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Phase Formation and Structure of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ $(R_E=La,Pr; M=Ca,Sr)$

The samples of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ are prepared by solid state reaction method. The single phase boundary of R_E and M in $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ is 1.0~2.0 and 0~1.0 respectively. In $(Pr,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$, the phase boundary of Sr is 0~1.0. The structure of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ belongs to the structure type of 212 cuprate superconductors with space group I4/mmm.

Keywords: phase formation, structure, cuprate

1. Introduction

SHAPLYGIN et al. reported on the synthesis of compounds with the formaula $(La,Sr)_2CuO_{4+\delta}$ (SHAPLYGIN et al.). Raveau et al. in have reported on the preparation and characterization of the series of compounds with the formula $La_{2-x}A_{1+x}Cu_2O_{6-x/2+\delta}$ (La212) , where A=Ca,Sr (NGUYEN et al., MICHEL et al., DOVERSPIKE et al.). These compounds represent oxygen defect intergrowths of compounds crystallizing with the $Sr_3Ti_2O_7$ structure.

After the first synthesis of $La_{2-x}Ca_{1+x}Cu_2O_6$, the structure and phase formation have been extensively investigated (DOVERSPIKE et al., IDEMOTO et al., IZUMI et al.), because it was expected to become superconducting with Tc around 60~90 K when appropriately doped as its structure contains two CuO_2 layers separated by a Ca^{2+} sheet. Finally, Cava et al. succeed in inducing superconductivity with Tc=60 K by annealing the synthesized compounds in high pressure oxygen (CAVA et al.). Following Cava's discovery, several studies have also induced superconductivity to La212 by changing composition, annealing in different high pressure oxygen or oxidized with $KMnO_4$ (ADACHI et al., KINOSHITA et al., LIU et al., SAKURAI et al.).

The structure and phase formation in La212 have been extensively investigated because superconductivity has continued to be of interest as it is a simplest double layer 212 type superconductor (CAVA et al., CHE et al.).

In order to search a new superconductor in typical 212 type compounds and furtherly study the relations between superconducting mechanism and structure, it is necessary to investigate the phase formation and structure of R_E212 type compounds with different rare earth element. This paper investigated the phase formation of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ $(R_E=Pr,La)$ and their structure.

2. Experimental

Samples of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ are prepared by solid state reaction method. The starting material are $SrCO_3$, $CaCO_3$, CuO, Pr_6O_{11} and La_2O_3 with purity >99.9%. Pr_6O_{11} and La_2O_3

were calcinated at 850-900 °C for 20~30 h in air in order to eliminate absorbed or chemically bound impurities. Then the starting material were weighed, mixed, ground and calcinated at 920°C for 25h. The materials were re-ground thoroughly and pressed into pellets. The pellets were sintered at 980~1030°C for 40h and cooled slowly to room temperature in air.

X-ray diffraction analyses (XRD) were performed on a MXP18A-HF type diffractometer with CuKα-radiation. RIETVELD, FINAX and LAZY programs were used for the lattice parameter and the structure determination. The traditional four-probe technique was used for the electrical resistance measurements.

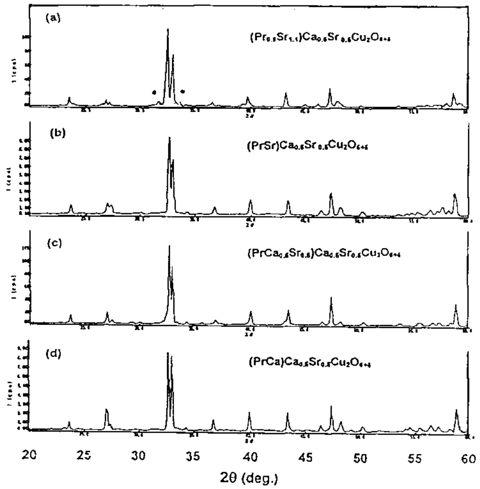

Fig. 1: The XRD pattern of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$

3. Results and Discussion

3.1 Phase formation of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$

Fig.1 shows the typical XRD pattern of $La_{2-x}Ca_{1+x}Cu_2O_{6+\delta}$ (CAVA et al.). The other parts of Fig.1 contain the XRD patterns of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$. From Fig.1 it can be seen that single or nearly single phase samples are obtained and the 212 type compounds can be formed in $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$. Fig.1 shows that a purer phase of typical 212 type compounds occurs with the increase of content of R_E (R_E=Pr or Pr and La). A little of $(La,Pr,Sr,Ca)_2CuO_{4+\delta}$ phase (with marks of asterisks) appears when the content of R_E decreases to 0.9. So the phase boundary of R_E in $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ is 2.0~1.0 .Fig.1 also shows that there is a purer phase of 212 type compounds with the decrease of content of M (M=Ca,Sr).

