

## Synthesis and characterization of the superconducting cuprates $(\text{Pb,Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_z$

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Single-phase ceramics of superconducting Pb-based layered copper oxides  $(\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$  ( $x=0-0.35$  and  $z \approx 7$ ) are successfully synthesized in an oxidizing atmosphere. The compounds that contain appropriate amounts of Ca ( $x > 0.2$ ) exhibit superconductivity when annealed in air and subsequently quenched into liquid nitrogen. The superconductivity transition temperature increases with increasing  $x$  and is raised to 52 K for nearly single-phase samples with  $x=0.4$ . It is shown that, when the sample with  $x=0.35$  is quenched, the oxygen content  $z$  decreases from 7.10 to 6.99, which is practically equal to the stoichiometric value of 7. It is shown that the length of the  $a$  axis is nearly independent of the value of  $x$ , being constant at a fixed value for each set of as-sintered and quenched samples and that the  $a$  axis of the crystal is shrunken by quenching compared with that of a crystal slowly cooled.

### INTRODUCTION

Since the first superconducting Pb-based layered copper oxides,  $\text{Pb}_2\text{Sr}_2(\text{Y,Ca})\text{Cu}_3\text{O}_8$  of the 2:2:1:3 phase, which had superconductivity transition temperatures ( $T_c$ 's) near 70 K were discovered by Cava *et al.*,<sup>1</sup> a variety of lead cuprates have been synthesized.<sup>2-15</sup> Since they have the same or similar crystallographic structures to the Bi- and Tl-based layered copper oxide superconductors [some of which have  $T_c$ 's higher than 100 K (Refs. 16-18)], such lead cuprates are thought to be promising candidates for new superconductors which have  $T_c$ 's higher than 100 K.

Cava *et al.*,<sup>1</sup> Subramanian *et al.*,<sup>2</sup> and Lee *et al.*<sup>5</sup> independently discovered Pb-based copper oxides in the  $(\text{Pb,Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_7$  system. Those groups<sup>2,5,19</sup> analyzed the crystallographic structure using single crystals of those compounds by means of x-ray diffractometry (XRD) and concluded that the compounds had the same crystallographic structure as  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$  (i.e., the 1:2:2:2 structure). However, it was reported that those Pb-based cuprates were not superconducting. Later, Rouillon *et al.*<sup>7</sup> reported that, by firing green samples of the nominal composition of  $(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_7$  which were encapsulated in evacuated silica tubes, a superconducting Pb-based 1:2:1:2 phase resulted. We previously reported that Pb-based 1:2:1:2 compounds were formed in an oxidizing atmosphere and that none of the samples of nominal compositions of  $\text{Pb}_{0.5}(\text{Sr,Y,Ca})_{3.5}\text{Cu}_2\text{O}_z$  were of the 1:2:1:2 single phase.<sup>9</sup> For some of the multiphase samples, we observed a superconductivity transition with an onset temperature of 26 K and a zero-resistivity temperature of 16 K. Recently, we successfully synthesized single-phase ceramics of the 1:2:1:2 structure for the chemical composition of  $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_z$  and concluded that both Ba substitution for Sr and Ca substitution for Y were necessary to make the ceramics superconducting.<sup>11</sup> Ono and Uchida<sup>20</sup> reported that  $(\text{Pb}_{0.65}\text{Cu}_{0.35})\text{Sr}_2(\text{Y}_{0.7}\text{Ca}_{0.3})\text{Cu}_2\text{O}_z$  became superconduct-

ing when quenched into liquid nitrogen from a high temperature. However, this Pb compound has not yet been characterized in detail.

In the present work, single-phase ceramics of Pb-based layered copper oxides given by the formula  $(\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$  ( $x=0-0.35$  and  $z \approx 7$ ) are successfully synthesized. Superconductivity is observed for samples with  $x > 0.2$  which are annealed in air and then quenched into liquid nitrogen. The highest  $T_c$  (onset) obtained is 52 K of the nearly single-phase sample with  $x=0.4$ .

