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Effect of Pr substitution on the superconducting properties of $(Pb_{0.5}Cd_{0.5})SrLaCuO_z$

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Abstract

The effects of Pr substitution on the structural and the superconducting properties for Pb-based 1201 cuprates with compositions of $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$ ($0 \leq x \leq 0.25$) and $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ ($0 \leq y \leq 0.1$) were investigated. It is found that T_c decreases as the Pr-doping content x increases in the $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$ samples, whereas T_c of $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ samples increases as the La-doping content y increases. The experimental results were discussed in connection with the change in hole concentration of the samples.

Keywords: Pb-based 1201 cuprate;; Pr doping ; $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$;superconductivity

1. INTRODUCTION

Soon after the discovery of the first Pb-based cuprate superconductors $(Pb_2Cu)Sr_2(Ca,Y)Cu_2O_z$(Pb-3212) by Cava et al. [1], new Pb-based layered cuprates of $(Pb_{0.5}Cu_{0.5})(Sr_{2-y}La_y)CuO_z$((Pb,Cu)-1201) were synthesized [2, 3]. The crystal structure of the (Pb,Cu)-1201 compound consists of a (Pb/Cu)-O mono-layer and a Cu-O octahedron as shown in Fig. 1 and it has the simplest unit cell among the Pb-based layered cuprates. Later, Cu sites in the mono-layers of (Pb/Cu)-O were found to be replaced by Cd [4], Zn [4] and B [5]. However, few studies have been made to replace Pb by other elements except Hg [6]. Among the several possible elements, Pr ion is an interesting candidate because the mercury-based 1201 phase is formed when Pr is substituted for Hg [7]. In the present study, we have prepared $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$ and $(Pb_{0.5-x}PrxCd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ and investigated the effect of Pr substitution for Pb on the phase formation and the superconducting properties of the system.

2. EXPERIMENTALS

Polycrystalline samples with nominal compositions of $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$ ($0 \leq x \leq 0.25$; A series) and $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-x}La_{1+x})CuO_z$ ($0 \leq y \leq 0.1$; B series) were prepared by using a solid-state reaction from starting powders of PbO, Pr_4O_7, CdO, $SrCO_3$, La_2O_3 and CuO with purities above 99.9%. The powders were mixed, ground, and heated at 800℃ for 10 h in air. The resultant powders were re-ground, pressed into pellets, and sintered either at 965℃ (B series) or 998℃ (A sereies) for 10 h in an oxygen atmosphere and then slowly cooled to below 200℃ in a furnace. The samples were characterized by X-ray diffraction (XRD) at room temperature by using a powder diffractometer (X'pert-pro MPD) with Kα radiation to determine their purity and the lattice parameters. The resistivity measurements were made on rectangular specimens cut from the sintered pellets, by employing a conventional four probe technique in the temperature range of about 10 K – 300 K. The measuring current was 10 mA. The room-temperature thermoelectric power measurements were carried out using the standard differential technique.

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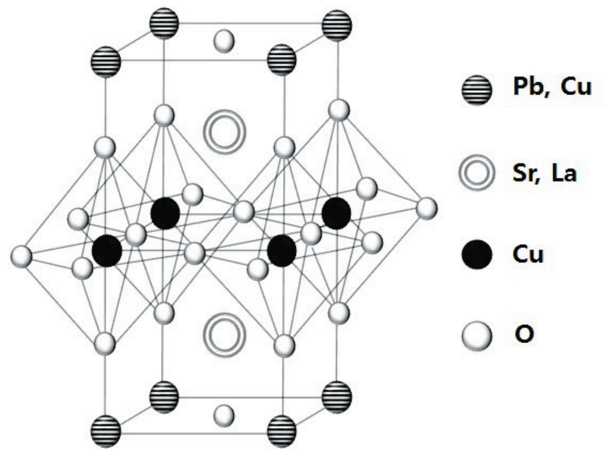

Fig. 1. Crystal structure model of $(Pb_{0.5}Cu_{0.5})SrLaCuO_z$.