Fig. 2 contains the XRD patterns of $(Pr,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ (M=Ca,Sr). It shows there is a purer phase of typical 212 type compounds with the decrease of content of Sr. A little of $(La,Pr,Sr,Ca)_2CuO_{4+\delta}$ phase appears when the content of Sr increases to 1.1 . So the phase boundary of Sr in $(Pr,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ is 0~1.0 .

3.2 Structure Analyses

The crystallographic unit cell of $La_{2-x}Ca_{1+x}Cu_2O_{6+\delta}$ is body-centered tetragonal with a=3.825 and c=19.428 (x=0.25) (CAVA et al., LIANG et al.). Our study of the XRD patterns indicates that the symmetry and lattice centering are maintained in the solid solution compounds $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$. Table 1 lists the lattice parameters of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$. It is found that the lattice parameters of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ are larger than those of $La_{2-x}Ca_{1+x}Cu_2O_{6+\delta}$. This may come from the radii of Pr^{3+} ions and Sr^{2+} ions which are larger than those of La^{3+} and Ca^{2+}, respectively.

Samples No.	Formula	a(Å)	c(Å)	V(Å^3)
1	$(Pr_{0.8}La_{1.2})Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$	3.8361	19.5351	287.48
2	$(Pr_{1.5}La_{0.2}Sr_{0.3})Ca0_{.5}Sr_{0.5}Cu_2O_{6+\delta}$	3.8370	19.6218	288.88
3	$(Pr_{1.5}Sr_{0.5})Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$	3.8408	19.6498	289.86
4	$(Pr_{1.2}Ca_{0.5}Sr_{0.3})Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$	3.8342	19.5291	287.08
5	$(PrSr)Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$	3.8361	19.5620	287.86
6	$(PrCa_{0.5}Sr_{0.5})Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$	3.8333	19.6166	288.25
7	$(PrCa)Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$	3.8386	19.5790	288.49

Table 1: The lattice parameters of $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$

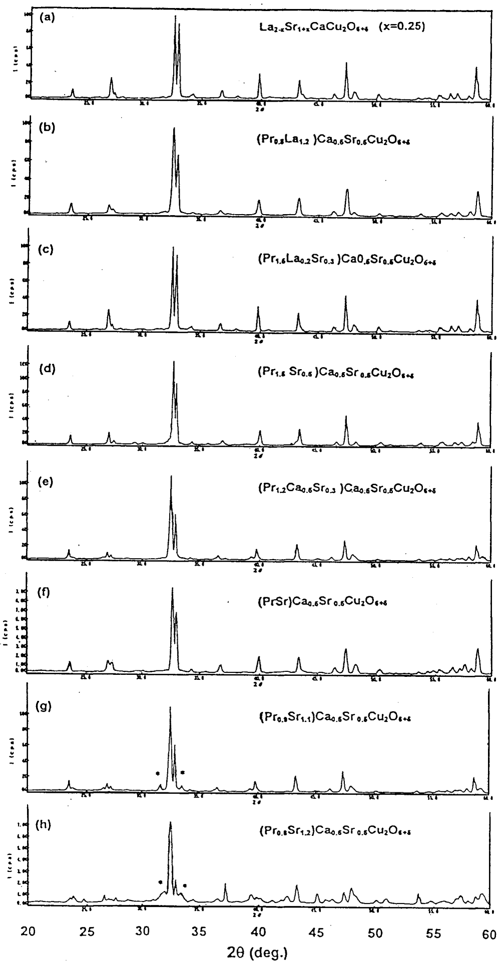

Fig. 2: The XRD pattern of $(Pr,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$

Based on the structure models for $(La,Sr)_2CaCu_2O_{6+\delta}$ reported (Cava et al., Idemoto et al., Liu et al., Kinoshita et al., Sakurai et al.), the crystal structure refinements are made with the Rietveld and LAZY programs by us. Table 2 shows the crystallographic parameters adopted by us. Fig.3 shows the structure representation of $(Pr_{1.5}Sr_{0.5})Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ .The calculated and observed peak intensities and interplane distance values, d, are given in Table 3. The discrepancy (R) factor ($\sum | I_{obs} - I_{cal} | / \sum I_{obs}$) of the refinement was 3.9 %. Table 3 indicates the good agreement between the observed and calculated patterns obtained for $(Pr_{1.5}Sr_{0.5})Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$, which supports the idea that the structure being similar to $La_{2-x}Ca_{1+x}Cu_2O_{6+\delta}$ is correct.

