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LETTER TO THE EDITOR

Stabilisation of the 110 K phase in Pb-substituted Bi–Sr–Ca–Cu–O

B Jayaram†, P C Lanchester†, M T Weller‡, J R Grasmeyer‡,
P A J de Groot† and G P Rapson†

† Department of Physics, The University, Southampton SO9 5NH, UK

‡ Department of Chemistry, The University, Southampton SO9 5NH, UK

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Abstract. A number of samples of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ ($0 \leq x \leq 0.8$) have been prepared by solid state reaction. All major peaks in the powder diffraction spectra of samples with $x = 0.2$ and 0.4 could be attributed to the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ phase with slight orthorhombic distortion. Resistivity measurements of these samples showed zero resistance at 100 K with onset of superconductivity around 110 K. The effect of variations of sintering and annealing have been studied in order to optimise conditions for obtaining the 110 K phase. From flux exclusion measurements the volume fraction of the high- T_c phase is estimated to be around 40% at best. These studies tentatively indicate that Pb substitutes preferentially on the Ca site rather than the Bi site in the Bi–Sr–Ca–Cu–O lattice. Samples with $x = 0.0$ and $x > 0.4$ showed zero resistance around 70 K with no indication of a phase with a higher T_c .

The discovery of superconductivity around 105 K in a likely multiphase sample of $\text{BiSrCaCu}_2\text{O}_y$ [1] has enlarged the scope for the search for materials possessing exceptionally high values of the superconducting transition temperature (T_c). The composition and structure of the phase in this sample with zero resistance around 75 K were quickly determined by several groups [2, 3]. Shortly afterwards the Tl–Ba–Cu–O system was discovered and, apart from having slightly enhanced T_c -values, this was shown to be similar to the Bi–Sr–Ca–Cu–O system in respect of the number of phases, crystal structure and microstructural characteristics. It is now known that, unlike the La–Sr–Cu–O and Y–Ba–Cu–O systems, at least three distinct superconducting phases exist in the bismuth system. Phase 1 has a composition $\text{Bi}_2\text{Sr}_2\text{CuO}_y$ (2201). It contains a single layer of copper oxide in the unit cell and T_c is less than 22 K [4]. Phase 2 has a composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (2212), contains two copper oxide planes and has a T_c of 75 K [2, 3]. Finally, phase 3 has a composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (2223), contains three copper oxide planes and is expected to have a T_c of 116 K [5]. Heat treatment schedules for the formation of single phases of $\text{Bi}_2\text{Sr}_2\text{CuO}_y$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ [6] are now well established; however, for the 2223 phase there is as yet no consensus on starting composition, sintering temperature and annealing schedule. There have been several reports of samples containing sufficient amounts of 110 K phase to show resistivity drops as well as diamagnetism at 110 K, but in all these cases zero resistance is observed only below 80 K [7–13]. Single crystals grown from $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_y$ precursor showed zero resistance above 100 K [14, 15], but the temperature corresponding to zero resistance in these crystals decreased with increase in the magnitude of sample current. This was

thought to be due to the low current carrying capacity of shells of 110 K phase formed around cores of low- T_c phase. It has been suggested that substitution of Pb in the Bi–Sr–Ca–Cu–O system encourages stabilisation of 110 K phase [16], and we have carried out a systematic investigation of the $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ system, with $n = 2$ to 4. In this Letter we report results of the resistivity, magnetisation and preliminary x-ray studies of the $n = 4$ system.

