

Preferential occupancy and composition-driven *c*-axis variation in $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr},\text{Y},\text{Ca})_3\text{Cu}_2\text{O}_{7-\delta}$

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(Received 13 September 1994; revised manuscript received 4 November 1994)

The effects of chemical substitution on the crystal structure and superconducting properties of $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr},\text{Y},\text{Ca})_3\text{Cu}_2\text{O}_{7-\delta}$ have been studied in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$, $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1-u+x}\text{Ca}_u\text{Cu}_2\text{O}_{7-\delta}$ ($u=0.0,0.3,0.5$), and $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_{v+x}\text{Y}_{1-v}\text{Cu}_2\text{O}_{7-\delta}$ ($v=0.0,0.1,0.3$). The single-phase region of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{3-x-y}\text{Ca}_x\text{Y}_y\text{Cu}_2\text{O}_{7-\delta}$ is $0 \leq x \leq 0.5$ and $0.8 \leq y \leq 1.0$. In $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$, the lattice parameter *c* anomalously decreases while *a* remains nearly unchanged with the substitution of Ca for Y ($0 \leq x \leq 0.2$). This phenomenon is related to the decrease of the oxygen content. The investigations of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1-u+x}\text{Ca}_u\text{Cu}_2\text{O}_{7-\delta}$ ($u=0.0,0.3,0.5$) reveal that it is difficult for Y to enter the Sr site (2*h*) and Ca can enter the Sr site (2*h*). The chemical formula of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1-u+x}\text{Ca}_u\text{Cu}_2\text{O}_{7-\delta}$ ($u=0.3,0.5$) for the $x > 0$ sides can be written as $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr}_{2-x}\text{Ca}_x)(\text{Y}_{1-u+x}\text{Ca}_{u-x})\text{Cu}_2\text{O}_{7-\delta}$ ($u=0.3,0.5$). Besides, we have also studied the relationships between the lattice parameters and chemical substitution, and found that the substitution of Ca for Sr in the Y site (1*d*) and Ca for Sr in the Sr site (2*h*) has different influence on the lattice parameters. The variations of lattice parameters with composition are linear for $x < 0$ or $x > 0$. The $\Delta c/\Delta x$ values are -0.12 \AA and -0.32 \AA for $x \leq 0$ and $x \geq 0$, respectively.

I. INTRODUCTION

Since Cava *et al.* discovered the first lead-based copper oxide superconductor $\text{Pb}_2\text{Sr}_2\text{ACu}_3\text{O}_{8+\delta}$ (*A* is a lanthanide or a mixture of Ln+Sr or Ca),¹ a variety of other lead-based cuprates have been synthesized successively. The lead-based cuprates are very rich in their structures, and can be classified into three categories according to layer blocks, i.e., $\text{Pb}_2\text{Sr}_2\text{ACu}_3\text{O}_{8+\delta}$ (Pb-3212),¹ $\text{Pb}_2\text{SrLaCu}_2\text{O}_6$ (Pb-3201),² $\text{Pb}_2\text{Sr}_2(\text{Ln},\text{Ce})_n\text{Cu}_3\text{O}_z$ (Pb-32*n*2, $n=2,3,4,\dots$),^{3,4} with PbO-Cu-PbO blocks; $\text{Pb}(\text{Ba},\text{Sr})_2(\text{Y},\text{Ca})\text{Cu}_3\text{O}_7$ (Pb-2212),⁵ $\text{Pb}(\text{Ba},\text{Sr})_2(\text{Ln},\text{Ce})_n\text{Cu}_3\text{O}_z$ (Pb-22*n*2, $n=2,3,4,\dots$),^{4,6} with (Pb,Cu)O bilayer blocks; and $(\text{Pb},\text{Cu})\text{Sr}_2(\text{Y},\text{Ca})\text{Cu}_2\text{O}_7$ (Pb-1212),^{7,8} $(\text{Pb},\text{Cu})\text{SrLaCuO}_5$ (Pb-1201),⁹ $(\text{Pb},\text{Cu})(\text{Sr},\text{Pr})_2\text{Pr}_2\text{Cu}_2\text{O}_9$ (Pb-1222),¹⁰ with (Pb,Cu)O monolayer blocks. For these lead-based cuprates, those containing the PbO-Cu-PbO blocks and (Pb,Cu)O bilayer blocks were prepared in a mildly reducing atmosphere and the valence states of the Pb, and Cu ions in the PbO-Cu-PbO blocks and (Pb,Cu)O bilayer blocks are +2 and +1, respectively,^{1,5,6} while those contain-

ing (Pb,Cu)O monolayer blocks were synthesized in an oxidizing atmosphere and the Pb and Cu ions in the monolayer blocks are in tetravalent and divalent states, respectively.^{9,11}

Among these lead-based cuprates, Pb-1212 has been given more attention. Many investigations have been made in order to optimize the superconducting properties. These included exploring the adequate synthesis conditions,^{11,12} finding the optimal ratio of Ca and Y,^{13,14} and carrying out different chemical substitutions,¹⁴⁻¹⁶ especially in the rock-salt-type (Pb,*M*)O layers (*M*=divalent metal element, such as Cu, Cd, and others). $(\text{Pb},\text{M})\text{Sr}_2(\text{Y},\text{Ca})\text{Cu}_2\text{O}_7$ has a space group *P4/mmm*; its structure resembles that of $\text{TiBa}_2\text{CaCu}_2\text{O}_7$. Different *M* can bring about different local structures in the rock-salt-type (Pb,*M*)O layers. For instance, in (Pb,Cu)-1212, there are excess oxygen atoms present in the (Pb,Cu)O layers, interstitially occupying the 2*f* site $(0, \frac{1}{2}, 0)$,¹⁷ while in (Pb,Cd)-1212 no excess oxygen atoms exist in the (Pb,Cd)O layers because of the closed-shell 4*d*¹⁰ electronic configuration of Cd²⁺.

In the (Pb,*M*)-1212 family, (Pb,Cd)-1212 is compara-

tively easy to prepare and exhibits good superconducting properties. In our previous work, we have systematically studied the synthesis conditions, crystal structure, chemical substitutions, and superconducting properties of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$.^{14,18,19} In this paper, we have carried out different substitutions on $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr},\text{Y},\text{Ca})_3\text{Cu}_2\text{O}_{7-\delta}$, and found that Sr and Ca can enter the Y site (1d), and Ca can enter the Sr site (2h), while it is difficult for Y to enter the Sr site (2h). This has been proved from different aspects in the present study. Investigations of the relationships between the lattice parameters and chemical substitutions show that the substitutions of Ca for Sr in the Y site (1d) and Ca for Sr in the Sr site (2h) have a different influence on the lattice parameters.

