NaBiO_3$ .

moreover this material shows a pronounced edge shift in its spectrum, when compared with all other samples, indicating a clear difference in the valence state. These results suggest that the valence state of Bi in  $BaBiO_3$  system does not resemble that of  $Bi_2O_3$  (Bi(III)) or  $NaBiO_3$  (Bi(V)). In figure 3 we compare Pb spectra ( $L_{III}$  edge) in  $BaBi_{1-x}Pb_xO_3$  with  $PbO$  (Pb(II)) and  $PbO_2$  (Pb(IV)). The Pb spectrum in  $BaBi_{1-x}Pb_xO_3$  resembles that of  $PbO_2$  suggesting that the valence state of Pb in  $BaBi_{1-x}Pb_xO_3$  is close to (IV). It is also of interest to compare the Bi spectra (in all  $BaBiO_3$  compounds) with the Pb spectra in  $PbO_2$  and  $BaBi_{1-x}Pb_xO_3$ . We find that the spectra for the two edges are very similar which suggests that both species have the same valence state of IV.

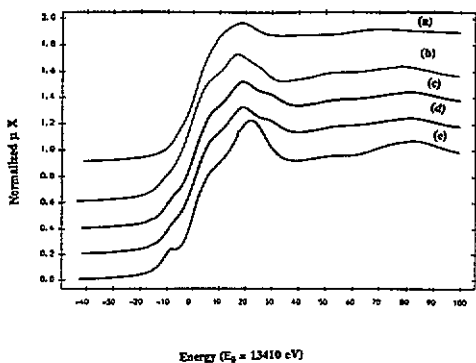


Figure 2. The x-ray absorption at the Bi  $L_{III}$  edges of (a)  $Bi_2O_3$ , (b)  $BaBiO_3$ , (c)  $Ba_{0.6}K_{0.4}BiO_3$ , (d)  $Ba_{0.5}K_{0.5}BiO_3$  and (e)  $NaBiO_3$ .

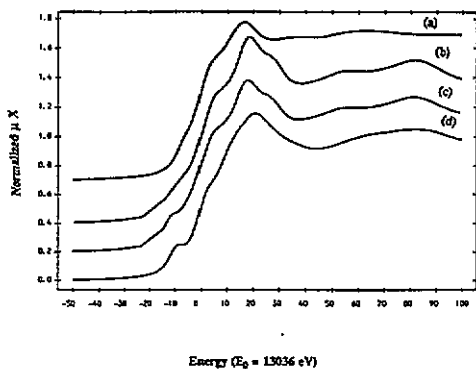


Figure 3. The x-ray absorption at the Pb  $L_{III}$  edges of (a)  $PbO$ , (b)  $BaBi_{0.25}Pb_{0.75}O_3$ , (c)  $BaBi_{0.3}Pb_{0.7}O_3$  and (d)  $PbO_2$ .

In summary, our XANES spectroscopic studies suggest that the Bi valence state is close to (IV) both in doped (Pb, K) and in pure  $BaBiO_3$ . Our conclusions coincide with those of Hedge *et al* (1989) who on the basis of XPS data concluded that there was no evidence for charge disproportionation in  $BaBiO_3$ , but disagree with those of Flavell *et al* (1992) who reported that Pb doping increases Bi(V) in  $BaBi_{1-x}Pb_xO_3$ . This disagreement can be attributed at least in part to differences in the quality of the data. Our spectra were collected on SRS station 9.2 (Wiggler line), giving data which are better resolved and able to show the

edge features which distinguish Bi(III) from Bi(V) valence states; whereas data of Flavell et al (1992) which were collected on station 7.1 do not clearly show these features. Both Bi and Pb have valence states close to (IV), therefore, when Pb is substituted at Bi sites, isovalent substitution occurs. In contrast when  $K^+$  is doped at  $Ba^{2+}$  sites, a species with an effective negative charge is created. If this effective charge is compensated electronically, a hole species must be formed. The Bi XANES are unaffected by K doping suggesting that such holes are formed on the oxygen sublattice, a result that is consistent with predictions of Zhang and Catlow (1991).

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