### EXPERIMENTAL PROCEDURE

The samples were prepared by a solid-state reaction method using high pure (>99.9%) powders of  $\text{PbO}$ ,  $\text{SrCO}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$ . These powders are mixed into nominal compositions of  $(\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$  ( $x=0-0.4$ ). The mixed powders were calcined at 850°C for 10 h in air, and then pressed into parallelepiped bars of  $3 \times 3 \times 20$  mm<sup>3</sup>. The bars were fired at 1000-1050°C for 1 h in air or  $\text{O}_2$  gas flow and then rapidly cooled to 900°C in 5-10 min. Subsequently, the samples were slowly cooled from 900°C to room temperature at a rate of 60°C/h. Some of the as-sintered samples were then annealed at 800°C for 1 h in air and then quenched into liquid nitrogen.

The samples were characterized by powder XRD using  $\text{Cu } K\alpha$  radiation. The temperature dependence of electrical resistivity was measured by a conventional four-probe method in the temperature range from room temperature down to 4.2 K. The measurements of dc-magnetic susceptibility with respect to temperature were made using a SQUID magnetometer.

### RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the crystallographic structures of Pb-based layered copper oxides of the 1:2:1:2 type<sup>2,5</sup> and of the 2:2:1:3 type,<sup>1</sup> respectively. There is a

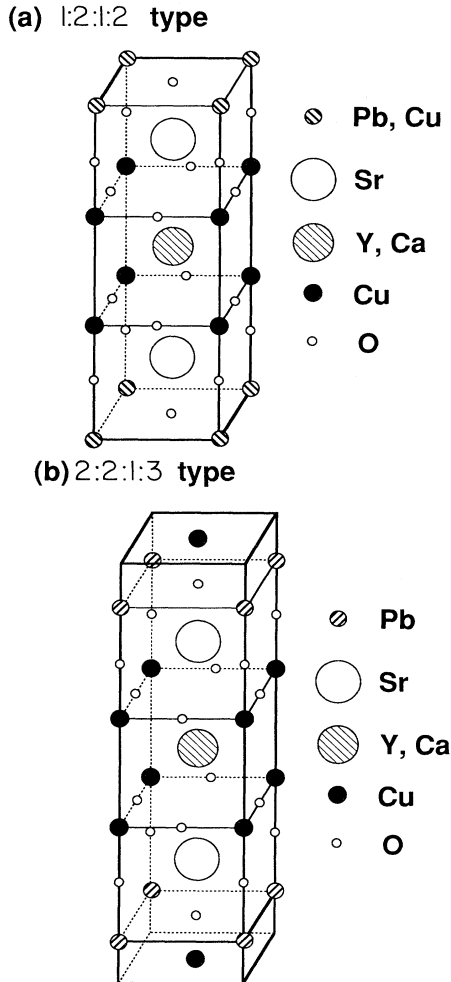


FIG. 1. Schematic representation of crystallographic structure of the Pb-based layered copper oxides of (a) 1:2:1:2 type and (b) 2:2:1:3 type.

little difference among the two crystallographic structures. That is, two  $\text{CuO}_2$  planes which are believed to be responsible for superconductivity are located between two (Pb,Cu)O rock-salt-type layers in the former structure and between two (PbO)-Cu-(PbO) stacking layers in the latter. In the 2:2:1:3 phase, the Cu and Pb ions, which the (PbO)-Cu-(PbO) stacking layers consist of are supposed to be monovalent and divalent, respectively. Thus, it was thought that, for the formation of the 2:2:1:3 phase, both firing of the green samples in a mildly reducing atmosphere [typically in ( $\text{N}_2 + 1 \text{ mol \% O}_2$ ) gas flow] and quenching of them to room temperature were essential.<sup>1</sup> On the contrary, since the Cu and Pb ions in the (Pb,Cu)O layers of the 1:2:1:2 phase were thought to be nearly divalent and tetravalent, respectively, the 1:2:1:2 phase can be formed in an oxidizing atmosphere.<sup>9,11</sup>

Figure 2 shows powder XRD patterns for as-sintered samples of  $(\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$  with  $x=0-0.4$  which were slowly cooled down to room temperature. It is seen that, up to  $x=0.35$ , single-phase samples of the Pb-based 1:2:1:2 compounds were obtained. The XRD patterns for the quenched samples were simply parallel to those for as-sintered samples. All the diffraction lines were indexed for a tetragonal unit cell with the lattice constants,  $a \approx 3.8 \text{ \AA}$  and  $c \approx 11.7 \text{ \AA}$ . It should be noted that, when Ca was doped, no single-phase samples were obtained for the Pb/Cu ratio of 1/1 in the (Pb,Cu)O plane while the Ca-free  $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_z$  was of single phase.<sup>11</sup>

