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LETTER TO THE EDITOR

Synthesis of Cuprates of Perovskite Structure in the Ba–Pb–Cu–O, Ba–Bi–Cu–O, and Ba–Pb–Tl–Cu–O Systems: Possible High T_c Superconductivity in a Perovskite-like Phase in the Ba–Pb–Tl–Cu–O System[1]

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Cubic cuprates ($a \sim 18.6$ Å) with a $BaCuO_2$-type structure were obtained in the Ba–Pb–Cu–O and Ba–Bi–Cu–O systems by the reaction of the component oxides at a high temperature (1370–1420 K), followed by quenching. By annealing these phases in oxygen at 1070–1120 K, perovskite-like phase ($a \sim 4.3$ Å) of the formulae $BaPb_{1-x}Cu_xO_{3-y}$ and $BaBi_{1-x}Cu_xO_{3-y}$ ($0 < x \leq 0.5$) were obtained. A perovskite of nominal composition $BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$, prepared by a similar procedure, was found to be superconducting with a T_c of ~ 70 K. © 1994 Academic Press, Inc.

$BaPbO_3$ and $BaBiO_3$ are two well-known perovskites with widely different properties. While $BaPbO_3$ is metallic (1), $BaBiO_3$ is an insulator consisting of Bi(III) and Bi(V) ordered at unique sites (2). More importantly, the solid solution between the two, $BaPb_{1-x}Bi_xO_3$, becomes superconducting when $x \sim 0.25$ (3) with a T_c of 12 K. $Ba_{1-x}K_xBiO_3$ is also superconducting witha T_c of 30 K (4). In contrast to these three-dimensional superconducting oxides, all the known high-T_c cuprate superconductors discovered in recent years possess layered structures consisting of CuO_2 sheets (5–8). As part of our continuing efforts to understand the chemistry of oxide superconductors, we have explored the possibility of synthesizing perovskite-like oxides containing copper along with bismuth/lead/thallium at the *B* site. We considered it to be feasible to synthesize such cuprates, since it is known that Cu(II/III) and Pb(IV) occupy the same sites in oxides such as (Pb, Cu)Sr_2(Ca, Y) $Cu_2O_{7-\delta}$ (9). It is also known that Pb(IV) in the layered perovskite $Ba_4Pb_3O_{10}$ (10) can be substituted for by Cu(II). We have therefore attempted to prepare perovskite-like phases in the $BaPb_{1-x}Cu_xO_{3-y}$ and $BaBi_{1-x}Cu_xO_{3-y}$ systems over the composition range ($0 < x \leq 0.5$) by a technique which involves quenching these compositions from 1370–1420 K, followed by annealing in oxygen at 1070–1120 K. Encouraged by the formation of perovskite-like phases in the Ba–Pb–Cu–O and Ba–Bi–Cu–O systems, we attempted to prepare perovskite phases in the Ba–Tl–Cu–O and Ba–Pb–Tl–Cu–O systems. We have indeed been able to prepare a perovskite-like phase with the nominal composition $BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$ ($y \sim 0.85$) by quenching the product of the reaction at 1220 K, followed by postannealing. This perovskite cuprate is superconducting, unlike members of the Ba–Pb–Cu–O and Ba–Bi–Cu–O system. We believe that the formation of perovskite-like phases in the Ba–Pb–Tl–Cu–O systems incorporating copper along with lead/bismuth/thallium at the *B*-site is of considerable interest. The observation of high-T_c superconductivity in $BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$ would indeed be significant, if further studies could fully establish the three-dimensional nature of this cuprate.

