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J. Phys.: Condens. Matter 7 (1995) 5975–5982. Printed in the UK

Crystal structure and superconductivity of new Pb-based 1222 cuprate $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$

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Received 16 May 1995, in final form 15 June 1995

Abstract. A new superconductor $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ has been prepared. The compound has higher T_c values when it is synthesized in O_2 than in air. Besides, the O_2-synthesized sample exhibits metallic behaviour, while the air-synthesized sample exhibits semiconducting behaviour in their normal state. It has a typical metal–insulator transition with the increase of the carrier concentration, which is proven by our calculation results of the bond valence sums of the Cu ions in the conducting CuO_2 planes. $(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Eu_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$ is an analogous compound of (Pb, Cd)-1222. (Pb, Cd)-1222 has higher superconducting transition temperatures than (Pb, Cu)-1222. This difference can be explained from the viewpoint of charge transfer between the charge reservoir (Pb, Cu)O layers and the conducting CuO_2 planes. The crystal structure of $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ has been refined by the Rietveld method. The refinement results indicate that both (Pb, Cd) and O(3) in the (Pb, Cd)O layer are displaced from their ideal sites.

1. Introduction

Since the first high-temperature superconductor was discovered in the La–Ba–Cu–O system by Bednorz and Müller [1], a great variety of other high-T_c copper oxides have been synthesized one after another in recent years. All these copper oxides have a common structure feature, i.e., layered structures. The layered structures can be regarded as alternating stacks of different block layers, such as rock-salt-type layers, perovskite-type layers and/or fluorite-type layers. In general, those compounds containing fluorite-type layers have lower T_c than the corresponding compounds containing no fluorite-type layers. For example, Tl-1212 has an onset T_c of about 100 K [2], while Tl-1222 just an onset T_c of about 40 K [3].

In 1990, Adachi *et al* discovered the first non-superconducting Pb-1222 phase $(Pb, Cu)(Sr, Pr)_2Pr_2Cu_2O_9$ [4]. The crystal structure of the (Pb, Cu)-1222 phase is derived from $(Pb, Cu)Sr_2(Y, Ca)Cu_2O_7$ with the oxygen-deficient (Y, Ca) layer replaced by the fluorite-type $(Ln, Ce)_2O_2$ layer. Since then, careful research has been carried out in the system $(Pb, Cu)(Sr, Ln)_2(Ln, Ce)_2Cu_2O_9$ (Ln = lanthanide elements), and a series of superconducting (Pb, Cu)-1222 compounds has been obtained [5–7]. Up to now, the highest

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onset T_c of 32 K was reported in $(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Nd_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$ [7]. At the same time, another kind of Pb-1222 phase $(Pb,Cu)(Sr,La)_2(Ln,La)_2Cu_2O_9$ (Ln = trivalent lanthanide ions) was reported by Sasakura *et al* [8], which does not contain any tetravalent lanthanide ions such as Ce^{4+} or Pr^{4+}. No superconductivity was discovered in this kind of Pb-1222 compound.

In this paper, the crystal structure and superconductivity of $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ is reported, which has higher superconducting transition temperatures than $(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Nd_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$. To our knowledge, the superconducting transition temperatures of the present compound are comparable to, or even higher than, those of the Tl-1222 phase [3].

2. Experimental details

Samples were prepared by the solid state reaction method using PbO, CdO, $SrCO_3$, Eu_2O_3, CeO_2 and CuO as starting materials. Stoichiometric amounts of starting materials were appropriately weighed, and ground together in an agate mortar. The well mixed powders were calcined at 900 °C in air overnight and then furnace cooled to room temperature. The prereacted material was reground and pressed into pellets. The pellets were sintered at 1050 °C in air for 8 hours. Finally, the pellets were ground another time, and then pressed and sintered at 1050 °C in air and flowing O_2, respectively.

X-ray powder diffraction (XRD) analyses were performed on an M18AHF x-ray diffractometer with Cu Kα radiation (50 kV × 200 mA). The structure refinement data were collected on the same diffractometer at ambient temperature. The scattering slit is 0.50°, the divergence slit 0.50° and the receiving slit 0.15 mm. The scanning step width is 0.02° in 2θ and the sampling time is 2 s per step. The 2θ range is from 10 to 110°. A standard four-probe method was used for electrical resistivity measurements.

