

# Effects of Cd substitution on the superconducting properties of $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$

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## Abstract

To understand the effects of Cd substitution for Cu,  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  ( $x = 0 \sim 0.5$ ) compounds were synthesized and the structural and superconducting properties of the compounds were characterized. Resistivity data revealed that superconducting transition temperature rises initially up to  $x = 0.25$  and then decreases as the Cd doping content increases. Room-temperature thermoelectric power decreases at first up to  $x = 0.25$  and then increases with higher Cd doping content, indicating that the change in  $T_c$  is mainly caused by the change in the hole concentration on the superconducting planes by the Cd doping. The non-monotonic dependence of the lattice parameters and the transition temperature with Cd doping content is discussed in connection with the possible formation of  $\text{Pb}^{+2}$  ions and the removal of excess oxygen caused by Cd substitution in the charge reservoir layer. A correlation between transition temperature and  $c/a$  lattice parameter ratio was observed for the  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  system.

**Keywords :** (Pb,Cu)-1212, Cd substitutions, superconductivity, structure

## 1. INTRODUCTION

Soon after the discovery [1] of the first lead-based superconducting cuprates  $\text{Pb}_2\text{Sr}_2(\text{Ca},\text{Y})\text{Cu}_3\text{O}_8$  (Pb-3212), (Pb,Cu)-1212 compounds with a nominal composition of  $(\text{Pb}_{0.71}\text{Cu}_{0.29})\text{Sr}_2(\text{Ca}_{0.27}\text{Y}_{0.73})\text{Cu}_2\text{O}_z$  [2] and  $(\text{Pb}_{0.23}\text{Cu}_{0.77})\text{Sr}_2(\text{Ca}_{0.15}\text{Y}_{0.85})\text{Cu}_2\text{O}_z$  [3] were synthesized. However, these compounds did not reveal superconductivity. Later, Rouillon *et al.* [4] discovered a new superconducting (Pb,Sr)-1212 compound with a nominal composition of  $(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{Ca}_{0.5}\text{Y}_{0.5})\text{Cu}_2\text{O}_z$ . Thereafter, extensive efforts have been devoted to the study of this kind of material and several superconducting lead-based 1212 cuprates  $(\text{Pb},\text{M})\text{Sr}_2(\text{Ca}_{1-x}\text{R}_x)\text{Cu}_2\text{O}_z$  ( $\text{R} = \text{rare-earth element, M} = \text{Cu}$  [5,6],  $\text{Ca}$  [7],  $\text{Mg}$  [8],  $\text{Cd}$  [9],  $\text{V}$  [10],  $\text{Ti}$  [11],  $\text{Sn}$  [12]) have been discovered. In spite of the greater flexibility of the rock-salt-type (Pb, M)O layer in the 1212 cuprates, most of these compounds, except  $\text{M} = \text{Cd, V, Ti}$  and  $\text{Sn}$ , were found to be difficult to prepare and only exhibited superconductivity when synthesized in a sealed quartz tube [4,7] and either annealed in high-pressure oxygen [8] or quenched to ambient temperature [5,6]. In particular, it was reported that the electrical resistance of Cd-containing lead cuprate  $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Ca}_{0.3}\text{Y}_{0.7})\text{Cu}_2\text{O}_z$  exhibited an onset  $T_c$  around 90 K [9]. Although the improved superconducting properties of cuprates induced by Cd substitution in the charge reservoir layer have often been reported [13-15], the precise role of Cd is not well understood. To obtain

further insight into the role of Cd in the charge reservoir in (Pb,M)-1212 cuprates, we investigated the effects of Cd substitution for Cu in the  $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  system.

