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Tl, Bi, and Pb Doping in $Ba_4BiPb_2TlO_{12-\delta}$

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To determine the effects of different 6s metal concentrations on the superconducting nature of $Ba_4BiPb_2TlO_{12-\delta}$, materials produced via four doping schemes were examined: $Ba_4Bi(Pb,Tl)_3O_{12-\delta}$, $Ba_4(Bi,Pb)_3TlO_{12-\delta}$, $Ba_4(Bi,Tl)_2Pb_2O_{12-\delta}$, and $Ba_4Bi_xPb_{4-2x}Tl_xO_{12-\delta}$. For the parent compound a value of $\delta = 0.91$ was observed, indicating that approximately $^1/_4$ oxygen atom was missing per cubic subsection of the unit cell. For all samples, the symmetry of the parent compound changed from orthorhombic to tetragonal as the system moved away from the ideal composition. This was usually accompanied by the loss of superconductivity, which exhibited a maximum T_c of 10.5 K for the parent compound $Ba_4BiPb_2TlO_{12-\delta}$. Also reported are high-temperature magnetic susceptibility results, which are used to determine the effect of metal substitution on the density of states at the Fermi level. For each set of variants on the parent composition, the onset of superconductivity was accompanied by a significant decrease in the size of the Pauli paramagnetic signal.

Introduction

Several 6s and 5s valence cubic perovskite systems have now been shown to exhibit superconductivity. The first such system to be discovered was $Ba(Pb,Bi)O_3$, which exhibits a peak T_c of 13.5 K.[1] Following this were the $(Ba,K)BiO_3$ (peak T_c 29.8 K)[2] and $Ba(Pb,Sb)O_3$ (peak T_c 3.2 K)[3] systems. It has also been reported that $BaPbO_3$ exhibits superconductivity at 0.5 K,[4] but this result has proven difficult to reproduce.[3,5]

To determine the relationship between properties and composition in the recently discovered superconductor $Ba_4BiPb_2TlO_{12-\delta}$,[6] four systems were prepared: $Ba_4BiPb_{3-x}Tl_xO_{12-\delta}$ (system 1), $Ba_4Bi_{3-x}Pb_xTlO_{12-\delta}$ (system 2), $Ba_4Bi_{2-x}Pb_2Tl_xO_{12-\delta}$ (system 3), and $Ba_4Bi_xPb_{4-2x}Tl_xO_{12-\delta}$ (system 4), corresponding to substitution of Tl into the Pb sites (**1**), Bi into the Pb sites (**2**), and Tl into the Bi sites (**3**). In addition, on the basis of recent results from our laboratory on anomalous properties of $BaBi_{0.5}Tl_{0.5}O_{3-y}$[7] as a function of oxygen content, the properties of samples in which equal amounts of Tl and Bi were doped into $BaPbO_3$ were examined (**4**). The structural and superconducting properties and paramagnetism of these systems have been measured.

It has been previously reported from this laboratory[6] that doping of Tl in place of Pb in the known superconductor $BaBi_{0.25}Pb_{0.75}O_3$ results in a conversion from orthorhombic to tetragonal symmetry, as well as loss of superconductivity at $BaBi_{0.25}Tl_{0.13}Pb_{0.62}O_3$; this is in general agreement with the results of Wang et al.[8] The subsequent reappearance of superconductivity at a Tl content of 0.25 was accompanied by a return to orthorhombic symmetry, indicating the existence of a new phase that is structurally and electronically distinct from the known $Ba(Bi,Pb)O_3$ superconductor.

Experimental Section

Synthesis. Samples were prepared in sintered Al_2O_3 crucibles or boats starting with 99.999% Bi_2O_3, 99% PbO_2, 98% Tl_2O_3, and 99.99% BaO, all supplied by Aldrich. Stoichiometric amounts of dry powders were ground in a wiggle bug for 4 min. A 33% excess of Tl_2O_3 was used to compensate for loss during the reaction process. The mixtures were loaded into Al_2O_3 crucibles and placed in a quartz tube for 1.25 h under flowing argon (5–10 cm^3/min) at 850 °C and then quenched by immediate removal from the oven. The prereacted mixtures were then reground by hand and pressed into pellets that were loaded into boats for rapid (15 min) heating to 800 °C under flowing argon. After rapid cooling to 450 °C, the argon flow was replaced by oxygen at the rate of 5–10 cm^3/min. Subsequently, the temperature was reduced to 425 °C and maintained for 1.5 h, followed by slow cooling (1.5 h) back to room temperature. The parent compound was also prepared using argon in place of oxygen in the final low-temperature annealing step to determine the effect of reducing conditions upon the structure and nature of $Ba_4BiPb_2TlO_{12-\delta}$. All samples were roughly polished with 600-grit Al_2O_3 sandpaper before analysis to remove surface defects.