In order to prepare members of the Ba–Pb–Cu–O and Ba–Bi–Cu–O systems corresponding to the nominal compositions $BaPb_{1-x}Cu_xO_{3-y}$ and $BaBi_{1-x}Cu_xO_{3-y}$, mixtures of BaO_2, PbO_2/Bi_2O_3, and CuO of appropriate compositions were heated in air at 1070–1170 K. Since the products obtained at 1070–1170 K were multiphasic, the solid state reaction was next carried out at higher temperatures (1370–1420 K), followed by quenching the samples in liquid N_2/air to obtain single-phase products. The quenched products were then annealed at 1070–1120 K in flowing oxygen. Synthesis of thallium-containing samples in the Ba–Tl–Cu–O and Ba–Pb–Tl–Cu–O systems was carried out in sealed silver tubes. The oxygen content (oxidizing power) of the samples was determined by iodometric titration. X-ray powder diffraction patterns were recorded with a JEOL JDX-8P diffractometer using Cu*Kα* radiation. Electrical resistivities were measured by a four-

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probe method using sintered pellets. Magnetic susceptibility measurements were carried out with a Lewis Coil magnetometer (Series 300) at an applied field of 10 Oe down to 15 K.

Our initial efforts to prepare perovskite phases corresponding to the nominal compositions $BaPb_{1-x}Cu_xO_{3-y}$ and $BaBi_{1-x}Cu_xO_{3-y}$ for $0 < x \leq 0.5$ by reacting BaO_2, PbO_2/Bi_2O_3, and CuO in air at 1120–1170 K were not successful, the products being multiphasic and consisting mainly of $BaCuO_2$ and a perovskite-related phase. For instance, the X-ray powder diffraction pattern of the nominal composition, $BaPb_{0.5}Cu_{0.5}O_{3-y}$, synthesized at 1170 K in air (Fig. 1a), showed low-angle reflections at $d \sim 17.8$, 8.9, and 5.9 Å, indicative of the formation of a perovskite superstructure as in $Ba_2Tl_2O_5$ (11). Since we could not obtain single-phase materials under these conditions, we carried out the reaction at higher temperatures (1370–1420 K), close to the melting point of the reaction mixtures, followed by quenching. X-ray powder diffraction patterns of the products thus obtained were completely different. A typical pattern for the nominal composition $BaPb_{0.75}Cu_{0.25}O_{3-y}$ is shown in Fig. 1b. This pattern could be indexed on a cubic, $BaCuO_2$-like unit cell with $a = 18.62$ Å. This phase, however, transformed to a perovskite-like structure upon heating in O_2 at 1070–1120 K. We show the X-ray diffraction pattern of the perovskite-

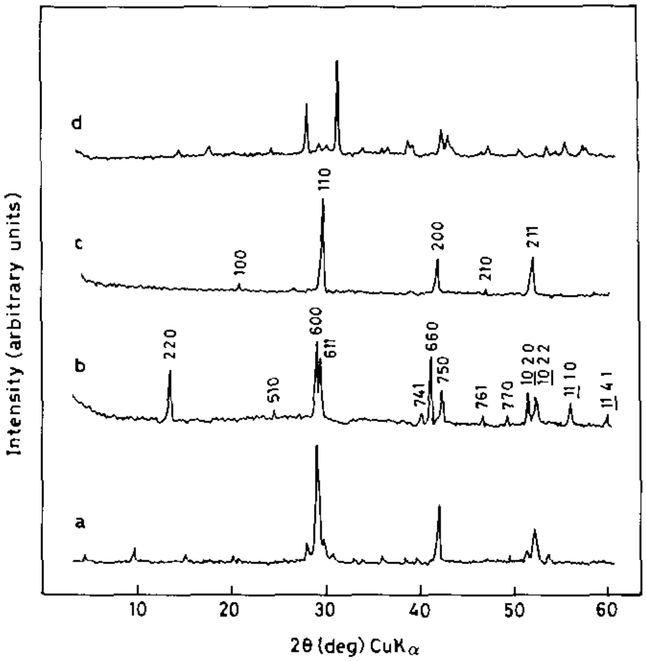

FIG. 1. X-ray powder diffraction patterns of nominal compositions of (a) $BaPb_{0.5}Cu_{0.5}O_{3-y}$ synthesized at 1170 K in air, (b) $BaPb_{0.75}Cu_{0.25}O_{3-y}$ quenched in liquid N_2 from 1370 K, (c) sample (b) annealed in oxygen at 1070 K. The X-ray diffraction pattern of $BaCuO_2$ quenched from 1370 K is shown in (d).

