



A new type of layered cuprates with 1222 structure. (CdCe)Sr₂(LnCeSr)₂Cu₂O_y (Ln = Nd, Y)

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Abstract

A new family of layered cuprates with the 1222 structure (CdCe)Sr₂(LnCeSr)₂Cu₂O_y (Ln = Nd, Y) has been successfully synthesized and identified. The diffraction patterns can be indexed by the tetragonal lattice parameters $a = 3.801 \pm 0.001$ Å, $c = 29.31 \pm 0.005$ Å (Ln = Y) and $a = 3.844 \pm 0.001$ Å, $c = 29.38 \pm 0.005$ Å (Ln = Nd), respectively. The space group is 14/mmm which is consistent with that of Pb-1222. The resistivity measurement showed that the two compounds were narrow-gap semiconductors.

1. Introduction

Since the discovery of Tl-1222 [1], some analogs such as Pb-1222 [2] have been synthesized. These compounds contained Tl-O and (Pb/Cu)-O rock-salt-type monolayers, respectively. By substituting the perovskite layer, Li et al. [3] prepared Ta-1222 which contains the SrTaO₃ block.

The Cd²⁺-doped superconducting cuprates are particularly interesting for investigation due to the position of Cd in the periodic table, its ionic size and its intrinsic chemical reactivity. Niu et al. [4] have synthesized the La_{2-x}Cd_xCu₂O_{4-δ} phase. Later, much works on Cd²⁺ doping have been reported [5,6]. Superconducting compounds such as (Bi,Cd)Sr₂(Y,Ca)Cu₂O_y [7], (Tl_{1.75}Cd_{0.25})Ba₂CuO_{6+δ} [8] and (Pb_{0.5}Cd_{0.5})Sr₂(Y_{0.7}Ca_{0.3})Cu₂O_y [9] have been synthesized. In the above systems, Cd²⁺ ions mainly

substitute Bi³⁺, Tl³⁺ or Pb⁴⁺ in the rock-salt-type layers.

In this work, we synthesize a type of layered cuprate Cd-1222. The structure analysis combined with chemical analysis results indicate that the compounds can be expressed as (Cd,Ce)-1222: (Cd_{0.844}Ce_{0.156})Sr₂(Y_{1.248}Ce_{0.676}Sr_{0.078})Cu₂O_y and (Cd_{0.797}Ce_{0.203})Sr₂(Nd_{1.155}Ce_{0.743}Sr_{0.101})Cu₂O_y.

2. Experimental

The samples with nominal composition Cd-Sr₂Y_{1.2}Ce_{0.8}Cu₂O_y or CdSr₂Nd_{1.1}Ce_{0.9}Cu₂O_y were prepared using high-purity compounds of SrCO₃ (99%), Nd₂O₃ (99.99%), CeO₂ (99.99%), CuO (99%), Y₂O₃ (99.99%) and CdO (99%). Appropriate amounts of SrCO₃, CeO₂, CuO, Nd₂O₃ and Y₂O₃ or CdO were mixed and ground well in an agate mortar. The mixtures were preheated at 930°C in air for 48 h. After that the samples were pressed into pel-

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lets, calcined in air at 980°C for another 48 h and then cooled to room temperature in the furnace. The X-ray diffraction (XRD) patterns were taken by a Japan Rigaku Dmax diffractometer with high intensity Cu K α radiation at a scan rate of 0.05°/s and a 2 θ range of 5° to 65°. Silicon powder was used as an internal standard to determine the lattice parameters. The compositions of the compounds were measured by inductively coupled plasma analysis (Plasma 100, America). The resistivity of the samples was measured by the standard four-probe method with indium contacts, down to 16 K.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns of the samples which can be indexed by a least-root-mean-square refinement procedure [10] with a tetragonal cell as: $a = 3.801 \pm 0.001$ Å, $c = 29.31 \pm 0.005$ Å (Ln=Y) and $a = 3.844 \pm 0.001$ Å, $c = 29.38 \pm 0.005$ Å (Ln=Nd), respectively. The parameters are close to that of Pb-1222 (3.88 Å, 29.14 Å) [2]. Since only the peaks that satisfy the condition $h+k+l=\text{even}$ are observed, the lattice type is I. The space group of 14/mmm was chosen.

