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Oxygen-deficient barium lead oxide perovskites

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Through careful selection of reduction conditions it is found that both $BaPbO_3$ and $Ba_4Pb_3O_{10}$ can be prepared with significant amounts of oxygen deficiency. In both cases, crystallographic unit cells and resistivities change with oxygen content. Hall-effect measurements, however, indicate that the oxygen nonstoichiometry does not change the mobile-carrier concentration, suggesting that the electrons introduced are strongly trapped. The oxygen-deficient materials $BaPbO_{2.90}$ and $Ba_4Pb_3O_{9.86}$ are not superconducting down to 70 mK.

The simple perovskite semimetal $BaPbO_3$ is the basis for the 3.5- and 12-K superconductors $BaPb_{0.75}Sb_{0.25}O_3$ and $BaPb_{0.75}Bi_{0.25}O_3$,[1,2] materials which, along with $Ba_{0.6}K_{0.4}BiO_3$ [$T_c=30$ K Ref. (3)], are of interest in comparison to copper-oxide superconductors. Sb and Bi doping add one electron per substituted Pb into an electronic band which is of strongly hybridized Pb 6s-O 2p character.[4] Although $BaPbO_3$ itself was once reported to be superconducting at 0.5 K,[5] more recent studies[1,6] have instead found it to be a normal metal down to significantly lower temperatures. An alternative to electron doping of $BaPbO_3$ by M^{5+} for Pb^{4+} substitution is to remove oxygen, chemically reducing the Pb^{4+} formally present to $Pb^{4-\delta+}$ with 2e doping per oxygen removed. Oxygen deficiency in layered Ba-Pb-oxides has been explored theoretically[7] and suggests that this might be a fruitful doping method. Here we show that careful selection of reducing atmosphere and temperature can yield chemical reduction without decomposition for both $BaPbO_3$ and the related triple layer phase[8] $Ba_4Pb_3O_{10}$. In the simple perovskite, sufficient oxygen can be removed ($BaPbO_{2.87}$) to yield the same chemical doping level as is achieved through Bi and Sb substitution for Pb in the optimal superconductors. The color of the material changes from the brownish black of $BaPbO_3$ to the bluish black of $BaPb_{0.75}Sb_{0.25}O_3$, but superconductivity is not induced. The Hall-effect measurements show that the chemically induced charge does not take part in conductivity, a probable explanation for the absence of superconductivity.

Polycrystalline samples of $BaPbO_3$ and $Ba_4Pb_3O_{10}$ were synthesized by ceramic processing methods. Starting materials were $Ba(OH)_2 8H_2O$ and Pb_3O_4 for $BaPbO_3$, and $BaCO_3$ and $Pb(NO_3)_2$ for $Ba_4Pb_3O_{10}$. For $BaPbO_3$, slow heating and 12-h soaks at 600, 700, and 750°C in O_2 with intermediate grindings yielded single-phase material. Pellets were then pressed and buried in powder of like composition and heated in O_2 at 825°C for 2 h followed by 500°C for 5 h. $Ba_4Pb_3O_{10}$ required higher temperatures and longer times; it was heated in O_2 twice (after initial slow heating) at 825°C for 15 h, then at 950°C for 48 h, with intermediate grinding. Pellets were then made, buried in powder of like composition, and heated in O_2 again for 48 h at 950°C, then for 5 h at 850°C and 500°C.

Weight loss experiments in a commercial thermogravimetric analyzer (TGA) indicated that reversible oxygen depletion was possible for both $BaPbO_3$ and $Ba_4Pb_3O_{10}$ on heating in either N_2 or an Ar-0.1% H_2 mixture. (The small H_2 content of Ar scrubs the gas stream of any O_2 that might be introduced by minor leaks.) Representative data for $BaPbO_3$ heated in N_2 are shown in Fig. 1. The sample was heated at 10°/min to a final temperature where it was held isothermally. At 700°C the data show reduction of oxygen content to a stoichiometry $BaPbO_{2.9}$. Oxygen was then introduced, replacing the N_2 and the sample very quickly recovered a significant fraction of its weight. On cooling to room temperature at 5°C/min all of the initial weight is recovered, indicating reversible oxygen insertion and removal. At 800°C in N_2, weight loss is more pronounced, but on introduction of oxygen and subsequent cooling to room temperature all the weight is not recovered, indicating some reductive decomposition of $BaPbO_3$ under these conditions, probably to BaO+PbO. Treatment temperatures up to 725°C in N_2 were possible without decomposition. To prepare samples for physical property studies, pellets were buried in powder of $BaPbO_3$ and heated at temperatures between 600 and 725°C for 4 h yielding $BaPbO_x$ for approximately $3.0 \geq x \geq 2.8$. Final oxygen content was determined by