Methods. X-ray data were obtained on a Scintag powder diffractometer with a scan rate of 2°/min over a 2θ range of 5–75° in 0.01° steps. The resulting powder patterns were indexed and analyzed by a Fortran IV X-ray fitting program.[9]

Resistivity data were measured on a four-probe resistivity system using a Lake Shore temperature sensor with a calibrated Si diode (±0.05 K) and a 20 mA (±0.02 mA) constant-current source. Resulting voltages were measured with a Keithley voltmeter with a sensitivity of 0.5 μV.

Susceptibility data were obtained on a S.H.E. magnetic susceptometer operating at 20 G to detect superconducting transitions and at 25 kG for bulk magnetic susceptibility from 50 to 300 K. All transition temperatures were assigned based upon the crossover point to diamagnetism for each sample. The value of the Pauli paramagnetism was determined by the linear portion of the magnetic data between the temperatures of 50 and 200 K.

Flame atomic emission (FAE) data were measured on a Perkin-Elmer 510 atomic absorption instrument, equipped with an acetylene/nitrous oxide gas mixture. All samples were weighed in triplicate prior to dissolving them in aqua regia. All analytical data are reported based on a content of 4.0 Ba/formula unit. For all values of x, FAE indicated that the observed Tl content was within ±0.09% of the expected percentage. Oxygen contents were determined by difference using the measured Ba, Tl, Bi, and Pb percentages; estimated errors are ±0.39% or a $\Delta\delta = \pm 0.047$. (Because of the volatility of Tl_2O and secondary chemical interferences, direct determination of the O content by previously published techniques is not feasible.) As expected, the value of δ is low after the low-temperature oxygen annealing. The degree of oxygen vacancy in the parent compound was found to be $\delta = 0.91$, or approximately 0.23 oxygens missing per cubic unit of the

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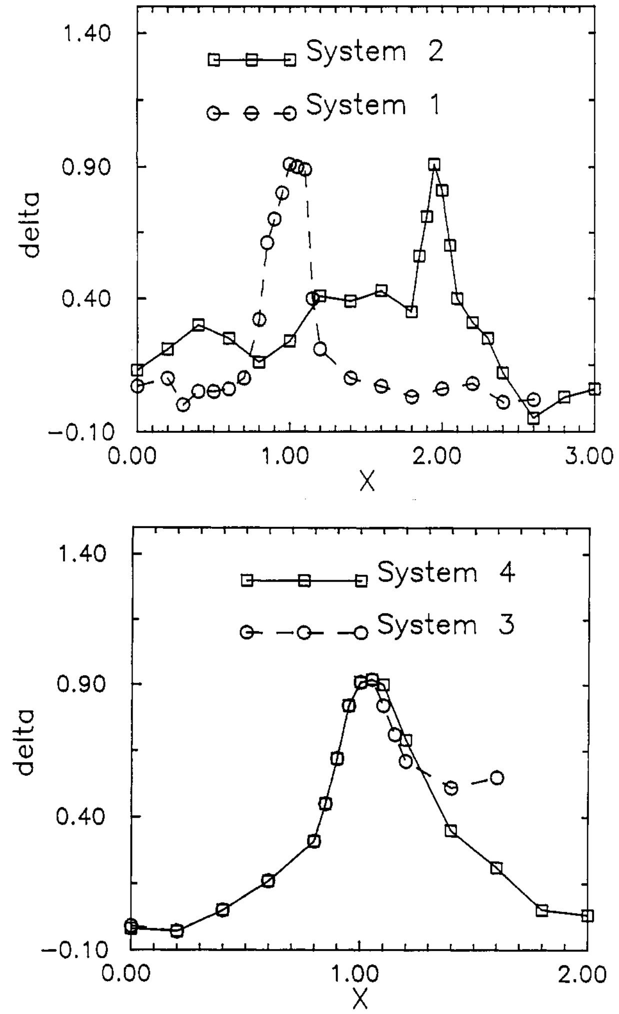

Figure 1. (a, top) Plot of δ vs x for $Ba_4BiPb_{3-x}Tl_xO_{12-\delta}$ (system 1) and $Ba_4Bi_{3-x}Pb_xTlO_{12-\delta}$ (system 2). (b, bottom) plot of δ vs x for $Ba_4Bi_{2-x}Pb_2Tl_xO_{12-\delta}$ (system 3) and $Ba_4Bi_xPb_{4-2x}Tl_xO_{12-\delta}$ (system 4).