Samples of nominal composition $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$, with $0 \leq x \leq 0.8$, were prepared by solid state reaction in air. Appropriate quantities of the starting materials, Bi_2O_3 , PbO , SrCO_3 , and CuO were thoroughly mixed and reacted at 850°C for 65 h. The reacted powder lump was then pulverised and cold pressed into pellets. Final sintering and annealing was performed in the temperature range 820 – 860°C , followed by slow cooling at the rate of 2°C min^{-1} down to 400°C inside the furnace. Below 400°C the cooling rate was governed by the natural radiation of the furnace. An INEL CPS-120 x-ray diffractometer using $\text{Cu K}\alpha$ radiation was used to record powder diffraction spectra. Four-probe DC resistivity measurements were performed on rectangular slabs cut from pellets, the temperatures of which were monitored with a miniature diode thermometer. With our apparatus the smallest measurable resistance corresponds to a sample voltage of less than 100 nV with a measuring current of 10 mA. The temperature at which the sample resistance falls to less than this has been used to determine the superconducting transition temperature (T_c). Magnetisation studies were performed with a home-built SQUID magnetometer.

The x-ray powder diffraction pattern of a $\text{Bi}_2\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ sample annealed at 840°C for 36 h is shown in figure 1(a). Almost all peaks of this spectrum can be identified with the 2212 phase. However, the appearance of a new set of peaks in addition to peaks due to the 2212 phase can be seen in the diffraction pattern of a $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ sample (figure 1(b)), which has been heat treated at 860°C for 16 h. On reducing the annealing temperature to 840°C and increasing the time to 36 h, the new pattern, as shown in figure 1(c), becomes more prominent and the 2212 phase peaks disappear. All significant peaks in figure 1(c) can be indexed satisfactorily to a tetragonal unit cell with parameters $a = 5.377 \pm 0.002 \text{ \AA}$ and $c = 36.95 \pm 0.02 \text{ \AA}$. A small improvement in the fit was obtained assuming orthorhombic symmetry, but the orthorhombic distortion was only slight. It has been shown from transmission electron microscopy studies that the c axis increases by 3 \AA due to inclusion of a layer of either Cu, Ca or Sr in Bi–Sr–Ca–Cu–O superconductors. Based on this observation, an increment of 6 \AA in the c axis of the 2212 phase with respect to the 2201 phase was attributed to incorporation of an extra layer of Ca and CuO_2 in the atomic layer sequence of the 2201 phase [6]. Continuing this sequence it is predicted that the 2223 phase should have a c axis of 36 \AA . Although some reports confirm this prediction [7–12], the samples used showed signs of more than one superconducting transition. The present results clearly identify a single superconducting phase with $c = 36.9 \text{ \AA}$.

The temperature variation of resistance of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ ($0 \leq x \leq 0.8$) samples which were sintered at 860°C for 16 h are shown in figures 2(a) and 2(b). It is evident that the temperature coefficient of resistance changes from positive to negative as the concentration of Pb is increased from 0.0 to 0.8. The normal state resistivity (measured at 110 K) increases only slowly with x up to $x = 0.4$ and more rapidly thereafter. As shown in figure 2(b) samples with $x = 0.2$ and 0.4 exhibit drops in resistivity of about 50% around 110 K and zero resistance at 86.9 K and 85.2 K respectively. These temperatures are considerably higher than the zero-resistance temperature of 75 K for single-phase $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$. The large width of the resistive transition indicates either

