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Journal of Alloys and Compounds 228 (1995) 45–48

Journal of ALLOYS AND COMPOUNDS

Formation of the (Pb, Cd)-1212 phase in the $(Pb_{0.5}Cd_{0.5})Sr_2RCu_2O_7$ system

G.C. Che, Y.C. Lan, Z.X. Zhao

National Laboratory for Superconductivity, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 27 January 1995; in final form 14 March 1995

Abstract

The formation of the (Pb, Cd)-1212 phase in the $(Pb_{0.5}Cd_{0.5})Sr_2RCu_2O_7$ system was investigated systematically. It is found that the (Pb, Cd)-1212 phase can be formed for all R (R is a rare earth element) except La and Ce. The structure of $(Pb_{0.5}Cd_{0.5})Sr_2TbCu_2O_7$ is refined. The refined structure parameters are nearly the same as those of $(Pb_{0.5}Cd_{0.5})Sr_2YCu_2O_7$.

Keywords: (Pb,Cd)-1212 phase; HT superconductors

1. Introduction

After the discovery of the Pb-based superconductor $Pb_2Sr_2(Ca, Y)C_3O_8$ by Cava et al. [1], $(Pb, M)Sr_2(R_{1-x}Ca_x)Cu_2O_7$ (M is a divalent metal element, such as Cu, Cd, Zn, Hg and Sr; R is a rare earth element) has received much attention and careful investigations have been carried out. These have included exploring the reasonable synthesis conditions, finding the optimal ratio of Ca and Y, and carrying out different chemical substitutions, especially in the rock-salt-type (Pb, M)O layers [2–23].

Among the (Pb, M)-1212 family, (Pb, Cd)-1212 is comparatively easy to prepare as single-phase samples and exhibits good superconducting properties. In previous work, $(Pb, Cd)Sr_2(R, Ca)Cu_2O_7$, R ≡ Y and Lu, has been investigated [5,8,21,24–26].

In this work, we investigated systematically the formation of the (Pb, Cd)-1212 phase. The results are useful for the preparation of $(Pb, Cd)Sr_2(R, Ca)Cu_2O_7$ superconductors.

2. Experimental

Samples with the nominal composition $(Pb_{0.5}Cd_{0.5})Sr_2RCu_2O_7$ (R ≡ Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) were prepared by the conventional solid state reaction method. Stoichiometric powders of PbO, CdO, $SrCO_3$, CuO and rare earth oxides with purities higher than 99.9% were mixed by grinding in an agate mortar. The mixed powders were first sintered at 810–850 °C for 5–10 h in air. The products were reground and pressed into pellets, and sintered at 870–910 °C for 40 h. It should be noted that it is difficult to obtain single-phase $(Pb, Cd)Sr_2RCu_2O_7$ when R ≡ Tb, Yb. Their sintering temperature is relatively low (870 °C), and regrinding and resintering several times are necessary to form the single phase.

X-ray diffraction analysis was carried out on a MXP18Hf type diffractometer using Cu Kα radiation. The lattice parameters were determined using FINAX and LAZY programs. The structure refinement data were collected by the same diffractometer at ambient temperature. The scanning step was 0.02° in 2θ and the scanning time was 2 s per step. The 2θ range was 10°–110°.

3. Results and discussion

The X-ray powder diffraction patterns of $(Pb_{0.5}Cd_{0.5})Sr_2RCu_2O_7$ samples are shown in Fig. 1. It indicates that single-phase or nearly single-phase samples are obtained. It is observed that the weights of the samples have not changed significantly after sintering. Therefore, the sample compositions are still approximately stoichiometric.

