

Synthesis and Crystal Structure of New Pb-Based Copper Oxides (Pb_{0.5}M_{0.5})(Sr_{0.9}Ho_{0.1})₂(Ho_{0.7}Ce_{0.3})₂Cu₂O_y (M = Pb and Cd)

H. M. Luo,*†¹ Z. X. Zhao,* G. C. Che,* F. Wu,* H. Chen,* C. Dong,* Z. Y. Chen,†‡ and Y. T. Qian†‡

*National Laboratory for Superconductivity, Institute of Physics Academia Sinica, Beijing 100080, People's Republic of China; †Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China; and ‡Structure Research Laboratory, University of Science and Technology of China, Academia Sinica, Hefei, Anhui 230026, People's Republic of China

Received September 18, 1995; in revised form January 24, 1996; accepted February 12, 1996

New Pb-based copper oxides (Pb_{0.5}M_{0.5})(Sr_{0.9}Ho_{0.1})₂(Ho_{0.7}Ce_{0.3})₂Cu₂O_y (M = Pb and Cd) have been synthesized successfully. The structure of the compounds has been determined using the powder X-ray diffraction data. It is found that the lattice parameters are $a = 3.8368 \text{ \AA}$ and $c = 29.1894 \text{ \AA}$ for the compound with M = Pb and $a = 3.8168 \text{ \AA}$ and $c = 29.3372 \text{ \AA}$ for M = Cd. XRD results show that the structure is isostructural with (Pb, Cu) (Sr, R)₂(R', Ce)₂Cu₂O_z (R, R' = rare earth elements). © 1996 Academic Press, Inc.

INTRODUCTION

The first nonsuperconducting (Pb, Cu)-1222 phase (Pb, Cu) (Sr, Pr)₂Pr₂Cu₂O_z was discovered by Adachi in 1990 (1). This phase is isomorphous to TlSr₂(Nd, Ce)₂Cu₂O_z (Tl-1222) (2) and contains [CuO₅] square pyramids, (Pb, Cu)-O monolayers, and fluorite-type layers in the structural unit. Careful research was carried out on the system (Pb, Cu) (Sr, R)₂(R', Ce)₂Cu₂O_z (R, R' = rare earth elements), and a series of single-phase and superconducting (Pb, Cu)-1222 compounds were obtained (3). Considering the similar chemical properties of Cd and Cu ions and that Cd partially replaces Pb as well as Cu in the Pb-based "1212" compounds (4, 5), the (Pb, Cd)-1222 phase should be formed. However, up to now the (Pb, Cd)-1222 phase has not been reported. Additionally, the cations in the insulating layer of many Pb-based copper oxides consist of mixed ions, such as (Pb, Cu) and (Pb, Cd); the question thus arises whether compounds with the cations in the insulating layer consisting of pure Pb could be synthesized. In this paper, we selected R = R' = Ho as an example in the (Pb, M) (Sr, R)₂(R', Ce)₂Cu₂O_y (M = Pb and Cd) system, and successfully synthesized the new compounds (Pb_{0.5}M_{0.5})(Sr_{0.9}Ho_{0.1})₂(Ho_{0.7}Ce_{0.3})₂Cu₂O_y (M = Pb and Cd), with cations in the Pb-containing block layers con-

sisting of pure Pb and (Pb, Cd), respectively. We also determined the structure of the compound with M = Cd using the X-ray diffraction data. The XRD results show that Pb-1222 and (Pb, Cd)-1222 phases can be formed, as well as the (Pb, Cu)-1222 phase.

