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Modulation-free bismuth-lead cuprate superconductors: $BiPbSr_{1+x}L_{1-x}CuO_6$ and $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$

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Modulation-free $BiPbSrLCuO_6$ (L = La, Pr, Nd) and $BiPbSr_2YCu_2O_8$, which are isotypic with the $n = 1$ and 2 members of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ family, have been prepared and characterized. These parent compounds are nonsuperconducting, but when doped with holes by substitution chemistry give modulation-free superconducting cuprates of the general formulas $BiPbSr_{1+x}L_{1-x}CuO_6$ and $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$, exhibiting maximum T_c's of 24 and 85 K, respectively. Significantly, the hole concentration at the maximum T_c is 0.12 in the cuprate family with a single Cu-O layer and 0.22 in that with two Cu-O layers.

Since the discovery of high-temperature superconductivity in the Bi-Sr-Ca-Cu-O system by Maeda *et al.*,[1] a homologous series of oxides of the ideal formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ has been characterized for $n = 1$, 2, and 3 with maximum superconducting transition temperatures (T_c) of 10, 85, and 110 K, respectively.[2,3] The bismuth cuprates possess the same structural unit as that in the superconducting 2:1:4 (La_2CuO_4 related) and 1:2:3 ($LBa_2Cu_3O_7$, L = Y or rare earth) materials, viz., CuO_2 sheets with axial oxygen atoms giving CuO_5 pyramids or CuO_6 octahedra.[4,5] The structure of the bismuth cuprates is, however, more complex exhibiting an incommensurate modulation along the orthorhombic b direction. The modulation is approximately four and five times the subcell repeat in the $n = 1$ and 2 materials, respectively.[6,7] The modulation arises from the displacements of Bi, Sr, and Cu from their ideal positions in the subcell.[6] While the exact mechanism of the modulation is not fully understood, it is believed that insertion of extra oxygens in the BiO bilayers is the main cause of modulation.[7,8]

It was thought for some time that the modulation was related to the superconductivity of the bismuth cuprates. It is now known that compounds such as $Bi_2Sr_2LCu_2O_8$ (L = rare earth) which are not superconducting also exhibit superlattice modulation, similar to the $n = 2$ member of the superconducting bismuth cuprate family.[9] Superconductivity with $T_c = 14$ K has, however, been reported in a modulation-free $n = 1$ member of the Bi-Pb-Sr-Cu-O system.[10] Recently, modulation-free nonsuperconducting oxides of the type $BiPbSr_2MO_y$ (M = Mn, Fe, Co) have also been characterized.[11]

The modulated superstructure and the associated nonstiochiometry in chemical composition tend to mask the real mechanism of the doping of holes in bismuth cuprates. Thus, while the relationship between chemical substitution and hole concentration is known in the 2:1:4 and the 1:2:3 superconductors,[12] the mechanism of doping in the bismuth cuprate family is not yet clear. For example, stoichiometric $Bi_2Sr_2CaCu_2O_8$ should be a Mott-Hubbard insulator just as La_2CuO_4 or $YBa_2Cu_3O_6$; experimentally, however, the ideal $Bi_2Sr_2CaCu_2O_8$ which should be an antiferromagnetic insulator has not been prepared so far. Therefore, we considered it important to synthesize nonsuperconducting modulation-free parent compounds which are isotypic with the bismuth cuprates; these compounds could then be doped with holes by appropriate chemical substitution to impart superconductivity.

In this Rapid Communication, we report the synthesis and characterization of two series of superconducting bismuth cuprates of the formulas $BiPbSr_{1+x}L_{1-x}CuO_6$ (L = La, Pr, or Nd) and $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$ which are totally free of modulation. These cuprates are isotypic with the $n = 1$ and 2 members of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ cuprate family (which exhibit modulation). Establishing the occurrence of superconductivity in the two series of modulation-free bismuth cuprates reported here completes all the possible combinations between modulation and superconductivity, the presence of the former without the latter as well as the co-occurrence or absence of both having been known earlier.

Oxides of nominal composition $BiPbSr_{1+x}L_{1-x}CuO_6$ (L = La, Pr, Nd) ($n = 1$) and $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$ ($n = 2$) where prepared by heating the binary oxides and carbonates at 1100–1200 K for 24 h in air. Formation of desired phases was investigated by powder x-ray diffraction. Lattice parameters were derived by least-squares refinement of the powder-diffraction data of single phases. Magnetic susceptibility was measured by using a Model-300 Lewis Coil Force Magnetometer at an applied field of 10 Oe. Electrical resistivity of sintered pellets was measured by four-probe method. Hole concentration (formal Cu^{III} content) was determined by titration using a standard Fe^{II} solution. Electron-diffraction patterns were recorded using a JEOL JEM 200 CX electron microscope operating at 200 kV.