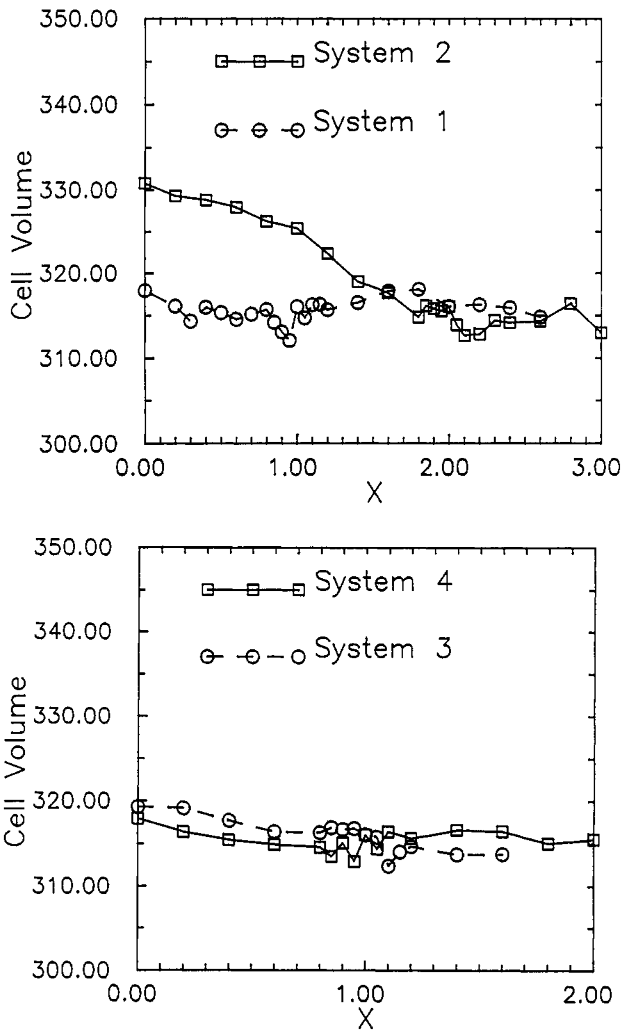

Figure 2. (a, top) Cell volume in Å^3 for $Ba_4BiPb_xTl_{3-x}O_{12-\delta}$ (1) and $Ba_4Bi_{3-x}Pb_xTlO_{12-\delta}$ (2). (b, bottom) Cell volume in Å^3 for $Ba_4Bi_{2-x}Pb_2Tl_xO_{12-\delta}$ (3) and $Ba_4Bi_xPb_{4-2x}Tl_xO_{12-\delta}$ (4).

unit cell, which is slightly higher than the value of 0.13 found by neutron diffraction data.[10] Argon annealing significantly increased the value of δ to 2.21, indicating a high concentration of oxygen vacancies. In general, as the material was doped toward the superconducting region, the degree of oxygen vacancy reached a maximum in the superconducting region (Figure 1).

Results and Discussion

Prior to a discussion of our results, a consideration of previous doping studies of the $Ba(Bi,Pb,Tl)O_3$ system is required. Recently, Hull et al.[8] described doping experiments on the $BaPb_{0.73-a}Bi_{0.27}Tl_aO_3$ and $BaPb_{0.55}Bi_{0.45-b}Tl_bO_3$ systems. For doping of Tl into the known superconductor $Ba(Bi,Pb)O_3$ their data agree with our results in that increasing Tl lowers T_c. However, their data indicated a loss of superconductivity at $a = 0.2$, whereas our results indicate a loss of superconductivity at $a = 0.075$ (system 1, $x = 0.3$) followed by the reappearance of superconductivity at $a = 0.225$ (system 1, $x = 0.9$). For doping of Tl into the Bi sites of $BaPb_{0.55}Bi_{0.45}O_3$, they report the observation of superconductivity from $b = 0.1$ to $b = 0.2$, with a peak T_c of ≈7 K. However, their reported preparation of the materials was done without the presence of excess Tl and, although at a lower temperature, for a much longer reaction period (over 13 h). Despite the fact that the reported temperatures are below the vaporizing point of Tl_2O_3, gradual loss of Tl still occurs well below 750 °C due to the high vapor pressure of the metal oxide. Therefore, given the different stoichiometries investigated, the lack of magnetic data on the volume of sample exhibiting superconductivity, and the absence of elemental analysis results, we feel that the data presented below are not necessarily incompatible with those previously reported.

All samples exhibited either tetragonal or orthorhombic symmetry; no monoclinic distortions were observed. Cell volume calculations for systems 1 and 2 (Figure 2a) and for systems 3 and 4 (Figure 2b) indicate that the cell volume changes as expected as elements of different size are substituted (see below).

