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Neutron diffraction study of Nd-substituted $FeSr_2YCu_2O_{6+\delta}$ magnetic superconductor

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ABSTRACT

$FeSr_2YCu_2O_{6+\delta}$ with tetragonal $Ba_2YCu_3O_{6+\delta}$-type structure exhibits superconductivity around 60 K, only when it is annealed in reduced atmosphere and subsequently in oxidized atmosphere. However, $FeSr_2NdCu_2O_{6+\delta}$ with the substitution of lanthanoid with large ionic radius for Y do not exhibit superconductivity even if it is annealed in the same process as superconducting $FeSr_2YCu_2O_{6+\delta}$. We have performed neutron powder diffraction of the $FeSr_2Y_{1-x}Nd_xCu_2O_{6+\delta}$ solid solution system to investigate the effect of the Nd substitution on structure and superconductivity. The structure analysis indicates that the disorder of Sr and Nd, of oxygen on double superconducting CuO_2 sheets and of Cu and Fe prevents exhibiting superconductivity in the Nd-substituted system.

1. Introduction

Coexistence of superconductivity and ferromagnetism has been discovered in $RuSr_2GdCu_2O_8$ with the substitution of the RuO_6 octahedron for the CuO_δ chain in the $Ba_2YCu_3O_{6+\delta}$-type high-T_c superconductor, which exhibits superconductivity at 16 K and ferromagnetic order of Ru at 133 K by the careful sample preparation process [1]. Meanwhile, $FeSr_2YCu_2O_{6+\delta}$ is known as the $Ba_2YCu_3O_{6+\delta}$-related compound with the substitution of the oxygen-deficient $FeO_{4+\delta}$ octahedron with the magnetic transition element Fe for the CuO_δ chain [2,3]. Although $FeSr_2YCu_2O_{6+\delta}$ was expected to exhibit superconductivity as $Ba_2YCu3O_{6+\delta}$, as-sintered $FeSr_2YCu_2O_{6+\delta}$ compound did not exhibit superconductivity due to the substitution of Fe on the superconducting CuO_2 sheets. However, $FeSr_2YCu_2O_{6+\delta}$ exhibits superconductivity around 60 K, only when it is properly annealed in N_2 atmosphere and subsequently in O_2 atmosphere [4]. Neutron powder diffraction study indicated that the N_2-annealing causes order of Cu and Fe atoms to prevent the substitution of Fe on the CuO_2 sheets, and that the O_2-annealing supplied enough carrier on the CuO_2 sheets to exhibit superconductivity [5]. Although other lanthanoid elements (Nd, Sm, Eu, Gd, Dy, Ho, Er and Tm) can be substituted for Y in $FeSr_2YCu_2O_{6+\delta}$ like $Ba_2YCu_3O_{6+\delta}$, $FeSr_2NdCu_2O_{6+\delta}$ and $FeSr_2SmCu_2O_{6+\delta}$ do not exhibit superconductivity and $FeSr_2EuCu_2O_{6+\delta}$ exhibit superconductivity at lower temperature than T_c of $FeSr_2YCu_2O_{6+\delta}$, even if those are annealed along the same process as superconducting $FeSr_2YCu_2O_{6+\delta}$ [6]. Those indicate that the ionic size at the Y site is effective on superconductivity unlike $Ba_2YCu_3O_{6+\delta}$. Since the change of the ionic size at the Y site affects the crystal structure including the oxygen site, we need to analyze the detailed crystal structure with neutron powder diffraction. However, we cannot use neutron powder diffraction for $FeSr_2SmCu_2O_{6+\delta}$ and $FeSr_2EuCu_2O_{6+\delta}$ because of extremely strong absorption of neutron by Sm and Eu. To investigate the structural effect of the lanthanoid substitution on superconductivity, we have performed the neutron powder diffraction study of the $FeSr_2Y_{1-x}Nd_xCu_2O_{6+\delta}$ solid solution system, which ionic size at the Y site varies systematically.