We have been able to prepare cuprates of the formula $BiPbSrLCuO_6$ (L = La, Pr, Nd) possessing an orthorhombic structure ($a = 5.318$ Å, $b = 5.379$ Å, $c = 24.51$ Å for the La compound) similar to $Bi_2Sr_2CuO_y$ [the $n = 1$ member of the $Bi_2(Ca,Sr)_{n+1}Cu_nO_{2n+4}$ series]. These BiPb cuprates, which are different from the La-substituted derivatives of $Bi_2Sr_2CuO_y$ reported in the literature,[13] are nonsuperconducting above 10 K and have a hole concentration of ~0.05 as determined by redox titrations. These phases may accordingly be regarded as the normal-valence compounds where copper is present essentially in the II state. Solid solutions of the type $BiPbSr_{1+x}L_{1-x}CuO_6$ were prepared by us with the idea of doping holes in the CuO_2 sheet in the parent cuprates. We could obtain a series of monophasic cuprates with x up to 0.5 when $L = La$ and up to $x = 0.3$ when $L = Pr$. In Fig. 1 we show the variation of the orthorhombic lattice parameters of $BiPbSr_{1+x}L_{1-x}CuO_6$ with x; the c parameter increases with increasing x, while the a and b parameters diverge due to the increasing orthorhombic distortion arising from the increasing size difference of the ions at the Sr and L sites. We show the variation of the hole concentration in $BiPbSr_{1+x}L_{1-x}CuO_6$ with the composition in Fig. 2. The hole concentration determined by titration in this series is smaller than the value expected for the ideal composition indicating that the samples are likely to be oxygen deficient. Thus, for the $x = 0.5$ member in $BiPbSr_{1+x}La_{1-x}CuO_y$, the copper valence should be 2.5 if $y = 6$, but the measured hole concentration corresponds to a valence of 2.2; this would imply that $y < 6$. Such oxygen deficiency has indeed been reported in $Bi_2Sr_2CuO_y$.[14]

We could prepare $BiPbSr_2YCu_2O_8$ [$n = 2$ analog of the $Bi_2(Ca,Sr)_{n+1}Cu_nO_{2n+4}$ family] which also possesses an orthorhombic structure. A similar Y derivative has been reported in the literature[15] as a member of the series $Bi_{2-x}Pb_xSr_2Ca_{1-x}Y_xCu_2O_{8+y}$. $BiPbSr_2YCu_2O_8$ prepared by us is, however, nonsuperconducting above 10 K,

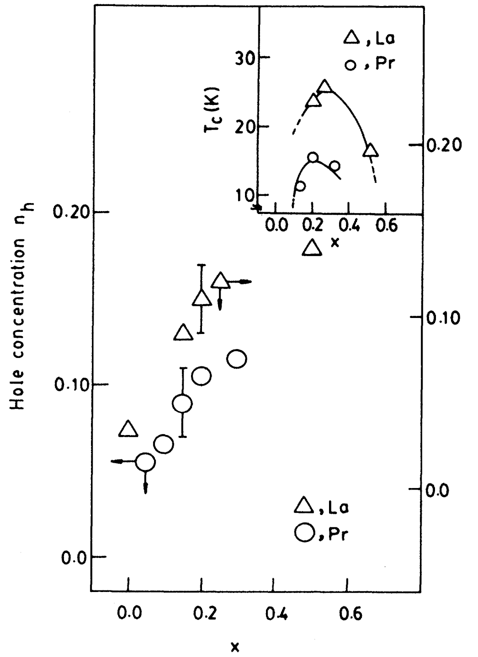

FIG. 2. Variation of hole concentration with x in the series $BiPbSr_{1+x}L_{1-x}CuO_6$. Triangles, $L = La$; circles, $L = Pr$. Inset shows a variation of T_c with x.

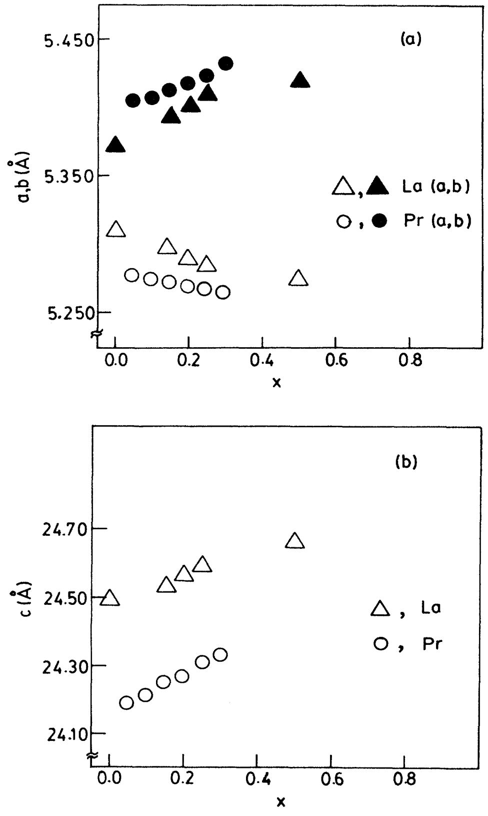

FIG. 1. Variation of the lattice parameters of $BiPbSr_{1+x}L_{1-x}CuO_6$ with composition.