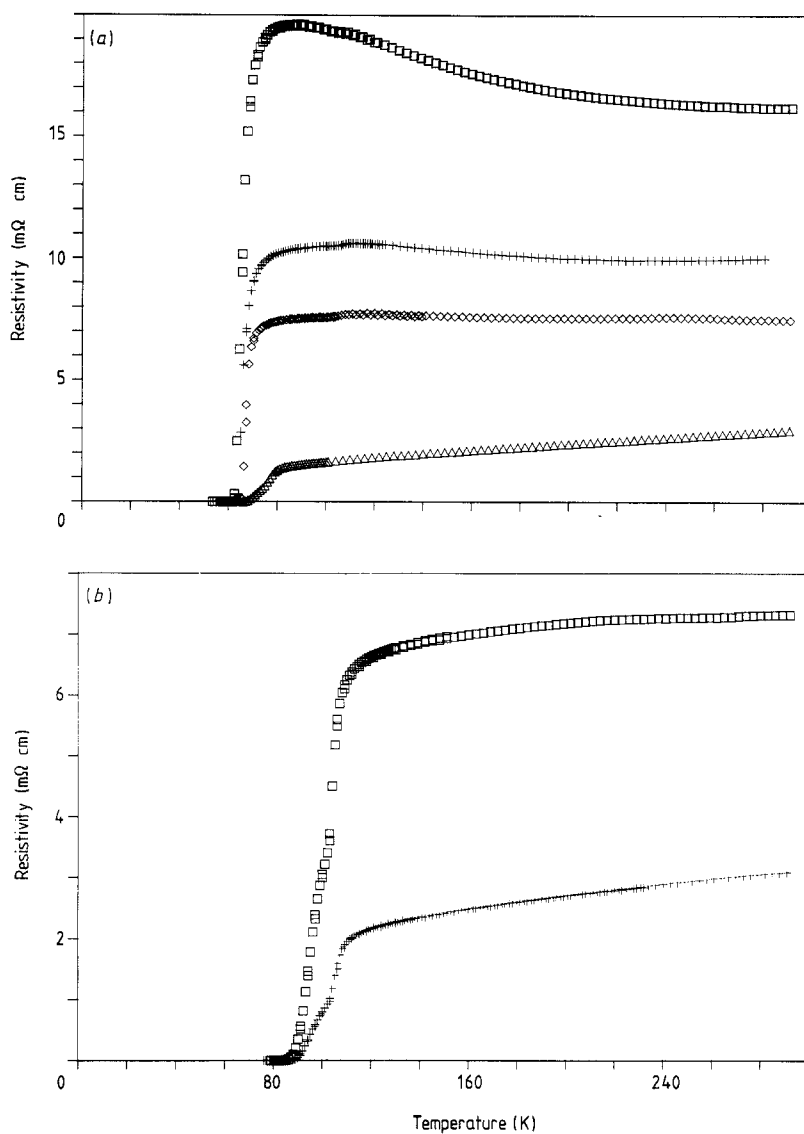


Figure 2. The temperature dependence of resistivity of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ ($0 \leq x \leq 0.8$) samples annealed at 860°C for 16 h. (a) $x = 0$ (Δ), $x = 0.5$ (\diamond), $x = 0.6$ ($+$), $x = 0.8$ (\square); (b) $x = 0.2$ ($+$), $x = 0.4$ (\square).

Table 1. Summary of sintering conditions adopted for $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_x$ samples and their T_c -values.

Sintering conditions	$x = 0.0$	$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$	$x = 0.5$
$840^\circ\text{C}/\text{air}/36\text{ h}$	68.8	65.5	93.3	94.6	100.0	61.3
$840^\circ\text{C}/\text{air}/36\text{ h} +$ $500^\circ\text{C}/\text{air}/3\text{ h}$	69.6	62.7	95.3	96.1	97.2	—
$840^\circ\text{C}/\text{air}/54\text{ h}$	—	71.8	98.5	96.8	92.8	—
$820^\circ\text{C}/\text{air}/33\text{ h}$	—	73.8	99.3	91.5	96.1	—