From Fig. 1, it can be sen that (Pb, Cd)-1212 phases

SSDI 0925-8388(95)01637-6

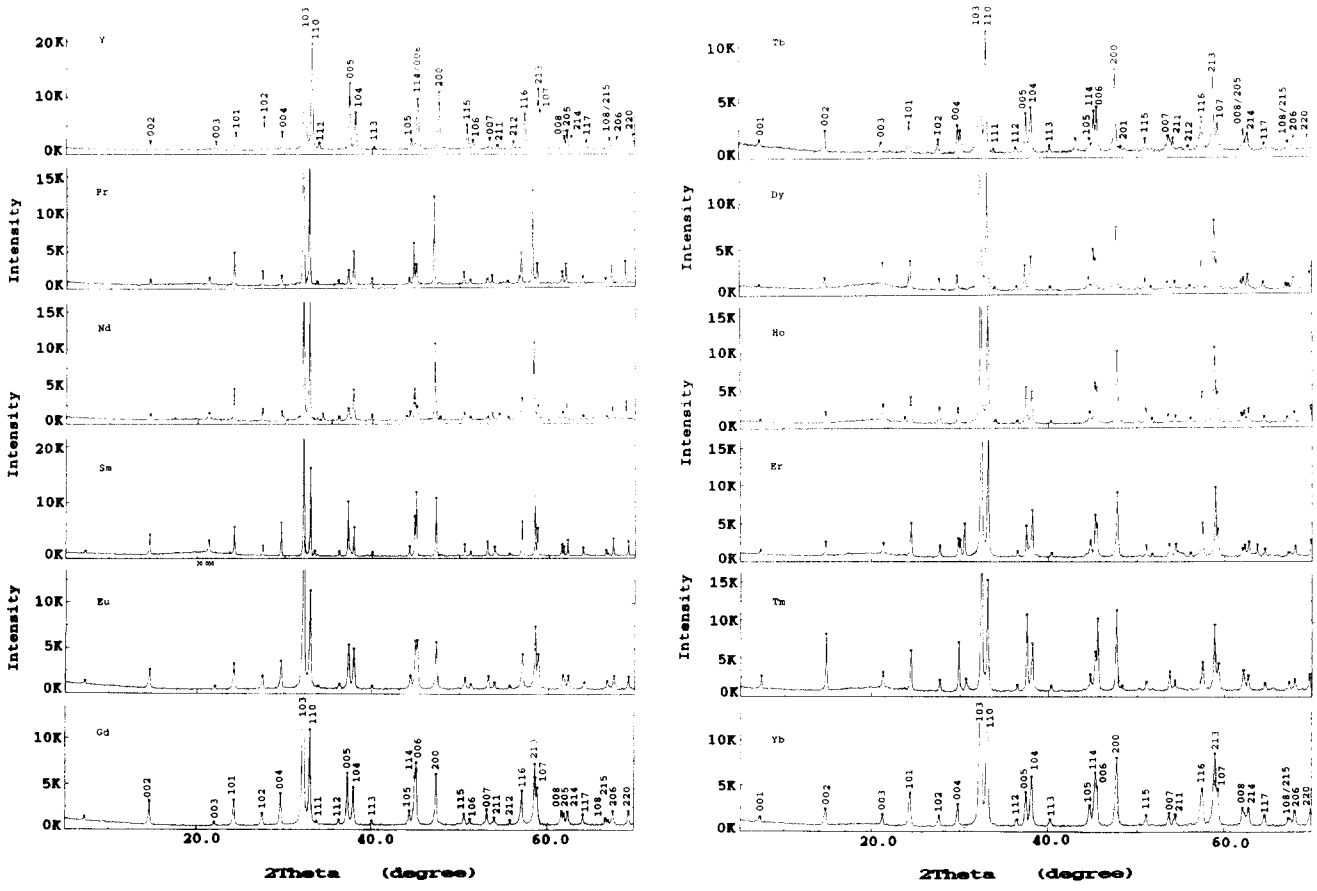

Fig. 1. X-ray powder diffraction patterns of the (Pb, Cd)-1212 phase in the $(Pb_{0.5}Cd_{0.5})Sr_2RCu_2O_7$ system.

can be formed for all R except La and Ce. The formation of the (Pb, Cd)-1212 phase in the $(Pb_{0.5}Cd_{0.5})Sr_2RCu_2O_7$ system is different from that of 123 phases in the $RBa_2Cu_3O_7$ system. It is well known that Ce-123 and Tb-123 phases cannot be formed. however, in the (Pb, Cd)$Sr_2RCu_2O_7$ system, the (Pb, Cd)-1212 phase can be formed for Tb, although the structure of the (Pb, Cd)-1212 phase is very similar to that of R-123.

According to the structure model of 1212 type cuprates, such as $TlBa_2CaCu_2O_7$, (Pb, Cu)-1212 and $(Pb_{0.5}Cd_{0.5})Sr_2(R, Ca)Cu_2O_7$ [27], we refined the structure of $(Pb_{0.5}Cd_{0.5})Sr_2TbCu_2O_7$ (Tb-1212) to make a definite diagnosis of this structure and its composition. Refined structure parameters obtained by the Rietveld method are listed in Table 1, and a schematic representation of the Tb-1212 structure is shown in Fig. 2.

The structure refinement results show that the structure parameters for $(Pb_{0.5}Cd_{0.5})Sr_2TbCu_2O_7$ are nearly the same as those for $(Pb_{0.5}Cd_{0.5})$-$Sr_2(Y, Ca)Cu_2O_7$ [26].

Table 2 and Fig. 3 show the lattice constants a, c and the unit cell volume V of the (Pb, Cd)-1212 phase in the $(Pb_{0.5}Cd_{0.5})Sr_2RCu_2O_7$ system. Fig. 3 shows that the lattice constants decrease with an increase in the atom number of R. However, the lattice parameter c of $(Pb_{0.5}Cd_{0.5})Sr_2TbCu_2O_7$ is anomalously small. We have not found a reasonable explanation for this anomaly.