EXPERIMENTAL

Samples with nominal compositions (Pb_{0.5}M_{0.5}) (Sr_{0.9}Ho_{0.1})₂(Ho_{0.7}Ce_{0.3})₂Cu₂O_y (M = Pb and Cd) were prepared by the solid state reaction method using PbO, CdO, SrCO₃, Ho₂O₃, CeO₂, and CuO as starting materials. Stoichiometric amounts of starting materials were well mixed and preheated at 830°C for 24 h in air and then pressed into pellets. The pellets were sintered at 850°C for 10 h in air, and then slowly cooled to room temperature at a rate of 30°C/h. For comparison purposes, we also prepared the sample (Pb_{0.5}Cu_{0.5}) (Sr_{0.9}Ho_{0.1})₂(Ho_{0.7}Ce_{0.3})₂Cu₂O_y by the same experimental procedure.

X-ray powder diffraction (XRD) analyses were performed on a MXP18HF-type diffractometer with CuK_α radiation (50 kV × 200 mA). The structural parameters were determined by FINAX, FHKL, and LAZY programs.

RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns for (Pb_{0.5}M_{0.5}) (Sr_{0.9}Ho_{0.1})₂(Ho_{0.7}Ce_{0.3})₂Cu₂O_y (M = Cd, Pd, and Cu). The sample with M = Cd is practically single phase; all peaks can be indexed on the basis of a tetragonal unit cell with $a = 3.8168 \text{ \AA}$ and $c = 29.3372 \text{ \AA}$. Figure 1a shows that the XRD pattern for (Pb, Cd) (Sr, Ho)₂(Ho, Ce)₂Cu₂O_y is similar to that for (Pb, Cu)-1222 samples (1, 3, 6–8). This result suggests that the (Pb, Cd)-1222 phase can be formed and that the (Pb, Cd)-1222 compound has a crystal structure similar to that of the (Pb, Cu)-1222 compound. The sample with M = Pb contains a Pb-1222 phase as the main phase and only a small amount of all impurity phase (marked with asterisk in the pattern). This result also shows

¹ Communication address: Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R.China.