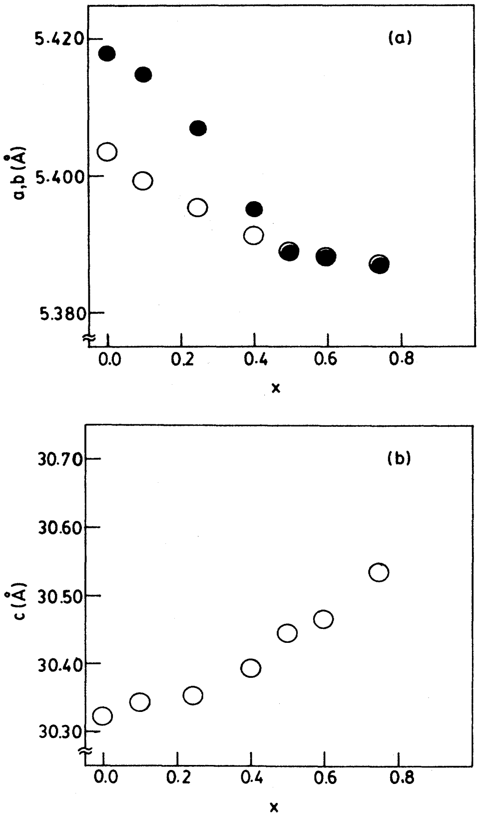

FIG. 3. Variation of the lattice parameters of $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$ with composition.

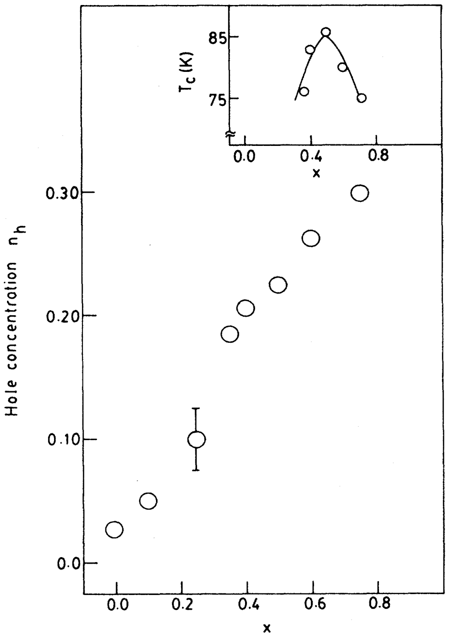

FIG. 4. Variation of the hole concentration with x in $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$. Inset shows a variation of T_c with x.

the hole concentration being less than 0.05. We have substituted Ca for Y to obtain the series $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$. Powder x-ray-diffraction data revealed that isostructural phases exist up to $x = 0.8$ showing systematic variation in the lattice parameters (Fig. 3). That the substitution of Y by Ca has enabled us to dope holes is evidenced from Fig. 4.

Electron-diffraction patterns reveal that the parent compounds as well as the hole-doped compositions in $BiPbSr_{1+x}L_{1-x}CuO_6$ and $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$ systems are free from the modulated superstructure that is characteristic of the $Bi_2(Ca,Sr)_{n+1}Cu_nO_{2n+4}$ family. In Fig. 5, we show the a^*-b^* reciprocal-section electron-diffraction patterns of two compositions to demonstrate the absence of superstructure modulation in the a and b directions. The absence of modulation in the Pb-substituted $Bi_2Sr_2CuO_y$ and in $BiPbSr_2MO_y$ (M = Mn, Fe, Co) which are isostructural with $Bi_2Sr_2CuO_y$ has been reported in the literature.[11,16] The reason for the absence of modulation when Bi is replaced by Pb in this family of oxides appears to be related to the decrease in the size mismatch between the rocksalt BiO bilayers and perovskitelike cuprate sheets. Structural modulation occurs in bismuth cuprates where the mismatch is compensated by the insertion of extra oxygen atoms in the BiO bilayers.