Since Cd²⁺ could be evaporated after heat-treatments at high temperature, a inductively coupled plasma (ICP) analysis was carried out. ICP analysis indicates that the recoveries of all metal elements after heat-treatments are Cd (81.2% \pm 0.1%), Sr (99.9% \pm 0.1%), Y (100.0% \pm 0.1%), Ce (100.1% \pm 0.1%), Cu (98.5% \pm 0.1%), (Ln=Y), and Cd (75.8% \pm 0.1%), Sr (99.9% \pm 0.1%), Nd (100.1% \pm 0.1%), Ce (100.0% \pm 0.1%), Cu (97.9% \pm 0.1%), (Ln=Nd), respectively. In general, the average valence of cations in a rock-salt-type layer is more than 2+. Through the loss of Cd²⁺ some of the ions such as Ce⁴⁺, Y³⁺ or Nd³⁺ may have entered the rock-salt layers, since Ce⁴⁺, Y³⁺ and Nd³⁺ are high-valence ions and have a similar size to Cd²⁺. From the report on (Cd,Ce)-1212 [11], a (Cd,Ce)-O monolayer could exist in layered cuprates. Similarly we think that Ce⁴⁺ entered the rock-salt layers instead of Y³⁺. Thus, these compounds could be expressed by the formulae of (Cd_{0.844}Ce_{0.156})Sr₂(Y_{1.248}Ce_{0.676}Sr_{0.076})Cu₂O_y and (Cd_{0.797}Ce_{0.203})Sr₂(Nd_{1.156}Ce_{0.743}Sr_{0.101})Cu₂O_y.

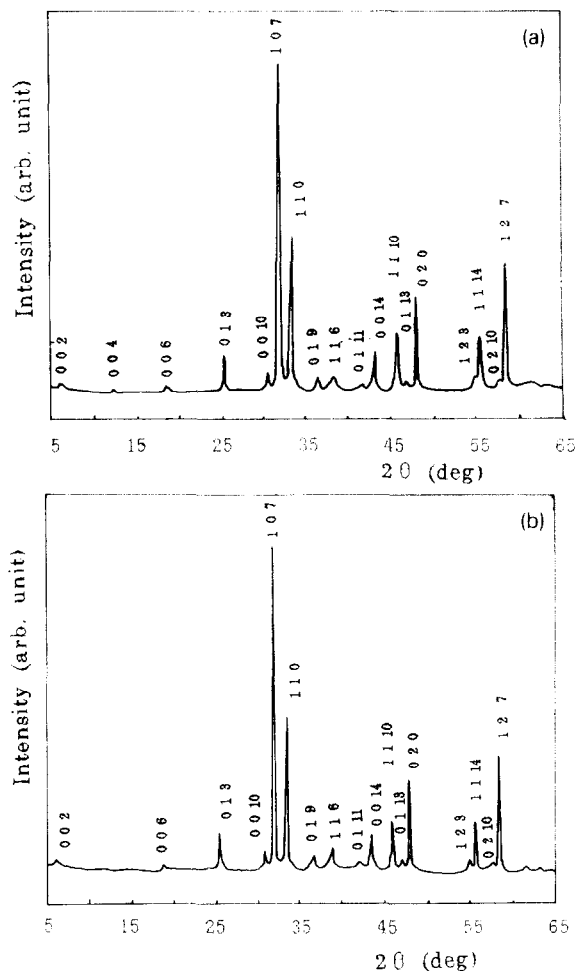


Fig. 1. Powder XRD patterns of the series (CdCe)Sr₂(LnCeSr)₂Cu₂O_{9- δ} samples with Ln=Y (a), Ln=Nd (b).

The diffraction peak intensities of (Cd,Ce)-1222 were calculated according to the model of Fig. 2, using the following equation [12]:

$$I_c = P'' L P F^2 \exp(-2B \sin^2 \theta / \lambda^2),$$

where I_c is the diffraction peak intensity, P'' a multiplicity factor, P a polarization factor, L the Lorentz factor, F a structure factor, B a temperature factor, λ the wavelength of the X-rays, 2θ the angle between incident and diffracted beams.

Table 1 lists the final refinement of the atomic positions. The discrepancy R factor ($\sum |I_c - I_0| / \sum I_0$) of the refinement is 6.54% (Ln=Y), and 7.23% (Ln=Nd). Considering that Y³⁺ might enter the

Table 1
Atomic positions of $(\text{CdCe})\text{Sr}_2(\text{LnCeSr})_2\text{Cu}_2\text{O}_y$

Atomic positions	x	y	z	
			Ln=Y	Ln=Nd
Ln/Ce/Sr (4e)	0.5	0.5	0.204 ± 0.005	0.205 ± 0.005
Sr (4e)	0.5	0.5	0.084 ± 0.005	0.084 ± 0.005
Cu (4e)	0	0	0.144 ± 0.005	0.145 ± 0.005
Cd/Ce (8i) ^a	0.02	0	0	0
O ₁ (8j) ^b	0.34	0.5	0	0
O ₂ (4e)	0	0	0.073 ± 0.005	0.074 ± 0.005
O ₃ (8g)	0	0.5	0.148 ± 0.005	0.150 ± 0.005
O ₄ (4d)	0	0.5	0.25	0.25

^a Split into four pieces by shifting from the ideal 2a site.

