Lanthanoid Substitution in $Sr_2YCu_2FeO_{6+\delta}$ System

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Abstract

The $Sr_2YCu_2FeO_{6+\delta}$ compound exhibits superconductivity around 50 K. We have synthesized the single phase sample of $Sr_2LnCu_2FeO_{6+\delta}$ (Ln=Nd, Er) where Ln is substituted for Y in $Sr_2YCu_2FeO_{6+\delta}$. While $Sr_2ErCu_2FeO_{6+\delta}$ exhibits superconductivity, $Sr_2NdCu_2FeO_{6+\delta}$ does not exhibit superconductivity. We have analyzed the crystal structure of $Sr_2LnCu_2FeO_{6+\delta}$ to compare with that of $Sr_2YCu_2FeO_{6+\delta}$ using X-ray and neutron powder diffraction. From these studies it was found that Cu was substituted for Fe and similarly Sr for Ln in $Sr_2NdCu_2FeO_{6+\delta}$, resulting in a severe reduction of T_c in this system.

Key words: Fe1212; magnetic superconductor; crystal structure; neutron diffraction

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1. Introduction

Superconductivity has been discovered around 50 K in $Sr_2YCu_2FeO_{6+\delta}$[1,2]. This compound exhibits superconductivity, only when it is properly annealed in N_2 atmosphere and subsequently in O_2 atmosphere. It has been shown by neutron powder diffraction study that N_2-annealing causes ordering of Cu and Fe atoms, and that O_2-annealing supplies the charge on the CuO_2 sheets. Although it is possible to substitute other lanthanoid elements for Y in $Sr_2YCu_2FeO_{6+\delta}$ like $Ba_2YCu_3O_{6+\delta}$, $Sr_2NdCu_2FeO_{6+\delta}$ does not exhibit superconductivity with the same annealing process as superconducting $Sr_2YCu_2FeO_{6+\delta}$. Therefore, we have performed the X-ray and neutron powder diffraction to investigate the difference in the crystal structure between superconducting $Sr_2LnCu_2FeO_{6+\delta}$ (Ln = Y and Er) and nonsuperconducting $Sr_2NdCu_2FeO_{6+\delta}$.

2. Experimantal

Samples were prepared by the solid-state reaction of stoichiometric mixture of $SrCO_3$, Ln_2O_3 (Ln = Y, Nd and Er), CuO and Fe_2O_3 powders. The mixture was calcined at 900°C for 24 h in air, ground and then pressed into pellets. The pellets were sintered at 1000°C for 24 h in air. The samples were subsequently annealed at 800°C for 24 h in an N_2 flow, at 300°C for 24 h in an O_2 flow, and finally at 350°C for 24 h in high oxygen pressure of 190 atm. The samples were characterized by X-ray and neutron powder diffraction, magnetic susceptibility and resistivity. Neutron diffraction were performed with high-resolution powder diffractometer, HRPD, at the research reactor, JRR-3M, in the Japan Atomic Energy Research Institute. The intensity data were collected using cold neutron radiation with wave length of 0.1825 nm in the case of $Sr_2YCu_2FeO_{6+\delta}$ and of 0.1823 nm in the case of $Sr_2LnCu_2FeO_{6+\delta}$ (Ln = Nd and Er) at room temperature.

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3. Structure Refinements

The structure of the $Sr_2LnCu_2FeO_{6+\delta}$ compounds was refined using the Rietveld refinement program RIETAN[3] on the basis of the tetragonal $Ba_2YCu_3O_{6+\delta}$-type structure model. The atomic coordinates are

Sr	in 2h: $\frac{1}{2}\ \frac{1}{2}\ z$,
Y	in 1d: $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$,
Cu(1), Fe(1)	in 1a: 0 0 0,
Cu(2), Fe(2)	in 2g: 0 0 z,
O(1)	in 2f: 0 $\frac{1}{2}$ 0,
O(2)	in 2g: 0 0 z,
O(3)	in 4l: 0 $\frac{1}{2}$ z.

The intensity data for the 2θ region between 20^o and 155^o were used for the refinement. Preliminary refinements revealed that the O(1) atom was shifted from 2f site (0, $\frac{1}{2}$, 0) to twofold split 4n site (x, $\frac{1}{2}$, 0) in all samples. This indicates that those atoms have large thermal motion in the ab-plane. In table 1 the final R factors, the lattice and structure parameters and their standard deviations are listed.