TABLE 1

Composition, Synthesis Condition, Lattice Parameter, and Oxygen Content for $BaPb_{1-x}Cu_xO_{3-y}$, $BaBi_{1-x}Cu_xO_{3-y}$, and $BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$ Oxides

Composition	Synthesis condition	y^a	Lattice parameter (Å)	Electrical property
$BaPbO_{3-y}$	1120 K, 24 hr, air	0.03	4.270(5)	Metallic
$BaPb_{0.75}Cu_{0.25}O_{3-y}$	1370 K, 12 hr, quenched in liquid N_2	0.85	18.62(2)	Insulating
$BaBi_{0.75}Cu_{0.25}O_{3-y}$	1420 K, 12 hr, quenched in air	0.74	18.46(5)	Insulating
$BaPb_{0.85}Cu_{0.15}O_{3-y}$	1370 K, 12 hr, quenched in liquid N_2; 1070 K, 24 hr, O_2	0.17	4.281(4)	Metallic
$BaPb_{0.75}Cu_{0.25}O_{3-y}$	1370 K, 12 hr, quenched in liquid N_2; 1070 K, 24 hr, O_2	0.29	4.294(6)	Metallic
$BaPb_{0.50}Cu_{0.5}O_{3-y}$	1370 K, 12 hr, quenched in liquid N_2; 1070 K, 24 hr, O_2	0.58	4.322(5)	Semiconducting
$BaBi_{0.85}Cu_{0.15}O_{3-y}$	1420 K, 12 hr, quenched in air; 1120 K, 24 hr, O_2	0.19	4.277(5)	Semiconducting
$BaBi_{0.75}Cu_{0.25}O_{3-y}$	1420 K, 12 hr, quenched in air; 1120 K, 24 hr, O_2	0.28	4.301(6)	Semiconducting
$BaBi_{0.50}Cu_{0.50}O_{3-y}$	1420 K, 12 hr, quenched in air; 1120 K, 24 hr, O_2	0.52	4.320(5)	Semiconducting
$BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$(I)	1220 K, 6 hr, sealed Ag tube, air-quenched; 870 K, 3 hr, O_2; 770 K, 12 hr, N_2	0.85	4.281(4)	Superconducting (T_c = 70 K)
$BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$(II)	1220 K, 6 hr, sealed Ag tube, air-quenched; 870 K, 3 hr, O_2; 770 K, 12 hr, N_2	0.89	4.289(7)	Superconducting (T_c = 72 K)

[a] Determined by iodometric titration. The uncertainty in y is within ±0.02.

like structure in Fig. 1c. We could prepare monophasic samples of $\mathrm{BaPb}_{1-y}\mathrm{Cu}_x\mathrm{O}_{3-y}$ in the perovskite-like structure over the composition range ($0 < x \leq 0.50$) by this procedure (involving initial heating at 1370–1420 K, followed by annealing in O_2 at 1070–1120 K).

