

## Characterization of a new Fe-1222 layered cuprate, $\text{FeSr}_2(\text{LnCe})_2\text{Cu}_2\text{O}_y$

Li Rukang, Zhu Yingjie, Zhang Daoyuan\*, Xu Chen<sup>†</sup>, Qian Yitai,  
Chen Zuyao and Zhou Guien<sup>†</sup>

Department of Applied Chemistry, \*Department of Physics, University of Science and  
Technology of China, <sup>†</sup>Structure Research Laboratory of Chinese Academy of Sciences,  
Hefei, Anhui 230026 (China)

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### Abstract

Four compounds in the  $\text{FeSr}_2(\text{LnCe})_2\text{Cu}_2\text{O}_y$  ( $\text{Ln} \equiv \text{Y, Nd, Sm, Dy}$ ) system have been prepared and characterized. The structure of the compounds is found to be the same as that of the Ti-, Pb-, Cu- and Ta-1222 phases. Typical cell parameters are obtained as  $a = 3.833 \text{ \AA}$  and  $c = 28.157 \text{ \AA}$  for the sample with  $\text{Ln} \equiv \text{Dy}$ , with a body-centred lattice and space group  $I4/mmm$ . Long-range magnetic order has not been detected by Mössbauer spectroscopy at room temperature.

### 1. Introduction

Most of the layered cuprates have been found to be high  $T_c$  superconductors since their first discovery [1]. Recently, one of us has found that all the layered cuprates can be classified as being composed of three basic block units, namely a  $\text{CuO}$  layer, connecting and separating layers [2]. In accordance with this classification, we have designed and succeeded in preparing a Ta-1222 compound  $\text{TaSr}_2(\text{NdCe})_2\text{Cu}_2\text{O}_y$  [3] which possesses a similar structure to that of  $\text{TiBa}_2(\text{LnCe})_2\text{Cu}_2\text{O}_y$  [4]. The main feature of the Ta-1222 structure is that it contains a connecting layer of perovskite,  $\text{SrTaO}_3$ , which links two  $\text{CuO}_5$  pyramid planes. In order to find more layered cuprates, a systematic search for other connecting layers has been performed in this laboratory [5].

In 1989 Sunshine *et al.* reported that doping other elements (iron, cobalt, aluminium, lead) into the copper sites may stabilize the formation of the Sr-123 (or 1212)  $\text{YSr}_2\text{Cu}_3\text{O}_7$  [6] phase, which cannot be formed under normal conditions. In addition, many doping experiments on  $\text{YBa}_2\text{Cu}_3\text{O}_y$  further concluded that the  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$  and  $\text{Al}^{3+}$  ions are mainly concentrated on the  $\text{Cu}(1)$  chain site [7]. Thus the  $\text{FeO}$ ,  $\text{CoO}$  and  $\text{AlO}$  layers which link the two  $\text{CuO}_5$  planes can also act as connecting layers in our view. A recent report on the Fe-1232 layered compound  $(\text{FeCu})\text{Sr}_2(\text{HoCe})_3\text{Cu}_2\text{O}_y$  [8] agrees with this opinion. Therefore layered M-1222  $\text{MSr}_2(\text{LnCe})_2\text{Cu}_2\text{O}_y$  ( $\text{M} \equiv \text{Fe, Co, Al}$ ) phases may also exist. In the present paper we report the preparation and characterization of the Fe-1222 compounds.

## 2. Experimental details

Samples with nominal compositions  $\text{FeSr}_2(\text{LnCe})_2\text{Cu}_2\text{O}_y$  ( $\text{Ln} \equiv \text{Y}$ , rare earth elements) were prepared by solid state reaction using the starting compounds  $\text{Fe}_2\text{O}_3$  (99.5% purity),  $\text{SrCO}_3$  (99%),  $\text{CuO}$  (99%) and the corresponding rare earth oxides (all higher than 99.5% purity) in stoichiometric ratios. The mixtures were well ground and preheated to 950 °C for 24 h in alumina crucibles followed by fast cooling to room temperature. The samples were ground again, pelletized into discs and further sintered at 1000 °C for 24–48 h. X-ray powder diffraction patterns of the samples were recorded in a Rigaku Dmax  $\gamma_A$  diffractometer with high intensity  $\text{Cu K}\alpha$  radiation and a graphite monochromator was set at the scattering beam path. To accurately determine the lattice parameters, the patterns were recorded at a scan rate of 0.05 deg s<sup>-1</sup> in the  $2\theta$  range from 3° to 65° and  $\text{KCl}$  was used as internal standard. The resistivities of the samples were measured by the standard four-probe method with soldered indium contacts in a helium cryostat down to 20 K. Mössbauer spectra were collected on a Model M-500 conventional constant-acceleration spectrometer operated in conjunction with a Canberra series 35 multichannel analyser. A 10 mCi  $^{57}\text{Co}$ –Rh matrix  $\gamma$  ray source was used. The isomer shifts were corrected relative to metallic iron. Selected area electron diffraction patterns were obtained in a Hitachi Model H-800 transmission electron microscope.