II. EXPERIMENTAL DETAILS

The samples were prepared by the solid-state reaction method using PbO , CdO , SrCO_3 , Y_2O_3 , CaCO_3 , and CuO as starting materials. Stoichiometric amounts of starting materials were appropriately weighted, and ground together in an agate mortar. The well-mixed powders were calcined at 850°C in air for 15 h and then furnace cooled to room temperature. The prereacted material was reground and pressed into pellets. The pellets were sintered at 950°C in air for 10 h and then furnace cooled to room temperature. This process was repeated several times in order to obtain homogeneous samples. A part of the samples was annealed in O_2 at 970°C for 2 h in order to induce and optimize superconductivity in the samples.

X-ray-diffraction (XRD) analyses were performed using a M18AHF x-ray diffractometer with $\text{Cu } K\alpha$ radiation ($50\text{ kV} \times 200\text{ mA}$). High-purity Si powder was added to the samples as an internal standard to correct the 2θ positions of the diffraction peaks. The lattice parameters were calculated using a standard least-squares refinement. The data for structure refinement were collected on the same diffractometer at ambient temperature with a scattering slit of 0.50° , a divergence slit of 0.50° , and a receiving slit of 0.15 mm . The scanning step is 0.02° in 2θ and the sampling time is 2 s per step. The 2θ range was from 10 to 110° . All samples for structure refinements were annealed in O_2 at 970°C for 2 h.

A standard four-probe method was used for electrical resistance measurements. The electrical contacts to the samples were made by fine copper wires with a conductive silver paint. The applied current was 1 mA. The oxygen content of samples were determined by iodometric titrations.⁵

III. RESULTS

A. Phase identification and the variations of lattice parameters with composition

The single-phase region of the (Pb,Cd)-1212 phase determined by XRD can be expressed as $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{3-x-y}\text{Ca}_x\text{Y}_y\text{Cu}_2\text{O}_{7-\delta}$ ($0 \leq x \leq 0.5$, $0.8 \leq y \leq 1.0$).

1. $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$

A series of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ samples has been prepared in air, and single-phase (Pb,Cd)-1212 samples are obtained between $x = 0$ and 0.2 . The phase purity of the (Pb,Cd)-1212 samples decreases with the decrease of the yttrium content although the 1212 phase remains the majority phase until $x = 0.7$. For the sample of composition $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$, the 1212 phase disappears. Thus, it seems that a certain amount of yttrium is necessary for the formation of the (Pb,Cd)-1212 phase.

The variations of the lattice parameters a and c with calcium content x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ are shown in Fig. 1. The estimated errors for a and c are about 0.001 and 0.005 \AA , respectively. It is interesting to note that c decreases and a is nearly a constant for $0 \leq x \leq 0.2$. In general, c will increase and a will decrease with the substitution of calcium for yttrium. The increase in c arises from the substitution of the larger Ca^{2+} (1.12 \AA , CN=8) for Y^{3+} (1.019 \AA , CN=8), and the decrease in the lattice parameter a can be attributed to an increase of the average copper-oxidation state, which results in shorter Cu-O distances in the copper-oxygen sheets. It has been proposed that the lattice parameter a is mainly determined by the Cu-O distances in the copper-oxygen sheets. The anomalous composition dependence of the lattice parameters in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ may be related to the oxygen content. The oxygen content measurements indicate that the oxygen contents of the $x = 0, 0.1$, and 0.2 samples are 6.98 , 6.94 , and 6.87 , respectively. Thus the oxygen content of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ ($0 \leq x \leq 0.2$) synthesized in air decreases with the increase of the calcium content in order to keep the charge equilibrium. It has been suggested that the decrease of oxygen content can cause the decrease of the lattice parameter c .

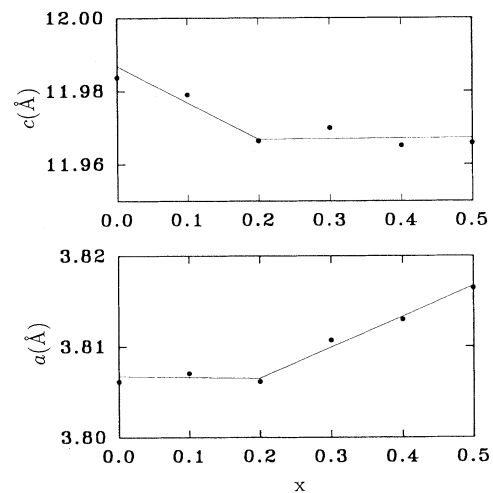


FIG. 1. The variations of the lattice parameters a and c with the calcium content x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$.

in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-d}$.²⁰ Therefore, the effect of oxygen content on the c value overwhelms the size effect in this system and leads to the decrease of c . At the same time, the average copper oxidation state is almost unchanged with the substitution of calcium for yttrium, and so the fact that a is nearly a constant is not difficult to understand. When $x > 0.2$, the constant c indicates that the solubility limit of Ca in the Y site is $x=0.2$.

2. $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1+u+x}\text{Ca}_u\text{Cu}_2\text{O}_{7-\delta}$ ($u=0.0, 0.3, 0.5$)

a. $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1+x}\text{Cu}_2\text{O}_{7-\delta}$. The $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1+x}\text{Cu}_2\text{O}_{7-\delta}$ samples have been prepared in air, and single-phase samples are obtained between $x = -0.2$ and 0. This indicates that Sr can enter the Y site (1d), while it is difficult for Y to enter the Sr site (2h). The Sr content that the Y site (1d) can accommodate is equal to the Ca content that the Y site (1d) can accommodate. $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{0.8}\text{Ca}_{0.2})\text{Cu}_2\text{O}_{7-\delta}$ exhibits weak superconductivity, while $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2.2}\text{Y}_{0.8}\text{Cu}_2\text{O}_{7-\delta}$ is a semiconductor. Figure 2 shows the x-ray-powder-diffraction patterns of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1+x}\text{Cu}_2\text{O}_{7-\delta}$. The sample with $x > 0$ contains the secondary phase Y_2O_3 and exhibits a trace of CdO .

Figure 3 shows the variations of the lattice parameters a and c as a function of x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1+x}\text{Cu}_2\text{O}_{7-\delta}$. As Sr enters the Y site (1d) ($x < 0$), both a and c increase because Sr has larger ionic radius than Y (1.26 and 1.019 Å for Sr^{2+} and Y^{3+} respectively, CN=8). But when $x > 0$, c decreases and a increases. Because it is difficult for Y to enter Sr site (2h), which results in the appearance of impurity phases, we infer that it is the excess Cu that enters the (Pb,Cd) site in place of Cd, and leads to the decrease of c and the increase of a . This is under-

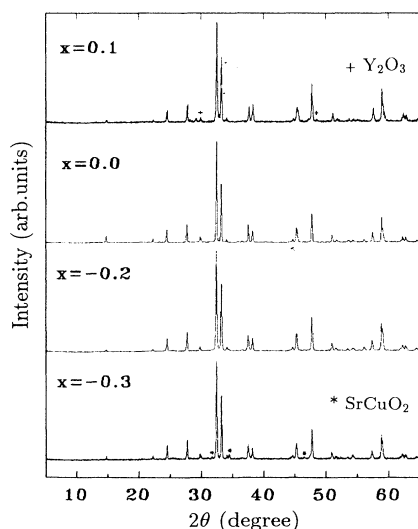


FIG. 2. X-ray-powder-diffraction patterns for $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1+x}\text{Cu}_2\text{O}_{7-\delta}$.

