

State of bismuth in BaBiO₃ and BaBi_{1-x}Pb_xO₃: Bi4f photoemission and BiL 3 absorption spectroscopic studies

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State of bismuth in BaBiO_3 and $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$: Bi 4f photoemission and Bi L_3 absorption spectroscopic studies

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The $2p\ 6d$ feature in the Bi L_3 spectra has different energies in the semiconducting ($0.0 \leq x < 0.7$) and the superconducting ($x = 0.75$) compositions of $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$. The Bi $4f$ core level spectrum shows distinct features ascribable to Bi III and Bi V in BaBiO_3 and in the semiconducting compositions; the width of the $4f$ peaks is also considerably larger in these compositions compared to that in $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$, which shows a single sharp Bi $4f$ feature.

$\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ is a classic example of an oxide system where superconductivity occurs at the metal-insulator boundary.¹⁻³ While BaPbO_3 ($x = 1.0$) with an empty Pb $6s$ band is metallic, BaBiO_3 ($x = 0.0$) is a semiconductor although it has a half-filled Bi $6s$ band. Semiconducting properties of the compositions from BaBiO_3 to $\text{BaBi}_{0.3}\text{Pb}_{0.7}\text{O}_3$ is due to the presence of Bi III and Bi V states giving rise to a charge-density wave. There is considerable evidence for the presence of a charge-density wave in this composition range.² Unlike in the semiconducting compositions ($0.0 \leq x < 0.70$), Bi in the superconducting compositions of $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ is expected to be in a delocalized IV state. There is increasing interest in the mechanism of superconductivity in the $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ system in recent months, but there has been no direct spectroscopic evidence for the disproportionation of Bi IV into Bi III and Bi V in the semiconducting compositions. In this communication, we discuss the results of our study of semiconducting and superconducting compositions of $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ by employing both x-ray absorption spectroscopy and x-ray photoemission spectroscopy, earlier reports^{4,5} based on such studies not being conclusive. Wertheim *et al.*⁵ found the Bi III and V states in BaBiO_3 to be marginally distinguishable and suggested the need for further investigation of the $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ system, with samples suitably prepared under vacuum.

$\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ compositions with $x = 0.0, 0.25, 0.5, 0.75$, and 1.0 were prepared by mixing appropriate quantities of Bi_2O_3 , BaO_2 , and PbO_2 and heating the mixture initially at $770\ \text{K}$ for $24\ \text{h}$ followed by regrinding, pelletizing, and heating the pellets at $1020\ \text{K}$ in a bed of powder of the same composition. The samples were characterized by powder x-ray diffraction and four-probe resistivity down to $4.2\ \text{K}$. The sample with the composition $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$ ($x = 0.75$) showed superconducting at $12\ \text{K}$. Bi L_3 and Pb L_3 absorption edge spectra were recorded using an x-ray absorption spectrometer (Rigaku, Japan) with a rotating anode x-ray generator (Ru-200B, Rigaku, Japan). A Si (440) crystal was used as a monochromator with a $0.1\ \text{mm}$ slit. Samples for these studies were prepared by sandwiching an appropriate amount of finely ground

powder between adhesive tapes, ensuring uniform thickness and an absorption jump of ~ 1.0 . X-ray photoemission spectra were recorded on a VG ESCA3 Mark II spectrometer using Mg $K\alpha$ radiation. The samples were scraped with a ceramic scraper at $300\ \text{K}$ in the high vacuum chamber (6×10^{-10} Torr).

In Fig. 1 we show the Bi L_3 absorption edge spectra of the two reference oxides, Bi_2O_3 and NaBiO_3 , where the Bi is in III and V states, respectively. In these two bismuth oxides, the main $2p\ 6p$ transition energy differs by $\sim 9\ \text{eV}$. The spectrum of NaBiO_3 shows an additional pre-edge feature due to the $2p\ 6s$ transition arising from the empty $6s$ band. This pre-edge feature cannot be used to distinguish the semiconducting and superconducting composition of $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ since the $6s$ state is partly or fully empty in all of them and would therefore show some intensity. What is interesting is that BaBiO_3 as well as the semiconducting $x = 0.25$ and $x = 0.5$ compositions show the $2p\ 6d$ feature in between that due to Bi III and Bi IV (Fig. 1). The $2p\ 6d$ feature in the superconducting $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$ has an energy closer to Bi V. We thus see a distinction in the $2p\ 6d$ transition energy of the superconducting ($x = 0.75$) and the semiconducting ($0.0 \leq x < 0.7$) compositions. This result is different from that of Cheson *et al.*⁴ who seem to find almost identical Bi L_3 spectra for BaBiO_3 and $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$. It should be noted, however, that in all the $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ compositions studied by us, the Pb L_3 spectra are comparable with the spectrum of BaPbO_3 (see inset of Fig. 1).