4. Discussion

The $Sr_2ErCu_2FeO_{6+\delta}$ compound has almost same structure as the $Sr_2YCu_2FeO_{6+\delta}$ compound. However, the $Sr_2NdCu_2FeO_{6+\delta}$ compound has the different structure from that, because R factors are reduced from $R_{wp} = 10.31\%$ to 8.91% by introduction of the O(4) site at (0, 0, $\frac{1}{2}$) between double CuO_2 sheets. This indicates that the CuO_2 sheets in the $Sr_2NdCu_2FeO_{6+\delta}$ compound may be disordered like $Nd_{2-x}Sr_{1+x}CuO_{6-\delta}$[4]. Moreover, larger thermal parameter of the O(3) site, $B_{O(3)}$, shows that the O(3) site may be deficient. Although neutron diffraction can not distinguish positions between Sr and Nd because the scattering length of Sr (7.02 fm) is close to that of Nd (7.69 fm), X-ray diffraction can do. X-ray diffraction study of the $Sr_2NdCu_2FeO_{6+\delta}$ compound shows that the Sr atoms substitute the Nd atoms. Therefore, the disordered distribution of the Sr and Nd atoms causes the introduction of the oxygen atom to the O(4) site, to suppress superconductivity. The occupation factors of the Cu(2) site, $g_{Cu(2)}$, indicate that it is easier to substitute Cu for Fe in $Sr_2NdCu_2FeO_{6+\delta}$ than in $Sr_2LnCu_2FeO_{6+\delta}$ (Ln = Y and Er). This also supports suppressing supercondcutivity in $Sr_2NdCu_2FeO_{6+\delta}$.

Table 1
Final results of the Rietveld refinements for the $Sr_2LnCu_2FeO_{6+\delta}$ (Ln = Nd, Y and Er, tetragonal, P4/mmm, Z=1) compounds. g is the occupation factor. B is the isotropic thermal parameter in nm^2. Numbers in parentheses are estimated standard deviations of the last digit, and those without deviations are fixed.

Ln	Nd	Y	Er
R_{wp}	8.91%	9.25%	10.05%
R_p	6.81%	6.88%	7.30%
R_R	15.91%	12.41%	15.73%
R_I	6.42%	2.76%	2.97%
R_F	5.02%	1.88%	1.97%
R_e	5.35%	6.49%	6.58%
S	1.66	1.43	1.53
a/nm	0.38436(1)	0.38220(1)	0.38158(1)
c/nm	1.14581(3)	1.13651(3)	1.13491(4)
z_{Sr}	0.1757(2)	0.1803(2)	0.1809(3)
B_{Sr}/nm^2	0.0125(4)	0.0091(4)	0.0087(5)
B_{Ln}/nm^2	0.0121(6)	0.0053(5)	0.0060(7)
$g_{Cu(1)}$	0.37(5)	0.19(3)	0.28(6)
$B_{Cu(1)}/nm^2$	0.0045(8)	0.0049(6)	0.0031(9)
$g_{Cu(2)}$	0.81(3)	0.90(2)	0.86(3)
$z_{Cu(2)}$	0.3400(2)	0.3497(2)	0.3502(2)
$B_{Cu(2)}/nm^2$	0.0084(5)	0.0049(1)	0.0049(6)
$g_{O(1)}$	0.436(7)	0.419(5)	0.412(9)
$x_{O(1)}$	0.061(2)	0.075(2)	0.082(2)
$B_{O(1)}/nm^2$	0.0188(16)	0.0188(15)	0.0152(23)
$z_{O(2)}$	0.1613(3)	0.1617(2)	0.1619(3)
$B_{O(2)}/nm^2$	0.0237(7)	0.0144(6)	0.0126(8)
$z_{O(3)}$	0.3549(2)	0.3723(1)	0.3729(3)
$B_{O(3)}/nm^2$	0.0174(7)	0.0074(4)	0.0066(5)
$g_{O(4)}$	0.378(10)	-	-
$B_{O(4)}/nm^2$	0.01	-	-

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