For doping of Tl into the Pb sites of $BaBi_{0.25}Pb_{0.75}O_3$ ($Ba_4BiPb_{3-x}Tl_xO_{12-\delta}$; system 1), the samples were multiphase with some lines belonging to $Ba_2Tl_2O_5$ evident for $x \geq 2.60$ (Figure 3a). As x was increased further, the samples exhibited tetragonal symmetry to the point where the system became superconducting, which was accompanied by conversion to an orthorhombic structure. Above the region of superconductivity attributed to $Ba_4BiPb_2TlO_{12-\delta}$ and before the system approached the composition of $BaBi_{0.25}Pb_{0.75}O_3$, tetragonal symmetry was again observed, which gave way to orthorhombic symmetry as the composition neared that of the known $BaBi_{0.25}Pb_{0.75}O_3$ superconductor. The overall lack of change in the unit cell axes and cell volume indicates that a simple substitution of Tl^{3+} for Pb^{4+} is not occurring, since Tl^{3+}

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[10] Iqbal, Z. *Bull. Mater. Sci.* **1990**, *25*, 1100.

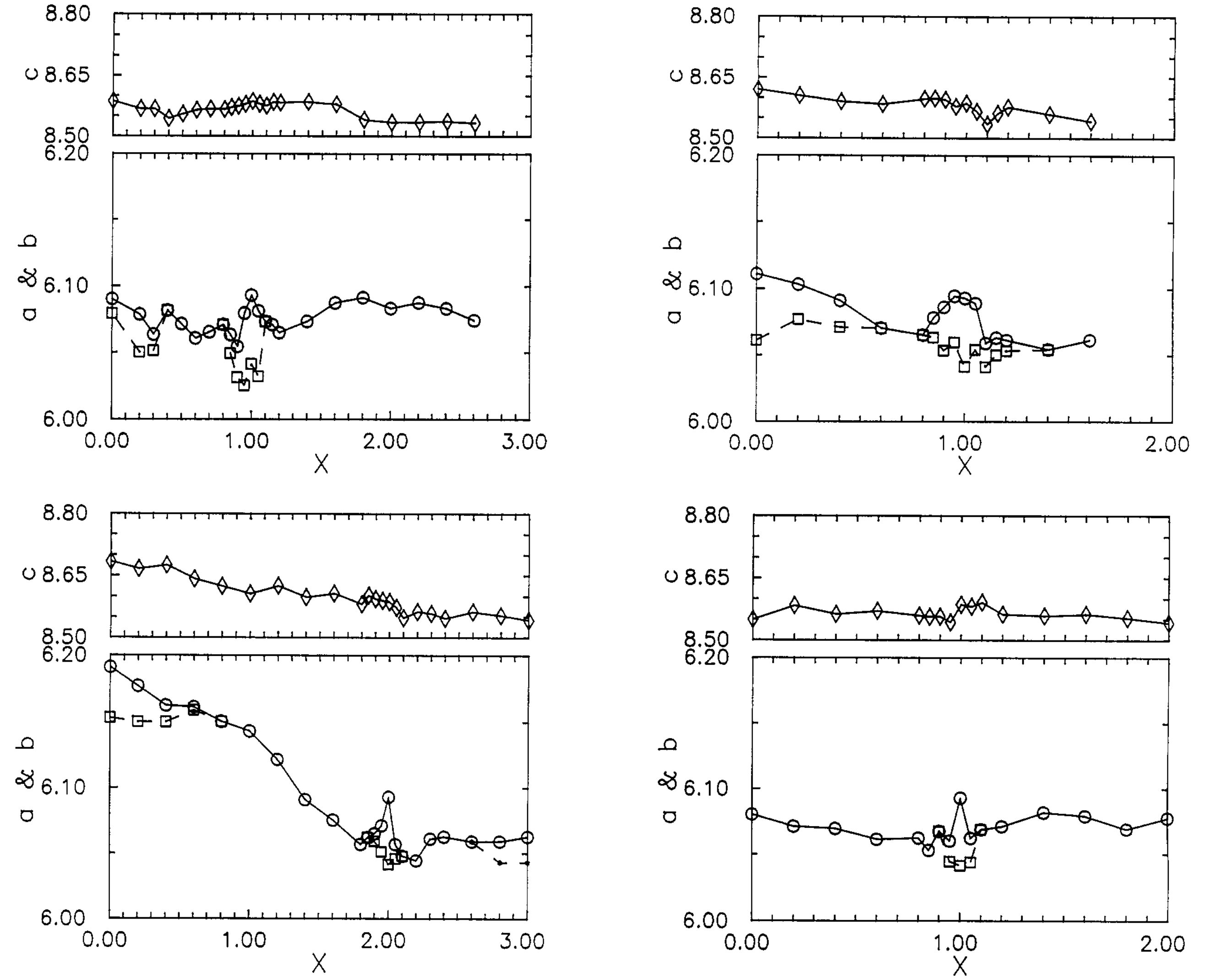

Figure 3. (a, top left) *a*, *b*, and *c* in Å for $Ba_4BiPb_{3-x}Tl_xO_{12-\delta}$. (b, bottom left) *a*, *b*, and *c* in Å for $Ba_4Bi_{3-x}Pb_xTlO_{12-\delta}$. (c, top right) *a*, *b*, and *c* in Å for $Ba_4Bi_{2-x}Pb_2Tl_xO_{12-\delta}$. (d, bottom right) *a*, *b*, and *c* in Å for $Ba_4Bi_xPb_{4-2x}Tl_xO_{12-\delta}$.

