Physica C 469 (2009) 960–964

Contents lists available at ScienceDirect

Physica C

journal homepage: www.elsevier.com/locate/physc

Effect of intervening structure between CuO_2 sheets in heavily Fe-substituted high-T_c superconductor $FeSr_2YCu_2O_{6+\delta}$

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ARTICLE INFO

Article history:
Available online 29 May 2009

PACS:
74.62.Dh
74.72.Bk

Keywords:
$FeSr_2YCu_2O_{6+\delta}$
Cationic order
Fluorite

ABSTRACT

Heavily Fe-substituted $Ba_2YCu_3O_{6+\delta}$-type compound $FeSr_2YCu_2O_{6+\delta}$ exhibits superconductivity around 60 K, only when it is annealed in N_2 and subsequently in O_2. Cationic distribution in this compound is strongly dependent on ionic radius at the Y site, and its superconducting properties are affected by the cationic distribution. In contrast, although the compound with the substitution of fluorite-type unit for Y has cationic order, it does not exhibit superconductivity. We have analyzed the crystal structure of the compounds with the substitution of other lanthanoid elements for Y and with substitution of fluorite-type unit for Y.

1. Introduction

Heavily Fe-substituted $Ba_2YCu_3O_{6+\delta}$-type compound $FeSr_2YCu_2O_{6+\delta}$ exhibits superconductivity around 60 K only when it is annealed in N_2 and subsequently in O_2, although the as-sintered $FeSr_2YCu_2O_{6+\delta}$ compound did not exhibit superconductivity [1]. Neutron powder diffraction study indicates that the N_2-annealing causes order of Cu and Fe to prevent the substitution of Fe for Cu on the superconducting CuO_2 sheets, and that the O_2-annealing supplied carrier on the CuO_2 sheet to exhibit superconductivity [2]. Although other lanthanoid elements (Nd, Sm, Eu, Gd, Dy, Ho, Er and Tm) can be substituted for Y in $FeSr_2YCu_2O_{6+\delta}$, the compounds with large ionic radius do not exhibit superconductivity or exhibits superconductivity at lower temperature than T_c of $FeSr_2YCu_2O_{6+\delta}$, even if those are annealed along the same process as superconducting $FeSr_2YCu_2O_{6+\delta}$ compounds [3]. We have investigated the correlation between the ionic size and superconductivity using neutron powder diffraction of $FeSr_2MCu_2O_{6+\delta}$ ($M = Y_{1-y}Nd_y$) with the variation of the ionic radius at the M site, because Sm and Eu have extremely strong absorption of neutron [4]. It indicates that the increase of the ionic size yields the change of the cationic distribution from order to disorder of Cu and Fe, and Sr and Nd, and accordingly T_c decreases.

Meanwhile, fluorite-type unit can be substituted for the M layer between adjacent CuO_2 sheets in $FeSr_2MCu_2O_{6+\delta}$ with the sheets stacked in the sequence $(FeO_\delta)_o(SrO)_c(CuO_2)_o(M)_c(CuO_2)_o(SrO)_c$, according to a descriptive method proposed by Santoro et al. [5]. The compound with the fluorite-type unit has the sheets stacked in the sequence $(FeO_\delta)_o(SrO)_c(CuO_2)_o(M')_c(O_2)(M)_o(CuO_2)_c(SrO)_o$ with the composition of $FeSr_2M'_2Cu_2O_{8+\delta}$ where M′ is $Ln_{1-y}Ce_y$ and Ln is lanthanoid element except for Ce. Fig. 1 shows both crystal structures of $FeSr_2MCu_2O_{6+\delta}$ and $FeSr_2M'_2Cu_2O_{8+\delta}$, which were drawn with the visualization program VESTA [6]. Yang et al. [7] reported the crystal structure and physical properties of $FeSr_2M'_2Cu_2O_{8+\delta}$ ($M' = Ln_{0.25}Ce_{0.75}$; Ln = Eu, Gd and Tb). While $FeSr_2(Eu_{0.25}Ce_{0.75})_2Cu_2O_{8+\delta}$ exhibits antiferromagnetic order below 25 K, other compounds show the Curie-type paramagnetic behavior. This indicates that the physical properties are sensitive to kind of lanthanoid element in the fluorite-type unit, like $FeSr_2MCu_2O_{6+\delta}$ with the substitution of lanthanoid elements [8]. We have succeeded in synthesis of the $FeSr_2M'_2Cu_2O_{8+\delta}$ compounds ($M' = Ln_{0.65}Ce_{0.35}$; Ln = Eu, Gd and Tb) with different composition from the previous report [7]. We cannot perform neutron diffraction