2. Experimental

The $FeSr_2Y_{1-x}Nd_xCu_2O_{6+\delta}$ samples ($x = 0$, 0.25, 0.5, 0.75 and 1) were prepared by the solid-state reaction of stoichiometric mixtures of Fe_2O_3, $SrCO_3$, Y_2O_3, Nd_2O_3 and CuO powders. The same process was performed to all samples as follows, to prepare the

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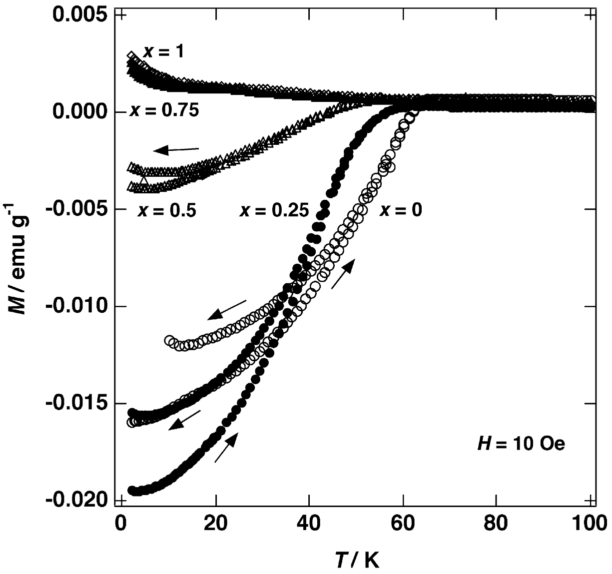

Fig. 1. Temperature dependence of the DC magnetization in magnetic field of 10 Oe for the oxidized $FeSr_2Y_{1-x}Nd_xCu_2O_{6+\delta}$ samples ($x = 0$, 0.25, 0.5, 0.75 and 1).

samples with fixed oxygen content, $6 + \delta$. The mixtures were sintered at 1000 °C for 12 h in air, ground and then pressed into pellets. The pellets were sintered at 1000 °C for 12 h in air. The as-sintered samples were subsequently annealed at 700 °C for 12 h in a nitrogen flow, at 300 °C for 24 h in an oxygen flow, and finally oxidized at 350 °C for 24 h in high oxygen pressure of 20 MPa. Fig. 1 shows the temperature dependence of the DC magnetization for the $FeSr_2Y_{1-x}Nd_xCu_2O_{6+\delta}$ samples ($x = 0$, 0.25, 0.5, 0.75 and 1). The samples with $x = 0$, 0.25 and 0.5 exhibit superconductivity at 65, 60 and 55 K, respectively, and the samples with $x = 0.75$ and 1 do not exhibit superconductivity. This indicates that the Nd substitution depresses the T_c value.

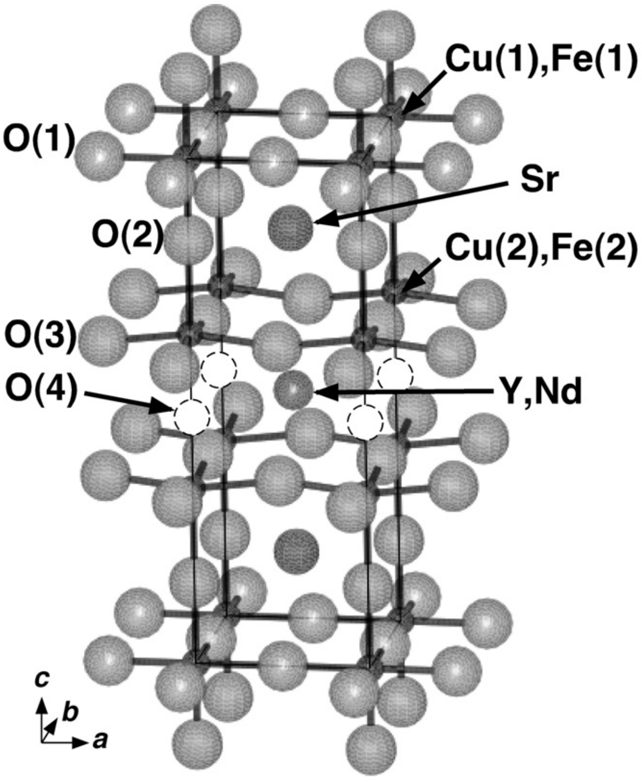

Fig. 2. Crystal structure of $FeSr_2Y_{1-x}Nd_xCu_2O_{6+\delta}$.