## 2. EXPERIMENTS

Polycrystalline samples were prepared by using a conventional solid-state reaction from starting powders of  $\text{PbO}$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CdO}$  and  $\text{CuO}$  with purities above 99.9%. In a preliminary study on the  $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Ca}_{1-y}\text{Y}_y)\text{Cu}_2\text{O}_z$  system, we found an optimal transition temperature,  $T_c$  for a sample with a value of  $y$  of about 0.3, so we prepared samples with nominal compositions of  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  ( $0 \leq x \leq 0.5$ ). The powders were mixed, ground, and heated at 800 °C for 7 h in air. The resultant powders were thoroughly re-ground, pressed into pellets, and sintered at 970 °C for 7 h in an oxygen atmosphere and then slowly cooled to a temperature below 200 °C in a tube furnace. The samples were characterized by X-ray diffraction (XRD) at room temperature by using a powder diffractometer (X'pert-pro MPO) with  $\text{K}\alpha$  radiation to determine their phase purity and lattice parameters. The lattice parameters were calculated from the diffraction peak positions by the method of least squares. The temperature dependence of the electrical resistivity was measured by using a conventional four-probe technique. The measuring current was 10 mA. Room temperature thermoelectric power (TEP) was measured relative to the copper electrodes using

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a dc differential method [16], and was then calculated by correcting for the TEP of copper.

### 3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns for  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  samples with  $x = 0, 0.2, 0.25, 0.3$  and  $0.5$ . The main diffraction peaks were indexed on the basis of a tetragonal unit cell (space group  $P4/mmm$  structure). The samples were seen to contain a slight trace of impurity phases, marked by \*, as reported by other authors. The main impurity phase was identified as the non-superconducting  $\text{Sr}_{5-x}\text{Pb}_{3+x}\text{Cu}_y\text{O}_{12-z}$  phase [9, 12]. The impurity content decreased slightly with the increase of  $x$  up to 0.25. The variation of the lattice parameters  $a$  and  $c$  with Cd doping content  $x$  is shown in Fig. 2. The lattice parameters obtained from the least square fitting method are  $a = 3.835(1) \text{ \AA}$  and  $c = 11.918(5) \text{ \AA}$  for the  $x = 0$  sample,  $a = 3.829(1) \text{ \AA}$  and  $c = 11.984(3) \text{ \AA}$  for the  $x = 0.25$  sample and  $a = 3.829(1) \text{ \AA}$  and  $c = 11.984(3) \text{ \AA}$  for the  $x = 0.5$  sample. One can notice that the partial substitution of Cd for Cu tends to result in a slight decrease in the  $a$  lattice parameter and an increase in the  $c$  lattice parameter compared to those of the  $x = 0$  or  $x = 0.5$  samples.

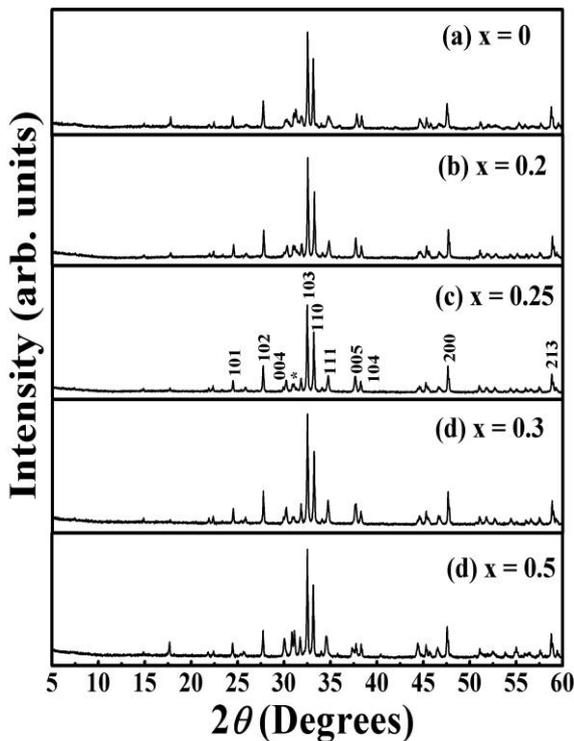


Fig. 1. Powder XRD patterns for  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  samples.