is 0.12 Å larger than Pb^{4+}.[11] Therefore, we conclude that doping of Tl into this system causes the Bi sites to undergo a disproportionation from the 4+ valence theorized for $BaPb_{0.75}Bi_{0.25}O_3$ into Bi^{3+} and Bi^{5+}, in order to accommodate the presence of the 3+ valence of Tl; similar results have been observed for Tl doping into $BaBiO_3$.[5,7] Thus, no significant alteration of the unit cell parameters is expected, since the presence of larger Tl^{3+} (0.96 Å)[11] is offset by the appearance of Bi^{5+} (0.74 Å).[11]

For doping of Pb into the Bi site of $BaBi_{0.75}Tl_{0.25}O_3$ ($Ba_4Bi_{3-x}Pb_xTlO_{12-\delta}$; system **2**), the known orthorhombic symmetry gave way to tetragonal symmetry at $x = 0.8$ (Figure 3b). However, at $x = 1.9$, orthorhombic symmetry was again observed. Incorporation of over 70% Pb ($x = 2.7$) induced a weak orthorhombic splitting after the orthorhombic symmetry of the parent compound had vanished. Previous work has indicated that $BaBi_{0.75}Tl_{0.25}O_3$ is more accurately written as $BaBi^{5+}{}_{0.5}Bi^{3+}{}_{0.25}Tl^{3+}{}_{0.25}O_3$.[5,7] Therefore, doping of Pb^{4+} into this system, which causes a decrease in the unit cell volume, results in a reduction in the amount of Bi^{3+} as opposed to Bi^{5+}, since Pb^{4+} (0.84 Å) is smaller than Bi^{3+} (0.96 Å) but larger than Bi^{5+} (0.74 Å).[11]

Doping of Tl into the Bi sites of $BaBi_{0.5}Pb_{0.5}O_3$ ($Ba_4Bi_{2-x}Tl_xPb_2O_{12-\delta}$; system **3**) induced a loss of orthorhombic symmetry at $x = 0.6$ (Figure 3c). The system returned to orthorhombic at $x = 0.85$, while high Tl levels ($x \geq 1.7$) resulted in a multiphase product. The lack of any significant reduction or enlargement of the unit cell parameters is best interpreted by viewing the parent system as $Ba_4Bi^{3+}Bi^{5+}Pb_2O_{12}$. Therefore, doping Tl^{3+} into the Bi^{3+} sites would not lead to any significant increase in the unit cell since these two elements possess nearly identical ionic radii (0.95 and 0.96 Å, respectively).

For the final system (**4**), in which equimolar amounts of Tl and Bi were doped into $BaPbO_3$, tetragonal symmetry was observed for all samples except when the Tl and Bi contents were within 1.25% ($x = 0.05$) of the parent $Ba_4BiPb_2TlO_{12-\delta}$ composition (Figure 3d). Again, the lack of any significant change in the overall cell parameters indicates that doping of Tl and Bi is occurring via a pseudodisproportionation scheme. Since 3+ is the highest valence of Tl, Bi would have to substitute in as Bi^{5+} in order to accommodate a nearly full amount of oxygen in the unit cell. Therefore, the average of these atomic radii (0.845 Å) is nearly identical to that of Pb^{4+} (0.84 Å), and no significant increase or decrease in the unit cell parameters is expected.

Resistivity data were used primarily to confirm the superconducting transitions and to demonstrate the narrow onsets. Zero resistance was observed for the superconducting samples, and a transition width of 0.5 K was viewed as evidence of a single-phase material. The parent

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[11] Table of Ionic Radii, *CRC Handbook of Chemistry and Physics*, 60th ed.; Weast, R., Ed.; CRC Press: Cleveland, 1981; p F-214.

compound displayed nearly temperature-independent resistivity at temperatures above the superconducting transition temperature, while samples near the composition of the parent compound exhibited weak metallic behavior, with resistivity decreasing as the temperature decreased. However, the rest of the samples exhibited behavior similar to the extremes of the doping region, i.e., semiconducting behavior for $Ba_4Bi_3TlO_{12}$ ($BaBi_{0.75}Tl_{0.25}O_3$)[7] and $Ba_4Bi_2Tl_2O_{12}$ ($BaBi_{0.5}Tl_{0.5}O_3$),[7] metallic conduction for $BaPbO_3$,[12] and semimetallic behavior for $Ba_4Bi_2Pb_2O_{12}$ ($BaBi_{0.5}Pb_{0.5}O_3$).[12]