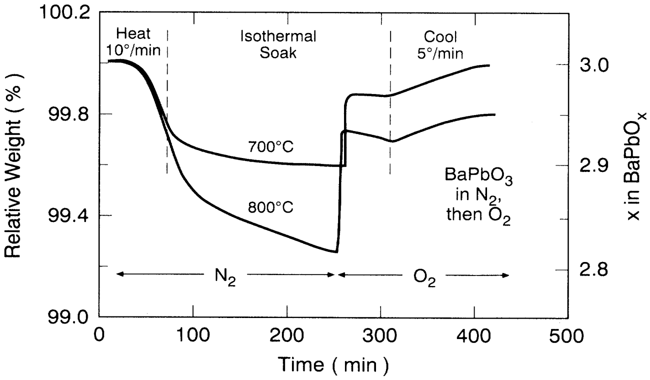

FIG. 1. Treatment of polycrystalline $BaPbO_3$ in a commercial TGA in N_2 then O_2. At 700°C the weight loss is entirely reversible, whereas at 800°C partial decomposition, leading to irreversible weight loss, is observed.

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measurement of the weight of the pellet before and after treatment.

For $Ba_4Pb_3O_{10-\delta}$,N_2 treatment did not prove to be sufficiently reducing in our experimental apparatus to yield $\delta > 0.10$, and so the 0.1% H_2 in Ar gas mixture was also employed. Curves similar to those in Fig. 1 were obtained, revealing a maximum treatment temperature of 700°C for reduction without decomposition. Samples of $Ba_4Pb_3O_x$ for experimental study in the range $10 \geq x \geq 9.9$ were obtained by 4-h treatment in N_2 of buried pellets at temperatures between 650 and 700°C. For $Ba_4Pb_3O_x$, $9.9 \geq x \geq 9.7$ treatments in 0.1% H_2-Ar for 4 h at temperatures between 600 and 700°C were employed. For both $BaPbO_x$ and $Ba_4Pb_3O_x$, TGA measurements indicated that somewhat more nonstoichiometry might be possible, to $x \approx 2.82$ for $BaPbO_3$ and $x = 9.57$ for $Ba_4Pb_3O_{10}$, but we could not obtain samples free from decomposition products for physical studies.

Characterization of the reduced $BaPbO_x$ and $Ba_4Pb_3O_x$ by conventional powder x-ray diffraction revealed subtle but unambiguous structural changes on oxygen removal. $BaPbO_3$ is a slightly rotationally distorted orthorhombic body-centered perovskite with $a = 6.056$, $b = 6.024$, $c = 8.506$ Å.[9] Figure 2 shows the (400), (224), and (040) reflections [derived from the (220) reflection of the basic cubic $a = 4.265$ subcell] for $BaPbO_x$. The data show that the unit cell becomes dimensionally more uniform on oxygen removal, perhaps tetragonal or cubic, apparently due to decreased rotational displacements of the PbO_6 octahedra, and that the cell size increases slightly, consistent with the introduction of Pb^{3+} into a Pb^{4+} array. Detailed structural study is necessary to fully characterize the new structures. For $Ba_4Pb_3O_x$ the situation is more straightforward, with the oxygen deficiency introducing no change in symmetry, only a change in cell dimension. For $Ba_4Pb_3O_{10}$, our powder x-ray cell refinement (16 reflections) yields $a = 4.289(1)$, $c = 30.278(8)$ Å for the tetragonal body-centered cell, and for $Ba_4Pb_3O_{9.84}$ (17 reflections) $a = 4.292(1)$ and $c = 30.305(9)$, revealing a very small increase in cell size on chemical reduction.

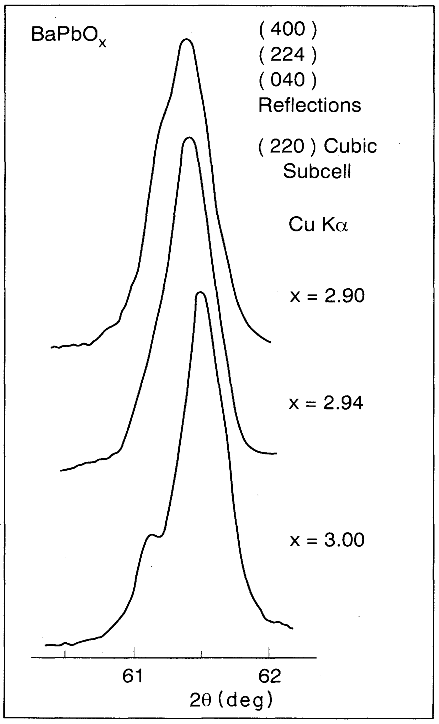

FIG. 2. The (220) cubic subcell reflection of $BaPbO_x$. For the true orthorhombic cell, three reflections are nearly degenerate. The unit cell becomes dimensionally more isometric and larger on oxygen removal.