3. Results and discussion

$(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ is very sensitive to sintering temperature and atmosphere as is $Pb(Sr,La)_2Ln_2Cu_2O_{9+\delta}$ (Ln = Gd, Dy, Eu and Pr) [9]. Therefore, inappropriate synthesis conditions will lead to the appearance of impurity phases. The optimal synthesis conditions for the present (Pb, Cd)-1222 are sintering at 1050 °C in oxidizing atmosphere (air or O_2). Figure 1 shows the resistivity versus temperature curves for $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$, which was synthesized in air and O_2, respectively. The room-temperature resistivities for the air-synthesized and O_2-synthesized samples are 1.2 mΩ cm and 5 mΩ cm, respectively. It can be seen from figure 1 that $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ has higher T_c values when it is synthesized in O_2 ($T_{c,onset}$ = 43 K, $T_{c,zero}$ = 35 K) than synthesized in air ($T_{c,onset}$ = 19 K, $T_{c,zero}$ = 12 K). Besides, the O_2-synthesized sample exhibits metallic behaviour in its normal state, while the air-synthesized sample exhibits semiconducting behaviour in its normal state. It was a typical metal–insulator transition for high-T_c superconducting copper oxides as the carrier concentration increases.

Maeda *et al* synthesized an analogous compound $(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Eu_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$ in O_2 [6]. This compound has an onset T_c of 25 K. Thus, (Pb, Cd)-1222 has higher superconducting transition temperatures than (Pb, Cu)-1222. In our previous work, we compared the structure difference between (Pb, Cd)-1212 and (Pb, Cu)-1212 [10]. From a structural viewpoint, lead prefers a rock salt structure environment, whereas copper prefers

a perovskite structure environment. The mixed occupation of Pb and Cu in the (Pb, Cu)O layer leads to extra oxygen atoms present in the (Pb, Cu)O layer in the (Pb, Cu)-1212 phase. Oxygen in this position tends to trap holes within the rock-salt-type (Pb, Cu)O layers and weakens the ability of charge transfer from the (Pb, Cu)O layers to the CuO_2 planes. For the (Pb, Cd)-1212 system, on the other hand, there will not exist such extra oxygen in the (Pb, Cd)O layers, because cadmium also prefers to form a rock salt structure like lead. Furthermore, the internal oxidation/reduction reaction between Pb^{4+} and Cu^{2+} also affects the charge transfer from the charge reservoir (Pb, Cu)O layers to the conducting CuO_2 planes. All these will naturally limit the T_c values of (Pb, Cu)-1212. For the same reason, it is suggested that the structure difference between (Pb, Cd)-1222 and (Pb, Cu)-1222 is parallel to that between (Pb, Cd)-1212 and (Pb, Cu)-1212. Thus, it is not difficult to understand why (Pb, Cd)-1222 has higher superconducting transition temperatures than (Pb, Cu)-1222.

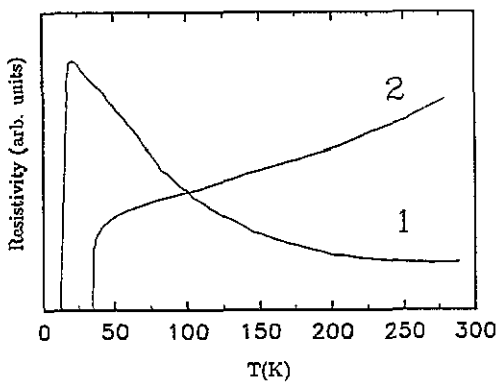

Figure 1. The temperature dependence of resistivity for $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$, which was synthesized in air (curve 1) and O_2 (curve 2), respectively.

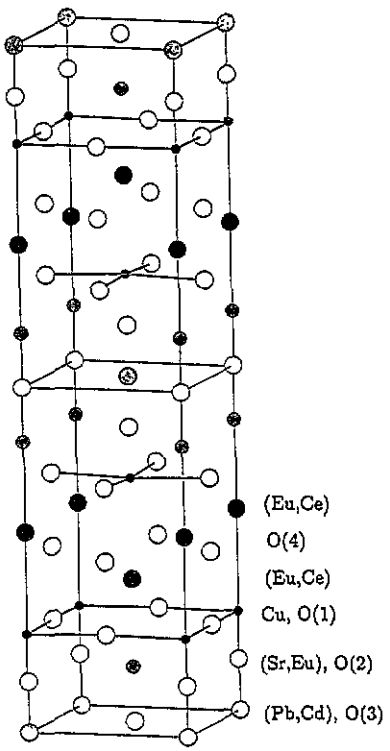

Figure 2. Schematic representation of the crystal structure of $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_9$.

