JMEPEG (2004) 13:374-378
DOI: 10.1361/10599490419243

Anomalies of Electrical Properties of Sm-Cuprate Oxides Substituted With Yttrium and Iron Oxides at Low Temperatures

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(Submitted 22 July 2003)

Samples of $Sm_{2-x}R_xCuO_4$ (R = Y and Fe), for x = 0.0 and 0.05, were prepared by standard solid-state reactions. The lattice parameters of the single-phase cuprates increased for the altered samples. The samples were studied by differential scanning calorimetry, scanning electron microscopy, electrical resistivity, and thermoelectric power measurements. The effect of substitution was found to increase compound stability, decrease the electrical resistivity, and change the sign of the thermoelectric power. The anisotropy field due to apical oxygen in the unaltered sample was not found.

Keywords: electrical resistivity, low temperatures, Sm-cuprate oxides, substitution, thermal analysis, thermoelectric power

1. Introduction

Sm-cuprate oxides with composition R_2CuO_4 (where R = Nd, Sm) have the tetragonal T′ structure and are n-type superconductors when suitably doped.[1-3] Sm_2CuO_4 consists of a single alternating perovskite $[SmCuO_2]^+$ and $[SmO_2]^-$ fluoride layers.[4] The perovskite layer is under tension and carries a net positive charge. Meanwhile, the fluoride layer is under compression and carries a net negative charge. Hong and Smyth[4] proposed that self-doping in the above cuprate oxides occurs as a result of reduction reaction with the formation of oxygen vacancies, V_o, and electrons:

$$O_O \leftrightarrow \tfrac{1}{2}\, O_2 + V_O^{2+} + 2e^- \qquad \text{(Eq 1)}$$

This reduction reaction results because the stability of these samples is less than the lower limit, $t = 0.85$.[5] This study was initiated to investigate the effect of substitution of magnetic (Fe) and non-magnetic (Y) for Sm on the electrical properties Sm-cuprate oxides at low temperature.

2. Experiment

Cuprate samples of the chemical formula $Sm_{2-x}R_xCuO_4$ (R = Y and Fe with x = 0.0 and 0.05) are prepared by the standard ceramic-processing techniques. High-purity oxides, 99.9% of Sm_2O_3, CuO, Y_2O_3, and Fe_2O_3, are mixed according to their molecular weight. The powders are presintered at 900 °C for 16 h followed by slow cooling to room temperature. The compacts are ground again to fine powders. The samples are disc-shaped, and 9 mm in diameter by 2 mm in thickness. They are then sintered at 1100 °C for 8 h and slowly cooled to room temperature. X-ray diffraction patterns were recorded using a diffractometer (X'pert-MPD system, Philips, Amsterdam, the Netherlands) with Cu-Kα radiation. A single-phase material was indicated. The apparent densities of the samples were measured using Archimedes method and were found to be higher than 90% theoretical. Polished and etched samples (boiling HCl) were prepared for microscopy. A scanning electron microscope (JEOL, JSM-5600 LV, Peabody, MA) was used. The calculated values of the average lattice parameters of cuprate Sm_2CuO_4 are given in Table 1. They are in agreement with those reported in the Joint Committee on Powder Diffraction Standard database. The lattice parameters for altered samples increased slightly. For measurements of the electrical resistivity, In-Hg is used as the electrode. The error in ρ was about ±1%. The temperature was measured using a K-type thermocouple. The activation energy is calculated using the equation $\rho = \rho_o \exp(E_\rho/\kappa T)$, where Eρ is the activation energy and is calculated from the slope of log ρ versus 1000/T. The thermoelectric power (α) was measured for all samples. A temperature difference of 5 °C was maintained during all α measurements. The percentage error in α values was 1%.

Table 1 The Average Lattice Parameters and T_N for Sm_2CuO_4, Y-, and Fe-Substituted Samples

Sample	a, Å	c, Å	T_N, K
$[Sm_2CuO_4]_{JCPDS}$	3.905	11.938	
Sm_2CuO_4	3.897 ± 0.005	11.935 ± 0.005	285
$Sm_{1.95}Y_{0.05}CuO_4$	4.008 ± 0.005	12.092 ± 0.005	278
$Sm_{1.95}Fe_{0.05}CuO_4$	4.025 ± 0.005	12.113 ± 0.005	255

3. Results

3.1 Electrical Properties of Sm_2CuO_4 at Low Temperature

Figure 1(a) shows the temperature dependence of log ρ for Sm_2CuO_4. The log ρ increases with decreasing temperature up to ~77 K. It is clear that the activation energy increases gradu-