^b Split into four pieces by shifting from the ideal 2b site.

Table 2
The bond lengths of the M–O bonds of $(\text{Cd}_{0.844}\text{Ce}_{0.156})\text{Sr}_2(\text{Y}_{1.248}\text{Ce}_{0.676}\text{Sr}_{0.076})\text{Cu}_2\text{O}_{9-\delta}$ (upper panel), and $(\text{Cd}_{0.797}\text{Ce}_{0.203})\text{Sr}_2(\text{Nd}_{1.156}\text{Ce}_{0.743}\text{Sr}_{0.101})\text{Cu}_2\text{O}_{9-\delta}$ (lower panel)

(Cd/Ce)–O ₁	2.256 ± 0.005	(Cd/Ce)–O ₂	2.141 ± 0.016
Cu–O ₂	2.052 ± 0.022	Cu–O ₃	1.903 ± 0.001
Sr–O ₁	2.536 ± 0.016	Sr–O ₂	2.707 ± 0.004
Sr–O ₃	2.670 ± 0.003	Y–O ₃	2.511 ± 0.022
Y–O ₄	2.330 ± 0.010	Y=Y/Ce/Sr	
(Cd/Ce)–O ₁	2.282 ± 0.005	(Cd/Ce)–O ₂	2.175 ± 0.017
Cu–O ₂	2.086 ± 0.031	Cu–O ₃	1.928 ± 0.002
Sr–O ₁	2.543 ± 0.011	Sr–O ₂	2.737 ± 0.003
Sr–O ₃	2.730 ± 0.004	Nd–O ₃	2.511 ± 0.020
Nd–O ₄	2.333 ± 0.010	Nd=Nd/Ce/Sr	

rock-salt layers, we also calculated the *R* factor according to $(\text{Cd},\text{Y})\text{Sr}_2(\text{SrYCe})_2\text{Cu}_2\text{O}_y$ or $(\text{Cd},\text{Nd})\text{Sr}_2(\text{SrNdCe})_2\text{Cu}_2\text{O}_y$, but obtained a larger *R* factor: 8.19% (Ln=Y), 9.46% (Ln=Nd). That indicates that Ce^{4+} entered the rock-salt layers instead of Y^{3+} or Nd^{3+} , too. In the present paper, we are not concerned with the oxygen deficiency. The lengths of the metal–oxygen bonds derived from the refined atomic positions are listed in Table 2.

Fig. 2 schematically shows the idealized crystal structure of $(\text{Cd},\text{Ce})\text{Sr}_2(\text{Ln},\text{Ce},\text{Sr})_2\text{Cu}_2\text{O}_y$, which is similar to that of Pb-1222 [2]. The structure of (Cd,Ce) -1222 can be described by a rock-salt-type block (Cd,Ce) –O layer between the apices of pyramidal CuO_5 . The bases of the pyramids are separated by a fluorite layer $(\text{LnO})_2$. In comparison with Ta-

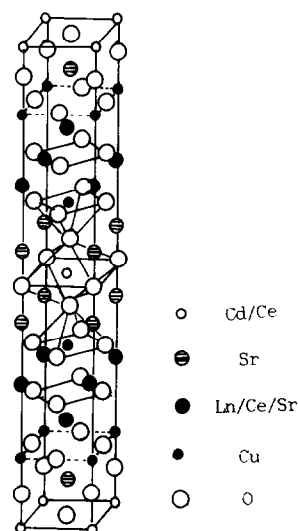


Fig. 2. Schematic representation of the ideal crystal structure of $(\text{CdCe})\text{Sr}_2(\text{LnCeSr})_2\text{Cu}_2\text{O}_{9-\delta}$.

1222 [3], the main difference between the two structures is that in (Cd,Ce) -1222, $(\text{Cd}^{2+}, \text{Ce}^{4+})$ forms a rock-salt-type layer but Ta^{5+} forms a perovskite octahedra TaO_6 in Ta-1222.