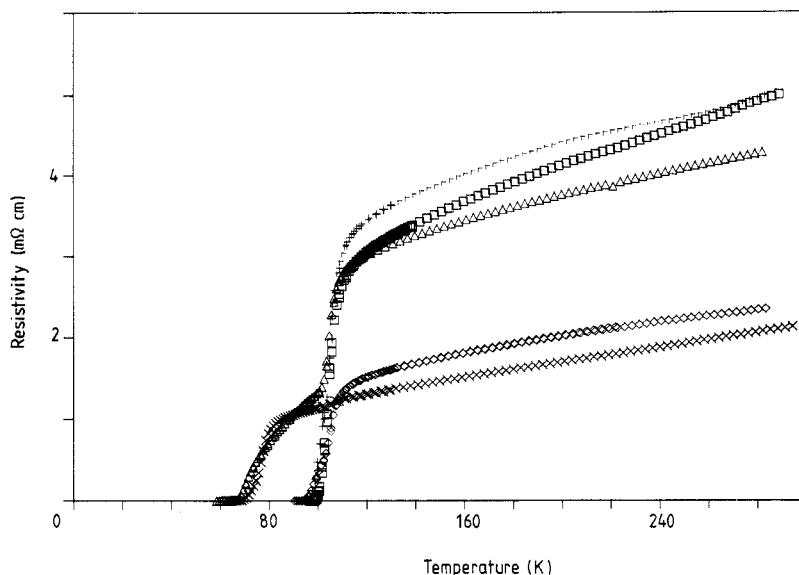


Figure 3. The temperature dependence of resistivity of $x = 0$ to 0.4 samples annealed at 840°C for 36 h. $x = 0$ (\times), $x = 0.1$ (Δ), $x = 0.2$ (\diamond), $x = 0.3$ ($+$), $x = 0.4$ (\square).

despite an initial 50% fall in resistance at 110 K. Another batch of samples were given additional annealing at 500°C for 3 h after the initial annealing at 840°C for 36 h. T_c -values of samples with $x = 0.2$, 0.3 and 0.4 remained above 95 K, but no marked improvement in transition width occurred. Extending the annealing time to 54 h at 840°C improved T_c -values for the $x = 0.1$ to 0.3 samples significantly, but decreased T_c for the $x = 0.4$ sample to 92.8 K. In a final experiment, the samples were annealed for 33 h at a further reduced temperature of 820°C . This heat treatment improved T_c for the $x = 0.2$ samples to 99.3 K, which is the best T_c for this composition over all sintering conditions tried (figure 4).

It is of interest to note that varying the Sr/Ca ratio from 0.75 to 0.70 had a deleterious effect on T_c irrespective of sintering temperature and time. Note too that by analogy with $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ compounds, it has been suggested that the high- T_c phase of the bismuth system differs from the low- T_c phase only in the oxygen content [15]. In view of this, we have annealed samples with $x = 0$ to 0.5 in oxygen over the temperature range 820 to 850°C . All samples, regardless of their annealing history, showed high room-temperature resistance.

Some representative plots of the magnetisation as a function of temperature of samples with $x = 0.2$ and 0.4 are shown in figure 5. Samples were initially cooled in zero field and magnetisation data was collected at a field of 0.18 mT. All samples with $x = 0.1$ to 0.4 showed diamagnetic behaviour around 110 K. The $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ sample in particular, which was annealed for 36 h at 840°C gave a sharp and strong diamagnetic signal at 110 K indicative of an almost pure phase. The volume fraction of high- T_c phase assuming an estimated density of 7 g cm $^{-3}$ is about 40% of a complete bulk superconductor at 80 K. Other samples of $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ which were annealed at 840°C for 54 h and 820°C for 33 h showed a second transition at 80 K corresponding to the 2212 phase. The volume fraction of high- T_c phase in these samples was about 20% and 8% respectively.

