

# Structural properties of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ nanostructures

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Electrical resistance as a function of temperature,  $R(T)$ , and X-ray powder diffractometry (XRD) patterns are reported for polycrystalline samples of the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  system.  $R(T)$  measurements conducted with single phase samples show metal-like behavior for  $\text{BaPbO}_3$ , superconductivity in the  $0.005 < x < 0.30$  range, and an insulating regime for  $x > 0.30$ . A careful analysis of the onset of the critical temperature ( $T_C$ ) reveals dependence on sample composition for  $0.005 < x < 0.30$ . We argue that the composition-dependence of  $T_C$  is related to the superconducting volume fraction which ultimately leads to connected or disconnected superconducting clusters, similar to granular superconductors.

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**Keywords:** Nanostructure; XRD; Superconductivity.

## 1. INTRODUCTION

In 1975, Sleight et al. discovered superconductivity in the Bi doped  $\text{BaPbO}_3$  perovskite phase [1]. Depending on the sample composition and heat treatment, the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  compound has maximum  $T_C$  near 13 K [2, 3]. By doping the insulator  $\text{BaBiO}_3$  with K in the Ba site, Cava et al. and Matheiss et al. reported a new high critical temperature oxide superconductor with  $T_C$  near 30 K [4-6]. As a consequence, some authors have referred to the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  and  $\text{BaBi}_{1-x}\text{K}_x\text{O}_3$  compounds as the precursors of the high- $T_C$  cuprates [6]. Some questions regarding structural distortions, doping effects, and  $T_C$  dependence on sample composition have also received some interest [2, 4,7-11]. Analyses of the electrical resistance as a function of temperature,  $R(T)$ , for the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  system have revealed that Bi substitution in the Pb site induced a superconductor-insulator transition

(SIT) close to the  $x = 0.30$  composition [11]. Several authors have dedicated great attention to the SIT in low and high temperature superconductors [12-18], however the mechanism of the SIT in the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  system is not completely understood [11]. As discussed by some authors, there are two possible mechanisms to explain disorder induced SIT in granular superconductors [18]. Basically, suppression of superconductivity can occur by the reduction of the amplitude and/or by changing the phase of the superconducting order parameter. Two examples of SIT for these cases are the  $R(T)$  curves obtained in homogeneous Bi and granular Ga films [12,13, 18]. In homogeneous superconductors, the SIT occurs with the reduction of the critical temperature of the samples [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 systematic structural characterization and measurements of electrical resistance as a function of temperature for the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  system. The results allow us to discuss some important aspects about  $T_C$ -dependence with sample composition and the influence of the Bi substitution to the Pb site on the transport properties of the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  system.