Table 1
Refined structure parameters for $(Pb_{0.5}Cd_{0.5})Sr_2TbCu_2O_7$, tetragonal system with $a = 3.822$ Å, $c = 11.951$ Å, space group $P4/mm$, $R_p = 6.15\%$, $R_{wp} = 7.45\%$, $R_{exp} = 3.74\%$

Atom	Site	X	Y	Z	g	B(Å^2)
Pb/Cd	4l	0.068	0	0	0.25	0.2
Sr	2h	0.5	0.5	0.208	1	0.5
Tb	1d	0.5	0.5	0.5	1	0.5
Cu	2g	0	0	0.360	1	0.5
O(1)	4i	0	0.5	0.375	1	1
O(2)	2g	0	0	0.164	1	1
O(3)	4n	0.332	0.5	0	0.25	1

4. Conclusion

The formation of the (Pb, Cd)-1212 phase in the $(Pb_{0.5}Cd_{0.5})Sr_2RCu_2O_7$ system was investigated systematically. It is found that the (Pb, Cd)-1212 phase can be formed for all R except La and Ce. The structure of $(Pb_{0.5}Cd_{0.5})Sr_2TbCu_2O_7$ was refined. The refined structure parameters of

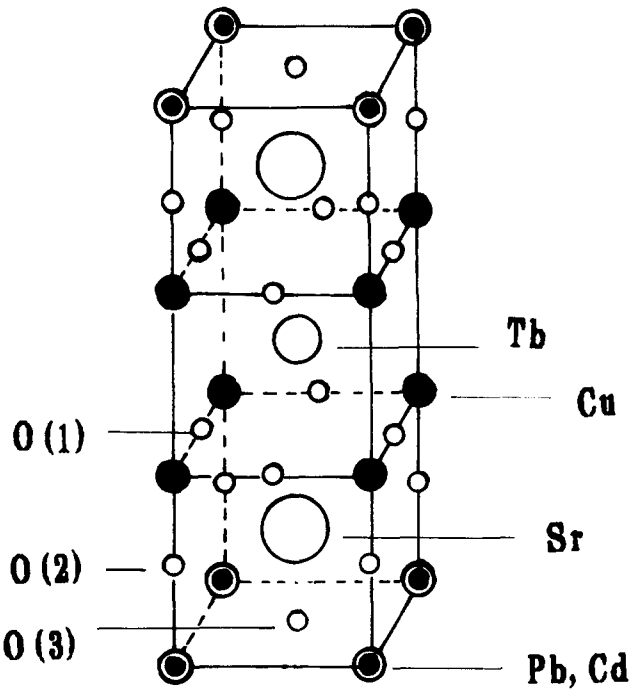

Fig. 2. Schematic representation of the crystal structure of $(Pb_{0.5}Cd_{0.5})Sr_2TbCu_2O_7$.

Table 2
Lattice parameters of $(Pb_{0.5}Cd_{0.5})Sr_2RCu_2O_7$ samples sintered at 910 °C in air

R	a(Å)	c(Å)	V(Å^3)
Pr	3.857	12.07	179.6
Nd	3.853	12.06	179.0
Sm	3.859	12.07	177.9
Eu	3.856	12.04	177.1
Gd	3.830	12.04	176.6
Tb	3.822	11.95	174.6[a]
Dy	3.816	12.01	174.8
Y	3.813	12.01	174.7
Ho	3.812	11.98	174.1
Er	3.809	11.97	173.6
Tm	3.803	11.96	172.9[a]
Yb	3.810	11.97	173.8[a]

[a] Sintered at 840 °C.

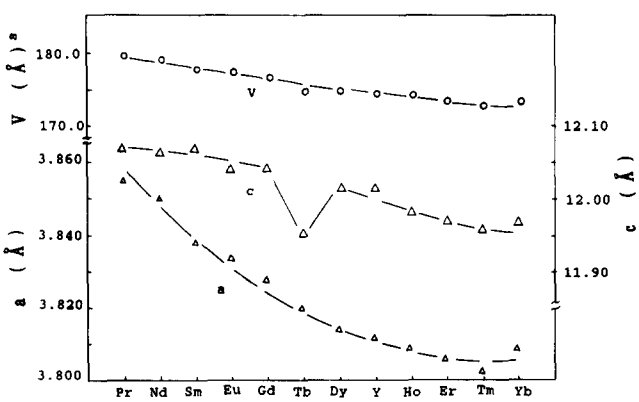

Fig. 3. Changes in the lattice parameters a, c and unit cell volume V in the $(Pb_{0.5}Cd_{0.5})Sr_2RCu_2O_7$ system.

$(Pb_{0.5}Cd_{0.5})Sr_2TbCu_2O_7$ are nearly the same as those of $(Pb_{0.5}Cd_{0.5})Sr_2YCu_2O_7$.

Acknowledgement

The authors would like to thank senior technician T.S. Ning for recording X-ray diffraction patterns.

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