From Fig. 2, one can see that the (Cd,Ce) -1222 phase contains four layers of CuO_5 pyramid planes in one unit cell. The CuO_5 planes may act as conducting paths for the carriers, thus the compounds will be a conductor or even a superconductor if the proper carrier concentration is achieved. In this study the electrical resistivity vs. temperature (*R*–*T*) curve of $(\text{Cd},\text{Ce})\text{Sr}_2(\text{Ln},\text{Ce},\text{Sr})_2\text{Cu}_2\text{O}_y$ (Fig. 3) showed

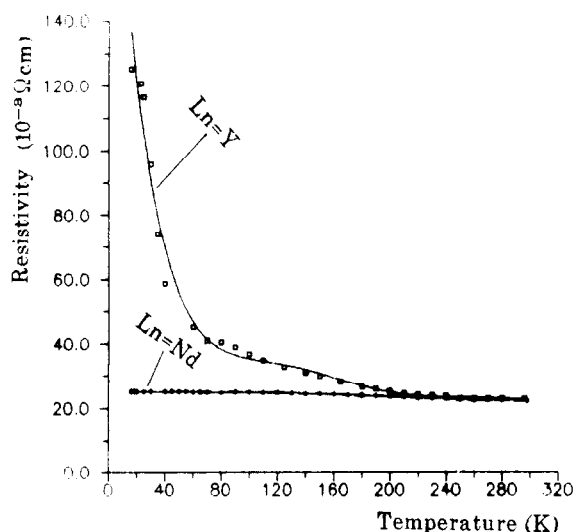


Fig. 3. Temperature dependence of electrical resistivity for $(\text{CdCe})\text{Sr}_2(\text{LnCeSr})_2\text{Cu}_2\text{O}_{9-\delta}$.

that resistivity is quite small and weakly dependent on temperature from room temperature 296 K ($0.023 \Omega \text{ cm}$ ($\text{Ln}=\text{Y}$), $0.021 \Omega \text{ cm}$ ($\text{Ln}=\text{Nd}$)) down to 16 K ($0.126 \Omega \text{ cm}$ ($\text{Ln}=\text{Y}$), $0.0252 \Omega \text{ cm}$ ($\text{Ln}=\text{Nd}$)) which shows a typical narrow-gap semiconductor-like behaviour.

4. Conclusion

The new family of $(\text{Cd,Ce})\text{Sr}_2(\text{Ln,Ce,Sr})_2\text{Cu}_2\text{O}_{9-\delta}$ ($\text{Ln}=\text{Y, Nd}$) was synthesized. The crystal structure of the two phases is similar to that of the Pb-1222

phase. A preliminary measurement shows that these compounds mentioned in the title are narrow-gap semiconductors in the temperature range of 296–16 K.

References

- [1] C. Martin, D. Bourgault, M. Hervieu, C. Michel, J. Provost and B. Raveau, *Mod. Phys. Lett. B* 3 (1989) 933.
- [2] S. Adachi, D. Inoue, S. Kawashima, H. Adachi, Y. Ichikawa, K. Setsune and K. Wasa, *Physica C* 168 (1990) 1.
- [3] Li Rukang, Zhu Yingjie, Qian Yitai and Chen Zuyao, *Physica C* 176 (1991) 19.
- [4] C.M. Niu, C.H. Kim, R. Kershaw, K. Dwight and A. Wold, *J. Solid State Chem.* 80 (1989) 201.
- [5] M.T. Andreas and A.I. Kingon, *Chem. Mater.* 3 (1991) 428.
- [6] K. Konstantinov and S. Karbanov, *Physica C* 165 (1990) 170.
- [7] Qian Yitai, Tang Kaibin, Yang Peidong, Chen Zuyao and Li Rukang, *Physica C* 209 (1993) 516.
- [8] J.B. Parise, N. Herron, M.K. Crawford and P.L. Gai, *Physica C* 159 (1989) 255.
- [9] 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 (1992) 47.
- [10] Li Rukang, Wu Xiao, Chen Zuyao, Qian Yitai, C. Zhu, H. Wei, S. Wang, J. Sha and J. Xia, *Phys. Lett. A* 144 (1990) 35.
- [11] T.P. Beales, C. Dineen, S.R. Hall, M.R. Harrison and J.M. Parberry, *Physica C* 207 (1993) 1.
- [12] H. Lipson, W.L. Bond, W. Cochran, B.F. Decker, A. Hargreaves, J. Kraut, C.E. Nordman and R.A.L. Sullivan, in: *International Tables for X-ray Crystallography*, Vol. 2, eds. J.S. Kasper and K. Lonsdale (Int. Union Crystallogr., Kluwer Press, Birmingham, UK, 1972) p. 237.