

A New Superconductor with the 1212 Structure (Pb,Sn)Sr₂(Ca,Lu)Cu₂O_z

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Received 31 May 2000

Abstract

New cuprates with the nominal composition (Pb_{0.75}Sn_{0.25})Sr₂(Ca_{1-x}Lu_x)Cu₂O_z (x=0.4~1.0) have been synthesized. These materials exhibit superconducting properties for 0.4 ≤ x ≤ 0.7. It is also observed that the superconductivity of the as-prepared sample is enhanced by post-annealing at high temperature followed by quenching. X-ray diffraction analysis reveals that the c lattice parameter decreases as x increases whereas the a lattice parameter is nearly independent of the value of x for both the as-prepared and the post-treated samples. The thermoelectric power measurements indicate that the post-heat-treatments result in an increase in the hole carrier density which account for the observed increase of T_c. Bulk superconductivity with a T_c value of 60 K is observed in this system.

Keywords : Synthesis, Superconductivity, (Pb,Sn)-1212 system, Thermoelectric power

I. Introduction

Soon after the discovery of the nonsuperconducting lead-based 1212 cuprates (Pb,Cu)Sr₂(CaY)Cu₂O_z [1], [2], extensive efforts have been devoted to the study of this kind of material because the lead-based cuprates have the same or similar crystallographic structures to the Bi₂Sr₂(Ca,Y)Cu₂O_z and TlSr₂(Ca,Y)Cu₂O_z superconductors. In (Pb,Cu)-1212, a (Pb,Cu) mixed layer replaces the Bi₂O₂ double layers or the TlO monolayer. Because of this structure, the Pb-based 1212 cuprates are thought to be promising candidates for new superconductors. Up to now, several superconducting lead-based 1212 cuprates (Pb,M)Sr₂(Ca_{1-x}Y_x)Cu₂O_z (M=Cu[3]-[5], Sr[6], Ca[7], Mg[8], Cd[9]) have been successfully synthesized. Despite the great flexibility of the rock-salt-type (Pb,M)O layers in the Pb-1212 cuprates, most of

these compounds except M=Cd are found to be difficult to prepare and only exhibit superconductivity when prepared in a sealed quartz tube[6], [7] and either annealed in high pressure-oxygen[5],[8] or quenched to ambient temperature[3], [4]. Recently, we have synthesized new Pb-based 1212 compounds of (Pb_{0.5}M_{0.5})Sr₂(Ca_{1-x}Y_x)Cu₂O_z with M=V[10] and Ti[11] under comparatively less critical conditions. As a part of the continued effort in this line, we tried atmospheric pressure synthesis of the (Pb,Sn)-1212 type of cuprates, (Pb,Sn)Sr₂(Ca,Lu)Cu₂O_z and report the observation of bulk superconductivity in this system.

II. Experiments

Samples with nominal compositions of (Pb_{1-y}Sn_y)Sr₂(Ca_{1-x}Lu_x)Cu₂O_z (x=0~1.0, y=0.1~0.5) were prepared by using a solid state reaction. The starting materials with the appropriate ratios of PbO, SnO₂,

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SrCO_3 , Lu_2O_3 , CaCO_3 , Y_2O_3 , and CuO were mixed in an agate mortar and heated at $780\text{ }^\circ\text{C} \sim 800\text{ }^\circ\text{C}$ in air for 10 h. The products were well ground, then pressed into pellets and sintered at $990\text{ }^\circ\text{C} \sim 998\text{ }^\circ\text{C}$ for 4 h in flowing O_2 followed by slow-cooling to room temperature at a rate of about $3\text{ }^\circ\text{C}/\text{min}$. The pellet samples were cut into rectangular specimens with dimensions of about $2\text{ mm} \times 2\text{ mm} \times 10\text{ mm}$ for measuring resistivity. In the post-heat-treatments, the sliced specimens were heated at $860\text{ }^\circ\text{C}$ for 3 h in an oxygen atmosphere and then quenched into liquid nitrogen. The sample purity was checked by X-ray powder diffraction (XRD) method. The electrical resistivity was measured in the range of $8\text{ K} \sim 300\text{ K}$ by the four-probe method. The measuring current was 5 mA. The dc magnetic susceptibility was monitored using a Quantum Design SQUID magnetometer. The thermoelectric power was measured by the differential method in the temperature range $30\text{ K} \sim 300\text{ K}$ using a closed cycle cryorefrigerator. One end of the rectangular specimen was attached to the cold head of the cryorefrigerator through a sapphire disk with 0.7 mm thick and the other free end to a thin Pt block containing a small heater. The sample was attached to the upper and lower blocks using silver paste. The thermoelectric voltage and temperature gradient (typically $\sim 2\text{ K}$) across the sample were measured [12] using two pairs of type T thermocouples which were glued to the sample. A Keithley nanovoltmeter was used to measure the thermoelectric voltage. The mean of the temperatures measured at the two thermocouples was chosen as the sample temperature. The thermoelectric power was corrected for the absolute thermoelectric power of Cu.