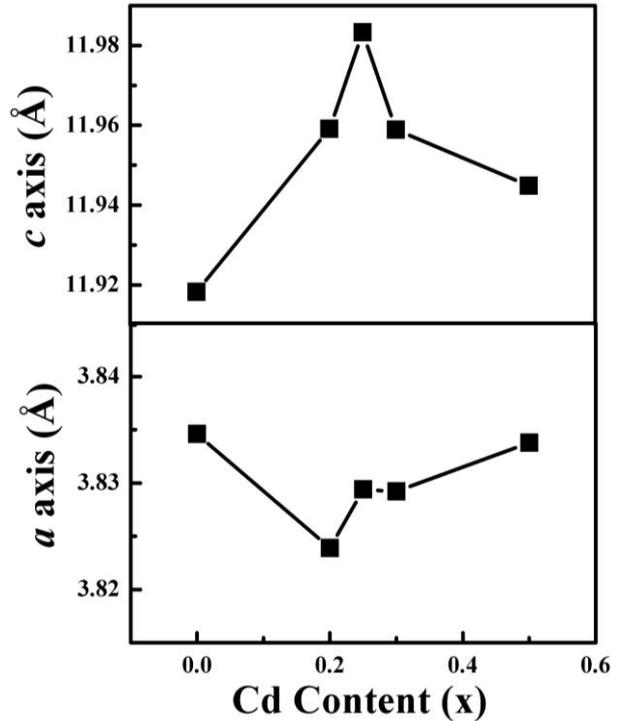


Fig. 2. Variation of the lattice parameters with Cd content,  $x$  for  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  samples.

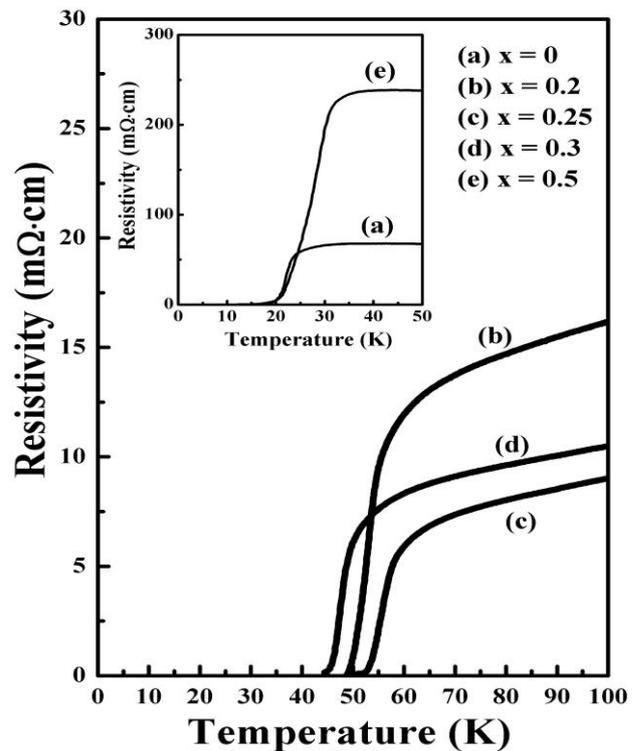


Fig. 3. Temperature dependence of the electrical resistivity for  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  samples.

Fig. 3 shows the temperature dependence of the electrical resistivity for  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  samples. The  $x = 0$  sample shows a superconducting onset temperature ( $T_c$  (onset)) at 31 K and reaches zero resistivity ( $T_c$  (zero)) at 16 K. The normal state resistivity was significantly decreased when Cd was partially substituted for Cu. However, when Cu is completely replaced by Cd ( $x = 0.5$  sample), the normal state resistivity prominently increases. The result in Fig. 2 indicates that the superconducting transition temperature rises initially up to  $x = 0.25$  and then decreases with increasing Cd doping content. The  $T_c$  (onset) and  $T_c$  (zero) are 64 K and 53 K for the  $x = 0.25$  sample, and 36 K and 20 K for the  $x = 0.5$  sample, respectively.