Unlike the case of the 2:2:1:3 phase, the Pb ions, form rock-salt-type layers together with Cu ions in the 1:2:1:2 phase. The ionic radii of  $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$  for the coordination number of 6 are 1.19 and 0.775  $\text{\AA}$ , respectively, and that of  $\text{Cu}^{2+}$  is 0.73  $\text{\AA}$  which is rather closer to the radius of  $\text{Pb}^{4+}$ .<sup>21</sup> Therefore, it is likely that the Pb ions in the (Pb,Cu)O layers are in the tetravalent state. Moreover, the fact that the Pb-based 1:2:1:2 phase can be formed in an oxidizing atmosphere suggests that the Pb

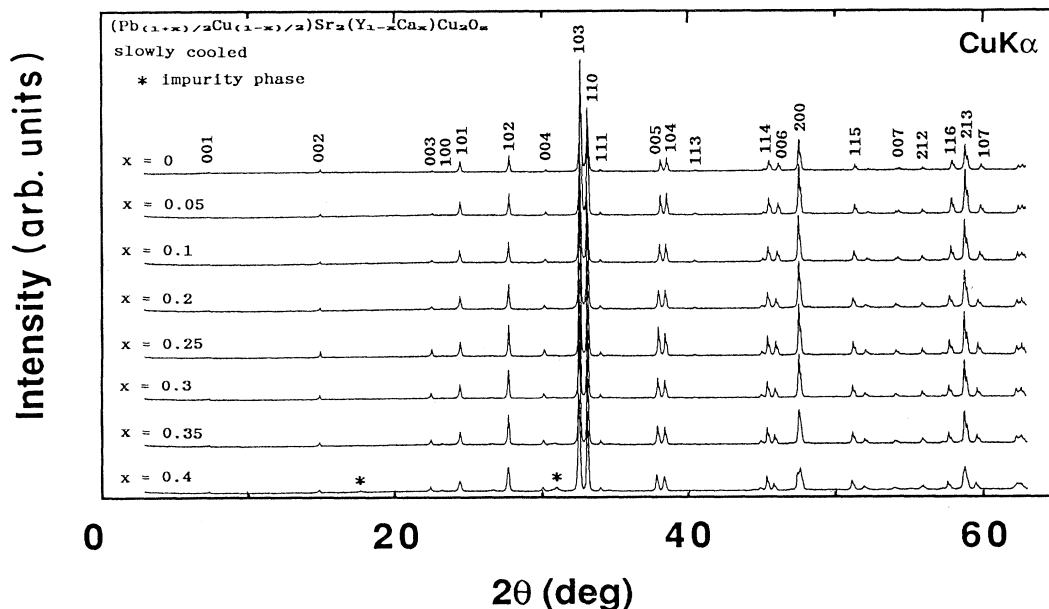


FIG. 2. Powder XRD patterns for the samples of  $x=0-0.4$  in  $(\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$ .

ions are tetravalent. Our preliminary ESCA (electron spectroscopy for chemical analysis) studies also support this result. Then, the decrease in the amount of positive charge due to the substitution of  $\text{Ca}^{2+}$  for  $\text{Y}^{3+}$  may be completely offset by the increase in the  $\text{Pb}^{4+}$ -to- $\text{Cu}^{2+}$  ratio for the  $(\text{Pb,Cu})\text{O}$  layers.

Figure 3(a) shows the temperature dependence of electrical resistivity of as-sintered samples which were slowly cooled down to room temperature. Although the electrical resistivity of the slowly cooled samples decreased as the Ca content  $x$  increased, none of the samples exhibited superconductivity down to 4.2 K. Figure 3(b) shows the temperature dependence of electrical resistivity of the samples quenched from 800 °C into liquid nitrogen. The magnitude of electrical resistivity decreased drastically compared with the case of the slowly cooled samples. Among the quenched samples, the increase in  $x$  resulted in a decrease in electrical resistivity. Finally, superconductivity was observed for the samples with  $x > 0.25$  when quenched from 800 °C. When quenched from temperatures higher than 800 °C, the sample with  $x = 0.25$ ,