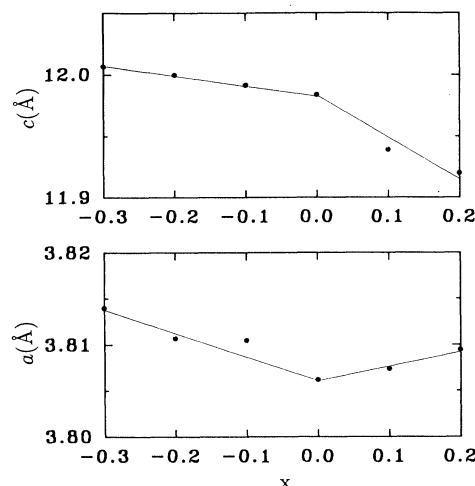


FIG. 3. The variations of the lattice parameters a and c with x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1+x}\text{Cu}_2\text{O}_{7-\delta}$.

standable from the a and c values of (Pb,Cd)-1212 and (Pb,Cu)-1212, i.e., $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$: $a=3.817$ Å, $c=11.966$ Å (this work); $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$: $a=3.824$ Å, $c=11.880$ Å.¹⁶

b. $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.7+x}\text{Ca}_{0.3}\text{Cu}_2\text{O}_{7-\delta}$. Figure 4 shows the variations of the lattice parameters a and c with x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.7+x}\text{Ca}_{0.3}\text{Cu}_2\text{O}_{7-\delta}$ synthesized in air. The single-phase samples are obtained between $x=0.1$ and 0.3. As Sr enters the Y site (1d) ($x < 0$), both a and c increase because of the substitution of larger Sr for Y. When $x > 0$, both a and c decrease. In fact, when $x > 0$ it is Ca ions that enter the Sr site (2h), and the chemical formula for the $x > 0$ samples can be written as $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr}_{2-x}\text{Ca}_x)(\text{Y}_{0.7+x}\text{Ca}_{0.3-x})\text{Cu}_2\text{O}_{7-\delta}$. This will be discussed in Sec. IV.

c. $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.5+x}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$. Figure 5 shows the variations of the lattice parameters a and c with x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.5+x}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$.

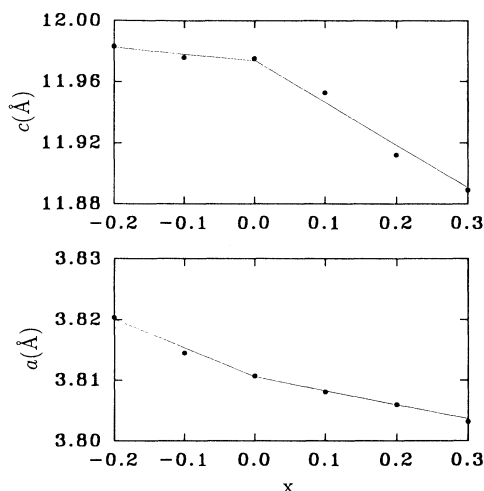


FIG. 4. The variations of the lattice parameters a and c with x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.7+x}\text{Ca}_{0.3}\text{Cu}_2\text{O}_{7-\delta}$.

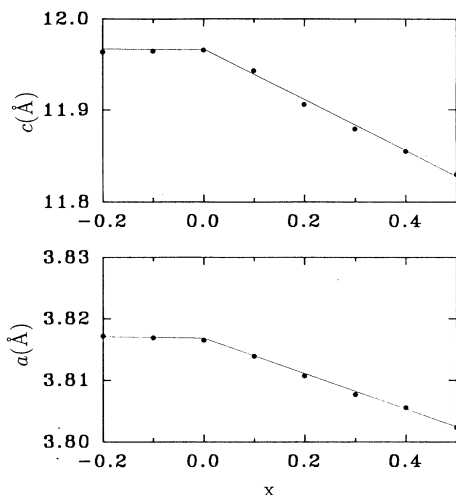


FIG. 5. The variations of the lattice parameters a and c with x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.5+x}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$.

synthesized in air. The single-phase region is $0.3 \leq x \leq 0.5$. When $x < 0$, both a and c are unchanged, which implies that the composition of the (Pb,Cd)-1212 phase is constant with the substitution. When $x > 0$, both a and c decrease, and the phase purity increases. Figure 6 shows the XRD patterns of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.5+x}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$. Like the above case, the chemical formula for the $x > 0$ samples can be written as $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr}_{2-x}\text{Ca}_x)(\text{Y}_{0.5+x}\text{Ca}_{0.5-x})\text{Cu}_2\text{O}_{7-\delta}$.

3. $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_v\text{Y}_{1-v}\text{Cu}_2\text{O}_{7-\delta}$ ($v=0.0, 0.1, 0.3$)

Figures 7, 8, and 9 show the x dependences of the lattice parameters a and c for $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}$

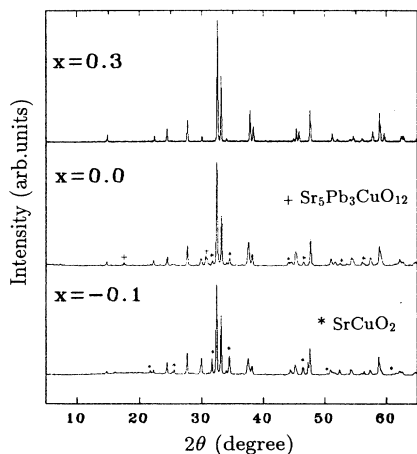


FIG. 6. X-ray powder diffraction patterns for $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.5+x}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$.

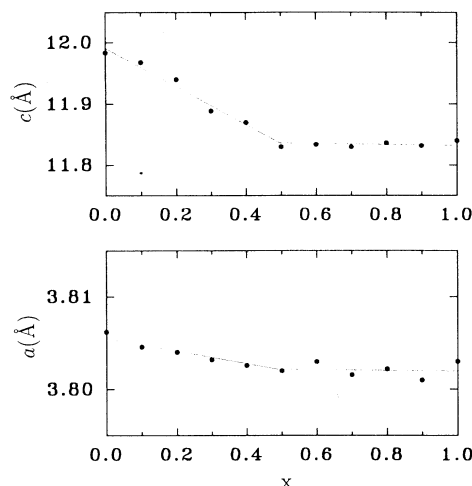


FIG. 7. The variations of the lattice parameters a and c with x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_x\text{YCu}_2\text{O}_{7-\delta}$.