For  $p$ -type high  $T_c$  cuprate superconductors, the hole concentration per  $\text{CuO}_2$  plane ( $p$ ) plays a very important role. It was found that  $T_c$  versus  $p$  shows a dome-shaped curve with a maximum transition temperature near  $p = 0.16$ . Modification of the hole concentration is usually done by the substitution of cations or by varying oxygen content, resulting in the change of the superconducting properties. It is possible to use TEP as a probe to determine the hole-doping state of the cuprates based on a systematic correlation [17] between room temperature TEP and the hole concentration in the superconducting planes. It has large positive values in the underdoped state and negative values in the overdoped state, with optimal doping being 1-2  $\mu\text{V}/\text{K}$ . The room temperature TEPs for the  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  samples with  $x = 0, 0.2, 0.25, 0.3$  and  $0.5$  are 31.2, 21.8, 19.5, 19.9 and 28.7  $\mu\text{V}/\text{K}$ , respectively. The corresponding hole concentration estimated from the TEP data for the  $x = 0, 0.2, 0.25, 0.3$  and  $0.5$  samples are 0.090, 0.100, 0.103, 0.102 and 0.093, respectively. Therefore, the enhancement of  $T_c$  (zero) for the  $x = 0.2, 0.25$  and  $0.3$  samples can be explained by the increase in hole concentration compared to those of the  $x = 0$  and  $0.5$  samples. At this time, the precise origin of the non-monotonic increase in hole concentration with the Cd doping content is unclear. However, this non-monotonic change in the hole concentration appears to be intimately related to the non-monotonic variation of the lattice parameters with Cd doping content, as is shown in Fig. 2. Liu *et al.* [18] observed that a complete replacement of Cu by Cd in  $(\text{Pb,Cu})$ -1212 compound resulted in an expansion in the  $c$  lattice parameter and a small contraction in the  $a$  lattice parameter. The expansion in the  $c$  lattice parameter for the Cd-substituted sample was attributed to the larger  $\text{Cd}^{+2}$  (0.95 Å, CN = 6) ion [19] substitution into the smaller  $\text{Cu}^{+2}$  (0.73 Å, CN = 6) ion. The contraction in the  $a$  lattice parameter can be attributed to an increase in the average copper oxidation state, leading to a shorter Cu-O distance in the  $\text{CuO}_2$  planes. In several Pb-based 1212 cuprates, it is well known that superconductivity is either enhanced or

induced in the as-prepared samples by post-annealing at an appropriate temperature above 800 °C and then quenching [5,6,10-12]. The improvement of superconductivity for the quenched sample was always accompanied by the contraction of the  $a$  lattice parameter [5,6, 10-12, 20] and was explained by the removal of excess oxygen in the as-prepared samples. Therefore, the contraction in the  $a$  lattice parameter and the improvement of superconductivity for partially Cd-doped samples shown in Fig. 2 and Fig. 3 is considered to be related to the removal of excess oxygen from the samples. Beales *et al.* [21] argued that both Pb and Cd prefer a rock-salt structure environment in the charge reservoir layer, whereas Cu prefers a perovskite structure environment. The resulting random arrangement of the oxygen ions in  $(\text{Pb,Cu})$ -1212 compounds would tend to trap holes within the charge reservoir layer and prevent their transfer into the  $\text{CuO}_2$  planes that carry the superconducting current. Therefore, the observation of superconductivity in the  $(\text{Pb,Cd})$ -1212 system without quenching experiments was attributed to the intrinsic removal effect of excess oxygen by Cd substitution in the charge reservoir layer. In this respect, the non-monotonic variation of the  $a$  lattice parameter with Cd doping content can be caused by the combined effects of the change in oxygen content and the ion size difference between Cd and Cu. On the other hand, the  $c$  lattice parameter of the quenched samples tended either to decrease slightly or to remain almost the same as those of the slowly cooled ones. Maignan *et al.* [22] suggested that the introduction of larger cations such as Cd or Sr in the charge reservoir layer in the Pb-based 1212 system would favor the formation of  $\text{Pb}^{+2}$ . Given the fixed oxygen content of a sample, the formation of  $\text{Pb}^{+2}$  ion means an increase in the hole concentration via an increase in the Cu oxidation state. The formation of  $\text{Pb}^{+2}$  ion in the Pb-1212 system is expected to result in an expansion of the  $c$  lattice parameter because the ionic size [19] of  $\text{Pb}^{+2}$  (1.19 Å, CN = 6) is larger than that of  $\text{Pb}^{+4}$  (0.775 Å, CN = 6). Consequently, the combined effect of the increased formation of  $\text{Pb}^{+2}$  and the removal of excess oxygen can be estimated by the ratio of the  $c$  and  $a$  lattice parameters ( $c/a$ ), and the increase in this ratio is expected to be correlated with the increase in the transition temperature of the underdoped Pb-based 1212 compound. Fig. 4 shows the dependence of the transition temperature on the  $c/a$  ratio for the  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  samples. One can see a good correlation between the transition temperature and the  $c/a$  ratio for the present Cd-doped compounds. Further studies on the possibility of application of this correlation to other Pb-based superconducting systems would be valuable to understand the role of Cd and to find improved superconducting materials.

