

Structural characterization and electrical resistance of the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system

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The electrical resistance $R(T)$ in function of temperature T , and X-ray powder diffraction (XRD) patterns of polycrystalline samples of the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system have been described. $R(T)$ measurements of single phase samples show that BaPbO_3 exhibits metal-like properties, and that the system exhibits superconductivity in the $0.005 < x < 0.30$ range, but insulating properties for $x > 0.30$. A careful analysis of the onset of the critical temperature (T_C) reveals its strong dependence on the sample composition in the range $0.005 < x < 0.30$ which may be related to the superconducting volume fraction ultimately leading to connected or disconnected superconducting clusters, similar to those observed in granular superconductors.

Keywords: *electrical conductance; XRD patterns; superconductivity; superconducting clusters*

1. Introduction

In 1975, Sleight et al. discovered superconductivity in Bi doped BaPbO_3 perovskite phase [1]. $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ compound exhibits a maximum T_C near 13 K depending on the sample composition and heat treatment [2, 3]. By doping the insulator BaBiO_3 with K at the Ba sites, Cava et al. and Matheiss et al. reported a new oxide superconductor having a very high critical temperature T_C near 30 K [4–6]. As a consequence, some authors referred to $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ and $\text{BaBi}_{1-x}\text{K}_x\text{O}_3$ as the precursors of the high T_C cuprates [6]. Some questions regarding how structural distortions, doping effects, and critical temperature T_C depend on the sample composition have also received some interest [2, 4, 7–11]. Studies [11] of temperature dependences of electrical resistance, $R(T)$, of the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system revealed that Bi substitution at Pb sites induces a superconductor–insulator transition (SIT) in compounds with x very close to 0.30. Several authors have focused great attention on the SIT in low and high temperature superconductors [12–18], however the SIT mechanism of the

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BaPb_{1-x}Bi_xO₃ system is not completely understood [11]. As discussed by some authors, two possible mechanisms may explain disorder induced SIT in granular superconductors [18]. Basically, superconductivity can be suppressed either by reducing the amplitude or changing the phase of the superconductor order parameter. Illustrative examples of both kinds of SIT are evident by observing the $R(T)$ curves obtained for homogeneous Bi and granular Ga films [12, 13, 18]. In homogeneous superconductors, SIT occurs when the critical temperature of the sample is reduced [13, 18]. On the other hand, disorder tuned SIT in granular samples occurs through a different mechanism. In such a case, suppression of long range order occurs as a consequence of the localization of the superconducting clusters without reduction of the T_C [12, 18].

In this paper, we present a systematic structural characterization of the BaPb_{1-x}Bi_xO₃ system and we describe its electrical resistance in function of temperature. The results allow us to discuss some important aspects concerning the dependence of T_C on the sample composition, and the influence of Bi substitution at Pb sites on the transport properties of the BaPb_{1-x}Bi_xO₃ system.

2. Experimental

Polycrystalline samples of BaPb_{1-x}Bi_xO₃ were fabricated by the solid state reaction technique using high purity PbO₂, Bi₂O₃, and BaCO₃ powders. The powders were compacted, calcined at 780 °C for 24 h, and finally heat treated at 800–850 °C for 24–48 h, depending on the sample composition. All samples were characterized by X-ray powder diffractometry using CuK α radiation. The diffractograms were indexed using a pseudocubic structure ($P23$) with the lattice parameter $a \approx 4.3$ Å [4, 6] and compared with simulations made with the powder cell program [19], utilizing *International Tables for X-ray Crystallography* [20]. A Perkin Elmer spectrometer (Analyst 800) was used to determine the composition of the samples after heat treatments. The electrical resistances of the samples in function of temperature were measured with a Maglab Oxford system, capable of generating the field strength of 9 T, and by employing the conventional four probe technique. Electrical terminals were prepared using low resistance (ca. 0.1 Ω) sputtered Au contacts.

3. Results

Results of chemical analyses revealed that the nominal composition of the samples was essentially unchanged during heat treatments. None of the analyzed samples exhibited statistically significant differences from the initial composition, within a standard deviation of 3%.

Figure 1 shows the X-ray diffractograms for samples that are representative of the full range ($0 < x < 1.0$) of Bi substitution. The diffractograms exhibit similar peaks, suggesting the samples have the same crystal structure. It is also visible that the dif-

fraction peaks shift with respect to the 2θ angle as the sample composition varies, hence indicating variations in the lattice parameters (notice, for example, how the peaks at $2\theta \sim 70^\circ$ shift systematically to the left as the Bi content x increases between 0 and 1). In spite of questions regarding structural distortions in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system to monoclinic, orthorhombic, or tetragonal [4, 6–8], we have analyzed diffractograms under the assumption that the unit cell is pseudocubic as others have also done [4, 6].