III. Results and Discussion

Following the above experimental procedure, samples with the nominal compositions $(\text{Pb}_{1-y}\text{Sn}_y)\text{Sr}_2(\text{Ca}_{0.5}\text{Lu}_{0.5})\text{Cu}_2\text{O}_z$ were prepared. XRD patterns showed that the Pb-1212 phase appeared in the range of $0.1 \leq y \leq 0.4$. However, the best-quality samples judged from the XRD patterns were obtained for $y=0.2\sim 0.3$. Comparing to the case of (Pb,V)-1212 system, this result suggests that the optimum composition in the rock-salt (Pb,M) layer to form a reasonably pure phase (Pb,M)-1212 sample depends on the

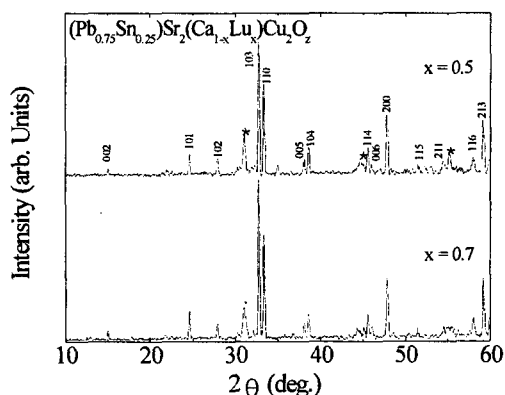


Fig.1. Powder XRD patterns of samples with nominal compositions of $(\text{Pb}_{0.75}\text{Sn}_{0.25})\text{Sr}_2(\text{Ca}_{1-x}\text{Lu}_x)\text{Cu}_2\text{O}_z$ with $x=0.5$ and $x=0.7$. Peaks due to impurity phases are shown by (*).

M ion. The Sn concentration was then fixed $y=0.25$ and the Ca/Lu ratio was varied to obtain $(\text{Pb}_{0.75}\text{Sn}_{0.25})\text{Sr}_2(\text{Ca}_{1-x}\text{Lu}_x)\text{Cu}_2\text{O}_z$. Figure 1 shows the powder XRD patterns of post-treated samples with $x=0.5$ and 0.7 . The diffraction peaks are indexed on the basis of a tetragonal unit cell. The impurity phases are marked by * and the main impurity phase is identified as $\text{Sr}_{5-x}\text{Pb}_{3+x}\text{Cu}_y\text{O}_{12-8}$ [13]. With the decrease of x below 0.4, the impurity content increases, although the 1212 phase remains the majority phase until $x=0.3$. The XRD patterns for the post-treated samples were nearly parallel to those for as-prepared samples.

Figure 2 shows the temperature dependence of electrical resistivity for as-prepared samples with $x=0.4\sim 0.7$. As the Lu content x decreases from 0.7 to 0.4, the normal state resistivity of the samples shows a transition from semiconducting behavior to metallic behavior. The decrease of x is also accompanied by the increase of the zero-resistivity transition temperature. The corresponding temperature dependence of electrical resistivity of the samples obtained by annealing the as-prepared samples at $860\text{ }^\circ\text{C}$ for 3 h in O_2 and then quenching them into liquid nitrogen is shown in Fig. 3. Comparing with the case of the as-prepared samples (Fig. 2), one can notice that superconducting transition behavior is enhanced in all samples after the post-heat-treatments.

Furthermore, contrary to the case of as-prepared samples, the superconducting transition temperature of the sample with $x=0.5$ is rather higher than that of the sample with $x=0.4$ after the post-heat-treatments.