By following the procedure employed for the preparation of $\mathrm{BaPb}_{1-x}\mathrm{Cu}_x\mathrm{O}_{3-y}$, we have prepared members of the $\mathrm{BaBi}_{1-x}\mathrm{Cu}_x\mathrm{O}_{3-y}$ family ($0 < x \leq 0.5$) as well. In Table 1 we list the compositions and unit cell parameters of the perovskite-like phases in the $\mathrm{BaPb}_{1-x}\mathrm{Cu}_x\mathrm{O}_{3-y}$ and $\mathrm{BaBi}_{1-x}\mathrm{Cu}_x\mathrm{O}_{3-y}$ families, along with the oxygen content obtained by idometric titration. We present in Fig. 2 the X-ray powder diffraction patterns of a few compositions of the perovskite-like phases. The actual structures of these phases are likely to be distorted to lower symmetry, as suggested by the broadening/splitting of the high-angle reflections in the X-ray diffraction patterns. It is difficult to visualize how a BaCuO_2-like phase transforms to a perovskite phase, since the two structures seem unrelated at first sight. A recent single crystal X-ray study (12) has shown that the structure of BaCuO_2 is quite complex, consisting of ordered as well as disordered parts where the square-planer copper takes up additional oxygen at apical positions, giving rise to a "perovskite-like configuration" of the copper atoms. It therefore seems feasible that the BaCuO_2-like phases (of the compositions $\mathrm{BaPb}^{\mathrm{II}}_{1-x}\mathrm{Cu}_x\mathrm{O}_{3-y}$ and $\mathrm{BaBi}^{\mathrm{III}}_{1-x}\mathrm{Cu}_x\mathrm{O}_{3-y}$) prepared at high temperatures pick up additional oxygen upon annealing at lower temperatures (1070–1120 K), thus transforming into a perovskite-like structure.

The oxygen content of the perovskite-like phases obtained by iodometric titration is listed in Table 1. We see that the oxygen content decreases with increasing x in both the series, $\mathrm{BaPb}_{1-x}\mathrm{Cu}_x\mathrm{O}_{3-y}$ and $\mathrm{BaBi}_{1-x}\mathrm{Cu}_x\mathrm{O}_{3-y}$, the oxygen deficiency y being approximately equal to x. The result is consistent with the replacement of Pb(IV)/Bi(III, V) in BaPbO_3/BaBiO_3 by Cu(II). Significantly, there is a systematic increase in the pseudocubic lattice parameter a with increasing x in both the series. The oxygen content of the corresponding samples quenched from 1370–1420 K is much lower (Table 1), suggesting that lead and bismuth are likely to exist essentially in the II and III oxidation states in the quenched samples.

Electrical resistivity measurements on perovskite-like $\mathrm{BaPb}_{1-x}\mathrm{Cu}_x\mathrm{O}_{3-y}$ show interesting results. The products obtained by quenching the BaCuO_2-like structures are generally semiconducting. The perovskite phases obtained after annealing in O_2 at 1070 K, however, show metallic behavior for $x \leq 0.25$ and semiconducting behavior for $x = 0.5$. On the other hand, $\mathrm{BaBi}_{1-x}\mathrm{Cu}_x\mathrm{O}_{3-y}$ mem-