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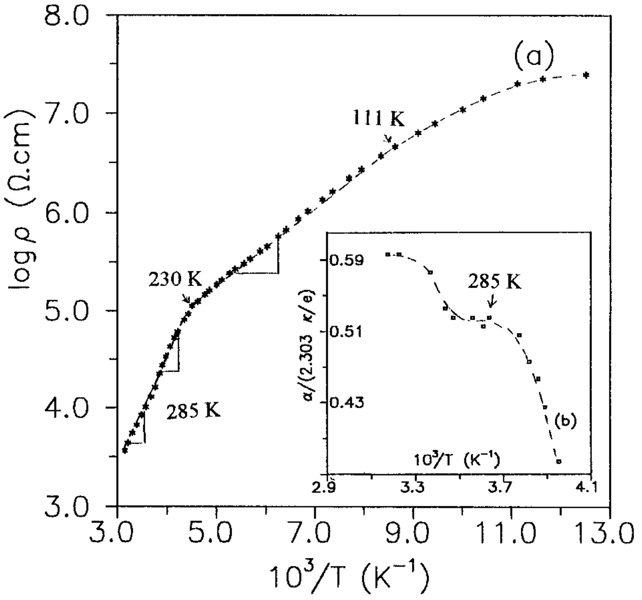

Fig. 1 Temperature dependence of (**a**) log ρ and (**b**) α for Sm_2CuO_4

ally with temperature up to ~111 K. For higher temperatures, different activation energies are noticed depending on the temperature range as shown in Fig. 1. For 230 K > T > 111 K, log ρ decreases with constant activation energy. For T > 230 K, there is a rapid decrease of log ρ with temperature. Another variation in activation energy is noted for T > 285 K.

Figure 1(b) illustrates the changes of α with temperature. Unfortunately, the measurements of α for T < 248 K could not be performed, and may be due to the charge localization. Similar results are reported for Nd_2CuO_4.[6] The values of α are found to be positive throughout the measured temperature range and increase with temperature. The rate of increase changes at 285 K.

To account for the high values of log ρ at low temperatures, one must consider the self-doping effect proposed by Hong and Smyth.[4] According to this effect, a reduction reaction increases the stability of Sm_2CuO_4, in which the calculated stability t = 0.825[7] is lower than the lower limit of t = 0.85.[5] This reaction produces oxygen as interstitials at the apical sites, which causes an anisotropy field. This leads to the localization of charge carriers in the CuO_2 planes and accounts on the increase in log ρ at low temperatures. The anisotropy field seems to decrease with increasing temperature due to the diffusion of oxygen (O) ions to sites along the c-axis. This causes delocalization of the charge carriers in the CuO_2 planes and explains the decrease in log ρ (Fig. 1a). The differential scanning calorimetry (DSC) scan (Fig. 2a) shows an exothermic peak at 196 K, which may be associated with the breakdown of the anisotropy field. This confirms our hypothesis and explains why the measurement of α at low temperatures cannot be performed. It seems that the anisotropy field vanishes at 230 K (i.e., the upper end of the exothermic peak). This causes more delocalization of the charge carriers due to the displacement of more O to the c-axis. Hence, it leads to a rapid decrease in the log ρ at T > 230 K and explains why α cannot be performed at temperatures of <235 K (Fig. 1b).