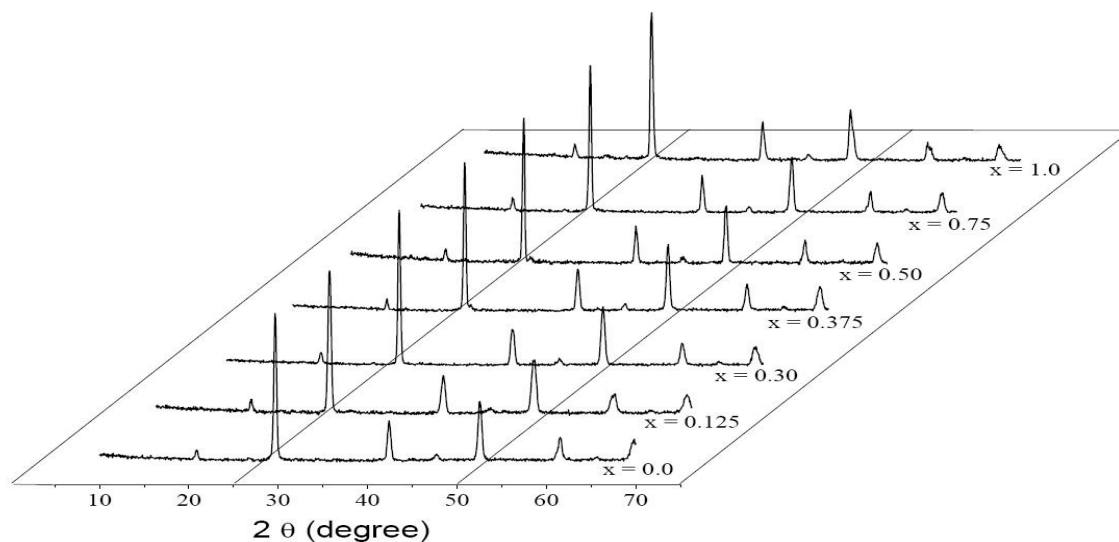
## 2. EXPERIMENTAL PROCEDURE

Polycrystalline samples of  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  were prepared by the solid-state reaction technique using high purity  $\text{PbO}_2$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{BaCO}_3$  powders. The powders were compacted, calcined at  $780^\circ\text{C}$  for 24 hours, and finally heat treated at  $800\text{-}850^\circ\text{C}$  for 24-48 hours depending on sample composition. All samples were characterized by X-ray powder diffractometry using  $\text{CuK}\alpha$  radiation. The diffractograms were indexed using a pseudo-cubic structure (P23) with lattice parameter  $a \sim 4.3 \text{ \AA}$  [4, 6] and compared with simulations from powder cell program [19] by using International Tables for X-ray crystallography [20]. Chemical analysis using atomic absorption spectrometry was performed in PerkinElmer equipment (Analyst 800) in order to confirm the composition of the samples after heat treatments. Measurements of the electrical resistance as a function of the temperature were carried out in a Maglab Oxford system, capable to applied fields of 9 T, by using of the conventional four probe technique. Electrical terminals were prepared using low resistance ( $\sim 0.1$ ) sputtered Au contacts.

## 3. RESULTS AND DISCUSSION

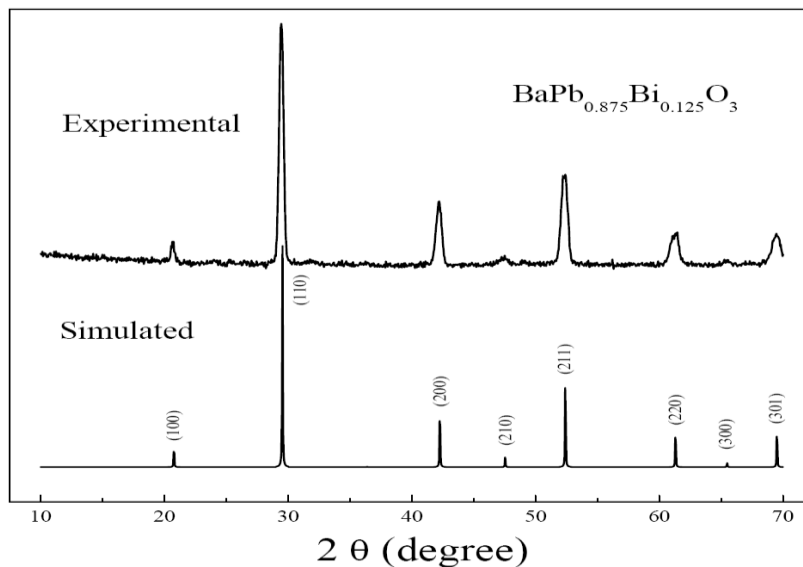
Results of chemical analysis revealed that the nominal composition of the samples was essentially unchanged during heat-treatments. No deviation from the starting composition was observed for all samples analyzed within the standard deviation of the technique (< 3 %).

In figure 1, X-ray diffractograms for samples with Bi composition ( $x$ ) in the full range of substitution ( $0 < x < 1.0$ ) are shown. We can see that the diffractograms present similar peaks suggesting the samples have the same crystal structure. It is also possible to observe shifting of the peaks along  $2\theta$  with the sample composition indicating lattice parameters variations (see, for example, systematic shifting to lower angles for increasing  $x$  of the peak at  $2\theta \sim 70^\circ$ ). 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 pseudo-cubic as other have done [4, 6].

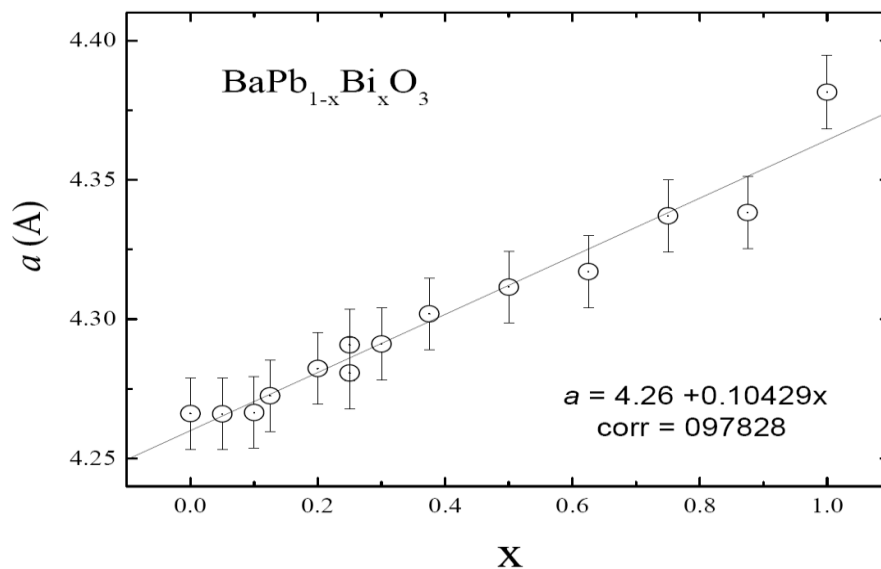


**Figure 1** X-ray powder diffractograms for samples with different Bi composition in the full range of substitution.

Figure 2 shows a comparison between experimental and simulated diffractograms for  $x = 0.125$ . We observe that the simulation is in good agreement with the experimental result. In Figure 3, the cubic lattice parameter is plotted as a function of composition. One can observe an approximately linear dependence suggesting complete substitutional solubility of Pb by Bi in  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ . This observation agrees with previous results published in the literature [6].