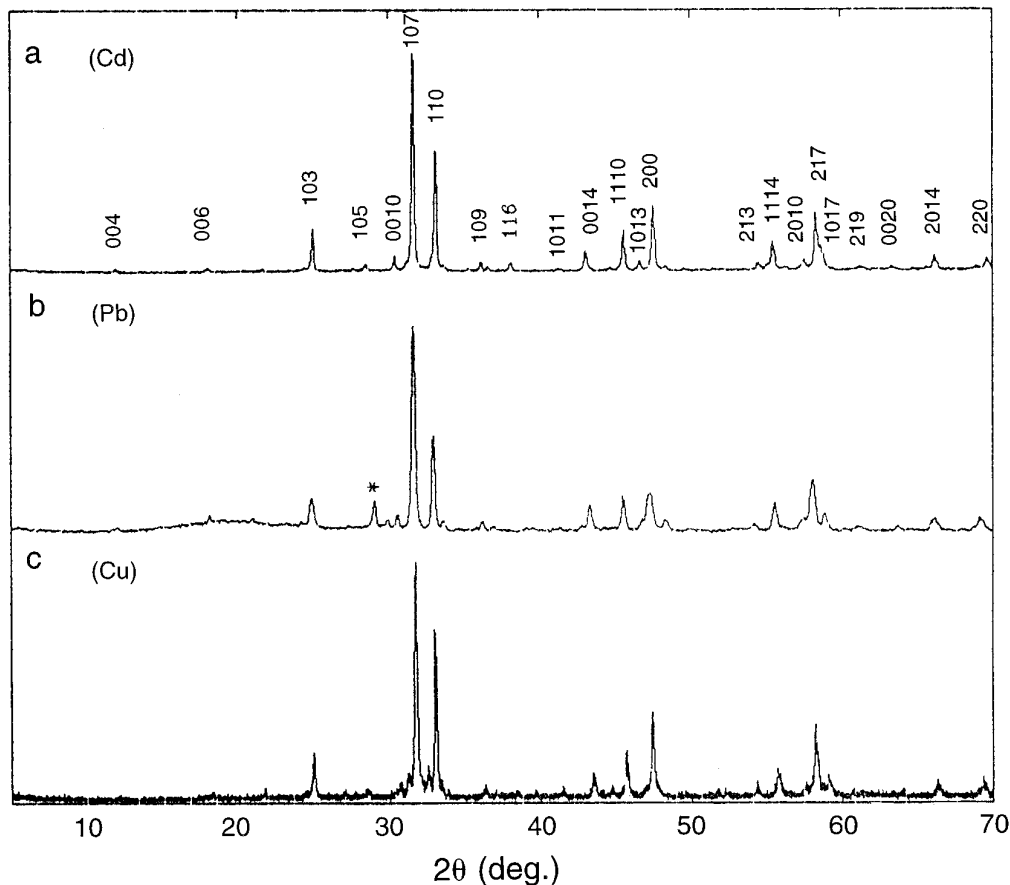


FIG. 1. The X-ray powder diffraction patterns for $(\text{Pb}_{0.5}M_{0.5})(\text{Sr}_{0.9}\text{Ho}_{0.1})_2(\text{Ho}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_9$ with (a) $M = \text{Cd}$, (b) $M = \text{Pb}$, and (c) $M = \text{Cu}$.

that the Pb-1222 phase can be formed. It is worth pointing out that in the present experiment the temperature of the (Pb, M)-1222 ($M = \text{Pb}$, Cd, and Cu) phase formation (850°C) is much lower than that of (Pb, Cu)-1222 as reported in Refs. (3, 6–8) (1080°C). That is to say, there is a wide range in the (Pb, M)-1222 phase formation temperature. The lattice parameters of these samples are listed in Table 1. The lattice parameter a of high- T_C layered copper oxides primarily depends on the Cu–O bond length. The lattice parameter c , on the other hand, is controlled by the sum of the thicknesses of the stacking layers involved in the high- T_C layered copper oxides. The c value of (Pb,

Cu)-1222 (29.0813 \AA for $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{0.9}\text{Ho}_{0.1})_2(\text{Ho}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_9$, 28.9862 \AA for $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{0.875}\text{Nd}_{0.125})_2(\text{Ho}_{0.69}\text{Ce}_{0.31})_2\text{Cu}_2\text{O}_z$, and 29.0116 \AA for $(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{0.875}\text{Eu}_{0.125})_2(\text{Eu}_{0.75}\text{Ce}_{0.25})_2\text{Cu}_2\text{O}_z$) is smaller than that of (Pb, Cd)-1222 (29.3372 \AA), owing to the difference in ionic radii between Cu ions (0.86 \AA) and Cd ions (0.97 \AA). The c value of Pb-1222 is also smaller than that of (Pb, Cd)-1222, which can be attributed to the large displacement of the Pb atoms in the PbO layers from their ideal site (9).

The structure of (Pb, Cd)-1222 compounds is determined based on the structure model of (Pb, Cu) $(\text{Sr}, \text{Eu})_2(\text{Eu}, \text{Ce})_2\text{Cu}_2\text{O}_z$ (3) and (Pb, Cu) $(\text{Sr}, \text{Nd})_2(\text{Ho}, \text{Ce})_2\text{Cu}_2\text{O}_z$ (8). Figure 2 shows a schematic representation of the crystallographic structure of (Pb, M) $(\text{Sr}, \text{Ho})_2(\text{Ho}, \text{Ce})_2\text{Cu}_2\text{O}_y$ with $M = \text{Pb}$, Cd, and Cu. The structure of the 1222 phase is similar to that of the 223 phase (7, 10). The only difference between the two structures is the position of the oxygen ions located in the middle plane of the unit cell shown in Fig. 2. In the 1222 structure, the (Pb, M)–O layers have a rock salt-type configuration, while in the 223 phase, the oxygen deficient Cu–O layers located between the apical oxygen ions of the Cu–O₅ pyramids have a perovskite-

TABLE 1
The Lattice Parameters for $(\text{Pb}_{0.5}M_{0.5})(\text{Sr}_{0.9}\text{Ho}_{0.1})_2(\text{Ho}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_y$ with $M = \text{Pb}$, Cd, and Cu