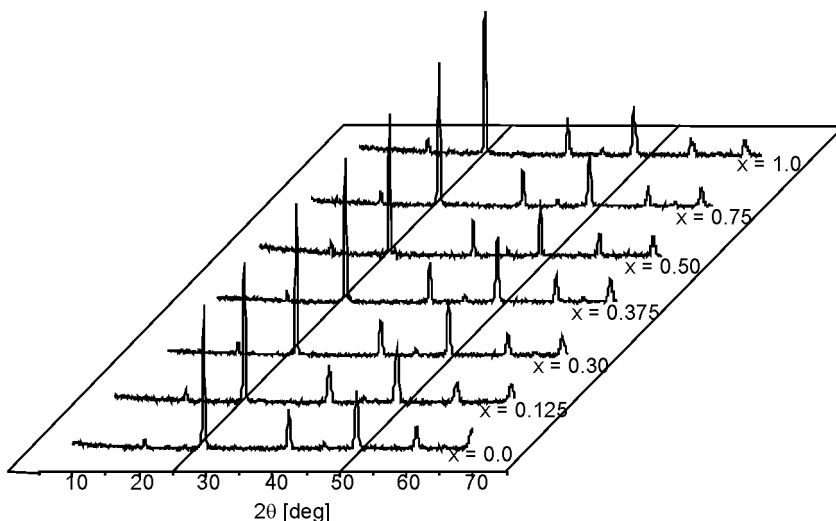


Fig. 1. X-ray powder diffractograms of samples with different Bi contents, over the full range of substitution

Figure 2 shows experimental and simulated diffractograms for $x = 0.125$. The simulated values are in close agreement with the experimental results. In Figure 3, the cubic lattice parameter is plotted against the level x of Bi in the sample. One can observe an approximately linear dependence, suggesting complete substitutional solubility of Bi in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$. This observation agrees with previous results published in the literature [6].

In order to study the transport properties of the samples, electrical resistance in function of temperature was measured. Figure 4 shows the electrical resistivity $R(T)$ plotted against temperature T of samples having compositions with $x \in \{0.0, 0.05, 0.15, 0.20, 0.30, 0.375\}$. It is possible to observe how resistivity changes from the metallic (BaPbO_3) to insulator ($x > 0.3$) as the content of Bi in the compound increases. In the $0.05 < x < 0.30$ range, the samples exhibit evidence of superconductivity.

In order to carefully identify the onset of the critical temperature for all superconducting samples, T_C has been defined as the point at which dR/dT versus T changes from normal to superconducting state. T_C defined in this way is plotted in Fig. 5 in function of x in the compound.

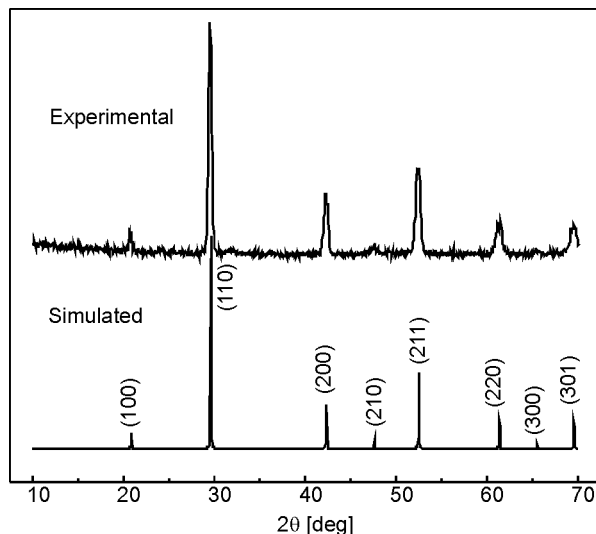


Fig. 2. Experimental and simulated diffractograms for the sample with $x = 0.125$

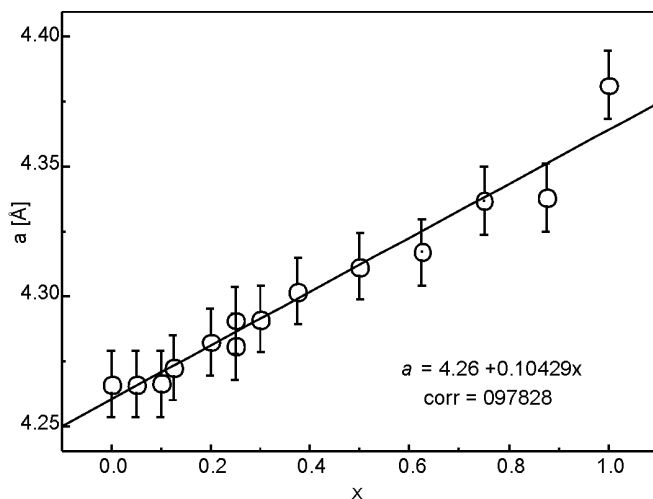


Fig. 3. Pseudocubic lattice parameters (calculated from the diffractograms of simulations) in function of the Bi content (x)

The superconducting critical temperature increases systematically from 11.2 K at $x = 0.005$ to ca. 12 K at $x = 0.15$, and decreases to 11.6 K at $x = 0.30$. Below $x = 0.005$ and above $x = 0.30$, superconductivity in the system vanishes (see Fig. 4). This behaviour is similar to results reported in the literature which show that T_C increases systematically from zero at $x = 0.0$ to ca. 12 K at $x \approx 0.20$, remaining constant until $x \approx 0.30$, and finally vanishing at $x > 0.30$ [2, 3]. As one can see from Fig. 4, the transition to the superconducting state does not reach zero resistance for samples having low Bi contents ($0.005 < x < 0.05$).