## 3. Results and discussion

The X-ray diffraction (XRD) pattern (Fig. 1(b)) of the  $\text{FeSr}_2(\text{NdCe})_2\text{Cu}_2\text{O}_y$  sample revealed that our first attempt at preparation was successful. It is similar to that of the corresponding Ta-1222 compound (Fig. 2) except for several peaks due to the 123 or Fe-1212 phase. These peaks cannot be removed by longer heating or treatment in oxygen. Thus we tried to prepare purer 1222 phase by using other rare earth ions with different radii, *e.g.* yttrium, dysprosium and samarium. It has been found that better purity can be obtained in particular for the composition  $\text{FeSr}_2(\text{DyCe})_2\text{Cu}_2\text{O}_y$  (Fig. 1(a)). On the basis of the space group  $I4/mmm$ , the XRD patterns can be indexed (Table 1) and refined by the least-squares method with the cell parameters  $a = 3.859$  Å and  $c = 28.294$  Å for  $\text{Ln} \equiv \text{Nd}$ , 3.833 and 28.157 Å for  $\text{Ln} \equiv \text{Dy}$  and 3.827 and 28.21 Å for  $\text{Ln} \equiv \text{Y}$ . The decreases in the  $a$  parameters and cell volumes are consistent with the decrease in the  $\text{Ln}^{3+}$  ion radii. Figure 3 gives the electron diffraction patterns of the sample with  $\text{Ln} \equiv \text{Nd}$ . From the pattern in the (010) direction one gets the cell parameters  $a = 5.6$  Å and  $c = 28$  Å, which means a unit cell with  $a = 2^{1/2}a_p$  must be chosen relative to the primitive unit cell ( $a_p$ ) of perovskite. The (001) $c$  zone diffraction pattern is even more complicated: the appearance of  $(\frac{1}{2}, \frac{1}{2}, 0)$  and  $(\frac{1}{4}, \frac{1}{4}, 0)$  spots means that a tetragonal supercell with  $a = 2^{3/2}a_p$  must be chosen. Since

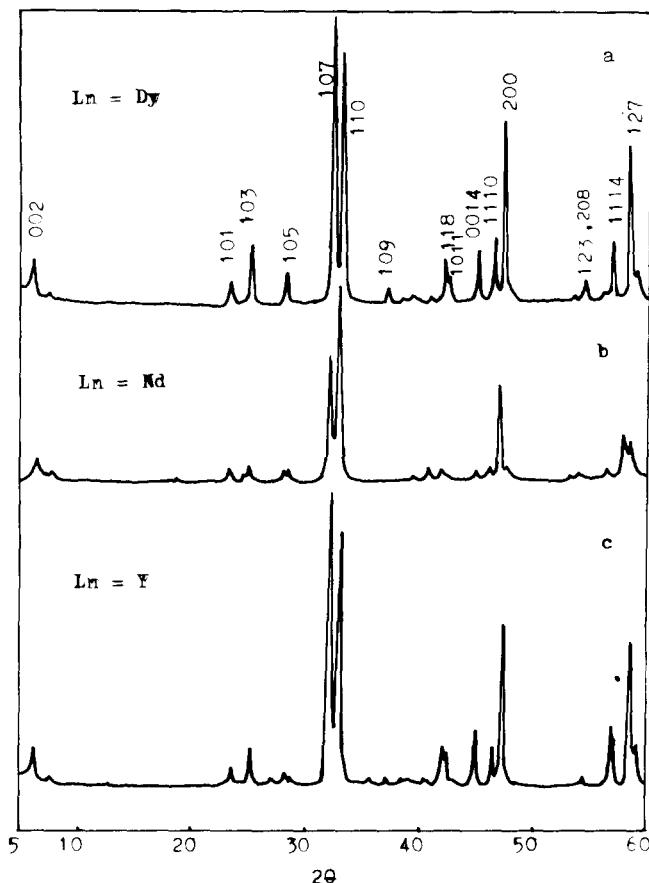


Fig. 1. X-ray powder diffraction patterns of  $\text{FeSr}_2(\text{LnCe})_2\text{Cu}_2\text{O}_y$ .