M	a (\AA)	c (\AA)	v (\AA^3)
Pb	3.8368	29.1894	429.71
Cd	3.8168	29.3372	427.38
Cu	3.8303	29.0813	426.66

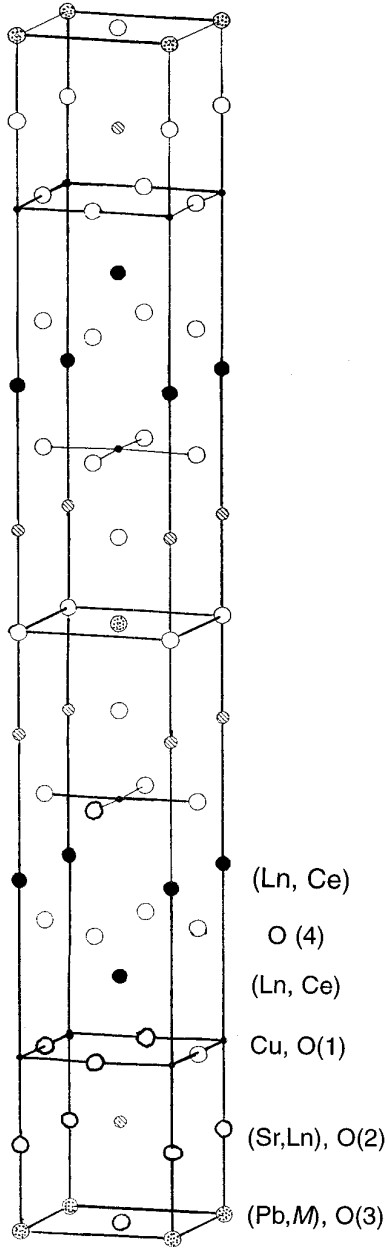


FIG. 2. Schematic representation of $(\text{Pb}, M)(\text{Sr}, \text{Ln})_2(\text{Ln}, \text{Ce})_2\text{Cu}_2\text{O}_9$ crystal structure ($M = \text{Pb}, \text{Cd}, \text{and Cu}$, $\text{Ln} = \text{rare earth element}$).

type configuration. The refined atomic parameters and the intensities and the interplanar distance d values for $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr}_{0.9}\text{Ho}_{0.1})_2(\text{Ho}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_9$ are listed in Table 2 and Table 3, respectively. (Pb, Cd) and O atoms in the $(\text{Pb}, \text{Cd})\text{O}$ monolayer in the (Pb, Cd) -1222 compound are displaced from their ideal sites and split into four parts: $2a \rightarrow 8i$ for (Pb, Cd) and $2b \rightarrow 8j$ for $\text{O}(3)$. Such atomic displacements are also observed in the $(\text{Pb}, \text{Cu})\text{O}$ monolayer of $(\text{Pb}, \text{Cu})(\text{Sr}, R)_2(R', \text{Ce})_2\text{Cu}_2\text{O}_z$. By

TABLE 2

The Atomic Parameters for $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr}_{0.9}\text{Ho}_{0.1})_2(\text{Ho}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_9$ (Space Group $I4/mmm$, $a = 3.8168 \text{ \AA}$, $c = 29.3372 \text{ \AA}$)

Atom	Site	Occupancy	x	y	z	$B (\text{Å}^2)$
(Pb, Cd)	$8i$	0.125/0.125	0.054	0.0	0.0	0.4
(Sr, Ho)	$4e$	0.9/0.1	0.5	0.5	0.0852	0.6
(Ho, Ce)	$4e$	0.7/0.3	0.5	0.5	0.2063	0.8
Cu	$4e$	1.00	0.0	0.0	0.146	0.5
$\text{O}(1)$	$8g$	1.00	0.0	0.5	0.145	1.0
$\text{O}(2)$	$4e$	1.00	0.0	0.0	0.073	1.0
$\text{O}(3)$	$8j$	0.25	0.45	0.5	0.0	1.0
$\text{O}(4)$	$4d$	1.00	0.0	0.5	0.25	1.0