Clearly, the presence of both lowered symmetry and oxygen vacancies are crucial to superconductivity in the $Ba_4BiPb_2TlO_{12-\delta}$ system. Since the appearance of orthorhombic symmetry and superconductivity for the parent compound is centered around a 1:2:1 Bi:Pb:Tl ratio, as is the appearance of the highest degree of oxygen vacancy (Figure 1), a comparison between the results obtained in this system and those obtained in an annealing study of $BaBi_{0.5}Tl_{0.5}O_{3-y}$ is warranted.[7] In the latter, y was found to be 0.0, 0.46, and 0.84 for low-temperature oxygen-, air-, and argon-annealed samples, respectively.

If the parent compound $Ba_4BiPb_2TlO_{12-\delta}$ is viewed as Pb-doped $BaBi_{0.5}Tl_{0.5}O_{3-y}$, then the anomalous carrier behavior reported for oxygen-deficient samples of $BaBi_{0.5}Tl_{0.5}O_{3-y}$[7] and the superconductivity in $Ba_4BiPb_2TlO_{12-\delta}$ can be attributed to the appearance of ordering of oxygen deficiencies or metal sites in systems where the amounts of Tl and Bi allow for such ordering. If it is assumed that this ordering is two-dimensional, Pb substitution can initially eliminate the stoichiometry necessary to achieve such ordering, until the next stoichiometric combination that could lead to a two-dimensional system is reached. In the case of a cubic derivative system with three metals, written as $Ba_ABi_XPb_YTl_ZO_{3A}$, the lowest value of A that can produce a centrosymmetric layered system is 4. In such a system, the three possible combinations are $Ba_4Bi_2PbTlO_{12}$, $Ba_4BiPbTl_2O_{12}$, and the known superconductor $Ba_4BiPb_2TlO_{12-\delta}$. The unique aspect of $Ba_4BiPb_2TlO_{12-\delta}$, as opposed to the two other systems that also fill the requirements, is that it is the only one possessing equimolar amounts of Tl and Bi. On the basis of superconductivity in this system, as well as the anomalous carrier behavior for $BaBi_{0.5}Tl_{0.5}O_{3-y}$,[7] ordering of the oxygen vacancies or the metal centers remains a strong possibility. There appears to be a correlation between the percentage of oxygen deficiencies in the lattice (15% for $BaBi_{0.5}Tl_{0.5}O_{2.54}$ vs 7.6% for $Ba_4BiPb_2TlO_{11.09}$) and the fraction of metal sites occupied by Bi andTl, suggesting that the pure Bi/Tl perovskite can tolerate a higher degree of oxygen vacancies. Finally, the similarity between the change from orthorhombic symmetry of the superconducting parent compound to tetragonal symmetry with a larger c axis (approximately 0.23 Å) for the argon-annealed sample is similar to the increase in the unit cell symmetry seen between air- and argon-annealed $BaBi_{0.5}Tl_{0.5}O_{3-y}$.[7] Here, the system changes from orthorhombic symmetry for $BaBi_{0.5}Tl_{0.5}O_{3-y}$ (y = 0.46) to tetragonal symmetry for the argon-annealed sample (y = 0.84), which is accompanied by a 0.37-Å increase in the c axis. These results strongly suggest that a similar type of ordering of the oxygen vacancies or metal centers may be occurring in both materials.