$\text{Ca}_x\text{YCu}_2\text{O}_{7-\delta}$, $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_{0.1+x}\text{Y}_{0.9}\text{Cu}_2\text{O}_{7-\delta}$, and $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_{0.3+x}\text{Y}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$, respectively. All these samples were prepared in air. The single-phase regions for $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_x\text{YCu}_2\text{O}_{7-\delta}$ and $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_{0.1+x}\text{Y}_{0.9}\text{Cu}_2\text{O}_{7-\delta}$ are $0 \leq x \leq 0.5$ and $-0.1 \leq x \leq 0.4$, respectively. No single-phase samples are obtained in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_{0.3+x}\text{Y}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$. It can be seen from Fig. 7 that both a and c decrease with the substitution of Ca for Sr for $0 \leq x \leq 0.5$, and a and c are constant when $x \geq 0.5$. This result coincides with the phase identification results by XRD; i.e., only when $0 \leq x \leq 0.5$ can single-phase samples be obtained in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_x\text{YCu}_2\text{O}_{7-\delta}$. From the three figures, the following conclusions can be reached.

- (1) The variations of the lattice parameters a and c

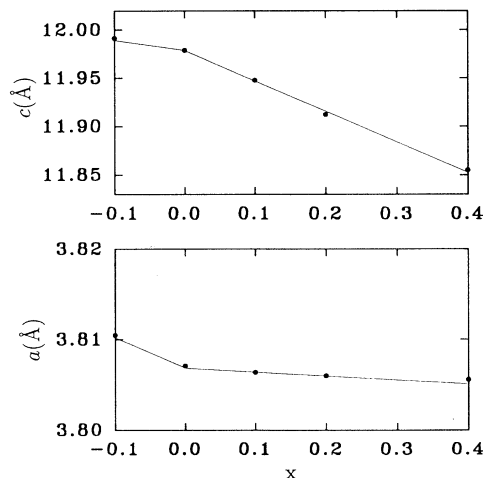


FIG. 8. The variations of the lattice parameters a and c with x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_{0.1+x}\text{Y}_{0.9}\text{Cu}_2\text{O}_{7-\delta}$.

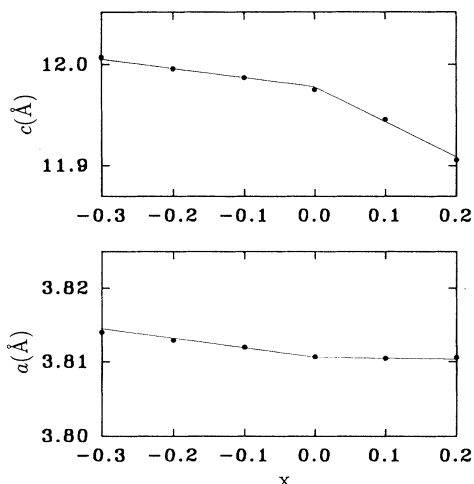


FIG. 9. The variations of the lattice parameters a and c with x in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_{0.3+x}\text{Y}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$.

with x have kinks at $x=0$. The substitutions of Sr for Ca in the Y site ($1d$) ($x < 0$) and Ca for Sr in the Sr site ($2h$) ($x > 0$) have a different influence on the lattice parameters. This will be further discussed in Sec. IV.

(2) The solubility of Ca in the Sr site ($2h$) is correlated with the Ca content in the Y site ($1d$). For example, the solubility of Ca in the Sr site ($2h$) in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_x\text{YCu}_2\text{O}_{7-\delta}$ is $x=0.5$, while in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_{0.1+x}\text{Y}_{0.9}\text{Cu}_2\text{O}_{7-\delta}$ it is $x=0.4$.

B. Superconducting properties

In order to induce and optimize the superconductivity of the (Pb,Cd)-1212 phase, we have investigated the effects of different heat treatments on $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$, and found an optimal heat treatment condition: annealing the sample in O_2 at 970°C for 2 h.¹⁸ In $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$, the samples with $x=0.0, 0.1$ are not superconducting. The resistivity measurements of the samples with $x=0.2, 0.3$ show a drop at about 15 K, but zero resistance is not achieved. The sample with $x=0.4$ only exhibits weak superconductivity. When the calcium content reaches 0.5, the transition temperatures have a sharp increase, and further substitution of calcium for yttrium has little effect on the superconducting transition temperatures. When all yttrium is replaced by calcium, superconductivity disappears, which indicates that the superconductivity is attributed to the (Pb,Cd)-1212 phase, and the calcium content in the Y site ($1d$) is a key factor in controlling the superconductivity of the (Pb,Cd)-1212 phase. As mentioned above, the Y content helps the formation of the (Pb,Cd)-1212 phase, while the calcium content contributes to the superconductivity of the (Pb,Cd)-1212 phase. Thus how to synthesize a pure (Pb,Cd)-1212 phase with high calcium content is very

intriguing.

In $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.5+x}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$, the sample $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ has the highest transition temperatures ($T_{c,\text{onset}}=76$ K, $T_{c,\text{zero}}=51$ K). The superconductivity deteriorates as x deviates from 0.0, and the decrease of T_c 's is more rapid for $x > 0$ than for $x < 0$ due to the increasing yttrium content in the Y site ($1d$). Taking into account the fact that the superconductivity deteriorates in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.5+x}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$ when $x < 0$, $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2.2}\text{Y}_{0.8}\text{Cu}_2\text{O}_{7-\delta}$ is a semiconductor, and $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{0.8}\text{Ca}_{0.2})\text{Cu}_2\text{O}_{7-\delta}$ exhibits a trace of superconductivity, we can conclude that the substitution of Ca for Y improves the superconductivity of (Pb,Cd)-1212, while the substitution of Sr for Y has detrimental effects on it.

In $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{0.5}\text{Ca}_{0.5+x}\text{Cu}_2\text{O}_{7-\delta}$, the superconductivity deteriorates as x deviates from 0, although the effect is very small. This indicates that Ca replaces Sr in the $2h$ site and Sr replaces Ca in the $1d$ site, all destroying the superconductivity of the (Pb,Cd)-1212 phase.

C. Crystal structure

The structure refinements of the lead-based 1212 compounds $(\text{Pb}_{0.69}\text{Cu}_{0.31})\text{Sr}_2(\text{Y}_{0.85}\text{Ca}_{0.15})\text{Cu}_2\text{O}_{6.8}$, $(\text{Pb}_{0.71}\text{Cu}_{0.29})\text{Sr}_2(\text{Y}_{0.73}\text{Ca}_{0.27})\text{Cu}_2\text{O}_7$, $(\text{Pb}_{0.65}\text{Cu}_{0.35})\text{Sr}_2(\text{Y}_{0.7}\text{Ca}_{0.3})\text{Cu}_2\text{O}_{7+\delta}$, and $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ have been reported by Subramanian *et al.*,⁷ Lee *et al.*,⁸ and Maeda *et al.*,¹⁷ respectively. A few common conclusions have been reached that these lead-based 1212 compounds have a $P4/mmm$ space group and their crystal structure resembles that of $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-\delta}$, which has a $\text{YBa}_2\text{Cu}_3\text{O}_7$ -like arrangement of metal atoms. Figure 10 shows a schematic representation of the crystal structure of $(\text{Pb},M)\text{Sr}_2(\text{Y},\text{Ca})\text{Cu}_2\text{O}_7$ (M =divalent metal ion). Besides, the site refinements indicate that the O(3) atom is remarkably displaced from its ideal $1c$ site to the $4n$ site, and the Pb and M (Cu or Cd) atoms in the rock-salt-type $(\text{Pb},M)\text{O}$ layers are displaced from their ideal $1a$ site to the $4l$ site.