The resistivities of polycrystalline pellets of single phase $BaPbO_x$ and $Ba_4Pb_3O_x$ were measured in a conventional four probe configuration between 300 and 4.2 K and for one stoichiometry of each type down to 70 mK. The results are summarized in Figs. 3 and 4. Within a naive rigid-band picture, oxygen deficiency in this class of compounds would be expected to provide electrons to a Pb6*s*-O2*p* σ^* band. For both $BaPb_{1-x}Bi_xO_3$ and $Ba_4Pb_{3-x}Bi_xO_{10}$, however, where electrons are provided to the same σ^* band by Bi or Pb substitution, the materials become more resistive on doping, and eventually experience a metal-to-semiconductor transition. The oxygen-deficient materials become more resistive with increasing oxygen deficiency, but at the nonstoichiometries obtained semiconducting behavior has not clearly developed. The resistivities are typical of those observed for poor metals. The resistivity rises faster per electron, more accurately per defect, for the layered $Ba_4Pb_3O_x$ case than the fully three-dimensional $BaPbO_x$ case. The effect of dimensionality on the doping-induced increased resistivity has not been explored in detail for this class of materials, but has been ascribed in the Pb-Bi case[10] to the well-known increased tendencies for charge-density-wave (CDW) formation or

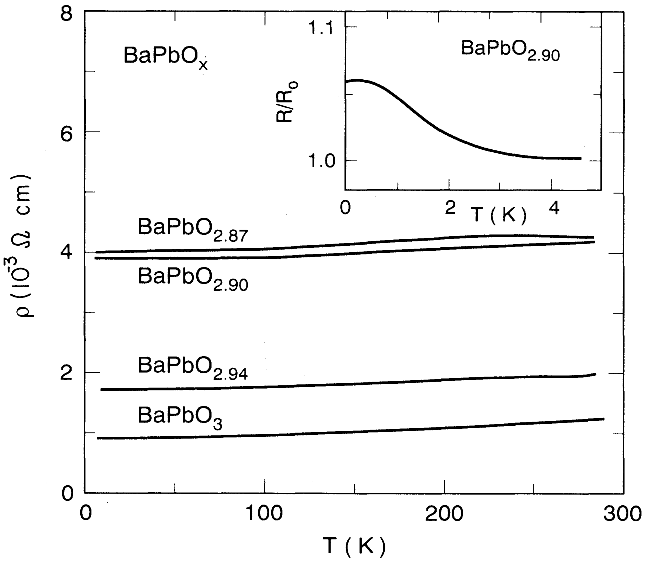

FIG. 3. Temperature-dependent resistivities of polycrystalline samples of $BaPbO_x$. Main figure, 4.2–300 K; inset resistance of $BaPbO_{2.90}$ below 5 K (to 70 mK).

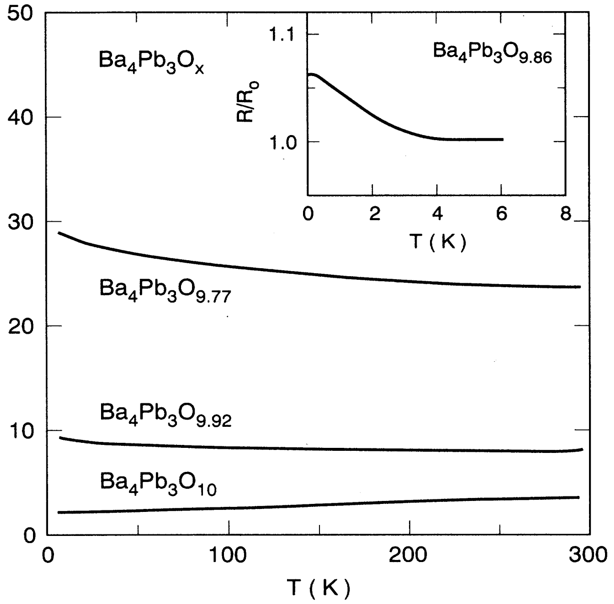

FIG. 4. Resistivities of polycrystalline samples of $Ba_4Pb_3O_x$. Main figure, 4.2–300 K; inset resistance of $Ba_4Pb_3O_{9.86}$ below 6 K (to 70 mK).