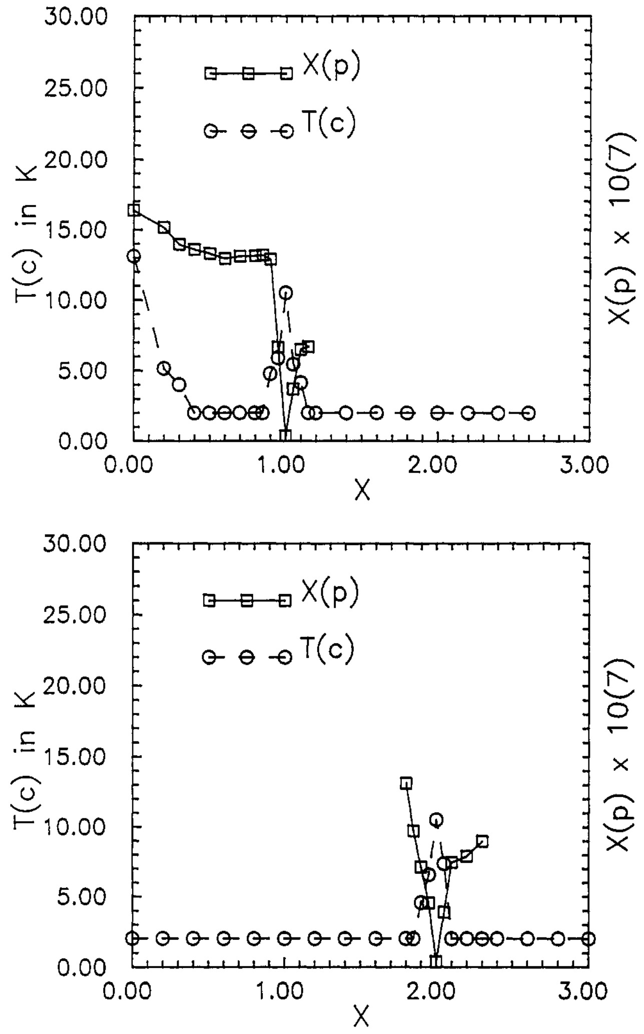

Figure 4. (a, top) T_c in K and χ_p in emu/gm × 10^7 for $Ba_4BiPb_{3-x}Tl_xO_{12-\delta}$. (b, bottom) T_c in K and χ_p in emu/gm × 10^7 for $Ba_4Bi_{3-x}Pb_xTlO_{12-\delta}$.

Since the valence of Tl and Bi in $BaBi_{0.5}Tl_{0.5}O_3$ is 3+ and 5+, respectively, then for $Ba_4BiPb_2TlO_{12}$ with no oxygen deficiencies the valence of these elements would have to be the same if Pb is assigned as 4+. If this is the case, however, then the actual number of 6s valence electrons would be zero, since Tl^{3+}, Bi^{5+}, and Pb^{4+} are all $6s^0$ states. Clearly, the presence of oxygen vacancies is a requirement for superconductivity in this system as opposed to $(Ba,K)BiO_3$ and $Ba(Bi,Pb)O_3$, in that it causes a repopulation of the 6s band, which leads to superconductivity as in the other $BaMO_3$ systems.

However, the susceptibility data seem to contradict the view of increasing density of states at the Fermi surface (E_f) giving rise to superconductivity in this system, as predicted by BCS theory.[13] The sharp superconducting transitions observed, as well as the large Meissner volume (>90%), indicate that the observed inverse correlation between T_c and the strength of the Pauli paramagnetism is associated with the changes in the electronic structure of the material as the metal concentrations are changed. For all samples, the observed increase in the Pauli paramagnetism and the decrease in the transition temperature (Figures 4 and 5) indicate that the number of electrons at the Fermi surface decreases[14] as the structure changes from

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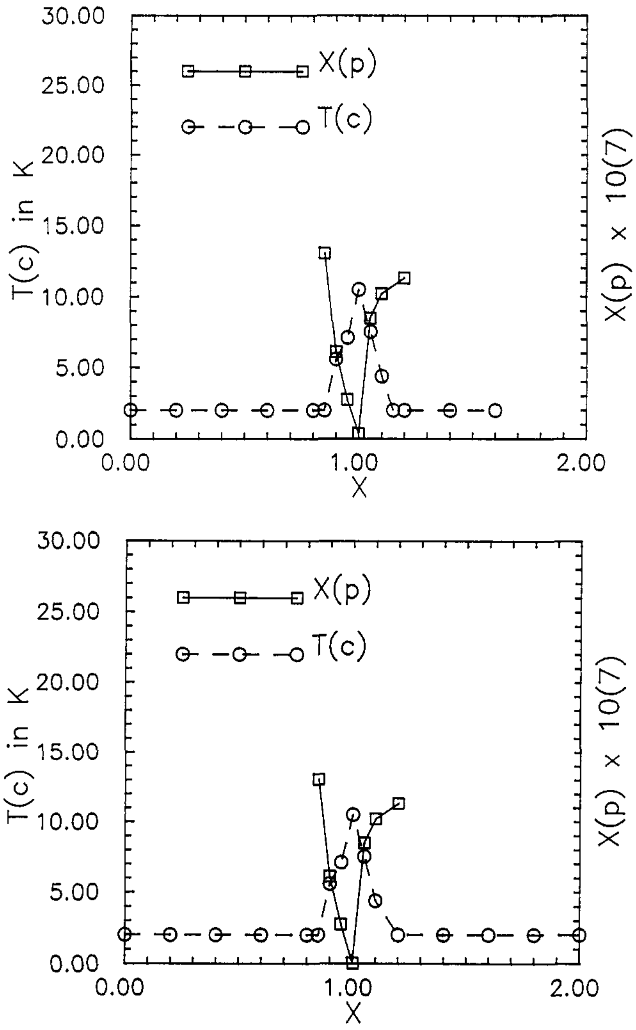

Figure 5. (a, top) T_c in K and χ_p in emu/gm × 10^7 for $Ba_4Bi_{2-x}Pb_2Tl_xO_{12-\delta}$. (b, bottom) T_c in K and χ_p in emu/gm × 10^7 for $Ba_4Bi_xPb_{4-2x}Tl_xO_{12-\delta}$.

orthorhombic to tetragonal and the number of oxygen vacancies decreases.