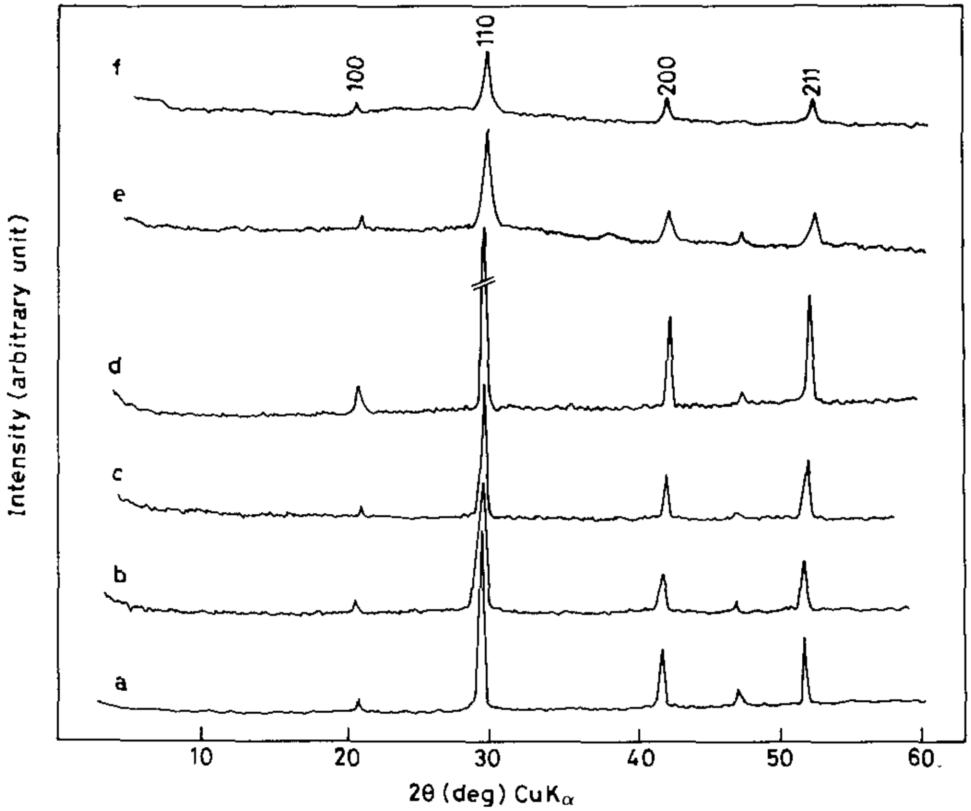

FIG. 2. X-ray powder diffraction patterns of perovskite-like phases (a) $\mathrm{BaPb}_{0.75}\mathrm{Cu}_{0.25}\mathrm{O}_{3-y}$, (b) $\mathrm{BaPb}_{0.5}\mathrm{Cu}_{0.5}\mathrm{O}_{3-y}$, (c) $\mathrm{BaBi}_{0.75}\mathrm{Cu}_{0.25}\mathrm{O}_{3-y}$, (d) $\mathrm{BaBi}_{0.5}\mathrm{Cu}_{0.5}\mathrm{O}_{3-y}$, (e) $\mathrm{BaPb}_{0.25}\mathrm{Tl}_{0.25}\mathrm{Cu}_{0.5}\mathrm{O}_{3-y}$, and (f) sample (e) annealed in nitrogen at 770 K.

bers are insulating or semiconducting, just as is the parent $BaBiO_3$, independent of the structure. Typical resistivity-temperature curves of these pervoskites are shown in Fig. 3.

We investigated the formation of perovskite-like phases in the Ba–Tl–Cu–O and Ba–Pb–Tl–Cu–O systems by employing a method of synthesis similar to that described earlier for the perovskite-like phases in the Ba–Pb–Cu–O and Ba–Bi–Cu–O systems. Since Tl_2O_3 is volatile, we carried out the synthesis in sealed silver tubes by quenching the samples from 1120 K, followed by oxygen annealing at 770 K. While we could not prepare a perovskite-like phase in the Ba–Tl–Cu–O system by this procedure, we did not obtain a perovskite-like phase of nominal composition $BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$. We show the X-ray diffraction pattern of this cuprate in Fig. 2e. This material exhibited metallic behavior.

On annealing metallic $BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$ in nitrogen at 770 K, the material became superconducting without any significant change in the X-ray diffraction pattern (Fig. 2f). In Fig. 4, we show the electrical resistivity of the as-prepared, as well as N_2-annealed, samples of $BaPb_{0.25}Tl_{0.25}Cu_{0.5})O_{3-y}$. The bulk nature of the superconductivity was confirmed by dc magnetic susceptibility measurements (see inset in Fig. 4). Iodometric titrations showed that the oxygen content of superconducting $BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$ was considerably lower than that of the other perovskite phases (see Table 1).