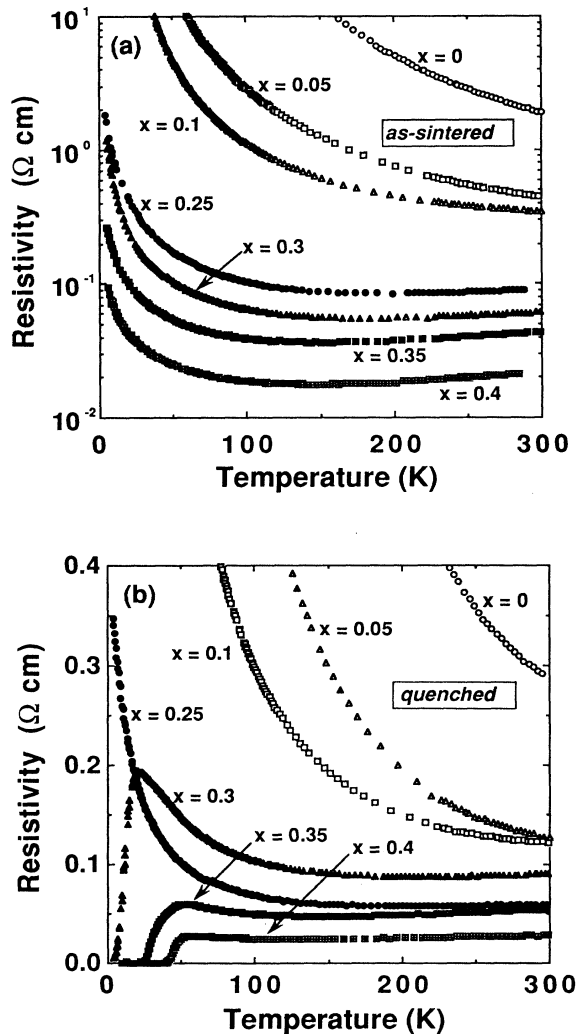


FIG. 3. Temperature dependence of electrical resistivity for the (a) slowly cooled and (b) quenched samples.

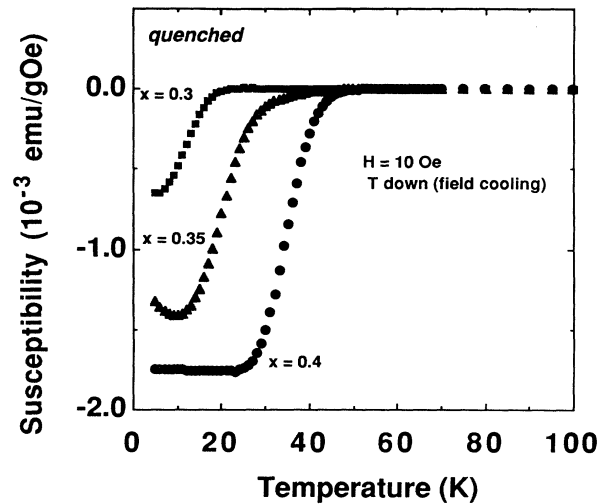


FIG. 4. Temperature dependence of dc-magnetic susceptibility for the samples of  $x = 0.3, 0.35,$  and  $0.4$

which was a nonsuperconductor when quenched from 800 °C, exhibited superconductivity. The highest  $T_c$  (onset) was obtained at 52 K for nearly single-phase samples with  $x = 0.4$  quenched from 800 °C. Figure 4 shows the temperature dependence of dc-magnetic susceptibility of the samples with  $x = 0.3, 0.35,$  and  $0.4$  measured at a magnetic field of 10 Oe. All the samples exhibited bulk superconductivity.

The dependence of the lattice constants  $a$  and  $c/3$  on the Ca content  $x$  for the samples both slowly cooled and quenched is shown in Fig. 5. For the slowly cooled samples, the  $c$  axis tended to become longer as  $x$  increased. The  $c$  axes of the quenched samples remained almost the same as those of the slowly cooled ones. In contrast, the  $a$  axes were nearly independent of the value of  $x$  for both slowly cooled and quenched samples, and were obviously shrunk to be about 3.815 Å for the quenched samples.