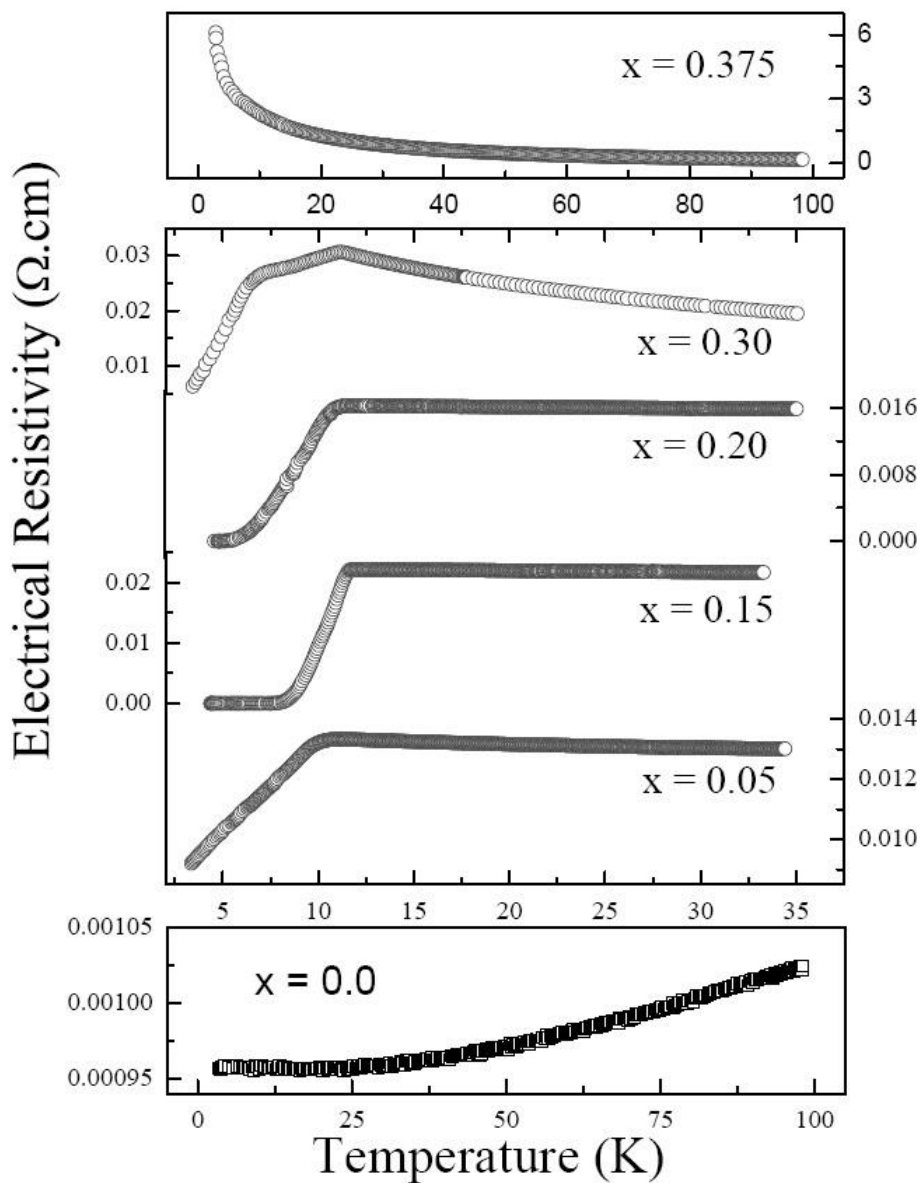
**Figure 2** Comparison between experimental and simulated diffractograms for the sample with  $x = 0.125$ .



**Figure 3** Pseudo cubic lattice parameters (calculated from diffractograms simulations) as a function of Bi composition.