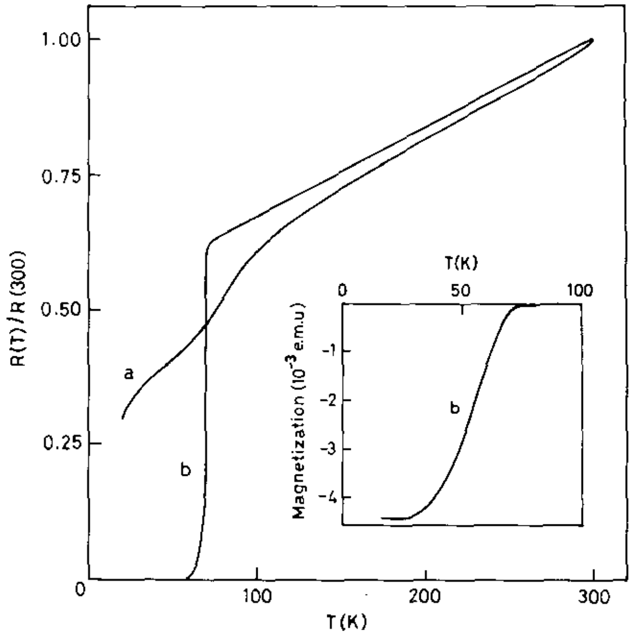

FIG. 4. Temperature dependence of the normalized resistance of $BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$; (a) as-prepared sample, (b) sample (a) annealed in nitrogen. Inset shows the temperature variation of the dc magnetic susceptibility for the superconducting composition (b).

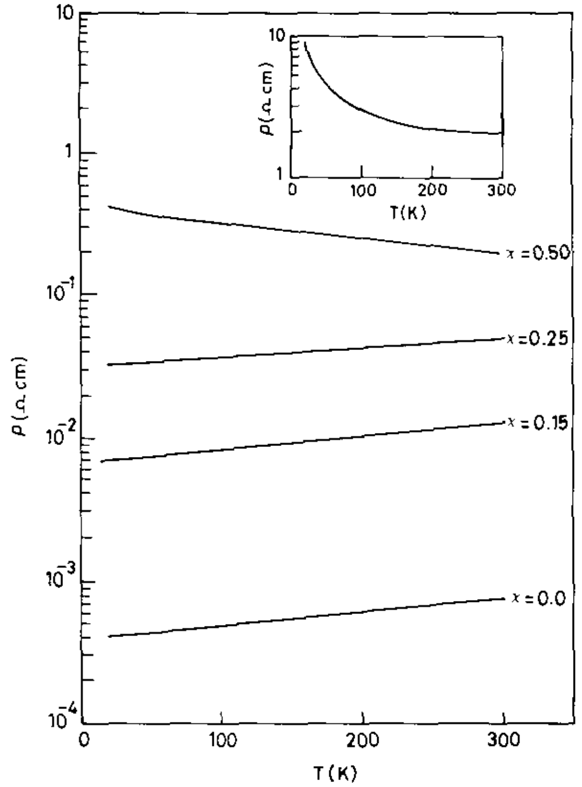

FIG. 3. Temperature dependence of the electrical resistivities of $BaPb_{1-x}Cu_xO_{3-y}$ perovskites. The temperature dependence of the electrical resistivity of the $BaBi_{0.75}Cu_{0.25}O_{3-y}$ perovskite is shown in the inset.

Superconductivity of $BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$ cannot be due to the impurity of layered $Ba_2Tl_2CuO_6$ (*I4/mmm*, $a = 3.87$, $c = 23.24$ Å), since such a phase is not likely to be formed with the low Tl content employed in the present preparation. We do not see any evidence for this phase nor for the nonsuperconducting Ba_2TlCuO_5 in the X-ray diffraction patterns (Figs. 2e and 2f). It seems that $BaPb_{0.25}Tl_{0.25}Cu_{0.5}O_{3-y}$ is a new superconducting cuprate with a defect-perovskite structure. We believe that the occurrence of superconductivity in a perovskite-like phase in the Ba–Pb–Tl–Cu–O system is of special significance, requiring further investigation.

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