Note. $(\text{Pb}, \text{Cd}) 2a(0, 0, 0) \rightarrow 8i(x, 0, 0)$, $\text{O}(3) 2b(0.5, 0.5, 0) \rightarrow 8j(x, 0.5, 0)$.

comparison with the displacements of (Pb, Cu) and $\text{O}(3)$ atoms in the $(\text{PbCu})\text{O}$ monolayer in the $(\text{Pb}, \text{Cu})(\text{Sr}, \text{Eu})_2(\text{Eu}, \text{Ce})_2\text{Cu}_2\text{O}_z$ ($\text{Cu}1$) (3) and $(\text{Pb}, \text{Cu})(\text{Sr}, \text{Nd})_2(\text{Ho}, \text{Ce})_2\text{Cu}_2\text{O}_z$ ($\text{Cu}2$) (8) compounds, the displacements of (Pb, Cd) and $\text{O}(3)$ atoms in the $(\text{Pb}, \text{Cd})\text{O}$ monolayer in $(\text{Pb}, \text{Cd})(\text{Sr}, \text{Ho})_2(\text{Ho}, \text{Ce})_2\text{Cu}_2\text{O}_y$ (Cd) are smaller. For example, the (Pb, M) atom is displaced from the ideal $2a$

TABLE 3
Powder X-Ray Diffraction Data for $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr}_{0.9}\text{Ho}_{0.1})_2(\text{Ho}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_9$

hkl	d_{obs}	d_{calc}	I_{obs}	I_{calc}
0 0 4	7.393	7.334	1.6	1.3
0 0 6	4.916	4.890	1.8	1.7
1 0 3	3.563	3.556	19.8	22.8
0 0 10	2.938	2.934	6.5	6.2
1 0 7	2.826	2.822	100	100
1 1 0	2.702	2.699	54.9	50.6
1 0 9	2.481	2.479	4.0	2.3
0 0 12	2.450	2.445	2.0	1.0
1 0 11	2.184	2.186	1.0	1.0
1 1 8	2.175	2.174	0.8	1.1
0 0 14	2.097	2.096	8.9	10.0
1 1 10	1.987	1.986	18.6	19.8
1 0 13	1.944	1.943	4.0	4.4
2 0 0	1.909	1.908	30.4	27.3
2 1 3	1.682	1.682	2.9	4.4
1 1 14	1.656	1.655	12.6	13.9
2 0 10	1.600	1.600	3.8	3.8
2 1 7	1.581	1.581	25.6	29.9
1 0 17	1.570	1.572	6.4	8.0
2 1 9	1.512	1.512	1.7	0.9
0 0 20	1.467	1.467	1.7	1.5
2 0 14	1.411	1.411	6.4	8.7
2 1 13	1.361	1.361	1.3	2.0
2 2 0	1.349	1.349	6.7	6.8

Note. $R = \sum |I_{\text{obs}} - I_{\text{calc}}| / \sum |I_{\text{obs}}| = 9.65\%$.

TABLE 4
Bonds and Interatomic Distances for $(\text{Pb}_{0.5}\text{Cd}_{0.5})$
 $(\text{Sr}_{0.9}\text{Ho}_{0.1})_2(\text{Ho}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_y$

Bonds	Interatomic distance (Å)	<i>N</i>
(Pb, Cd)–O(2)	2.152	2
(Pb, Cd)–O(3)	2.699	4
(Sr, Ho)–O(1)	2.592	4
(Sr, Ho)–O(2)	2.723	4
(Sr, Ho)–O(3)	2.507	1
(Ho, Ce)–O(1)	2.622	4
(Ho, Ce)–O(4)	2.299	4
Cu–O(1)	1.909	4
Cu–O(2)	2.142	1