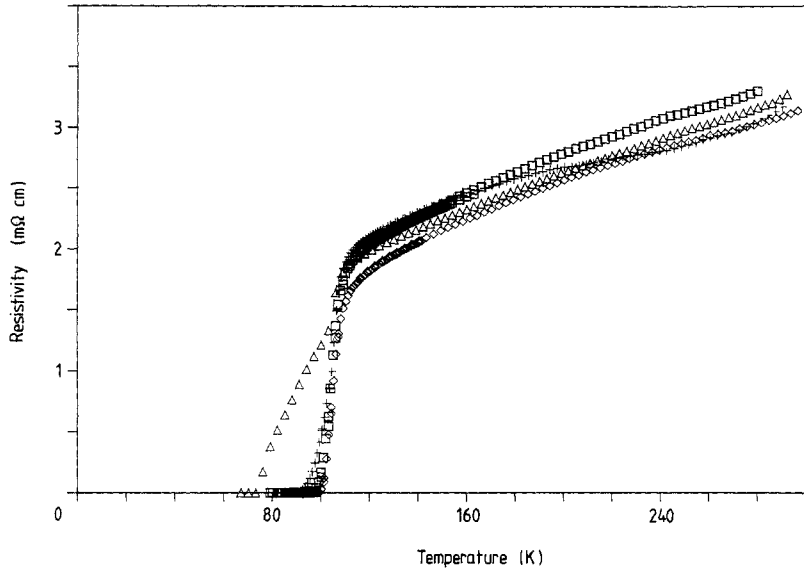


Figure 4. The temperature dependence of resistivity of $x = 0.1$ to 0.4 samples annealed at 820°C for 33 h. $x = 0.1$ (Δ), $x = 0.2$ (\diamond), $x = 0.3$ ($+$), $x = 0.4$ (\square).

Although the role of Pb substitution in $\text{Bi}_2\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ remains unclear, our results demonstrate that the presence of Pb is beneficial to the formation of the 110 K phase material at fairly low annealing temperatures. In the pure Bi–Sr–Ca–Cu–O system, samples were annealed at around 880°C , which is close to the melting point of the 2212 phase, in order to encourage growth of the 110 K phase from the low- T_c phase. However, the stability of the 2212 phase is such that it is formed inevitably for all compositions.

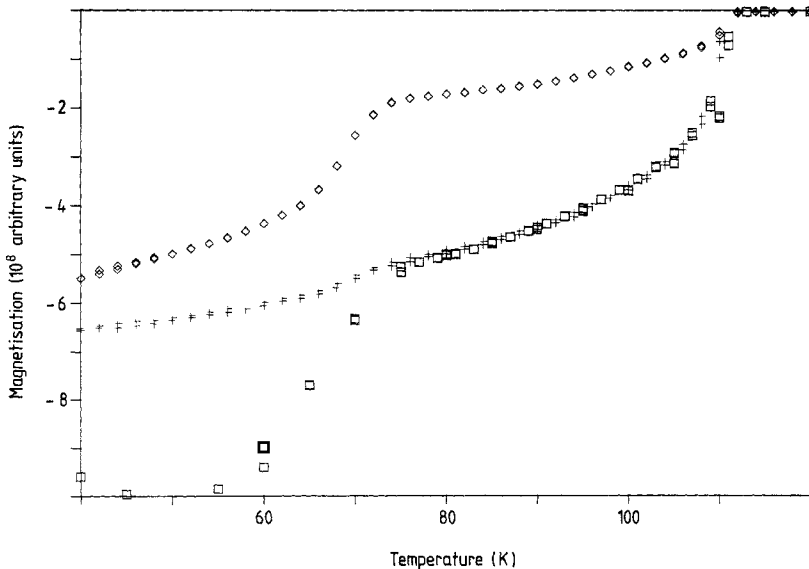


Figure 5. The temperature dependence of magnetisation of $x = 0.2$ and 0.4 samples. $x = 0.2$ ($840^\circ\text{C}/54$ h): \square , $x = 0.4$ ($840^\circ\text{C}/36$ h): $+$, $x = 0.4$ ($820^\circ\text{C}/33$ h): \diamond .