dc resistivity and magnetic susceptibility measurements show that the hole-doped materials are superconducting in both $BiPbSr_{1+x}L_{1-x}CuO_6$ and $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$. In the latter series, the parent compound is an antiferromagnetic insulator with a T_N of 42 K. On substitution of L by Sr in the former, we get a maximum T_c of 24 K when L = La (Ref. 17) at $x = 0.25$ and a maximum T_c of 15 K when L = Pr at $x = 0.20$. Superconductivity with a T_c of 24 K has been reported[13] in the modulated $Bi_2Sr_{1.5}La_{0.5}CuO_y$. The fact that we observe superconductivity in $BiPbSr_{1+x}La_xCuO_y$ with a similar T_c shows that structural modulation is not required for superconductivity. Although the hole concentration in $BiPbSr_{1+x}L_{1-x}CuO_6$, as determined by chemical titrations, increases continuously with x as expected, T_c shows a maximum around $x = 0.2$–0.25 where the hole concentration is around 0.12 (Fig. 2). In $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$, we see a continuous increase in the hole concentration with increasing x (Fig. 4). Superconductivity is, however, restricted to the composition range $0.35 \leq x \leq 0.75$ with the maximum $T_c = 85$ K occurring at $x = 0.5$. The hole concentration for the composition with maximum T_c is ~ 0.22. The Meissner fraction in these cuprates is similar to that in $Bi_2CaSr_2Cu_2O_8$.

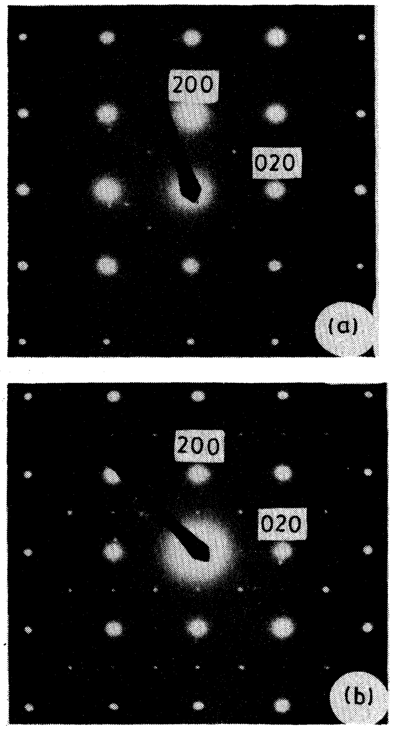

FIG. 5. Electron-diffraction patterns of (a) $BiPbSr_{1.2}La_{0.8}CuO_6$ and (b) $BiPbSr_2Y_{0.5}Ca_{0.5}Cu_2O_8$ recorded with the incident beam along the c axis.

In summary, we have prepared modulation-free $BiPbSrLCuO_6$ (L = La, Pr, Nd) and $BiPbSr_2YCu_2O_8$ which are isotypic with the $n = 1$ and 2 members of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ family. While these parent cuprates are nonsuperconducting, they could be doped with holes by substitution of Y or L by divalent Sr or Ca giving two series, $BiPbSr_{1+x}L_{1-x}CuO_6$ and $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$, where superconductivity is observed with maximum T_c's of 24 and 85 K, respectively. What is especially interesting is that the hole concentration corresponding to the maximum T_c is 0.12 in $BiPbSr_{1+x}L_{1-x}CuO_6$ containing a single Cu-O layer (just as in $La_{2-x}Sr_xCuO_4$) while it is 0.22 in $BiPbSr_2Y_{1-x}Ca_xCu_2O_8$ containing two Cu-O layers (just as in $YBa_2Cu_3O_7$).

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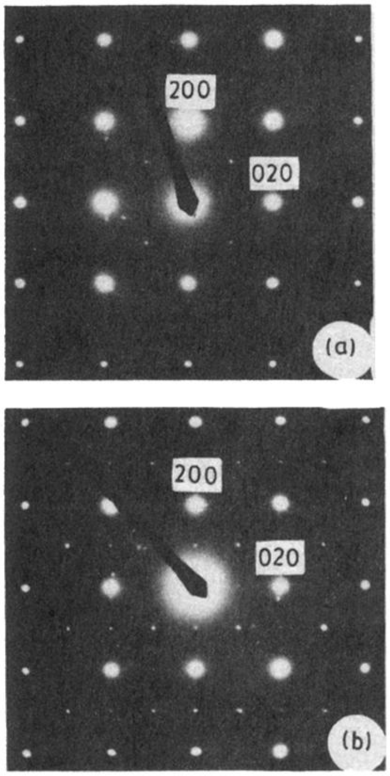
[17] We discounted the possibility of the presence of $La_{2-x}Sr_xCuO_4$ in the sample, since the x-ray-diffraction pattern showed the absence of a K_2NiF_4-like phase. Moreover, formation of isostructural phases with Pr and Nd clearly showed a different series of compounds in $BiPbSr\mathit{L}CuO_6$.



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