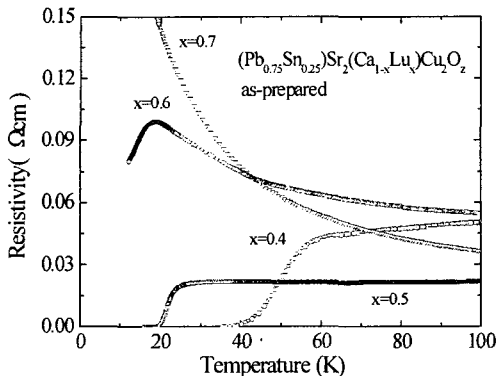


Fig.2. Temperature dependence of electrical resistivity for as-prepared $(\text{Pb}_{0.75}\text{Sn}_{0.25})\text{Sr}_2(\text{Ca}_{1-x}\text{Lu}_x)\text{Cu}_2\text{O}_z$ samples.

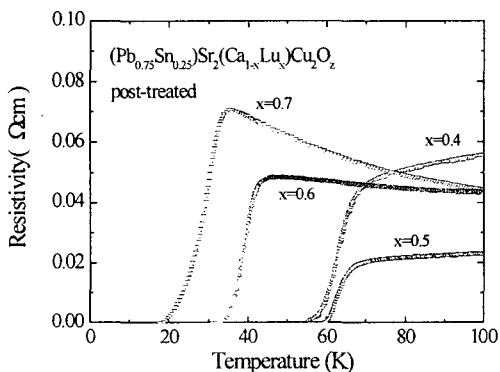


Fig.3. Temperature dependence of electrical resistivity for $(\text{Pb}_{0.75}\text{Sn}_{0.25})\text{Sr}_2(\text{Ca}_{1-x}\text{Lu}_x)\text{Cu}_2\text{O}_z$ samples annealed at 860°C for 3 h in O_2 and then quenched.

the sample with $x=0.4$ after the post-heat-treatments. This result suggests that the change in oxygen content induced by the post-heat-treatments as well as the Lu content in (Ca,Lu) site is a crucial factor in controlling the superconducting properties of the (Pb,Sn)-1212 system.

The highest superconducting transition temperature was observed in the post-treated sample with $x=0.5$. The onset, the midpoint and the zero-resistivity transition temperatures of this sample are 67 K, 63 K, and 60 K, respectively.

Figure 4 shows the field-cooled magnetic susceptibility of the sample with $x=0.5$ which was measured from 100 K down to 5 K with a Quantum Design SQUID magnetometer in a constant field of 10 Oe. The diamagnetic onset transition temperature of 60 K coincides with the zero-resistivity temperature

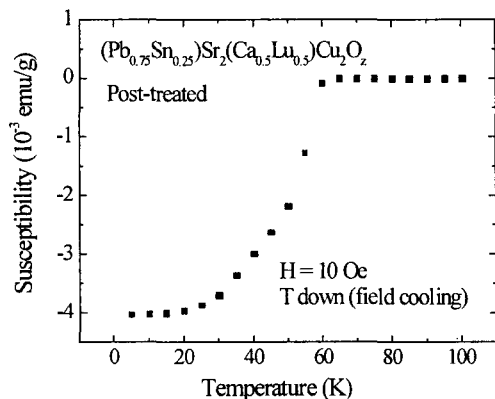


Fig.4. Temperature dependence of dc-magnetic susceptibility for $(\text{Pb}_{0.75}\text{Sn}_{0.25})\text{Sr}_2(\text{Ca}_{0.5}\text{Lu}_{0.5})\text{Cu}_2\text{O}_z$ sample annealed at 860°C for 3 h in O_2 and then quenched.

determined from the resistivity measurement. The superconducting volume fraction estimated from the susceptibility at 10 K and the crystal density is 35 % of perfect diamagnetism and indicates bulk superconductivity.

The dependence of lattice constants a and $c/3$ on the Lu content x is shown in Fig. 5. The c lattice parameter tends to decrease with x whereas the a lattice parameter is nearly independent of the value of x for both the as-prepared and the post-treated samples. The decrease of the c lattice parameter with x is expected because of the smaller ionic size of Lu^{+3} compared to that of for Ca^{+2} . For the post-treated samples, the a lattice parameters become shorter than those of the as-prepared samples. A very similar behavior was also observed in other Pb-based 1212 cuprates and the contraction of the a lattice parameter after the post-heat-treatments was explained as due to the decrease of the oxygen content of the sample[4], [10], [11].

The temperature variation of thermoelectric power, $S(T)$ for the Lu-doped samples with $x=0.4$ and 0.5 is shown in Fig. 6. For both the as-prepared and the post-treated samples, the thermopower sign is positive over the entire measured temperature range and $S(T)$ increases gradually with temperature after the steep rise near transition, passes through a broad maximum at $T=T_{\text{max}}$ and then decreases on further increase of temperature. After the post-heat treatments, the values of $S(T)$ for each sample are lower at all temperatures than those of the as-prepared sample and the T_{max} shifts to a lower temperature.