Based on the structure model described above, we refined the structure parameters of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_{7-\delta}$, $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{0.6}\text{Ca}_{0.4})\text{Cu}_2\text{O}_{7-\delta}$, $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$, $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{1.5}\text{Ca}_{0.5}\text{YCu}_2\text{O}_{7-\delta}$, and $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2.2}\text{Y}_{0.8}\text{Cu}_2\text{O}_{7-\delta}$ by the Rietveld method²¹ using powder-x-ray-diffraction data. $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{0.6}\text{Ca}_{0.4})\text{Cu}_2\text{O}_{7-\delta}$ and $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ were refined on a multiple-phase model because of the appearance of impurity phases in the two samples. The thermal parameters (B) were assumed to be isotropic, and the thermal parameters of all oxygen atoms were arbitrarily fixed at 1 \AA^2 . Table I lists the final R factors, the refined lattice parameters, structure parameters, and their estimated standard deviations in parentheses for the five samples. The reasonably small R factors support the structure

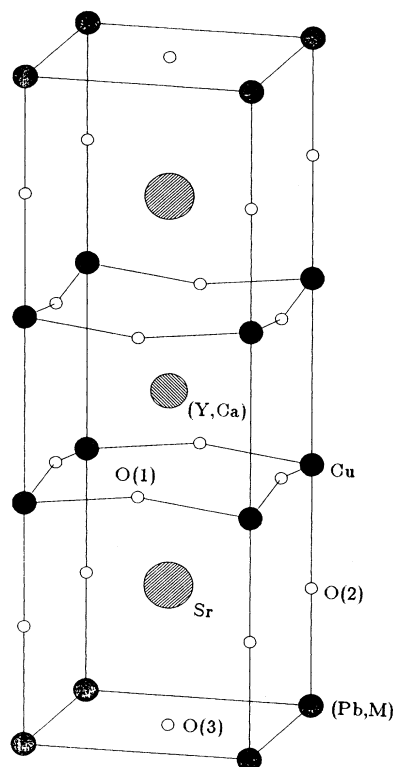


FIG. 10. The schematic representation of the crystal structure of $(\text{Pb},\text{M})\text{Sr}_2(\text{Y},\text{Ca})\text{Cu}_2\text{O}_7$ (M =divalent metal element).

model listed in Table I. Table II lists the selected metal-oxygen interatomic distances for these samples. For comparison, Table II also lists the bond valence sums for Cu ions.²²

During the refinements of the thermal parameters of the Pb and Cd atoms in the $(\text{Pb},\text{Cd})\text{O}$ layers, by assuming that they occupy the ideal 1a site, extraordinarily large thermal parameters are obtained for these atoms, which implies that a displacement of the (Pb,Cd) atoms from the ideal 1a site $(0,0,0)$ is necessary. Moreover, the O(3) atoms in the $(\text{Pb},\text{Cd})\text{O}$ layers are also displaced from the ideal 1c site $(\frac{1}{2}, \frac{1}{2}, 0)$ to the $4n$ site $(x, \frac{1}{2}, 0)$. Thus there exists a disorder in the $(\text{Pb},\text{Cd})\text{O}$ layers. We suggest that the disorder may be related to the coexistence of Pb^{4+} and Cd^{2+} in the $(\text{Pb},\text{Cd})\text{O}$ layers, which have different valences and different ionic radii (0.775 and 0.95 Å for Pb^{4+} and Cd^{2+} , respectively, CN=6). The mixed occupation of Pb and Cd in the $(\text{Pb},\text{Cd})\text{O}$ layers leads to the displacements of the (Pb,Cd) atoms and O(3) atoms. Besides, structural incompatibility, i.e., the difference between the interatomic distance required by the structure and the ideal distance, is also an important origin of the atomic displacements as is the case in $\text{Ti}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$. The ideal distance is approximately defined as the sum of the ionic radii. Generally, the lattice parameter a is determined primarily by the Cu-O distance, which is strong and is almost invariant through all the cuprate superconductors. So in (Pb,Cd) -1212, the

(Pb,Cd) -O distances are forced to be larger than the ideal distance.

The occupancy refinements of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{1.5}\text{Ca}_{0.5}\text{YCu}_2\text{O}_{7-\delta}$ indicate that the Y site (1d) is essentially occupied by Y atoms, while nearly all Ca atoms enter the Sr site (2h). This confirms our above-mentioned postulation that it is Ca that enters the Sr site (2h). The occupancy refinements of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2.2}\text{Y}_{0.8}\text{Cu}_2\text{O}_{7-\delta}$ indicates that Sr can enter the Y site (1d).

For $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_7$, it can be seen from Table II that as the calcium content increases, the interatomic distances between (Pb,Cd) atoms and O(2) atoms increase, while the distances between Cu atoms and O(2) atoms decrease. This implies that the substitution of Ca for Y induces the shift of O(2) atoms towards the CuO_2 planes. Consequently, it results in a charge transfer from the charge reservoir layers $(\text{Pb},\text{Cd})\text{O}$ to the conducting CuO_2 planes and the appearance of superconductivity. This result is consistent with the change of the bond valence sums of the Cu ions (Table II). As the calcium content increases, the average valence of Cu ions increases from 2.341 to 2.410 with hole carriers induced into the CuO_2 planes. Kosuge *et al.* have studied the Ca substitution effects on the transport properties in $(\text{Pb}_{(1+x)/2}\text{Cu}_{(1-x)/2})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_y$.²³ In that system the decreasing charge in the Y site (1d) is compensated by increasing the Pb/Cu ratio at the (Pb,Cu) site, and the oxygen content y is constant, regardless of the Ca content x . Therefore, they suggested that carrier doping in the chemical sense could not be obtained by increasing x . The hole carriers were introduced by "self-doping," i.e., by the decrease of the Cu valence in the (Pb,Cu) site from 2+ to 1+ or of the Pb valence from 4+ to 2+. In our system $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_7$, we have measured the oxygen content of the single-phase samples ($0 \leq x \leq 0.2$, synthesized in O_2) and found that the oxygen content of these samples is nearly constant and equal to 7.0, regardless of x . Therefore, we think that in our system the hole carriers may be created in two ways. One is the charge transfer from Pb ions to CuO_2 planes. The other is the substitution of lower valence Ca^{2+} for higher valence Y^{3+} .

IV. DISCUSSION

First we discuss whether Ca or Y enters the Sr site (2h) in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1-u+x}\text{Ca}_u\text{Cu}_2\text{O}_{7-\delta}$ ($u=0.3, 0.5$) when $x > 0$. We can infer that it is Ca, instead of Y, that enters the Sr site (2h) from the following facts.