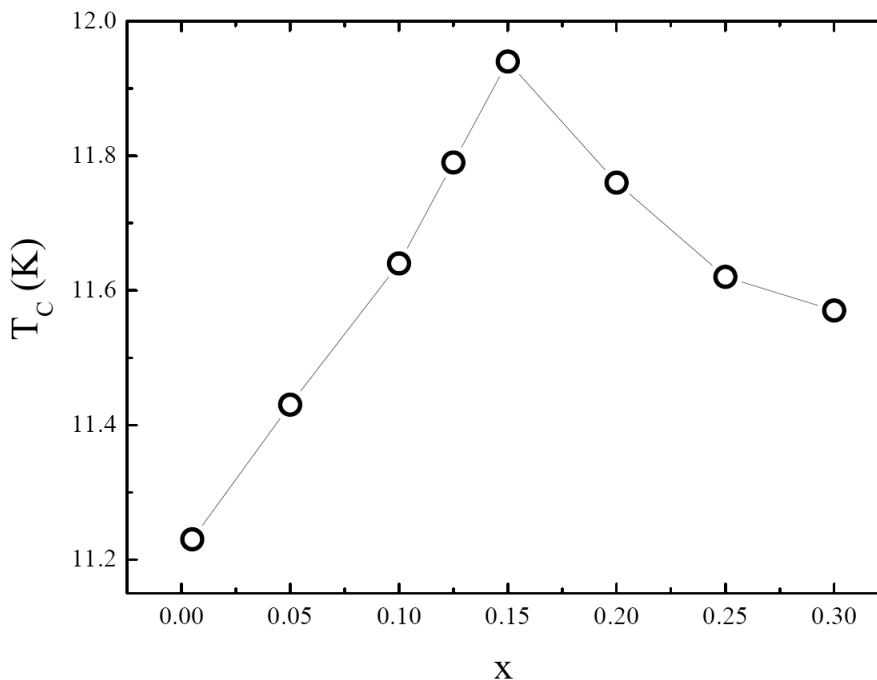
In order to study the transport properties of the samples, we measured electrical resistance as a function of temperature. In Figure 4, electrical resistivity,  $R(T)$ , for samples within the composition range from 0.0 to 0.375 are plotted. It is possible to observe a change in the resistive behavior from metallic ( $\text{BaPbO}_3$ ) to insulator ( $x > 0.3$ ) with increasing Bi composition. In the  $0.05 < x < 0.30$  range, the samples present evidence of

superconductivity.



**Figure 4:** Electrical resistivity as a function of temperature for samples ranging from  $x = 0.05$  to  $0.375$ .

In order to carefully obtain the onset of the critical temperature for all superconducting samples, we have defined  $T_C$  as the point in which  $dR/dT$  versus  $T$  changes from normal to superconducting state.  $T_C$  defined in such a way is plotted against Bi composition in Figure 5.



**Figure. 5:** Bi composition-dependence of  $T_C$ .

The superconducting critical temperature increases systematically from 11.2 K at  $x = 0.005$  to  $\sim 12$  K at  $x = 0.15$  and decrease to 11.6 K at  $x = 0.30$ . Below  $x = 0.005$  and above  $x = 0.30$ , superconductivity disappears in the system (see Figure 4). This behavior is similar to results reported in the literature which show that  $T_C$  increases systematically from zero at  $x = 0.0$  to  $\sim 12$  K at  $x \sim 0.20$ , remaining constant until  $x \sim 0.30$ , and finally vanishing at  $x > 0.30$  [2, 3]. As one can see, from Figure 4 (for low  $x$ ), the transition to the superconducting state does not reach zero resistance for low Bi composition samples ( $0.005 < x < 0.05$ ). Our interpretation regarding these results is that it is related to the fraction of superconducting clusters present inside of the samples. Results of transport properties for  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Pr}_x\text{Cu}_2\text{O}_{8+d}$  (Bi2212+Pr) polycrystalline samples have shown that the transition to the zero-resistance superconducting state depends on the fraction of superconducting clusters in the sample [21]. It was also observed that the zero-resistance superconducting state is only reached for 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 in  $R(T)$  curves must depend on the superconducting fraction. Therefore, for low Bi composition samples, this fraction must be small and zero resistance is not reached in agreement with the results in Figure 4. On the other hand, if the superconducting fraction is close to the percolation threshold a drop in the transition can be observed which provides information about the onset  $T_C$  value. This behavior 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 is reported for high- $T_C$  superconductors [21, 23].

#### 4. CONCLUSIONS

Analysis of X-ray powder diffractometric assuming a pseudo cubic crystal structure in the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  system reveals a linear dependence of the lattice parameter with Bi composition. This indicates complete substitutional solubility of Pb by Bi in this system. All prepared samples in the range  $0.005 < x < 0.30$  present evidence of superconductivity. Careful analysis of the  $T_C$  shows Bi composition dependence for superconducting samples. We have discussed this behavior within the context of inhomogeneous superconductivity. The  $T_C$  dependence with varying  $x$  indicates that the transition to the insulating state in the granular samples of the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  system occurs due to suppression of the superconducting coupling in a similar way as the granular superconductors.

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