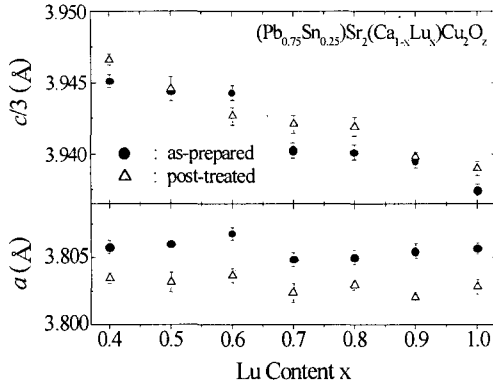


Fig.5. Variation of lattice parameters with Lu content, x for $(\text{Pb}_{0.75}\text{Sn}_{0.25})\text{Sr}_2(\text{Ca}_{1-x}\text{Lu}_x)\text{Cu}_2\text{O}_z$ samples.

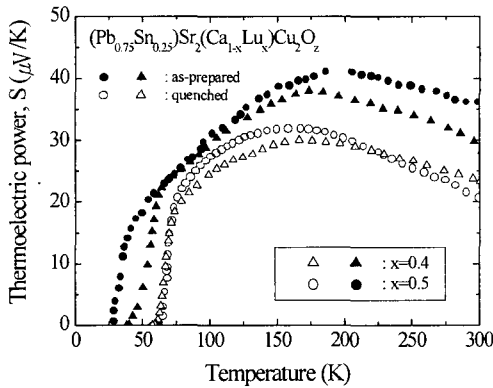


Fig.6. Temperature dependence of thermoelectric power for $(\text{Pb}_{0.75}\text{Sn}_{0.25})\text{Sr}_2(\text{Ca}_{1-x}\text{Lu}_x)\text{Cu}_2\text{O}_z$ samples with $x=0.4$ and 0.5 . The closed symbols refer to the as-prepared samples and the open symbols refer to the corresponding post-treated samples.

Although several models for $S(T)$ have been proposed in the past which involve mostly fitting of experimental data[14], the exact cause for the behavior of $S(T)$ with temperature is yet to be examined. However, Obertelli et al.[15] have demonstrated an universal correspondence of room-temperature thermoelectric power, $S(290\text{ K})$ on the charge(hole) carrier concentration of CuO_2 planes, p in several cuprate superconductors. According to their data, $S(290\text{ K})$ falls nearly exponentially with p from $S(290\text{ K})=500\ \mu\text{ V/K}$ for the undoped samples ($p=0$) towards $S(290\text{ K})=1\sim 2\ \mu\text{ V/K}$ in case of optimal doping($p=0.16$) and the change in sign of $S(290\text{ K})$ occurs when the sample is overdoped. As is seen in Fig. 7, there is no zero-crossing of thermoelectric

power below $T=300\text{ K}$ and the room temperature thermoelectric power is order of $10\ \mu\text{ V/K}$. Therefore, the present Pb-1212 compounds are considered to be underdoped. Further, the decrease of thermoelectric power after the post-heat-treatments indicates that there is an increase in the hole carrier density in the post-treated sample relative to the as-prepared sample that might also account for the increase in the T_c . Since the high temperature annealing following by quenching is expected to leave less oxygen in the as-prepared samples, both the improvement of T_c and the decrease of the thermoelectric power by the post-heat-treatments suggest that the excess oxygen which is present in as-prepared (Pb,Sn)-1212 samples effectively reduces the hole carrier concentration on CuO_2 layers[16]. Further study on the exact positions and the role of the excess oxygen may lead to better understanding of the underlying mechanism.

IV. Conclusion

A new type of Pb-based 1212 cuprates $(\text{Pb}_{0.75}\text{Sn}_{0.25})\text{Sr}_2(\text{Ca}_{1-x}\text{Lu}_x)\text{Cu}_2\text{O}_z$ has been synthesized under ambient pressure of oxygen. It was found that the superconducting transition temperature varies with Lu content x and post-heat-treatments. The thermoelectric power measurements indicated that the as-prepared samples are underdoped and the doping level is improved by the post-heat-treatments. Bulk superconductivity of a T_c value of 60 K has been observed for a post-treated sample with $x=0.5$.

Acknowledgements

The authors would like to thank Korea Basic Science Institute for the help in SQUID measurements.

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