As previously mentioned, the Pb ions are thought to be nearly tetravalent in the Pb-based 1:2:1:2 phase. Ono and Uchida<sup>20</sup> pointed out that holes responsible for superconductivity were introduced by the  $\text{Ca}^{2+}$  substitution for  $\text{Y}^{3+}$ . However, the decrease in positive charge due to the  $\text{Ca}^{2+}$  substitution for  $\text{Y}^{3+}$  was offset by the increase in the  $\text{Pb}^{4+}$ -to- $\text{Cu}^{2+}$  ratio in the  $(\text{Pb,Cu})\text{O}$  layers. That is, the Ca substitution does not seem to work for hole doping into the  $\text{CuO}_2$  planes. A Coulometric titration for the oxygen analysis<sup>22,23</sup> for the samples with  $x = 0.3$  showed that the  $z$  value for  $(\text{Pb}_{0.65}\text{Cu}_{0.35})\text{Sr}_2(\text{Y}_{0.7}\text{Ca}_{0.3})\text{Cu}_2\text{O}_z$  decreased from 7.10 (for slowly cooled nonsuperconducting samples) to 6.99 (for quenched superconducting samples) which was nearly equal to the stoichiometric value of 7. Although it is likely that the change in oxygen content induced by quenching is the most crucial factor for the appearance of superconductivity in the Pb-based 1:2:1:2 phase, the real reason why only quenched samples with relatively high Ca content exhibited superconductivity is unknown. In the case of so-called 3:2:6 compounds such as  $\text{La}_2\text{SrCu}_2\text{O}_z$  and  $\text{La}_2\text{CaCu}_2\text{O}_z$ , an excess amount of oxygen is also contained, which is thought to be unfavor-

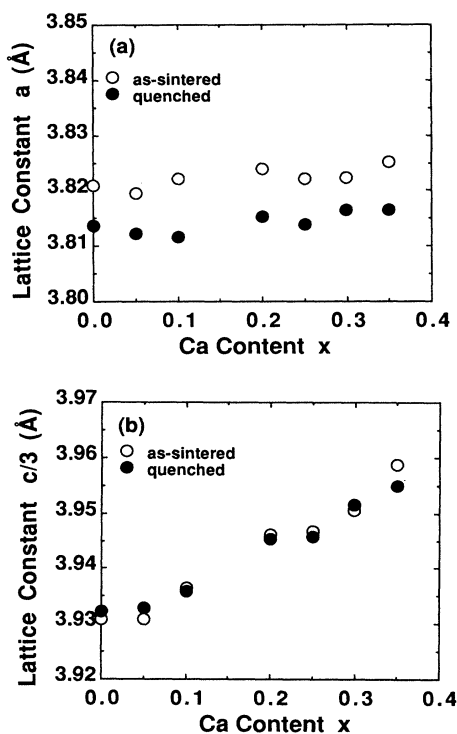


FIG. 5. The Ca-content,  $x$ , dependence of the lattice constants of (a)  $a$  and (b)  $c/3$  for both samples slowly cooled and quenched.

able for the occurrence of superconductivity.<sup>24</sup> For the Pb-based 1:2:1:2 compounds, it seemed that the quenching procedure removed the excess oxygen which was present in the slowly cooled nonsuperconducting samples and made the compounds superconducting. It should be noted that the superconducting 3:2:6 compound which was recently reported<sup>25</sup> has an  $a$  axis rather shorter than

nonsuperconducting 3:2:6 compounds.<sup>26</sup> The present results for the Pb-based 1:2:1:2 compounds shown in Fig. 5 are consistent with this observation. While the origin of the holes which are responsible for superconductivity in the Pb-based 1:2:1:2 phase is not very clear, our preliminary results of the Coulometric titration suggested that the partial reduction of Pb ions, such that the formal valence of a Pb ion was about 3.6+, induced such holes.

#### CONCLUSION

Single-phase ceramic samples of new 1:2:1:2 Pb-based layered copper oxides,  $(\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$  ( $x=0-0.35$ ), were synthesized and characterized. It was thought that Pb ions in the (Pb,Cu)O layer were tetravalent. Although the  $\text{Ca}^{2+}$  substitution for  $\text{Y}^{3+}$  did not seem to work for hole doping, superconductivity was observed for samples with  $x > 0.2$  when they were annealed in air and then quenched into liquid nitrogen. It was strongly indicated that the removal of excess oxygen to obtain stoichiometric 1:2:1:2 compounds with the oxygen content  $z=7$  was essential for having the 1:2:1:2 samples superconducting. As the excess oxygen was removed by quenching, the length of the  $a$  axis became shorter and nearly constant around 3.815 Å, while that of the  $c$  axis remained rather unchanged. The highest  $T_c$  (onset) observed in the present study was 52 K for a nearly single-phase sample with  $x=0.4$ .

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