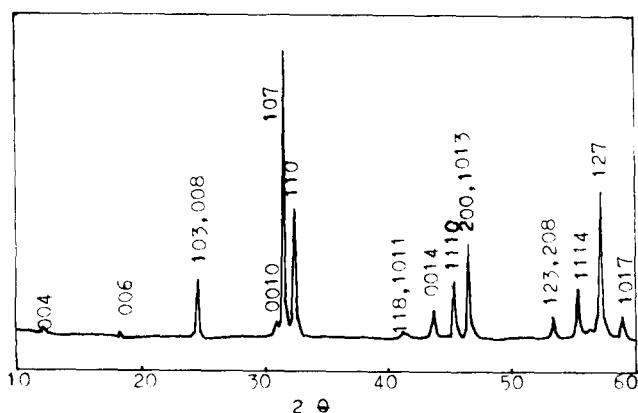


Fig. 2. X-ray powder diffraction pattern of  $\text{TaSr}_2(\text{NdCe})_2\text{Cu}_2\text{O}_y$ .

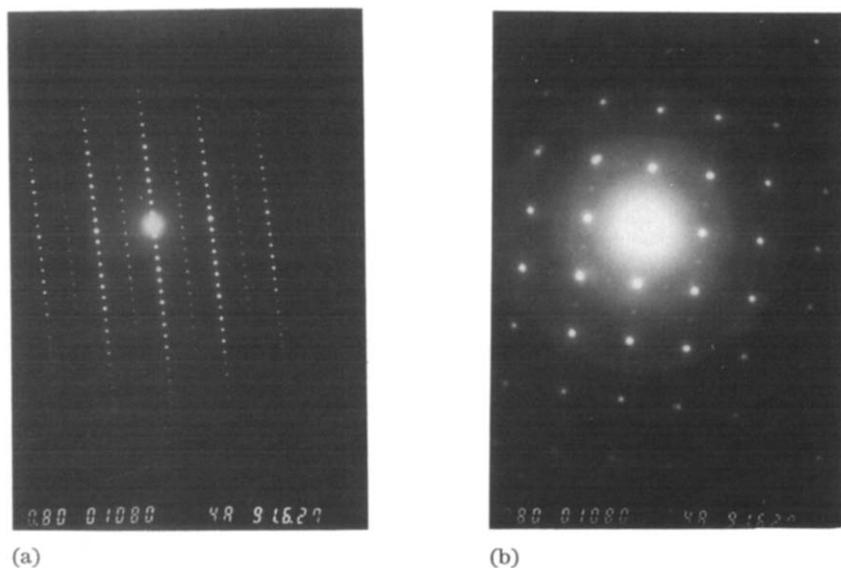
TABLE 1

Calculated and observed XRD peaks of  $\text{FeSr}_2(\text{DyCe})_2\text{Cu}_2\text{O}_y$  with space group  $I4/mmm$ ,  $a = 3.833 \text{ \AA}$ ,  $c = 28.157 \text{ \AA}$  and  $Z = 2$

$h \ k \ l$	$d_c (\text{\AA})$	$d_0 (\text{\AA})$	$I_0$
0 0 2	14.08	14.17	19.3
1 0 1	3.798	3.800	6.9
1 0 3	3.549	3.548	13.4
1 0 5	3.169	3.170	8.0
1 0 7	2.775	2.775	100
1 1 0	2.710	2.709	56.2
1 0 9	2.424	2.422	5.5
1 1 6 } 0 0 12 }	2.347 } 2.346 }	2.346	2.6
1 1 8	2.147	2.147	9.8
1 0 11	2.129	2.126	6.6
0 0 14	2.011	2.011	9.6
0 0 10	1.953	1.953	14.6
2 0 0	1.917	1.916	30.7
2 0 2	1.899	1.897	5.6
2 0 6 } 1 1 12 }	1.774 } 1.774 }	1.775	3.6
1 2 1	1.711	1.711	3.8
1 2 3 } 2 0 8 }	1.686 } 1.683 }	1.685	6.0
1 2 5	1.640	1.640	4.3
1 1 14	1.615	1.615	14.3
1 2 7	1.577	1.576	29.2
0 0 18	1.564	1.564	8.0
1 0 17	1.520	1.521	6.1
1 2 9	1.503	1.502	4.1

such spots have not been observed in the Ta-1222 phase, the supercell must be assigned to an ordered arrangement of oxygen vacancies or an ordered occupation of copper and iron ions in the (110) direction. The small difference in scattering factor between iron and copper prevents us from determining whether the Fe and Cu atoms are randomly occupied or completely ordered.

