New Pb-based 1212 Cuprate Superconductors Containing Sulfur, 
(Pb_{0.75}S_{0.25})Sr_2(Y_{1-x}Ca_x)Cu_2O_z

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Abstract New Pb-based 1212 layered cuprates containing sulfur have been synthesized in the (Pb_{0.75}S_{0.25})Sr_2(Y_{1-x}Ca_x)Cu_2O_z system. X-ray diffraction analysis shows that the almost single-phase samples are obtained within a region of 0 ≤ x ≤ 0.5. The crystal structure of each sample has a tetragonal symmetry with the typical lattice constants a = 0.3837 nm and c = 1.186 nm. As Ca content x is increasing, the semiconductor-like behavior is suppressed. But after only annealing under ambient O_2 pressure, none of the samples show any trace of superconductivity. On the other hand, when the samples are annealed under high O_2 pressure of about 13.6 MPa, they show resistivity dropping phenomenon in a region of 0.5 ≤ x ≤ 0.7. Among them, the lowest resistivity sample with x = 0.6 has an onset temperature of the resistivity dropping at about 22.5 K. Moreover, this sample shows a diamagnetic signal at about 21.5 K. These phenomena are attributed to superconductivity.

Keywords New Pb-based cuprate · 1212 phase · Oxy-anion substitution · (Pb_{0.75}S_{0.25})Sr_2(Y_{1-x}Ca_x)Cu_2O_z system · Superconductivity

1 Introduction

Pb-based layered cuprate superconductors of (Pb_2Cu)_Sr_2ACu_2O_z (Pb-3212 compounds) were first discovered by Cava et al., where A stands for a rare earth element (RE) or a mixture of RE and Ca (or Sr) [1]. These Pb-3212 compounds have charge reservoir blocks of PbO–Cu–PbO triple layer in the crystal structure. Following this discovery, another new Pb-based layered cuprate superconductor of Pb_{0.5}Sr_{2.5}Y_{0.5}Ca_{0.5}Cu_2O_z (Pb-1212 compound), which has an onset temperature of the superconducting transition T_c = 100 K, was synthesized by Rouillon et al. [2].

The structure of this Pb-1212 compound resembles that of the Pb-3212 one. However, the charge reservoir block is (Pb, Sr)–O monolayer instead of PbO–Cu–PbO triple layer. Later, many Pb-1212 compounds having various monolayers expressed by (Pb, M)–O, where M stands for one of metal elements, were discovered. The chemical formula of Pb-1212 compounds can be expressed as (Pb, M)Sr_2ACu_2O_z. For the other Pb-1212 compounds, the samples with M = Ca [3], Cu [4–6], Cd [7, 8], Mg [9], In [10], V [11] have previously been reported.

By the way, the layered cuprate of YSr_2Cu_3O_5, which is the Ba-free analogue of YBa_2Cu_3O_7, has also the monolayers of Cu–O in the crystal structure (Cu-1212 compound). This cuprate was possible to synthesize only under very high O_2 pressure [12]. However, the compound could be synthesized even under ambient O_2 pressure if the Cu-sites in the Cu–O monolayers (Cu-chain sites) were substituted by some cations [13–15]. That is, such the cation substitutions for the Cu-sites make the Cu-1212 structure stable. Afterwards, it was reported that the partial substitution of oxy-aniions such as CO_3^{2–} [16], BO_3^{2–} [17], PO_4^{3–} [18], SO_4^{2–} [18], for Cu-sites in the monolayers stabilized the Cu-1212 phase, too. From these experimental results on the substitution elements for Cu-sites in the monolayers of the Pb-1212 and
Cu-1212 compounds, we expected that some of these oxy-anions could be used as substitution elements for Cu-sites of the monolayers expressed as (Pb, Cu)–O in the crystal structure of the Pb-1212 compound of (Pb, Cu) Sr2 (Y, Ca) Cu2O2. Based on this idea, we have explored new charge-reservoir blocking units containing various oxy-anions.