3. RESULTS AND DISCUSSION

The XRD patterns for the $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$ samples with x = 0, 0.05, 0.125, 0.1, 0.15, 0.2, and 0.25 are shown in Fig. 2. The Pr-free pristine sample (x = 0) shows a single-phase nature. This feature was also observed when the Pr-doping content increased up to x = 0.2, but a further increase in the Pr-doping content resulted in an increase in impurity peaks marked with asterisks as shown for the x = 0.25 sample in Fig. 2, suggesting the solubility limit of Pr ion is about x = 0.2. The main diffraction peaks for the samples could be indexed on the basis of a tetragonal unit cell as denoted in Fig. 2. The tetragonal cell parameters *a* and *c* are shown in Fig. 3. It can be seen that the *a* lattice parameter decreases and the *c* lattice parameter increases as the Pr-doping content x increases. The increase in the *c* lattice parameter with x seems to be consistent with the difference in ionic size [8] of Pr^{+3}/Pr^{+4} (0.99 Å/0.82 Å for CN = 6) when compared to that of Pb^{+4} (0.775 Å for CN = 6).

Fig. 4 displays the temperature dependences of the electrical resistivity for the $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$ samples. The sample with x = 0 exhibits the onset transition temperature, T_c(onset) = 38 K and zero-resistivity, T_c(zero) = 35.4 K. The onset transition temperature is similar to the value of 40 K reported by Beales *et al.*[4]. As the Pr-doping content increases, the samples with x = 0.05, 0.1, and 0.15 show a superconducting drop at about 24, 18 and 11 K, respectively. Zero-resistivity temperatures for the x = 0.05 0.1 and 0.15 samples are 15.5 K, 12.5 K and 9.6 K, respectively. The x = 0.2 sample reveals no superconducting transition behavior in the measuring temperature range.

For several cuprates, T_c is known universally and empirically to vary as an inverted parabolic function of the hole concentration (p) per CuO_2 plane and maximum T_c is observed near $p = 0.16$ [9]. Accordingly, the decrease in T_c can be caused by either a decrease in the hole concentration below the optimum hole concentration or an increase in the hole concentration above the optimum hole concentration.

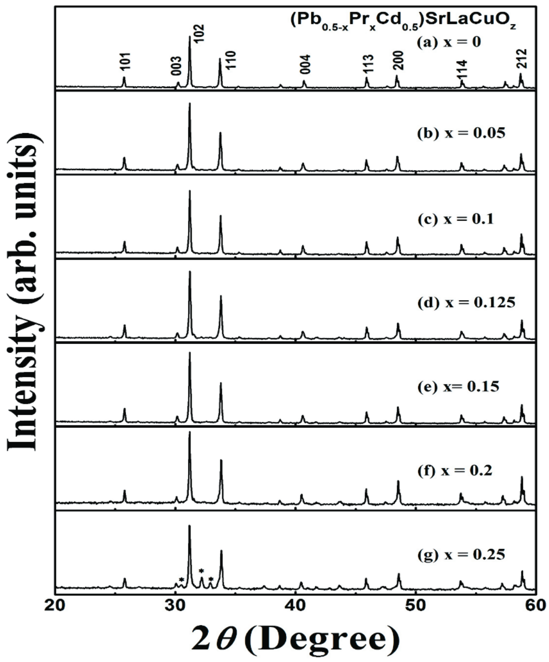

Fig. 2. Powder XRD patterns for the $(Pb_{0.05-x}Pr_xCd_{0.05})$ $SrLaCuO_z$ (x = 0 - 0.25) samples. Peaks due to impurity phases are marked with asterisks.

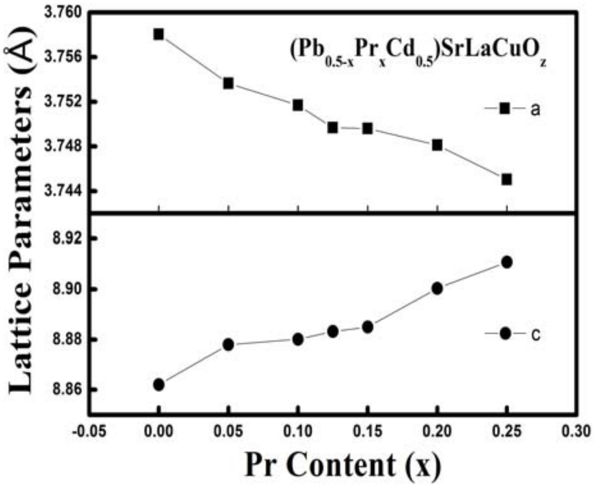

Fig. 3. Lattice parameters for the $(Pb_{0.05-x}Pr_xCd_{0.05})SrLaCuO_z$ (x = 0 - 0.25) samples.