The crystal structure of $(Pb, Cu)(Sr, Nd)_2(Ho, Ce)_2Cu_2O_{9.06}$ has been reported by Maeda *et al* [7]. According to this structure model, we have refined the structure parameters of $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ by the Rietveld method [11] using x-ray powder diffraction data. Figure 2 shows the schematic representation of the crystal structure of $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_9$. Larger Sr^{2+} was assumed to selectively occupy the nine-coordinated site in the rock-salt-type layers, and smaller Ce^{4+} was assumed to occupy the eight-coordinated site. Eu^{3+} was distributed in the two sites according to the

nominal composition. The thermal parameters (B) were assumed to be isotropic, and the thermal parameters of all oxygen atoms were arbitrarily fixed at 1 Å^2. Table 1 lists the final R factors, the refined lattice constants, structure parameters and their estimated standard deviations in parentheses for $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ synthesized in air and O_2. Table 2 lists the selected metal–oxygen interatomic distances of the two samples. For comparison, the corresponding data for $(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Eu_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$ [5] are also listed in tables 1 and 2, respectively. Figure 3 shows the Rietveld refinement patterns for $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$. The dotted lines represent the observed diffraction patterns, the solid lines represent the calculated patterns and the curves at the bottom of each figure represent the difference between the observed and calculated patterns. The short vertical lines mark the positions of possible Bragg reflections for the (Pb, Cd)-1222 phase. The remarkably good fit between the observed and calculated patterns supports the structure model listed in table 1.

During the refinement of the thermal parameter of the Pb and Cd atoms in the rock-salt-type (Pb, Cd)O monolayer in the present (Pb, Cd)-1222 compound assuming the ideal 2a site, an extraordinarily large thermal parameter is obtained for them, which implies a displacement of the Pb and Cd atoms from the ideal 2a site (0,0,0) to the 8i site (x,0,0). The O(3) atom in the (Pb, Cd)O layer is also displaced from the ideal 2b site ($\frac{1}{2}$,$\frac{1}{2}$,0) to the 8j site (x,$\frac{1}{2}$,0). This kind of atom displacement is a common feature for almost all 1212 and 1222 phases, and has been clearly elucidated by Min *et al* [12, 13].

In the bond valence model advanced by Brown and Altermatt [14], the atomic valence of an atom is assumed to be distributed between the bonds it forms. As a result, the atomic valence V_i is obtained by summing up the valences of the bonds formed by atom i given by

$$V_i = \sum_j S_{ij} \tag{1}$$

where V_i is the bond valence sums of atom i, and S_{ij} is the valence of the bond between atom i and j. The usefulness of this rule lies in the correlation observed between the length (R) and the valence (S_{ij}) of a bond as expressed by

$$S_{ij} = \exp((R_0 - R)/B) \tag{2}$$

where $B = 0.37$ Å and R_0 represents the length of the bond between atom i and j of unit valence.

Because R_0 depends on oxidation state, the oxidation states of the Cu atoms must be known before the bond valences can be calculated. However, the bond valences are needed in order to determine the oxidation states. This problem has been solved using the procedure developed by Brown [15,16]. Valences (S_{2+}) were calculated assuming that the copper was Cu^{2+}. Then the bond valence sum ($V_{2+} = \sum S_{2+}$) around a Cu atom was used to determine whether its oxidation state was greater than or less than two. Generally, the oxidation state of Cu ions in the hole-type superconducting copper oxides is greater than +2. In this case, the proportion (y) of Cu^{3+} was calculated using the equation

$$y = (V_{2+} - 2)/(V_{2+} + 1.0 - V_{3+}) \tag{3}$$

where V_{2+} is the bond valence sum calculated by assuming the copper is Cu^{2+} and V_{3+} the bond valence sum calculated by assuming the copper is Cu^{3+}.

The bond valence sums of Cu ions in the conducting CuO_2 planes for $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ and $(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Eu_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$ have been calculated using the above procedure and are listed in table 2. It is found that the bond valence sums of the Cu ions in the O_2-synthesized

Table 1. Refined structure parameters from powder x-ray Rietveld analysis for $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ synthesized in air; $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ synthesized in oxygen and $(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Eu_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$ (taken from [5]). Space group $I4/mmm$. $Z = 2$. The numbers in parentheses are estimated standard deviations in the last significant digit, and those without deviations were fixed. g denotes the site occupancy and B denotes the isotropic temperature factor with a unit of Å^2.