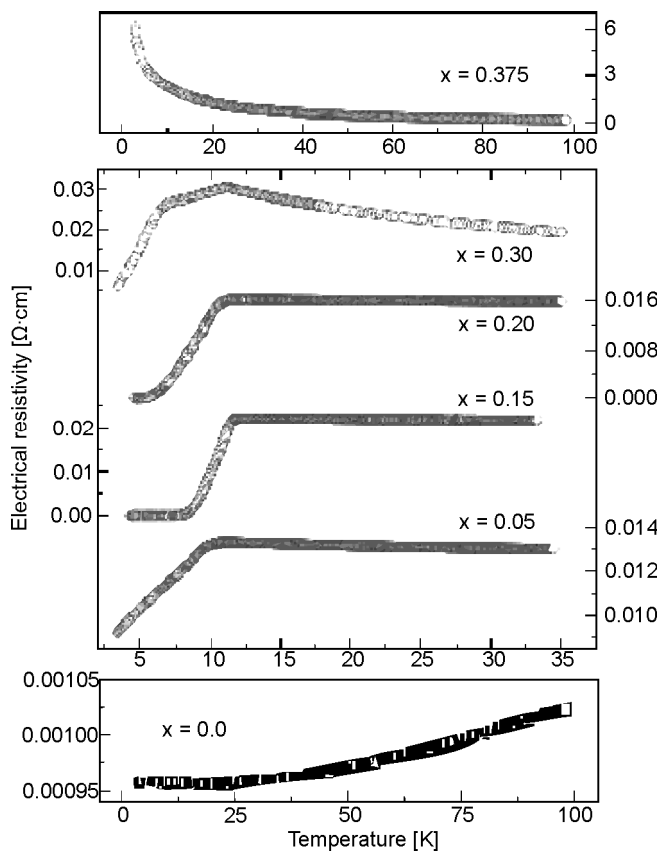


Fig. 4. Electrical resistivity in function of temperature for samples having Bi contents $x \in \{0.0, 0.05, 0.15, 0.20, 0.30, 0.375\}$

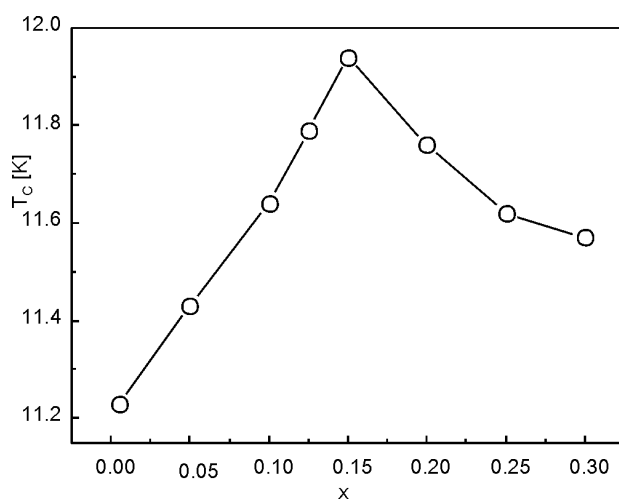


Fig. 5. The dependence of T_C on the Bi content x in the samples

Our interpretation of these results is that it is related to the fraction of superconducting clusters present in the samples. Research [21] on the transport properties of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Pr}_x\text{Cu}_2\text{O}_{8+d}$ ($\text{Bi2212} + \text{Pr}$) polycrystalline samples has shown that the transition to the zero resistance superconducting state depends on the fraction of superconducting clusters in the sample. It was also observed that the zero resistance superconducting state is only reached by samples with a large enough superconducting fraction [21, 22]. If we assume that the resistive transition in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system can be described by such a mechanism, the transition visible in $R(T)$ curves must depend on the superconducting fraction. Therefore, for samples with low Bi contents, this fraction must be small, and therefore zero resistance is not attained, which is consistent with the results shown in Fig. 4. On the other hand, if the superconducting fraction is close to the percolation threshold, a decrease in the transition intensity can be observed which provides information about the onset of the T_C value. This behaviour suggests that the existence of superconductivity in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system must be governed by the same mechanism of inhomogeneous superconductivity as that reported for high- T_C superconductors [21, 23].

4. Summary

Assuming the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system has a pseudocubic crystal structure, X-ray power diffraction data reveal there is a linear relationship between the lattice parameter and the content of Bi in the compound. This indicates complete substitutional solubility of Bi in this system. All prepared samples in the Bi range $0.005 < x < 0.30$ exhibit evidence of superconductivity. Careful analysis shows that, for superconducting samples, the critical temperature T_C depends strongly on the content of Bi. We have discussed this behaviour within the context of inhomogeneous superconductivity. The dependence of T_C on the Bi content x indicates that granular samples of the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system experience transition to the insulating state due to suppression of the superconducting coupling, much like the transition mechanism observed for granular superconductors.

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