(i) The x-ray-diffraction results of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1+x}\text{Cu}_2\text{O}_{7-\delta}$ indicate that it is difficult for Y to enter the Sr site (2h), because when $x > 0$, the impurity phase Y_2O_3 appears.

(ii) In $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1-u+x}\text{Ca}_u\text{Cu}_2\text{O}_{7-\delta}$ ($u=0.3, 0.5$), the phase purity increases when $x \geq 0$. Taking into account the conclusion obtained in the series $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ —i.e., the phase purity increases with the increasing yttrium content in the Y site (1d)—we can infer that, when $x \geq 0$, Ca enters the Sr site (2h), and the Y content in the Y site (1d)

TABLE I. Refined structure parameters for sample 1 ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_2\text{YCu}_2\text{O}_{7-\delta}$), sample 2 ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_2(\text{Y}_{0.6}\text{Ca}_{0.4})\text{Cu}_2\text{O}_{7-\delta}$), sample 3 ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$), sample 4 ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_{1.5}\text{Ca}_{0.5}\text{YCu}_2\text{O}_{7-\delta}$), and sample 5 ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_{2.2}\text{Y}_{0.8}\text{Cu}_2\text{O}_{7-\delta}$). Space group $P4/mmm$. The ratio of Pb and Cd in the (Pb,Cd)O layers is fixed at 0.5:0.5. The numbers in parentheses are estimated standard deviations of the last significant digit, and those without deviations were fixed. g denotes the site occupancy and B is the isotropic temperature factor in units of \AA^2 .

Atom	Site		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Pb/Cd	4l	(x)	0.0655(15)	0.0648(2)	0.078(3)	0.0711(17)	0.042(3)
		(B)	0.85(8)	0.54(1)	0.40(5)	0.59(1)	0.56(3)
		(g)	0.25	0.25	0.25	0.25	0.25
Sr	2h	(z)	0.2089(1)	0.2093(2)	0.2094(2)	0.2078(2)	0.2087(2)
		(B)	0.83(3)	0.76(1)	0.83(10)	0.63(2)	0.69(5)
		(g)	1	1	1	^a	1
Y/Ca	1d	(B)	0.81(2)	0.35(8)	0.61(8)	0.66(2)	0.71(2)
		(g)	1/0	0.74(1)/0.26(1)	0.72(1)/0.28(1)	0.983(9)/0.017(9)	^b
Cu	2g	(z)	0.3601(2)	0.3608(3)	0.3613(3)	0.3599(3)	0.3604(3)
		(B)	0.58(4)	0.72(1)	0.71(2)	0.58(3)	0.62(1)
		(g)	1	1	1	1	1
O(1)	4i	(z)	0.3783(5)	0.3758(8)	0.3789(10)	0.3758(8)	0.3768(7)
		(g)	1	1	1	1	1
O(2)	2g	(z)	0.1749(7)	0.1775(11)	0.1823(14)	0.1765(11)	0.1787(10)
		(g)	1	1	1	1	1
O(3)	4n	(x)	0.392(6)	0.383(10)	0.387(22)	0.388(8)	0.407(10)
		(g)	0.25	0.25	0.25	0.25	0.25
a (\AA)			3.8064(2)	3.8096(2)	3.8055(1)	3.8051(1)	3.8092(5)
c (\AA)			11.9758(5)	11.9658(5)	11.9410(1)	11.8541(2)	11.9924(14)
R_p (%)			5.84	7.01	9.07	6.60	6.65
R_{wp} (%)			7.80	10.23	13.04	9.61	8.96

^a Sr:Ca:Y=1.5:0.483(9):0.017(9).

^b Y:Sr=0.8:0.2.

increases which brings about the increase of the phase purity.

(iii) The occupancy refinements of ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_{1.5}\text{Ca}_{0.5}\text{YCu}_2\text{O}_{7-\delta}$) demonstrate that the Sr site (2h) is essentially occupied by Sr and Ca [Sr:Ca:Y=1.5:0.483(9):0.017(9)], and the Y site (1d) is essentially occupied by Y [Y:Ca=0.983(9):0.017(9)].

(iv) It has been indicated that the Ca content in the Y site (1d) plays an important role in the superconductivity of the (Pb,Cd)-1212 phase. Because the superconduct-

ing transition temperatures have only a little decrease in ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_{2-x}\text{Ca}_{0.5+x}\text{Y}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$) when x deviates from zero, whereas the superconducting transition temperatures have a faster decrease for $x > 0$ than for $x < 0$ in ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_{2-x}\text{Y}_{0.5+x}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$), we suggest that Ca enters the Sr site (2h) when $x > 0$, which results in the decrease of the Ca content in the Y site (1d), and the faster decrease of superconducting transition temperatures.

(v) Generally, Sr^{2+} is always ninefold coordinated,

TABLE II. Selected metal-oxygen interatomic distances (\AA) and bond valence sums of Cu ions in the CuO_2 planes for sample 1 ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_2\text{YCu}_2\text{O}_{7-\delta}$), sample 2 ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_2(\text{Y}_{0.6}\text{Ca}_{0.4})\text{Cu}_2\text{O}_{7-\delta}$), sample 3 ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$), sample 4 ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_{1.5}\text{Ca}_{0.5}\text{YCu}_2\text{O}_{7-\delta}$), and sample 5 ($\text{Pb}_{0.5}\text{Cd}_{0.5}\text{Sr}_{2.2}\text{Y}_{0.8}\text{Cu}_2\text{O}_{7-\delta}$). 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.

Bonds	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	N
(Pb,Cd)-O(2)	2.095	2.124	2.177	2.092	2.143	2
(Pb,Cd)-O(3)	2.692	2.694	2.691	2.691	2.694	4
Sr-O(1)	2.782	2.756	2.778	2.754	2.773	4
Sr-O(2)	2.722	2.721	2.710	2.716	2.717	4
Sr-O(3)	2.502	2.504	2.500	2.463	2.503	1
Y-O(1)	2.397	2.416	2.390	2.406	2.410	8
Cu-O(1)	1.916	1.913	1.914	1.912	1.915	4
Cu-O(2)	2.218	2.193	2.137	2.174	2.179	1
bond valence sums						
Cu	2.341	2.375	2.410	2.393	2.373	

while Y^{3+} is preferential for an eightfold-coordinated site in the 1212 phase, because of the larger ionic radii of Sr^{2+} than that of Y^{3+} .

(vi) It is well known that a common crystal-chemical feature for all copper oxide superconductors, except the infinite-layer compound,^{24,25} is that they all have intergrowth structures. The stabilization of such an intergrowth structure requires a bond-length matching across the intergrowth interface. The degree of the bond-length matching between the intergrowth layers is expressed in terms of the Goldschmidt tolerance factor t . For a ABO_3 -type perovskite,

$$t = d_{A-O}/\sqrt{2}d_{B-O}, \quad (1)$$

where A is the larger ion, B is the smaller ion, and the bond lengths of $A-O$ and $B-O$ have been taken as the sums of the ionic radii.