Figure 6 is a schematic illustration of the band structure previously proposed for $Ba(Bi,Pb)O_3$,[12] which should be generally applicable to systems such as $Ba_4BiPb_2TlO_{12-\delta}$. It has been suggested that $BaPbO_3$ becomes superconducting as the number of electrons in the 6s band increases upon doping with Bi^{4+}. Figure 6a represents $BaPbO_3$, where the 6s band is only slightly populated due to the covalent 6s–O 2p bonds. Figure 6b shows that, as Bi^{4+} is substituted for Pb^{4+}, the number of 6s electrons increases, resulting in a superconducting state. Figure 6a is also applicable to $Ba_4BiPb_2TlO_{12}$, where the population of the 6s band should also be small, as in $BaPbO_3$. For $Ba_4BiPb_2TlO_{12-\delta}$, population of the 6s band is attributed to the presence of oxygen vacancies, as illustrated in Figure 6b. A loss of oxygen vacancies should therefore decrease the number of 6s electrons, lowering the transition temperature and decreasing the Pauli paramagnetism. However, the Pauli paramagnetic signal actually increases as the composition is altered from a 1:2:1 Bi:Pb:Tl ratio, indicating an increasing number of conduction electrons (presumably 6s) for the system as the degree of oxygen vacancies and T_c decrease. Thus, the overall density of states at E_f not only is dependent upon the number of oxygen vacancies but also is highly sensitive to changes in the composition of the parent material. This suggests that structural changes due to order/disorder of the oxygen vacancies and/or metal sites may be important.

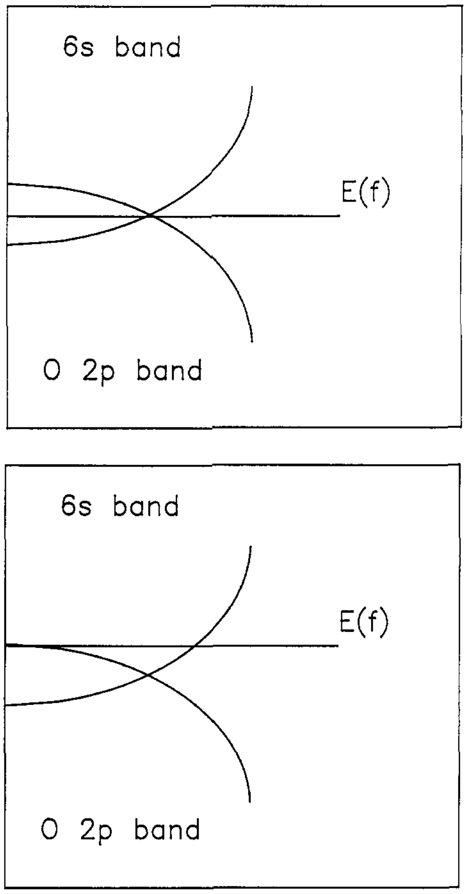

Figure 6. Schematic of 6s band overlap for (a, top) $BaPbO_3$ and $Ba_4(Tl,Pb,Bi)_4O_{12}$, nonsuperconducting and (b, bottom) $BaPb_{0.75}Bi_{0.25}O_3$ and $Ba_4(Bi,Pb,Tl)_4O_{12}$, superconducting.

Conclusion

The studies presented here demonstrate that the properties of the $Ba_4BiPb_2TlO_{12-\delta}$ system are extremely sensitive to the metal atom composition. This dependency appears to not be a simple valence charge effect. The present results, together with recent data for oxygen-deficient $BaBi_{0.5}Tl_{0.5}O_{3-y}$,[7] provide suggestive evidence for ordering of oxygen vacancies and/or metal sites. Unfortunately, the similarity in scattering power between the three metals makes the latter extremely difficult to address by X-ray or neutron crystallographic methods.

The observed relationship between T_c and the Pauli paramagnetism has been interpreted in terms of an interdependent relationship between the degree of overlap between the 6s and the 2p bands and E_f. In these metal oxide systems, the degree of overlap between the metal 6s and oxygen 2p bands, and the overlap between this region and the Fermi surface, appear to be crucial to superconductivity, and are significantly more important than the expected classic dependency on the density of states and T_c.[13]

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Registry No. $Ba_4BiPb_2TlO_{11.1}$, 143075-95-0.