Note. For the sake of convenience, the displaced atoms were displaced from their ideal positions while calculating the (Pb, Cd)–O(3) distance. *N* is the number of equivalent bonds.

site (0, 0, 0) to the 8*i* site (*x*, 0, 0) with *x* = 0.054 for Cd, while *x* = 0.070 for Cu1 and *x* = 0.062 for Cu2. The O(3) atom is displaced from the 2*b* site (0.5, 0.5, 0) to the 8*j* site (*x*, 0.5, 0) with *x* = 0.45 for Cd, while *x* = 0.18 for Cu1 and *x* = 0.32 for Cu2. The difference probably arises because Cd easily forms a rock salt-type configuration as well as Pb, while Cu more readily forms a perovskite-type configuration. Table 3 indicates the reasonable agreement between the observed and calculated patterns obtained for (Pb, Cd) (Sr, Ho)₂(Ho, Ce)₂Cu₂O_z. The discrepancy (*R*) factor ($\sum |I_c - I_o| / \sum I_o$) is 9.65%. This result strongly supports the idea that the structure model similar to (Pb, Cu)-1222 compound is correct. The selected interatomic distances calculated from the structure parameters for the (Pb_{0.5}Cd_{0.5}) (Sr_{0.9}Ho_{0.1})₂(Ho_{0.7}Ce_{0.3})₂Cu₂O_y compound are listed in Table 4.

Resistivity measurements showed that all these com-

pounds are semiconductors under present preparation conditions. However, these samples might become superconducting by adjusting of firing temperature or by post-annealing under high oxygen pressure. A series of single phase and superconducting compounds (Pb_{0.5}M_{0.5}) (Sr_{0.9}R_{0.1})₂(R'_{0.7}Ce_{0.3})₂Cu₂O_y (*M* = Pb and Cd, *R*, *R'* = rare earth elements) remains to be explored. Such experiments are in progress.

CONCLUSION

The synthesis and structure of the new compounds (Pb_{0.5}M_{0.5}) (Sr_{0.9}Ho_{0.1})₂(Ho_{0.7}Ce_{0.3})₂Cu₂O_y (*M* = Pb and Cd) have been studied by XRD. The results show that the Pb-1222 and (Pb, Cd)-1222 phases can be formed, as well as the (Pb, Cu)-1222 phase.

REFERENCES

1. S. Adachi, O. Inoue, S. Kawashima, H. Adachi, Y. Ichikawa, K. Setsune, and K. Wasa, *Physica C* **168**, 1 (1990).
2. C. Martin, D. Bourgault, M. Hervieu, C. Michel, J. Provost, and B. Raveau, *Mod. Phys. Lett. B* **3**, 993 (1989).
3. T. Maeda, K. Sakuyama, N. Sakai, H. Yamauchi, and S. Tanaka, *Physica C* **177**, 337 (1991).
4. T. P. Beales, C. Dineen, W. G. Freeman, S. R. Hall, M. R. Harrison, D. M. Jacobson, and S. J. Zammattio, *Supercond. Sci. Technol.* **5**, 47 (1992).
5. J. R. Min, J. K. Liang, X. I. Chen, C. Wang, C. Dong, and G. H. Rao, *Physica C* **229**, 169 (1994).
6. N. Sakai, T. Maeda, H. Yamauchi, and S. Tanaka, *Physica C* **212**, 75 (1993).
7. T. Maeda, K. Sakuyama, S. Koriyama, A. Ichinose, H. Yamauchi, and S. Tanaka, *Physica C* **169**, 133 (1990).
8. T. Maeda, N. Sakai, F. Izumi, T. Wada, H. Yamauchi, H. Asano, and S. Tanaka, *Physica C* **193**, 73 (1992).
9. J. R. Min, J. K. Liang, H. Jin, C. Wang, H. Chen, Y. D. Yu, C. Dong, and R. H. Rao, *Physica C* in press.
10. Y. Tokura, H. Takagi, and S. Uchida, *Nature* **337**, 345 (1989).