We have calculated the t values for the $-SrO-CuO_2$ - intergrowth structure unit and the $-SrO-(Pb,Cd)O$ - intergrowth structure unit assuming Sr, Ca, or Y occupying the Sr site (2h), and the t values for $-Y-CuO_2$ - intergrowth structure unit assuming Sr, Ca, or Y occupying the Y site (1d) (Table III). Because the oxide superconductors are of oxygen-deficient, distorted perovskite structure, the calculations of t values are very rough. Generally, the layered perovskite structure is stable in the limit $0.85 \leq t \leq 1.02$.²⁶ Thus we can speculate from the t values that it is difficult for Y to occupy the Sr site (2h), while Sr and Ca can enter the Y site (1d), and Ca can enter the Sr site (2h).

Based on the above facts, we can conclude that Ca will enter the Sr site (2h) in $(Pb_{0.5}Cd_{0.5})Sr_{2-x}Y_{1-u+x}Ca_uCu_2O_{7-\delta}$ ($u=0.3, 0.5$) when $x>0$, and the chemical formula for the $x>0$ compositions can be written as $(Pb_{0.5}Cd_{0.5})(Sr_{2-x}Ca_x)(Y_{1-u+x}Ca_{u-x})Cu_2O_{7-\delta}$ ($u=0.3, 0.5$).

Second, we discuss the relationships between the lattice parameters and chemical substitutions in $(Pb_{0.5}Cd_{0.5})(Sr,Y,Ca)_3Cu_2O_{7-\delta}$. As shown in Figs. 3–5 and 7–9, the variations of lattice parameters with composition are linear for $x < 0$ or $x > 0$, and the ratios $\Delta a/\Delta x$ and $\Delta c/\Delta x$ have been listed in Table IV. The $\Delta c/\Delta x$ values for $x \leq 0$ are about -0.12 \AA , while the $\Delta c/\Delta x$ values for $x \geq 0$ are about -0.32 \AA . The $\Delta c/\Delta x$ value for $x \leq 0$ in $(Pb_{0.5}Cd_{0.5})Sr_{2-x}Y_{1+x}Cu_2O_{7-\delta}$ is a little larger than the average value, because for Sr replacing Y, besides the size effect, there exists the effect

TABLE III. The tolerance factor t for the $-SrO-CuO_2$ - intergrowth structure unit and the $-SrO-(Pb,Cd)O$ - intergrowth structure unit assuming Sr, Ca, or Y occupying the Sr site (2h), and $-Y-CuO_2$ - intergrowth structure unit assuming Sr, Ca, or Y occupying the Y site (1d).

t	$-SrO-(Pb,Cd)O$	$-SrO-CuO_2$	$-Y-CuO_2$
Sr	0.85	0.93	0.92
Ca	0.81	0.89	0.87
Y	0.77	0.85	0.83

of the valence difference between Sr^{2+} and Y^{3+} as in $(Pb_{0.5}Cd_{0.5})Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$. The $\Delta c/\Delta x$ value for $x \leq 0$ in $(Pb_{0.5}Cd_{0.5})Sr_{2-x}Y_{0.7+x}Ca_{0.3}Cu_2O_{7-\delta}$ is larger than the average value because of the appearance of impurity phases. Because of the effect of the valence difference between Ca^{2+} and Y^{3+} in $(Pb_{0.5}Cd_{0.5})Sr_{2-x}Y_{1-u+x}Ca_uCu_2O_{7-\delta}$ ($u=0.3, 0.5$), the $\Delta c/\Delta x$ values for $x \geq 0$ in the two series are larger than the $\Delta c/\Delta x$ values in $(Pb_{0.5}Cd_{0.5})Sr_{2-x}Ca_{v+x}Y_{1-v}Cu_2O_{7-\delta}$ ($v = 0.0, 0.1, 0.3$).

It seems to us that, on the one hand, these systems obey the Vegard's law²⁷ in the variations of lattice parameters for $x \leq 0$ or $x \geq 0$. On the other hand, however, the variations have a kink at $x=0$. This kink may be related to different structural environments of the Sr site (2h) and the Y site (1d).

We choose the longitudinal section along the (020) plane of Fig. 10 as shown in Fig. 11. From Fig. 11, the lattice parameter c can be given by

$$\begin{aligned} c &= 2d_{Sr-O(3)} + 2d_1 + 2d_2 \\ &= 2\gamma_{Sr} + 2\gamma_{O^{2-}} + 2d_1 + 2d_2, \end{aligned} \quad (2)$$

where $d_{Sr-O(3)}$, d_1 , and d_2 are the c -axial Sr-O(3), Sr-O(1), and Y-O(1) distances, respectively, γ_{Sr} is the average ionic radius of the Sr site (CN=9), and $\gamma_{O^{2-}}$ is the ionic radius of O^{2-} (CN=6). For the sake of simplicity, we assume that the O(3) atom is in its ideal position in the calculations. First we discuss the case that Ca substitutes for Sr in the Sr site (2h) ($x > 0$). From the large $\Delta c/\Delta a$ values of $x > 0$ listed in Table IV, it is suggested that the variation of c is dominant in the case of substituting Ca for Sr. For the Δx of Ca replacing the Δx of Sr, i.e., $Sr_{2-\Delta x}Ca_{\Delta x}$, the change Δc in the lattice parameter c should be

TABLE IV. The $\Delta c/\Delta x$ values for $x \leq 0$ and $x \geq 0$ in $(Pb_{0.5}Cd_{0.5})Sr_{2-x}Y_{1-u+x}Ca_uCu_2O_{7-\delta}$ ($u=0.0, 0.3, 0.5$) and $(Pb_{0.5}Cd_{0.5})Sr_{2-x}Ca_{v+x}Y_{1-v}Cu_2O_{7-\delta}$ ($v=0.0, 0.1, 0.3$).