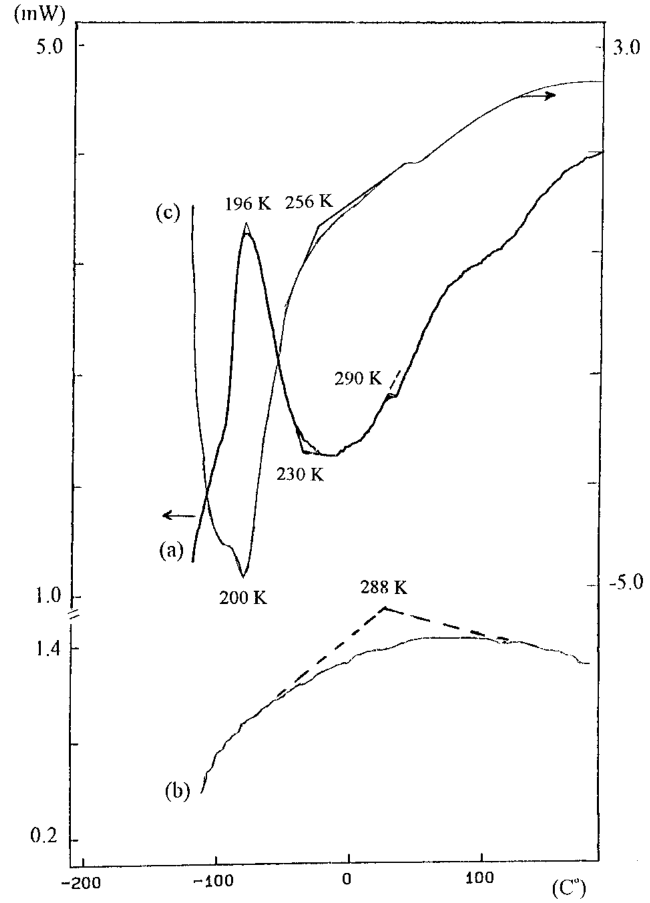

Fig. 2 DSC for (**a**) Sm_2CuO_4 and (**b**) $Sm_{1.95}Y_{0.05}CuO_4$ and $Sm_{1.95}Fe_{0.05}CuO_4$

It was reported by Skanthakumar et al.[8] and Wiegelmann et al.[9] that the Néel temperature (T_N) of Sm_2CuO_4 is 280 K and 285 K, respectively. At this temperature, Cu ions change from antiferromagnetic to paramagnetic. The magnetic transition is considered to be second order.[10] From thermodynamics, the second-order transition is accompanied by a volume expansion. This means that some amount of heat must be absorbed. Figure 2(a) shows a decrease in the heat absorbed at ~290 K. According to the above discussion, the changes in the heat absorbed at 290 K, and also the variations of Eρ and α at ~285 K, may be attributed to the order-disorder transition of the Cu ions.

Finally, the positive values of thermoelectric power indicate that the majority of charge carriers are holes. It was reported that the p-states of the oxygen sites are not filled due to the strong Cu-O covalent interaction in the CuO_2 plane.[11] This leads to the presence of holes at the O sites. In addition, the incorporation of Cu^{3+} ions in the sample due to the lower limit of stability account on the positive values of α.[5]

3.2 Effect of Substitution

Figure 3(a) illustrates the temperature dependence of log ρ for Y-sample, $Sm_{1.95}Y_{0.05}CuO_4$. One recognizes that log ρ decreases with increasing temperature up to 143 K with a con-

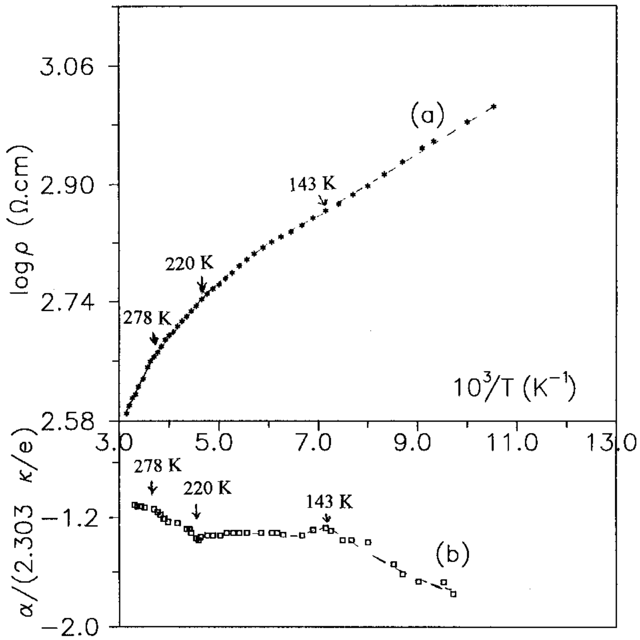

Fig. 3 Temperature dependence of (**a**) log ρ and (**b**) α $Sm_{1.95}Y_{0.05}CuO_4$

stant activation energy (E_ρ = 0.004 eV). For T > 143 K, the activation energy changes with temperature and again becomes constant at E_ρ = 0.009 eV for T ≥ 220 K.

Figure 3(b) shows the temperature dependence of α for the Y-substituted sample. One realizes that α is negative in the whole temperature range. This indicates that the majority of charge carriers are electrons. Thermoelectric power measurement shows distinct changes at 143 K, 220 K, and 278 K.

Figure 4(a) represents the temperature dependence of log ρ for an Fe-substituted sample, $Sm_{1.95}Fe_{0.05}CuO_4$. Obviously, log ρ decreases with temperature. The activation energy changes with temperature and becomes constant for T > 145 K. Its values change at 205 K and 255 K.