$(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ synthesized in air
$R_p = 9.50\%$, $R_{wp} = 13.31\%$, $a = 3.8443(4)$ Å, $c = 29.3937(11)$ Å

Atom	Site	x	y	z	g	B (Å^2)
Pb/Cd	8i	0.0540(26)	0	0	0.125/0.125	0.51(2)
Sr/Eu	4e	0.5	0.5	0.0848(1)	0.9/0.1	0.17(2)
Eu/Ce	4e	0.5	0.5	0.2066(1)	0.7/0.3	0.42(3)
Cu	4e	0	0	0.1468(3)	1	0.27(1)
O(1)	8g	0	0.5	0.1447(8)	1	1
O(2)	4e	0	0	0.0722(9)	1	1
O(3)	8j	0.4517(16)	0.5	0	0.25	1
O(4)	4d	0	0.5	0.25	1	1

$(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ synthesized in O_2
$R_p = 7.63\%$, $R_{wp} = 10.25\%$, $a = 3.8314(3)$ Å, $c = 29.3902(20)$ Å

Atom	Site	x	y	z	g	B (Å^2)
Pb/Cd	8i	0.0677(14)	0	0	0.125/0.125	0.23(3)
Sr/Eu	4e	0.5	0.5	0.0853(1)	0.9/0.1	0.33(3)
Eu/Ce	4e	0.5	0.5	0.2067(1)	0.7/0.3	0.41(4)
Cu	4e	0	0	0.1463(2)	1	0.19(1)
O(1)	8g	0	0.5	0.1449(5)	1	1
O(2)	4e	0	0	0.0726(6)	1	1
O(3)	8j	0.457(9)	0.5	0	0.25	1
O(4)	4d	0	0.5	0.25	1	1

$(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Eu_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$ synthesized in oxygen
$R_p = 5.09\%$, $R_{wp} = 7.16\%$, $a = 3.83795(5)$ Å, $c = 29.0116(5)$ Å

Atom	Site	x	y	z	g	B (Å^2)
Pb/Cu	8i	0.070(5)	0	0	0.125/0.125	0.5
Sr/Eu	4e	0.5	0.5	0.0841(4)	0.875/0.125	0.6(3)
Eu/Ce	4e	0.5	0.5	0.2060(2)	0.75/0.25	0.3(2)
Cu	4e	0	0	0.1440(8)	1	0.6(3)
O(1)	8g	0	0.5	0.145(2)	1	0.5
O(2)	4e	0	0	0.070(2)	1	0.5
O(3)	8j	0.18(3)	0.5	0	0.25	0.5
O(4)	4d	0	0.5	0.25	1	0.5

$(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ are higher than that in the air-synthesized $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$. This indicates that the O_2-synthesized sample has higher carrier concentration than the air-synthesized sample, which is consistent with the electrical resistivity measurement results. That is, the O_2-synthesized sample has high T_c values and exhibits metallic behaviour in its normal state, while the air-synthesized sample has low T_c values and exhibits semiconducting behaviour in its normal state. Comparing the bond valence sum of Cu ions in the O_2-synthesized $(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Eu_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$ with that in the O_2-synthesized

Table 2. Selected metal–oxygen interatomic distances and bond valence sums of Cu ions in the CuO_2 planes for 1: $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ synthesized in air; 2: $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ synthesized in oxygen and 3: $(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Eu_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$ synthesized in oxygen. For the sake of convenience, the displaced atoms were placed at their ideal positions while calculating the interatomic distances. N is the number of equivalent bonds.

	Distance (Å)			
Bonds	1	2	3	N
(Pb, Cd/Cu)–O(2)	2.121	2.134	2.031	2
(Pb, Cd/Cu)–O(3)	2.718	2.709	2.714	4
(Sr, Eu)–O(1)	2.606	2.595	2.608	4
(Sr, Eu)–O(2)	2.744	2.735	2.745	4
(Sr, Eu)–O(3)	2.493	2.508	2.440	1
(Eu, Ce)–O(1)	2.648	2.639	2.610	4
(Eu, Ce)–O(4)	2.306	2.301	2.305	4
Cu–O(1)	1.923	1.916	1.919	4
Cu–O(2)	2.195	2.164	2.147	1
Bond valence sums				
Cu	2.53	2.65	2.64	

$(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$, it is found that the bond valence sums of Cu ions in the two compounds are nearly equal. Namely, they have similar levels of carrier concentrations in the CuO_2 planes. But the latter has higher superconducting transition temperatures than the former, which give evidence that there exists hole trapping in the former as described above.

In conclusion, pure $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ has been prepared in the present work, which is very sensitive to sintering temperature and atmosphere. The optimal synthesis conditions for the (Pb, Cd)-1222 compound are sintering at 1050 °C in oxidizing atmosphere (air or O_2). The compound has higher superconducting transition temperatures when it is synthesized in O_2 ($T_{c,onset}$ = 43 K, $T_{c,zero}$ = 35 K) than in air ($T_{c,onset}$ = 19 K, $T_{c,zero}$ = 12 K). Besides, the sample synthesized in O_2 exhibits metallic behaviour in its normal state, while the sample synthesized in air exhibits semiconducting behaviour in its normal state. It is a typical metal–insulator transition with the increase of the carrier concentration, which is also proven by our calculation results of the bond valence sums of the Cu ions in the conducting CuO_2 planes.