The addition of Pb seems to alter the phase equilibrium leading to formation of the high- T_c phase even at 840 °C. The absence of PbO peaks in the powder diffraction spectra of all samples containing Pb suggests that Pb has been incorporated into the lattice of Bi–Sr–Ca–Cu–O, but it is not immediately obvious into which site it has been incorporated. Ideally this might be resolved by powder diffraction line profile analysis or by neutron diffraction data. Failing this there are other factors that bear consideration. Firstly, for the 2212 phase, a crystal structure analysis (not allowing for a possible incommensurate superstructure) has shown that as much as 6% Bi may be missing in the (BiO)₂ layers of the 2212 phase [17]. This together with the proximity of Bi to Pb in the periodic table and the comparable magnitudes of the ionic radii suggest that Pb simply substitutes for Bi as indicated by the formula. However, the electronic band structure obtained by local charge density calculations suggest that Bi–O layers contribute significantly to the density of states at the Fermi level. Furthermore, the Bi–O $pp\sigma$ states of (BiO)₂ planes are seen to give rise to strongly localised antibonding states which play a similar role to the $dp\pi$ one-dimensional states of the Cu–O linear chains in the YBa₂Cu₃O₇ compound [18, 19]. We expect therefore that the superconducting properties of the 2212 compound will be affected by changes in the (BiO)₂ planes in a similar way as the superconducting properties of YBa₂Cu₃O₇ are affected by doping in the Cu–O chains. In fact for YBa₂Cu₃O₇ it is well known that both T_c and the normal state resistivity depend strongly on the oxygen ordering and on substitution at the Cu sites in the chains [20, 21]. In contrast, as shown in figure 2 our low- T_c samples show some variation of normal state resistance with Pb concentration but T_c remains remarkably unaffected. Note that the results shown in figure 2(b) relate to the high- T_c (2223) phase and bear no relevance to the present discussion. From the observed insensitivity of T_c to Pb substitution we conclude that Pb occupies a site in the Bi–Sr–Ca–Cu–O lattice which is correspondingly unimportant to superconductivity. One possibility is the oxygen depleted Ca planes, the role of which, like the yttrium planes in YBa₂Cu₃O₇, appears to be limited to stabilising the lattice. Substitution at the Ca site is consistent with the relative ionic size and does not alter the local coordination. In this position it should not influence the electrical properties and in particular should not affect T_c significantly. The possibility that Pb enters the Ca site is also supported by the observation that Pb occupies a similar site in the Aurivillius phase Bi₂Nb₂PbTiO₉ [22]. The increase in the normal state resistivity with x contradicts this conclusion. However, it is clear from the difference between the stoichiometry of the starting mixture and the majority phase that there are impurity phases even in the best of our samples. These are likely to be poor conductors and may be dominant in determining the normal state resistivity.

The observed deterioration of the resistive and superconducting characteristics of Pb-substituted samples after oxygen annealing may be related to the way in which Pb is incorporated in the lattice. Thus if prior to annealing Pb lies mainly at the surface of the grains and subsequently diffuses in slowly during annealing, then it is reasonable to suppose that in the presence of oxygen Pb²⁺ ($r = 1.2 \text{ \AA}$) may be converted into Pb⁴⁺ ($r = 0.84 \text{ \AA}$) which, being smaller, enters the Cu²⁺ ($r = 0.72 \text{ \AA}$) site instead of the Ca²⁺ ($r = 0.99 \text{ \AA}$) site. Deterioration of superconductivity due to substitution at Cu sites in Y–Ba–Cu–O is well known [23].

A large number of samples containing varying amounts of Pb were prepared under different conditions in order to examine the stability of the 110 K phase in the Bi–Sr–Ca–Cu–O system. It has been established that Pb is essential in Bi₂Sr₂Ca₃Cu₄O_y in order to obtain a substantial proportion of the 110 K phase and that it is advantageous to reduce the reaction and annealing temperatures from 885 °C to 840 °C. The structure

of the high- T_c phase has been confirmed as that of the 2223 phase with some indication of a small orthorhombic distortion. It is argued that Pb may enter the Ca site rather than the Bi site and that the normal state resistivity may be dominated by impurity phases. Finally, it has been shown that annealing in oxygen causes the superconductivity characteristics to worsen, possibly due to displacement of Cu^{2+} by Pb^{4+} .

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Note added in proof. Since submitting this Letter we have become aware of a paper by Green and co-workers [24] which also reports on the beneficial effect of Pb substitution in obtaining zero resistance around 100 K. No structural data are given but the results are otherwise similar to those presented here.

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