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doi:10.1016/j.physc.2009.05.117

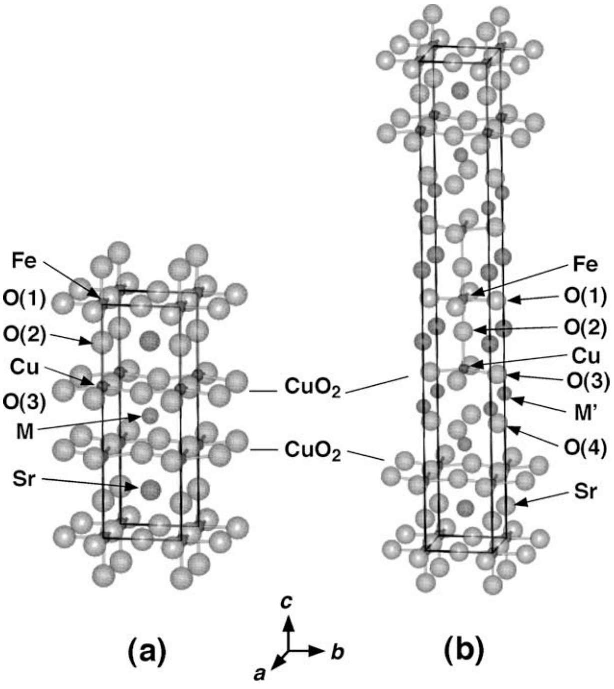

Fig. 1. Crystal structure of (a) $FeSr_2MCu_2O_{6+\delta}$ and (b) $FeSr_2M'_2Cu_2O_{8+\delta}$.

measurements for the Eu- and Gd-included compounds because Eu and Gd have extremely strong absorption of neutron. Therefore, we have performed high-resolution X-ray powder diffraction measurements to investigate the structural difference by the variation of the lanthanoid elements in the $FeSr_2M'_2Cu_2O_{8+\delta}$ system, as compared with $FeSr_2MCu_2O_{6+\delta}$.

2. Experimental

The $FeSr_2M'_2Cu_2O_{8+\delta}$ samples (M′ = $Ln_{0.65}Ce_{0.35}$; Ln = Eu, Gd and Tb) were prepared by the solid-state reaction of stoichiometric mixtures of Fe_2O_3, $SrCO_3$, Eu_2O_3, Gd_2O_3, Tb_4O_7 and CuO powders. The same process was performed to all samples as follows, to prepare the samples with fixed oxygen content, $8 + \delta$. The mixtures were sintered at 1050 °C for 24 h in air, ground and then pressed into pellets. The pellets were sintered at 1050 °C for 24 h in air. Finally, the as-sintered samples were oxidized at 350 °C for 24 h in high oxygen pressure of 20 MPa. The $FeSr_2M'_2Cu_2O_{8+\delta}$-type structure are stabilized in the limited composition range, and at least in our sintering condition this compound can be synthesized only when M′ = $Ln_{0.65}Ce_{0.35}$ and Ln = Eu, Gd and Tb. The DC magnetization of the oxidized samples was measured with a SQUID magnetometer. High-resolution X-ray powder diffraction data were taken with the imaging plate diffractometer at the BL15XU beamline at the synchrotron radiation facility, SPring-8, at Hyogo, Japan. The samples were put in the capillaries and the intensity data were collected using monochronized X-ray with the wavelength of 0.065300 nm at room temperature.