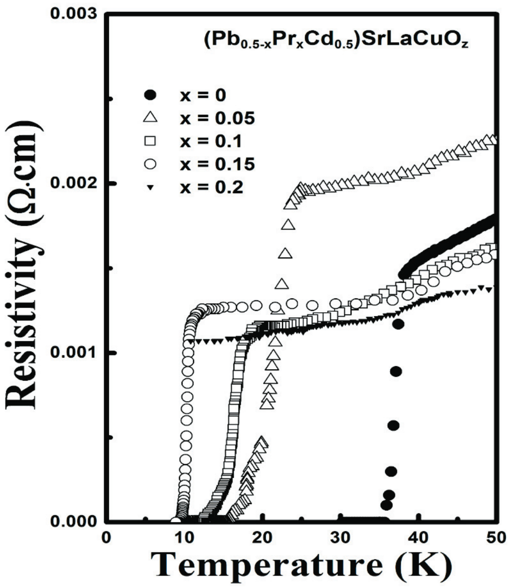

Fig. 4. Temperature dependences of the electrical resistivity of the $(Pb_{0.05-x}Pr_xCd_{0.05})SrLaCuO_z$ (x = 0 - 0.25) samples.

The room-temperature thermoelectric power (TEP) measurements are useful to estimate the carrier-doping level [9] of a sample, based on the correlation between the room-temperature TEP and the hole concentration. It has large positive values in the underdoped range and negative values in the overdoped range, with optimal doping being 1-2 μV/K. The room-temperature TEP values for the $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$ samples with x = 0, 0.05,0.125, 0.15, and 0.2 were -1.4, -2.1, -3.7, -4.0 and -3.3 μV, respectively (see also Fig. 7 (a)). This result suggests that the pristine sample (x = 0) is in an overdoped state and the Pr doping tends to increase the hole concentration of the sample in the solubility limit. Therefore, the decrease in the T_c caused by the Pr doping can be attributed to an increase in the hole concentration of the sample above the optimum hole concentration. This results seems to be also related to the contraction of the *a* lattice parameter with increasing the Pr-doping content as shown in Fig. 3.

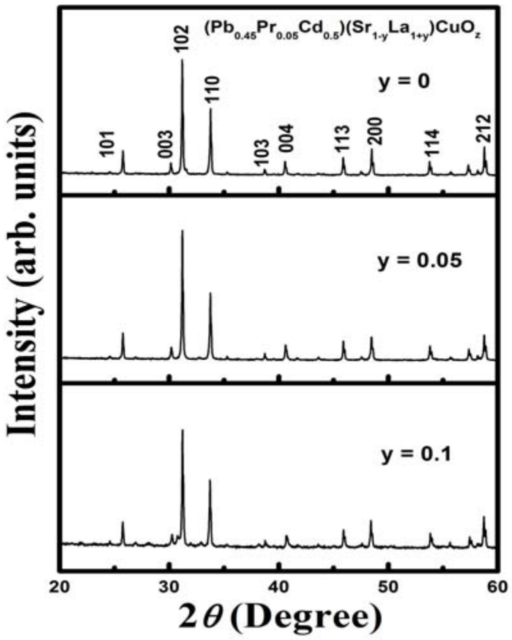

Fig. 5. Powder XRD patterns for the $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ (x=0-0.1) samples.

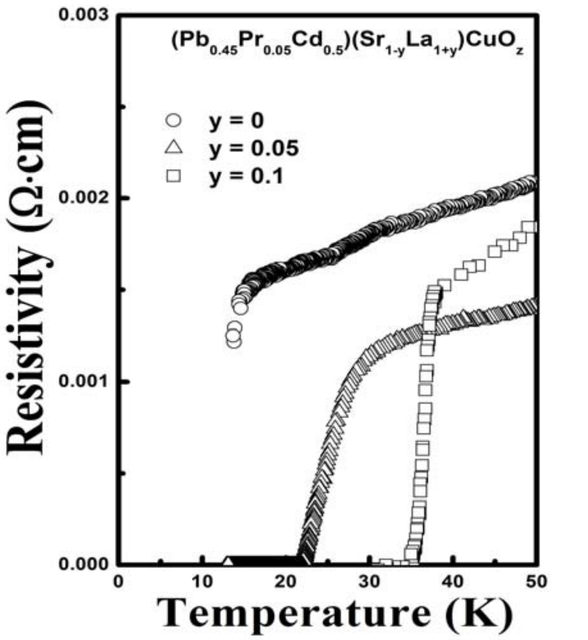

Fig. 6. Temperature dependences of the electrical resistivity of the $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ (x=0-0.1) samples.