The crystal structure of $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$ has been refined by the Rietveld method using x-ray powder diffraction data. The refinement results indicate that the Pb and Cd atoms in the rock-salt-type (Pb, Cd)O monolayer in the present (Pb, Cd)-1222 compound are displaced from the ideal 2a site (0,0,0) to the 8i site (x,0,0). The O(3) atom in the (Pb, Cd)O layer is also displaced from the ideal 2b site ($\frac{1}{2}$,$\frac{1}{2}$,0) to the 8j site (x,$\frac{1}{2}$,0). This kind of atom displacement is a common feature for almost all 1212 and 1222 phases.

$(Pb_{0.5}Cu_{0.5})(Sr_{7/8}Eu_{1/8})_2(Eu_{3/4}Ce_{1/4})_2Cu_2O_9$ is an analogous compound of (Pb, Cd)-1222. The superconductivity of the (Pb, Cu)-1222 compound and the present (Pb, Cd)-1222 has been compared in this paper. It is found that (Pb, Cd)-1222 has higher superconducting transition temperatures than (Pb, Cu)-1222. This difference can be explained from the viewpoint of charge transfer between the charge reservoir (Pb, Cu)O layers and the conducting CuO_2 planes.

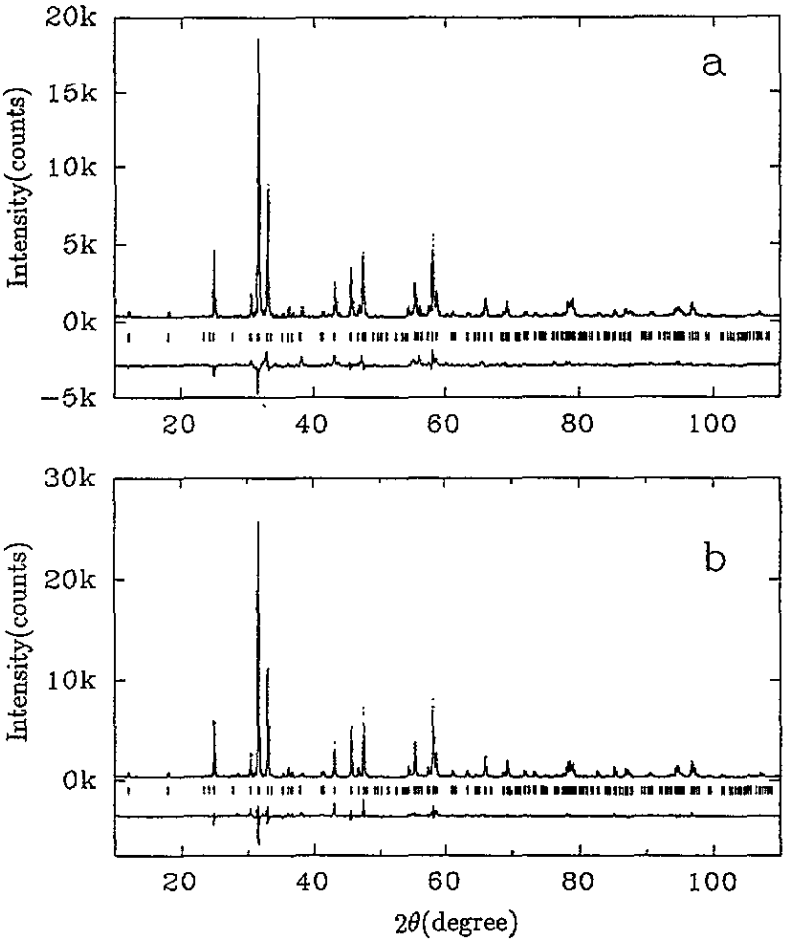

Figure 3. Rietveld refinement patterns for $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9+\delta}$, (a) synthesized in air; (b) synthesized in O_2. The dotted lines represent the observed diffraction patterns, the solid lines represent the calculated patterns and the curves at the bottom of each figure represent the difference between the observed and calculated patterns. The short vertical lines mark the positions of possible Bragg reflections for the (Pb, Cd)-1222 phase.

Acknowledgments

This work is supported by the National Centre for Research and Development of Superconductivity of China.

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