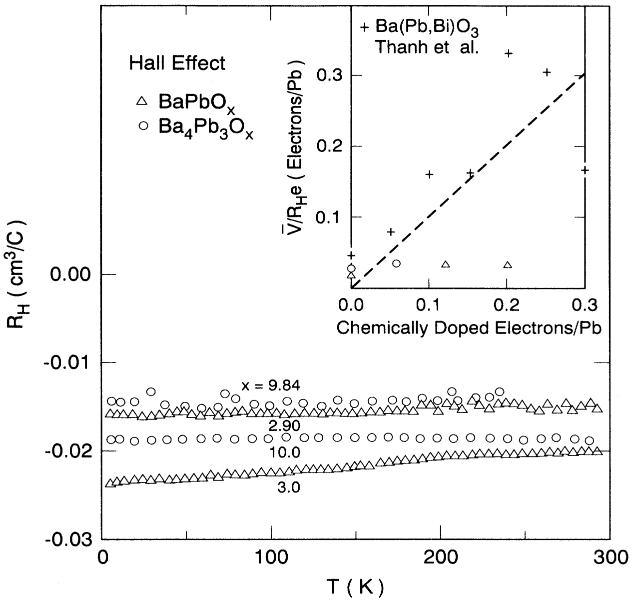

FIG. 5. Hall effect for several $BaPbO_x$ and $Ba_4Pb_3O_x$ stoichiometries. Inset: comparison of chemically induced charge and measured carrier concentration for reduced materials, and comparison to $BaPb_{1-x}Bi_xO_3$ (Ref. 11).

disorder-induced scattering in lower dimensions.

In both oxygen-deficient materials, normal metallic behavior is maintained to low temperatures, where the effects of carrier localization finally appear. No indication of superconductivity was observed down to 70 mK. In the $BaPbO_x$ case this is of particular interest, as due to chemical doping arguments alone the number of carriers is expected to be comparable with that of superconducting $BaPb_{0.75}Sb_{0.25}O_3$ and $BaPb_{0.75}Bi_{0.25}O_3$.

Hall-effect measurements were performed on polycrystalline samples of $BaPbO_x$ and $Ba_4Pb_3O_x$ at temperatures between 4.2 and 300 K at $H=10$ KOe. Figure 5 shows, in the main panel, the temperature dependencies of the Hall coefficients for several stoichiometries of $BaPbO_x$ and $Ba_4Pb_3O_x$. The Hall coefficients are negative and relatively temperature independent. The change in Hall coefficient with oxygen content is much less than is expected if the 2e per O vacancy, expected from chemical arguments, are doped into the σ^* band. A comparison of the chemically doped charge and the actual measured charge determined from Hall-effect measurements is shown in the inset to Fig. 5, and compared to the results for $BaPb_{1-x}Bi_xO_3$,[11] where the 1e per Bi doping is operating as expected, at least for the initial stages of doping. The data imply that the chemically induced charge is very strongly trapped for both oxygen-deficient materials $BaPbO_x$ and $Ba_4Pb_3O_x$ and does not contribute to the conductivity, with oxygen vacancies acting as stronger trapping centers than Bi substitutions. Further, the resistivity data, showing localization effects at low temperature, indicate that the oxygen vacancies act as scattering centers for the nontrapped charge present due to the overlap of the conduction band with the nonbonding oxygen bands. The continuous changes of the crystallographic unit cells with oxygen stoichiometry suggest that, for both $BaPbO_x$ and $Ba_4Pb_3O_x$, the oxygen vacancies are present in a classical random solid solution. Short-range ordering could, however, be present. High-resolution x-ray diffraction or electron microscopy studies would help resolve this issue.

In conclusion, we have shown that the simple perovskite $BaPbO_3$, and to a lesser extent the layered Ruddlesden-Popper phase $Ba_4Pb_3O_{10}$, can be made oxygen deficient through suitable mildly reducing chemical treatment. The increase in resistivity on going from $BaPbO_3$ to $BaPbO_{2.9}$ is considerably less than is encountered in the electronically equivalent $BaPbO_3$ to $BaPb_{0.8}Bi_{0.2}O_3$ doping[11] case. The same can be said for comparison of $Ba_4Pb_3O_{10}$, $Ba_4Pb_3O_{9.86}$, and $Ba_4(Pb_{0.9}Bi_{0.1})_3O_{10}$.[8] Oxygen vacancies therefore are weaker scattering centers for non-trapped carriers than are Bi atoms on Pb sites. $BaPbO_x$ and $Ba_4Pb_3O_x$ are not superconducting down to 70 mK when prepared as we describe: thus, the early report of superconductivity at 0.5 K in $BaPbO_3$ (Ref. 5) cannot be due to either $BaPbO_3$ itself or reduced material in the range $3 \geq x \geq 2.87$, or $Ba_4Pb_3O_{10}$ or reduced material in the range $10 \geq x \geq 9.86$. The Hall-effect results, which show that the chemically introduced charge does not contribute to the conductivity, e.g. that no electrons are introduced into the σ^* band, serve as a preliminary explanation for the absence of superconductivity in chemically reduced $BaPbO_x$ and $Ba_4Pb_3O_x$.

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