Table 1
Atomic coordinates of the tetragonal $Ba_2YCu_3O_{6+\delta}$-type structure model with the space group *P4/mmm*

Atom	Site	x	y	z
Sr	2h	1/2	1/2	z
$Y_{1-x}Nd_x$	1d	1/2	1/2	1/2
Cu(1), Fe(1)	1a	0	0	0
Cu(2), Fe(2)	2g	0	0	z
O(1)	2f	0	1/2	0
O(2)	2g	0	0	z
O(3)	4i	0	1/2	z
Split oxygen site				
O(1)	4n	x	1/2	0
O(2)	8r	x	x	z
Extra oxygen site				
O(4)	1b	0	0	1/2

Neutron powder diffraction data for all samples were taken with a high-resolution neutron powder diffractometer, HRPD, at the JRR-3 research reactor in the Japan Atomic Energy Agency. The intensity data were collected at room temperature and the crystal structure of the samples was refined with the Rietveld refinement program, RIETAN-2000 [7], on the basis of the tetragonal $Ba_2YCu_3O_{6+\delta}$-type structure with the space group *P4/mmm*. Fig. 2 shows the crystal structure and Table 1 shows the atomic coordinates of the structure model. Since mutual substitution of Cu and Fe is analyzed, four sites are assigned for Cu and Fe: 1a site for Cu(1) and Fe(1) and 2g site for Cu(2) and Fe(2), and those occupation factors, g, have the linear constrains

$$g_{\mathrm{Fe(1)}} = 1 - g_{\mathrm{Cu(1)}},$$
$$g_{\mathrm{Cu(2)}} = 1 - 0.5 g_{\mathrm{Cu(1)}},$$
$$g_{\mathrm{Fe(2)}} = 0.5 g_{\mathrm{Cu(1)}}.$$

3. Results and discussion

Table 2 lists the final R factors, the lattice and structure parameters and their standard deviation. Fig. 3 illustrates typical one of the Rietveld refinement patterns of the $FeSr_2Y_{1-x}Nd_xCu_2O_{6+\delta}$ samples. The structure model is supported by the good fit between the

Table 2
Final results of the Rietveld refinements for $FeSr_2Y_{1-x}Nd_xCu_2O_{6+\delta}$ (tetragonal, *P4/mmm*, $Z = 1$)

x	0	0.25	0.5	0.75	1
R_{wp}	7.01%	6.50%	6.43%	8.70%	7.07%
S	1.35	1.29	1.28	1.33	1.27
a (nm)	0.38169(1)	0.38307(1)	0.38307(1)	0.38420(1)	0.38435(1)
c (nm)	1.13546(2)	1.13884(3)	1.13886(3)	1.14133(2)	1.14623(2)
$g_{\mathrm{Cu(1)}}$	0.16(3)	0.10(4)	0.11(4)	0.09(4)	0.38(5)
$g_{\mathrm{Cu(2)}}$	0.92(2)	0.95(2)	0.94(2)	0.96(2)	0.81(3)
$g_{\mathrm{O(1)}}$	0.404(6)	0.402(6)	0.401(6)	0.389(7)	0.400(7)
$x_{\mathrm{O(1)}}$	0.076(1)	0.077(1)	0.076(1)	0.069(2)	0.063(2)
$x_{\mathrm{O(2)}}$	0.0	0.0	0.0	0.0	0.037(2)
$B_{\mathrm{O(2)}}$ (nm^2)	0.0131(5)	0.0167(6)	0.0165(2)	0.0185(7)	0.0163(12)
$B_{\mathrm{O(3)}}$ (nm^2)	0.0068(4)	0.0128(4)	0.0126(4)	0.0131(5)	0.0257(6)
$g_{\mathrm{O(4)}}$	0	0.081(9)	0.083(9)	0.153(10)	0.354(11)
$g_{\mathrm{Sr(1)}}$	1.0	0.941(10)	0.898(7)	0.876(14)	0.803(9)
$g_{\mathrm{Sr(2)}}$	0.0	0.118(20)	0.204(14)	0.248(28)	0.394(18)

g is the occupation factors. B is the isotropic atomic displacement parameter in nm^2. Numbers in parentheses are estimated standard deviations of the last significant digit, and those without deviations were fixed. $g_{\mathrm{Sr(1)}}$ and $g_{\mathrm{Sr(2)}}$ were refined from X-ray powder diffraction data, where four sites are assigned for Sr and Nd: 2h site for Sr(1) and Nd(1) and 1d site for Sr(2) and Nd(2).