The Mössbauer spectrum of  $\text{FeSr}_2(\text{YCe})_2\text{Cu}_2\text{O}_y$  is shown in Fig. 4. The four-peak splitting of the spectrum suggests that the iron ions in the compound are in at least two different environments. On the basis of the fitted parameters (Table 2), it may be concluded that the small quadrupole splitting is contributed by  $\text{Fe}^{3+}$  (HS) at the Cu(2) site and the larger splitting is due to  $\text{Fe}^{4+}$  or  $\text{Fe}^{3+}$  (LS) at a tetragonal or square planar coordinated site according to the assignment of ref. 9. The result of nearly 1:2 occupation of iron ions infers that the iron ions are almost homogeneously distributed at the Cu(1) and Cu(2) sites, which is different from the conclusions drawn from the Mössbauer spectra of the iron partially substituted 123 compounds [7]. Thus the semiconducting behaviour of all the samples (Fig. 5) may be due to the



(a)

(b)

Fig. 3. Electron diffraction patterns of  $\text{FeSr}_2(\text{DyCe})_2\text{Cu}_2\text{O}_y$ : (a) (010) zone pattern; (b) (001) $c$  zone pattern.

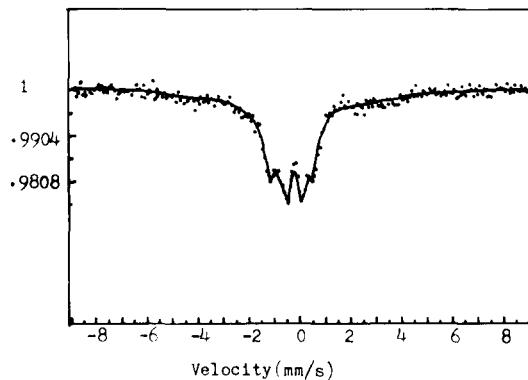


Fig. 4. Mössbauer spectrum of  $\text{FeSr}_2(\text{YCe})_2\text{Cu}_2\text{O}_y$ .

TABLE 2

Fitted parameters of Mössbauer spectra of  $\text{FeSr}_2(\text{LnCe})_2\text{Cu}_2\text{O}_y$

Ln	$IS_1$ (mm $\text{s}^{-1}$ )	$QS_1$ (mm $\text{s}^{-1}$ )	$IS_2$ (mm $\text{s}^{-1}$ )	$QS_2$ (mm $\text{s}^{-1}$ )	$A_1/A_2$ (%)
Dy	0.146	1.88	0.207	0.75	40
Nd	0.196	1.36	0.243	0.65	24
Y	0.167	1.65	0.247	0.58	74

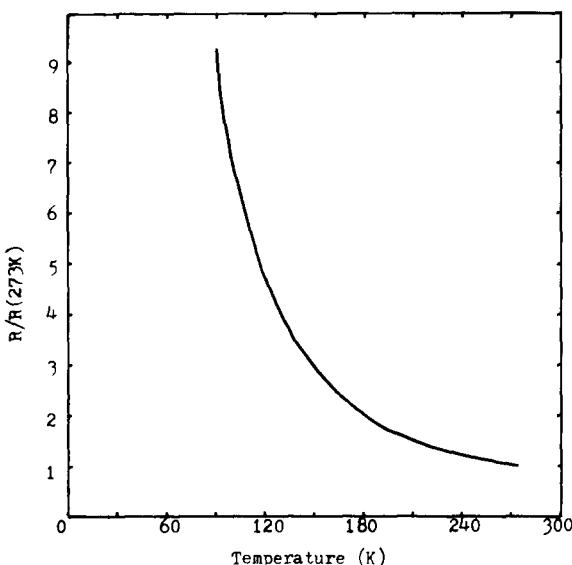


Fig. 5. Temperature-dependent resistivity of a typical  $\text{FeSr}_2(\text{DyCe})_2\text{Cu}_2\text{O}_y$  sample.

mobile carrier localization caused by the substitution of iron ions at copper sites or by the oxygen vacancies in the CuO planes.

#### 4. Conclusions

We have prepared mixed Fe–Cu layered compounds of the system  $\text{FeSr}_2(\text{LnCe})_2\text{Cu}_2\text{O}_y$  ( $\text{Ln} \equiv \text{Nd, Sm, Dy, Y}$ ) which have the 1222 structure. Since the pure cuprate  $\text{CuSr}_2(\text{LnCe})_2\text{Cu}_2\text{O}_y$  cannot be formed in the 1222 structure, we may conclude that the substitution of copper by iron can also stabilize the 1222 phase as has already been demonstrated for the 1212 and 1232 phases.

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