Sample	$x \leq 0$			$x \geq 0$		
	$\Delta a/\Delta x$	$\Delta c/\Delta x$	$\Delta c/\Delta a$	$\Delta a/\Delta x$	$\Delta c/\Delta x$	$\Delta c/\Delta a$
$(Pb_{0.5}Cd_{0.5})Sr_{2-x}Y_{1+x}Cu_2O_{7-\delta}$	-0.026	-0.077	2.96	0.017	-0.32	-18.82
$(Pb_{0.5}Cd_{0.5})Sr_{2-x}Y_{0.7+x}Ca_{0.3}Cu_2O_{7-\delta}$	-0.049	-0.04	0.82	-0.024	-0.29	12.08
$(Pb_{0.5}Cd_{0.5})Sr_{2-x}Y_{0.5+x}Ca_{0.5}Cu_2O_{7-\delta}$	0	0	/	-0.028	-0.27	9.64
$(Pb_{0.5}Cd_{0.5})Sr_{2-x}Ca_xYCu_2O_{7-\delta}$	/	/	/	-0.010	-0.31	31
$(Pb_{0.5}Cd_{0.5})Sr_{2-x}Ca_{0.1+x}Y_{0.9}Cu_2O_{7-\delta}$	-0.034	-0.13	3.82	-0.006	-0.34	56.67
$(Pb_{0.5}Cd_{0.5})Sr_{2-x}Ca_{0.3+x}Y_{0.7}Cu_2O_{7-\delta}$	-0.011	-0.106	9.64	0	-0.36	/

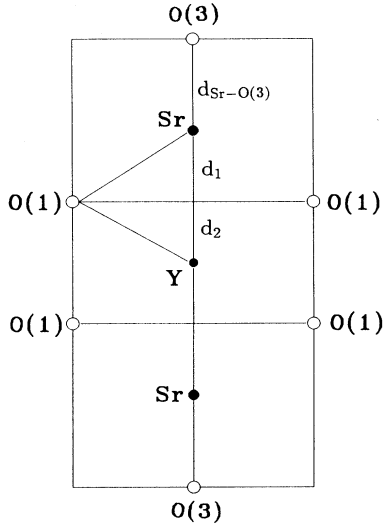


FIG. 11. The longitudinal section along the (020) plane of $(\text{Pb},\text{M})\text{Sr}_2(\text{Y},\text{Ca})\text{Cu}_2\text{O}_7$.

$$\begin{aligned}
 \Delta c &= 2\Delta\gamma_{\text{Sr}} + 2\Delta d_1 \\
 &= 2 \left(\frac{(2-\Delta x)\gamma_{\text{Sr}^{2+}} + (\Delta x)\gamma_{\text{Ca}^{2+}}}{2} - \gamma_{\text{Sr}^{2+}} \right) + 2\Delta d_1 \\
 &= \Delta x(\gamma_{\text{Ca}^{2+}} - \gamma_{\text{Sr}^{2+}}) + 2\Delta d_1 \\
 &= -0.13\Delta x + 2\Delta d_1.
 \end{aligned} \tag{3}$$

When we assume the lattice parameter a is still unchanged after the replacement [a equals the horizontal $\text{O}(1)\text{-O}(1)$ distance] and is equal to 3.806 [this value taken from the structure refinement results of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_{7-\delta}$], $2\Delta d_1$ can be calculated as follows:

$$\begin{aligned}
 2\Delta d_1 &= \Delta x [\sqrt{d_{\text{Ca-O}(1)}^2 - (a/2)^2} - \sqrt{d_{\text{Sr-O}(1)}^2 - (a/2)^2}] \\
 &= -0.187\Delta x,
 \end{aligned} \tag{4}$$

where $d_{\text{Sr-O}(1)}$ and $d_{\text{Ca-O}(1)}$ have been taken as the sums of the ionic radii, i.e., 2.71 and 2.58 Å for $d_{\text{Sr-O}(1)}$ and $d_{\text{Ca-O}(1)}$, respectively. Thus $\Delta c = -0.13\Delta x - 0.187\Delta x = -0.317\Delta x$, and the proportionality constant -0.317 is approximately equal to the $\Delta c/\Delta x$ values experimentally observed in the plots of c vs x , which are listed in Table IV. This result is also proved by the structural refinements of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{1.5}\text{Ca}_{0.5}\text{YCu}_2\text{O}_{7-\delta}$. From Table II, it can be seen that the substitution of Ca for Sr leads to the decrease of the Sr-O(1) and Sr-O(3) bond lengths.

If we use the same method to calculate the change Δc when substituting Sr for Ca in the Y site (1d), $\Delta c = -0.414\Delta x$. This value seriously deviates from those values experimentally measured. Taking into account the fact that the $\Delta a/\Delta x$ for $x \leq 0$ is larger than the corresponding $\Delta a/\Delta x$ for $x \geq 0$ in the same se-

ries if the substitutions can take place, we assume that when Sr enters the Y site (1d), Sr repels O(1) along the Y-O(1) direction and leads to the simultaneous increase of a and c . Under the circumstances, we obtain $\Delta c = -0.183\Delta x$. The proportionality constant -0.183 is still a little smaller than the observed value -0.12 . The difference between the calculated $\Delta c/\Delta x$ and experimentally observed $\Delta c/\Delta x$ may be related to the repulsion not along the strict Y-O(1) direction. The structural refinements of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2.2}\text{Y}_{0.8}\text{Cu}_2\text{O}_{7-\delta}$ manifest that the substitution of Sr for Y results in the expansion of the Y-O(1) bond.

V. CONCLUSION

We have studied the effects of chemical substitutions on crystal structure and superconducting properties of $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr},\text{Y},\text{Ca})_3\text{Cu}_2\text{O}_{7-\delta}$ in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$, $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1-u+x}\text{Ca}_u\text{Cu}_2\text{O}_{7-\delta}$ ($u=0.0, 0.3, 0.5$), and $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Ca}_{v+x}\text{Y}_{1-v}\text{Cu}_2\text{O}_{7-\delta}$ ($v=0.0, 0.1, 0.3$), which were prepared in air by the solid-state reaction method. The single-phase region of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{3-x-y}\text{Ca}_x\text{Y}_y\text{Cu}_2\text{O}_{7-\delta}$ is $0 \leq x \leq 0.5$ and $0.8 \leq y \leq 1.0$. The investigation of $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ indicates that a certain amount of yttrium is necessary for the formation of a pure (Pb,Cd)-1212 phase, while the calcium content in the Y site (1d) plays a crucial role in controlling the superconductivity of the (Pb,Cd)-1212 phase. Thus how to synthesize a pure (Pb,Cd)-1212 phase with high calcium content is very promising to improve the superconducting transition temperatures. From the XRD results of the $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1+x}\text{Cu}_2\text{O}_{7-\delta}$, we find that Sr can enter the Y site (1d), whereas it is difficult for Y to enter the Sr site (2h). For $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_{2-x}\text{Y}_{1-u+x}\text{Ca}_u\text{Cu}_2\text{O}_{7-\delta}$ ($u=0.3, 0.5$), when $x>0$ it is Ca ions that enter the Sr site (2h), and the chemical formula for the $x>0$ compositions can be written as $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr}_{2-x}\text{Ca}_x)(\text{Y}_{1-u+x}\text{Ca}_{u-x})\text{Cu}_2\text{O}_{7-\delta}$ ($u=0.3, 0.5$). This has been proved by XRD, T_c measurements, and structure refinements.

The relation between the lattice parameters and chemical substitutions shows that the substitutions of Ca for Sr in the Y site (1d) and Ca for Sr in the Sr site (2h) have a different influence on the lattice parameters. The variations of lattice parameters with composition are linear for $x < 0$ or $x > 0$. The $\Delta c/\Delta x$ values for $x \leq 0$ are about -0.12 Å, while the $\Delta c/\Delta x$ values for $x \geq 0$ are about -0.32 Å.

ACKNOWLEDGMENT

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

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