In order to explore further the effect of Pr substitution on the superconducting properties of the Pb-1201 system, we prepared another series of samples with a nominal composition of $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ ($0 \le y \le 0.1$) and characterized their properties. As shown in Fig. 5, the XRD data of these samples show a nearly single-phase nature. Fig. 6 exhibits that the temperature dependences of the electrical resistivity for the $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ samples with y = 0, 0.05 and 0.1. The sample with x = 0 shows a superconducting drop at about 15 K. As the La-doping content x increases from 0 to 0.1, the samples with x = 0.05 and 0.1 reveal a superconducting drop at about 30 K and 38 K, respectively. The T_c (zero) of the y = 0.1 sample is 35.2 K which is comparable to that (35.4 K) of the Pr-free pristine sample (Fig. 4). Since the valence of La ion (La^{+3}) is higher than that of Sr ion (Sr^{+2}), La substitution for Sr is expected to decrease the hole concentration of the sample, if there is negligible change in the oxygen content of the sample. Fig. 7 shows the room-temperature TEP for the $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ samples and the estimated p values [9] are 0.215, 0.203, and 0.175 for the y = 0, 0.05, and 0.1 samples, respectively. Therefore, one can see that the La doping results in a decrease in the hole concentration of the sample as expected from the change in valence between La and Sr ions. This result also indicates that the effect of the increase in oxygen content caused by the La doping is not enough high to cancel the effect of the decrease in the hole concentration caused by the valence difference. Therefore, the results of Fig.6 and Fig. 7 clearly indicate that the excess carriers introduced by the Pr doping can be counter-balanced by the hole filling through the La doping in the $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ ($0 \le y \le 0.1$) samples.

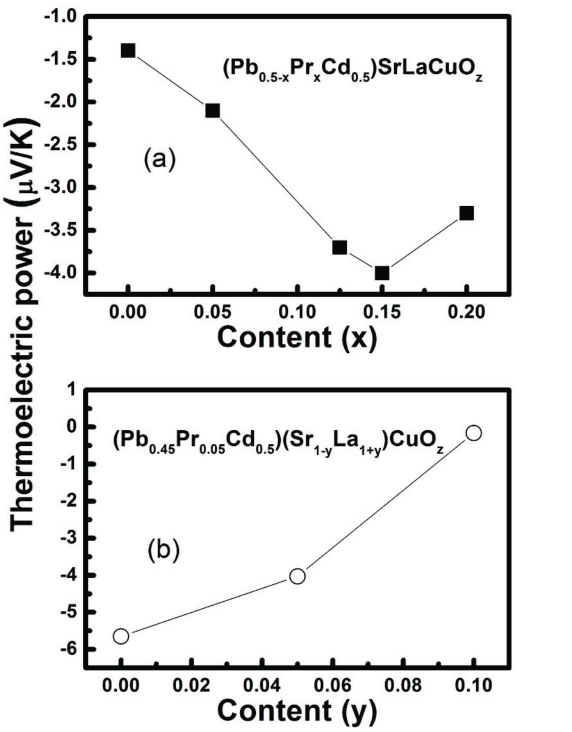

Fig. 7. Room-temperature thermoelectric powers for the (a) $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$ (x = 0 - 0.2) and (b) $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ (y = 0 - 0.1) samples.

4. CONCLUSIONS

The effect of Pr substitution for Pb on the superconducting properties of the $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$ ($0 \le x \le 0.25$) and $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ ($0 \le y \le 0.1$) samples were investigated. Almost single-phase samples could be obtained for the sample with x = 0 - 0.2 and y = 0 - 0.1. T_c decreased as the Pr-doping content x increased in the $(Pb_{0.5-x}Pr_xCd_{0.5})SrLaCuO_z$ samples, whereas T_c of the $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ samples increased as the La-doping content y increased. The experimental results suggested that the Pr doping in the Pb site of the (Pb,Cd)-1201 compounds introduced holes into the system and thereby, degrading superconductivity when the hole concentration was higher than the optimum value. Thermoelectric power measurements supported that the excess carriers introduced by the Pr doping could be counter-balanced by the hole filling through the La doping in the $(Pb_{0.45}Pr_{0.05}Cd_{0.5})(Sr_{1-y}La_{1+y})CuO_z$ ($0 \leq y \leq 0.1$) samples.

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