3. Results and discussion

Fig. 2 shows the temperature dependence of the DC magnetization in magnetic field of 10 Oe for the $FeSr_2M'_2Cu_2O_{8+\delta}$ samples, as compared with the oxidized $FeSr_2Y_{1-y}Nd_yCu_2O_{6+\delta}$ samples. While T_c of $FeSr_2Y_{1-y}Nd_yCu_2O_{6+\delta}$ decreases with the increase of the Nd content, y, corresponding to the ionic size at the M site, $FeSr_2M'_2Cu_2O_{8+\delta}$ does not exhibit superconductivity despite of the variation of the lanthanoid elements. While $FeSr_2(Gd_{0.65}Ce_{0.35})_2Cu_2O_{8+\delta}$ and $FeSr_2(Tb_{0.65}Ce_{0.35})_2Cu_2O_{8+\delta}$ exhibit the Curie-type paramagnetic behavior, $FeSr_2(Eu_{0.65}Ce_{0.35})_2Cu_2O_{8+\delta}$ exhibits the antiferromagnetic order at 17 K. Those results are consistent with the previous report [6], and indicate that oxidizing in high pressure to supply carrier onto the CuO_2 sheets is not effective on exhibiting superconductivity in $FeSr_2M'_2Cu_2O_{8+\delta}$ with the fluorite-type unit although it is effective in $FeSr_2YCu_2O_{6+\delta}$ without the fluorite-type unit. The appearance of the magnetic behavior in $FeSr_2M'_2Cu_2O_{8+\delta}$ is similar to that when superconductivity weakens in $FeSr_2MCu_2O_{6+\delta}$ [8].

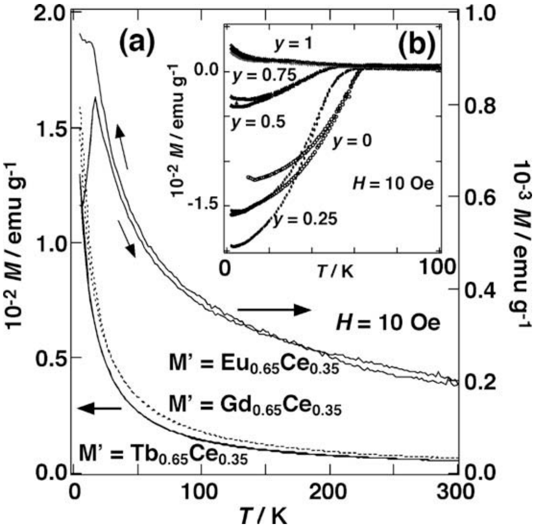

Fig. 2. Temperature dependence of the DC magnetization for (a) $FeSr_2M'_2Cu_2O_{8+\delta}$ (M′ = $Ln_{0.65}Ce_{0.35}$; Ln = Eu, Gd, Tb) and (b) $FeSr_2MCu_2O_{6+\delta}$. (M = $Y_{1-y}Nd_y$; y = 0, 0.25, 0.5, 0.75, 1).

Table 1
Final results of the Rietveld refinements for $FeSr_2M'_2Cu_2O_{8+\delta}$ (tetragonal, *I4/mmm*) where M′ = $Ln_{0.65}Ce_{0.35}$. B_m and B_o are the isotropic atomic displacement parameters at the metal and oxygen sites, respectively, in nm^2. Numbers in parentheses are estimated standard deviations of the last significant digit.

Ln	Eu	Gd	Tb
R_{wp}	3.00%	3.38%	4.75%
R_p	1.68%	1.94%	2.63%
R_R	14.35%	16.01%	21.58%
R_B	5.98%	5.77%	3.13%
R_F	3.93%	4.13%	1.97%
a (nm)	0.38418(1)	0.38375(1)	0.38372(2)
c (nm)	2.81445(5)	2.81248(7)	2.81347(18)
z_{Sr}	0.4258(1)	0.4257(1)	0.4264(1)
$z_{M'}$	0.2956(1)	0.2955(1)	0.2952(1)
z_{Cu}	0.1402(1)	0.1402(1)	0.1410(2)
$z_{O(2)}$	0.0663(4)	0.0675(4)	0.0649(7)
$z_{O(3)}$	0.1457(3)	0.1452(3)	0.1478(5)
B_m (nm^2)	0.0187(1)	0.0183(2)	0.0184(3)
B_o (nm^2)	0.0203(9)	0.0197(10)	0.0152(18)

The crystal structure of the $FeSr_2M'_2Cu_2O_{8+\delta}$ samples was refined using the Rietveld refinement program RIETAN-FP [9] on the basis of the tetragonal $(Ba_{1-x}Nd_x)_2(Nd_{1-y}Ce_y)_2Cu_3O_{8+\delta}$-type structure with the space group *I4/mmm* [10]. The atomic coordinates are

Sr	in 4*e*:	0	0	*z*,
M′	in 4*e*:	0	0	*z*,
Fe	in 2*a*:	0	0	0,
Cu	in 4*e*:	0	0	*z*,
O(1)	in 4*c*:	0	½	0,
O(2)	in 4*e*:	0	0	*z*,
O(3)	in 8*g*:	0	½	*z*,
O(4)	in 4*d*:	0	½	¼