Although Bi L_3 absorption spectroscopy delineates the semiconducting and the superconducting compositions of $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$, it does not provide a definitive proof for the occurrence of Bi III and Bi V states in the BaBiO_3 and the semiconducting compositions or for the delocalized Bi IV state in the superconducting compositions. We have, therefore, examined the Bi $4f$ photoemission spectra of these compounds. In Fig. 2, we show the Bi $4f$ photoemission spectra of BaBiO_3 and the superconducting $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$ along with the spectrum of NaBiO_3 . We also show the peak positions in the Bi $4f$ photoemission spectrum of Bi_2O_3 in the figure. We see that the energy corresponding to the main peak in the spectrum of BaBiO_3 as well as of the superconducting $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$ is close to that of Bi III in Bi_2O_3 . However, we see a distinct

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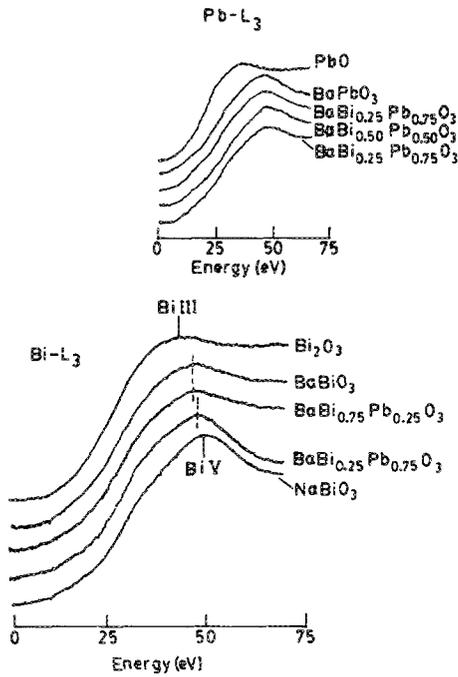


FIG. 1. Bi L_3 absorption spectra of $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ and of the reference oxides, Bi_2O_3 and NaBiO_3 . Inset shows Pb L_3 spectra of $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$.

shoulder-like feature on the high-energy side in BaBiO_3 close to where NaBiO_3 with Bi in the V state exhibits its main feature. Furthermore, the full width at half maximum (FWHM) in BaBiO_3 is quite large (2 eV). The Bi $4f$ spectra of the semiconducting $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ ($x = 0.25$ and 0.5) were similar to the spectrum of BaBiO_3 with only a slightly smaller FWHM (1.8 eV). On the other hand, the Bi $4f$ peak of superconducting $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$ ($x = 0.75$) is narrower (FWHM, 1.6 eV) with no shoulder in the Bi V region (see Fig. 2), suggesting that there is no charge separation in this composition. It is to be noted that the FWHM in the case of NaBiO_3 is 1.5 eV. Broadening of the Bi $4f$ features in the spectrum of BaBiO_3 had been reported earlier,^{5,6} but the spectrum could not exactly be fitted by assuming the presence of two Bi states. Not much information is available from these studies on the Bi $4f$ spectra of $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ compositions, except that they were also broader. The present photoemission results, however, show that the state of bismuth in superconducting $\text{NiBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$ is clearly different from that in the semi-

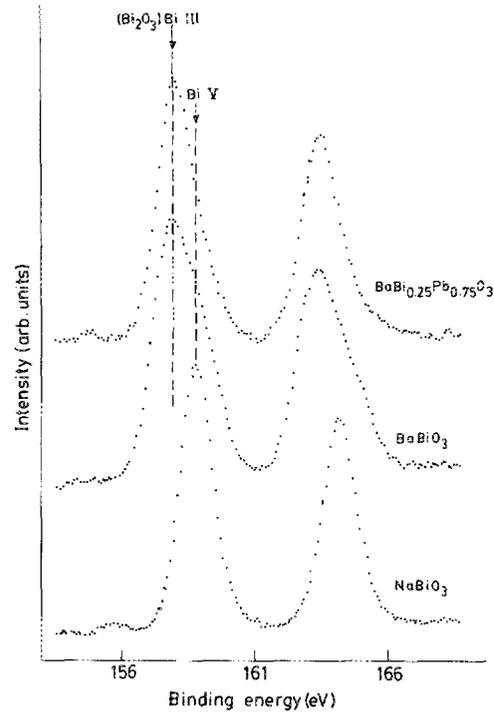


FIG. 2. Bi $4f$ core level spectra of BaBiO_3 , $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$, and NaBiO_3 . Positions of the features due to Bi III and Bi_2O_3 are also shown.

conducting compositions of $\text{BaBi}_{1-x}\text{Pb}_x\text{O}_3$ ($0.0 < x < 0.70$), the latter showing a shoulder in the region of Bi V of the Bi $4f$ spectrum in addition to a main feature appearing close to that of Bi III in Bi_2O_3 .

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