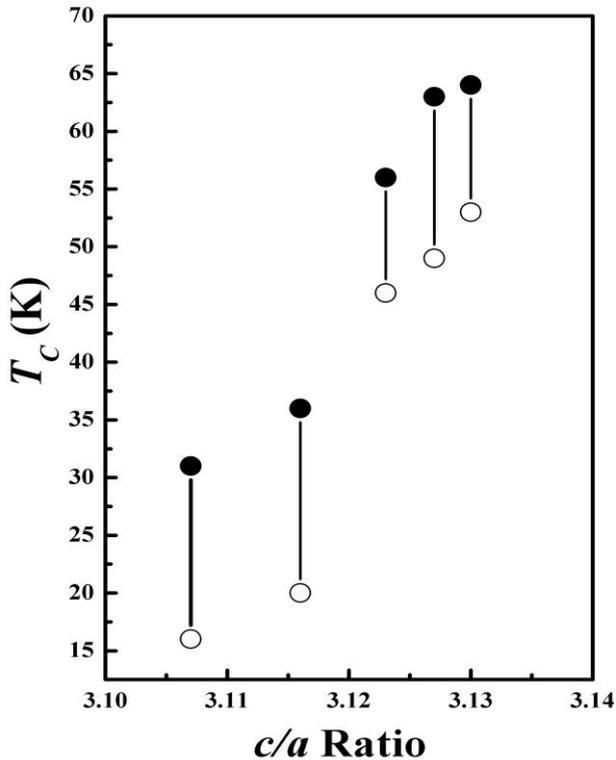


Fig. 4. Superconducting transition temperature versus  $c/a$  ratio.  $T_c$ (onset) and  $T_c$ (zero) are denoted with closed and open circles, respectively.

#### 4. CONCLUSION

The Pb-based compounds  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  ( $x = 0 \sim 0.5$ ) were synthesized through a solid-state reaction route and the effects of Cd substitution on structural and superconducting properties were studied. X-ray diffraction (XRD) patterns revealed that all the compounds were mainly crystallized in the space group  $P4/mmm$  structure. We found that the partial substitution of Cd for Cu tended to result in a slight decrease in the  $a$  lattice parameter and an increase in the  $c$  lattice parameter compared to those of the  $x = 0$  or  $x = 0.5$  samples. Resistivity data showed that superconducting transition temperature increased initially up to  $x = 0.25$  and then decreased as the Cd doping content increased. The change in the superconducting transition temperature caused by the substitution of Cd for Cu was discussed in connection with the non-monotonic changes in the structural parameters and the hole concentration of the compounds with the Cd doping content. A correlation between transition temperature and  $c/a$  lattice parameter ratio was observed for the  $(\text{Pb}_{0.5}\text{Cu}_{0.5-x}\text{Cd}_x)\text{Sr}_2(\text{Ca}_{0.7}\text{Y}_{0.3})\text{Cu}_2\text{O}_z$  system.

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