As previously reported, we had synthesized new Pb-based cuprates with oxy-anion substitution by the elements of BO3− and PO4− not only in Pb-1212 phase but also in Pb-1201, Pb-1222, and Pb-1232 phases. That is, (Pb0.5B0.5) (Sr, Ba)2 (Y, Ca) Cu2O2 [19], (Pb0.75P0.25) Sr2 (Y, Ca) Cu2O2 [20], (Pb0.5B0.5) (SrLa) CuO2 [21], (Pb0.5B0.5) Sr2 (RE, Ce, Sr)2Cu2O2 [22, 23], (Pb0.5B0.5) Sr2 (RE, Ce, Sr)3Cu2O5 [24], and so on.

More recently, we have successfully substituted M-site of (Pb, M)–O monolayer by other oxy-anion SO42−, and synthesized new Pb-based 1212 layered cuprates in the (Pb0.75Sr0.25) Sr2 (Y1−xCa, x) Cu2O2 system. And this Pb-1212 compounds show superconductivity by annealing under high O2 pressure. In this paper, we report on the results in detail.

2 Experimental

Polycrystalline samples with various x values for nominal composition of (Pb0.75Sr0.25) Sr2 (Y1−xCa, x) Cu2O2 were synthesized by conventional solid state reaction using high-purity powders of PbO, (NH4)2H2SO4, Sr2CuO3, Y2O3, Ca2CuO3, CuO as starting materials. Sr2CuO3 and Ca2CuO3 were obtained by reacting SrCO3 with CuO at 910 °C, and CaCO3 with CuO at 900 °C, respectively. The starting materials were thoroughly ground and pressed into disk-shaped pellets. The pellets were preheated at 800 °C for 3–5 h in air and cooled down to room temperature (first sintering). Then, the pellets were pulverized, mixed, ground, and pelletized again. The re-pelletized samples were sintered at 940 °C for about 12–15 h in air and cooled down to room temperature (second sintering). The second sintering was repeated twice to obtain homogeneous samples. Finally, two different annealing treatments were done for the resulting pellets. One was “AP annealing” which means the pellets were treated under ambient O2 pressure at 400 °C for 15 h. Another was “HP annealing” which means the pellets were treated under high O2 pressure of about 13.6 MPa at 400 °C for 4 h. After each annealing, the pellets were cooled down to room temperature at a rate of 0.5 °C/min.

X-ray powder diffraction (XRD) measurements using CuKα radiation were carried out to check the sample homogeneity and the purity. The diffraction intensities were collected by step-scanning at 0.02° intervals for 2 s in the 2θ range from 3° to 60°.

The temperature dependence of the electrical resistivity (ρ–T dependence) was measured by a standard four-probe method using silver paint for the contacts. Moreover, the temperature dependence of the DC magnetic susceptibility (χ–T dependence) was measured for the powdered samples using a SQUID magnetometer. The applied magnetic field was 10 Oe.

3 Results and Discussion

We carried out XRD analysis to investigate weather or not the Pb-1212 phase could be composed in contained sulfur (Pb, S) Sr2 Y Cu2O2 system. As a consequence, we obtained almost the single 1212 phase samples in the composition of (Pb0.75Sr0.25) Sr2 Y Cu2O2. The interesting thing is that the ratio of Pb:S to be 3:1 is analogous to that of Pb:P in the (Pb, P)-1212 phase as recently reported by us [20].

Figure 1 shows XRD patterns for the samples after the AP annealing with various Ca content values x = 0.0−0.7 in the (Pb0.75Sr0.25) Sr2 (Y1−xCa, x) Cu2O2 system. As seen from the figure, diffraction peaks for the sample with x = 0.0 can be indexed on the basis of a tetragonal unit cell with the lattice constants a = 0.3837 nm and c = 1.186 nm. For other samples, the diffraction patterns resemble that of the sample with x = 0.0 and almost all the diffraction peaks are attributed to those of the Pb-1212 phase. Exceeding x = 0.5, the samples start deviating from Pb-1212 single phase. Tiny peaks originated from impurity of Pb–Sr(Ca)–Cu–O solid solution [25] (marked by closed circles) are highly visible.