Element	Site	X/A	Y/B	Z/C	Occ.	B(Å^2)
Ca^{2+}	2a	0	0	0	0.500	0.700
Sr^{2+}	2a	0	0	0	0.500	0.700
Pr^{3+}	4e	0	0	0.176(2)	0.750	0.750
Sr^{2+}	4e	0	0	0.176(2)	0.250	0.750
Cu^{2+}	4e	0	0	0.590(7)	1.00	0.650
$O^{2-}(1)$	8g	0	0.5	0.082(5)	1.00	1.200
$O^{2-}(2)$	4e	0	0	0.702(7)	1.00	1.500

Table 2: The atom positions in $(Pr_{1.5}Sr_{0.5})Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$

h	k	l	d_{obs}	d_{cal}	I_{obs}	I_{cal}
1	0	1	3.7702	3.7644	58.8	53.6
1	0	3	3.3078	3.3064	225.9	246.3
0	0	6	3.2587	3.2603	45	42
1	0	5	2.7385	2.7391	1000	1000
1	1	0	2.6998	2.7125	751.1	745.1
1	1	2	2.6205	2.6139	60.1	61.3
0	0	8	2.4438	2.4453	88.5	79.7
1	1	4	2.3768	2.3721	12.5	16.1
1	0	7	2.2601	2.2588	202.9	211.1
1	1	6	2.0860	2.0852	211.9	200.8
0	0	10	1.9523	1.9562	48	46.6
2	0	0	1.9211	1.9181	420.8	403.3
1	0	9	1.8927	1.8911	118.7	128.8
2	0	2	1.8820	1.8822	1.0	2.0
1	1	8	1.8139	1.8162	60.8	62.3
2	0	4	1.7871	1.7856	18.0	25.9
2	1	1	1.7102	1.7090	10.2	11.4
2	1	3	1.6573	1.6591	80.8	72.4
2	0	6	1.6520	1.6532	32.9	28.1
0	0	12	1.6318	1.6302	67.5	61.4
1	0	11	1.5159	1.6134	50.2	38.6
1	0	10	1.5902	1.5866	68.2	57.8
2	1	5	1.5728	1.5711	331.8	346.4

Table 3: The calculated and observed peak intensities and interplane distance values, d, of $(Pr_{1.5}Sr_{0.5})Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$
a = b = 3.8408 Å, c= 19.6498 Å, V= 287.86 Å^3 , S.G.= I4/mmm
$R = \sum | I_{obs} - I_{cal} | / \sum I_{obs} = 3.9$ %

Because $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ has the same structure as $La_{2-x}Ca_{1+x}Cu_2O_{6+\delta}$, $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ may be a candidate for a superconductor if the proper carrier concentration is achieved. The temperature dependence of the normalized resistance for

$(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ shows that these samples are semiconductors with a narrow gap. When the samples was annealed in flowing O_2 gas, their room-temperature resistivity are far smaller than those of samples only synthesized in air. Taking into consideration that the La212 type cuprates become superconductors when treated under high pressure oxygen, we are expecting that the $(R_E,M)_2Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$ become new superconductors under proper high pressure oxygen and heat treatments.

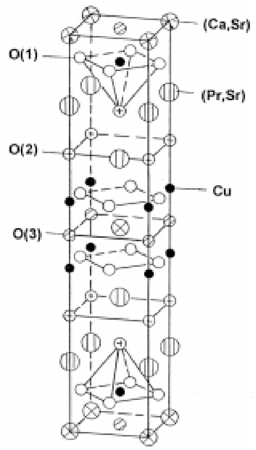

Fig. 3: The structure representation of $(Pr_{1.5}Sr_{0.5})Ca_{0.5}Sr_{0.5}Cu_2O_{6+\delta}$

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