Figure 4(b) shows the temperature dependence of α for the Fe-substituted sample. This sample possesses a similar behavior to that of the Y-substituted sample with changes in α at 145 K, 205 K, and 255 K. The values of α for T ≤ 120 K could not be determined.

The variations in log ρ and α of these chemically altered samples can be discussed by comparing their results with those of the base compound. Substitution of Y or Fe leads to the disappearance of the exothermic peak (Fig. 2b and c), observed at ≈196 K in Sm_2CuO_4 (Fig. 2a). This can be explained as follows. Zhou et al.[12] reported that for $R_2CuO_{4-\delta}$ the magnitude of δ increases as the a-lattice parameter increases. Table 1 shows the increase of the a-lattice and c-lattice parameters for Y/Fe samples.

The increase of the lattice parameters leads to the diffusion of apical O to positions along the c-axis and, hence, to the disappearance of localized charge carriers in CuO_2 planes. The increase of the a-lattice parameter (Table 1) leads to the increase in reduction reaction. According to Zhou et al.,[12] one can assume that Y (non-magnetic ions) and Fe (magnetic ions) enter into the $[SmO_2]^-$ layer because the ionic radii of Fe^{3+}

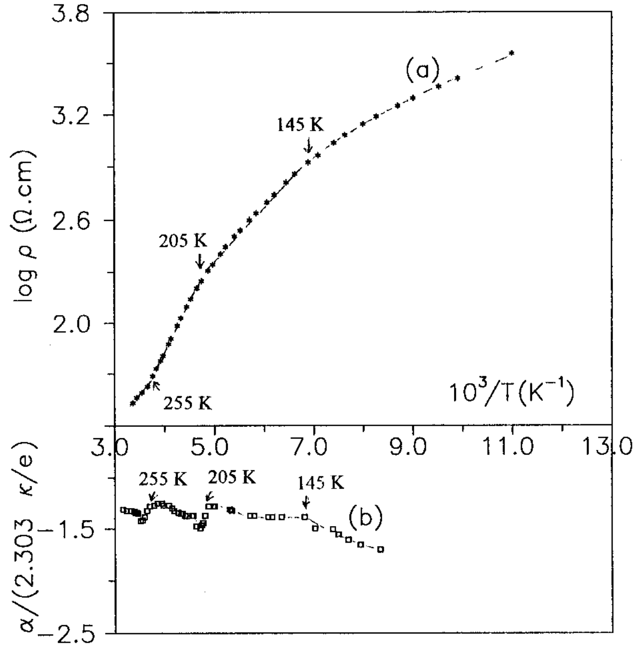

Fig. 4 Temperature dependence of (**a**) log ρ and (**b**) α $Sm_{1.95}Fe_{0.05}CuO_4$

(r = 0.64 Å) and Y^{3+} (r = 0.93 Å) are less than that of the Sm ions (r = 1.04 Å). This means that the substitution relieves the compression in these layers. Furthermore, as

$$Y_2O_3 \rightarrow 2Y + 3\ O_o \qquad \text{(Eq 2)}$$

and

$$Fe_2O_3 \rightarrow 2Fe + 3\ O_o \qquad \text{(Eq 3)}$$

provide additional self-doping results from O_o, as given by Eq 1. Thus, Y or Fe substitution leads to an increase in the number of electrons and vacancies in the alternating layers that relieves both stress and charges imbalances of (SS). This leads to an increase in stability of the compounds. Figure 5 shows the scanning electron microscope (SEM) photographs for unsubstituted sample, Sm_2CuO_4 and substituted $Sm_{1.95}Fe_{0.05}CuO_4$. The grains in the unsubstituted sample are inhomogenous, i.e., the grains are affected by certain stress (Fig. 5a). The grains for the Fe substituted sample are nearly homogenous due to the decrease of stress. These photographs confirm the above results that the stability increased for substituted samples. Similar results were reported by Idemoto et al.[13] They found that the addition of CeO_2 to Ln_2CuO_4 increases the chemical stability. Moreover, Yang et al.[14] reported that for $(Sm_{1-x}Y_x)_2CuO_4$, with x = 0 up to 0.5 at step increments of 0.1, the lattice parameters decreased with increasing values of x. For x ≥ 0.3, the samples exhibited a weak ferromagnetic component due to local structural distortions in the CuO_2 planes. This led to the absence of superconductivity in these samples. According to the above discussion, and noting that the altered samples possess opposite behavior, as the lattice parameters increase, the distortion in CuO_2 planes disappears. This may be due to the

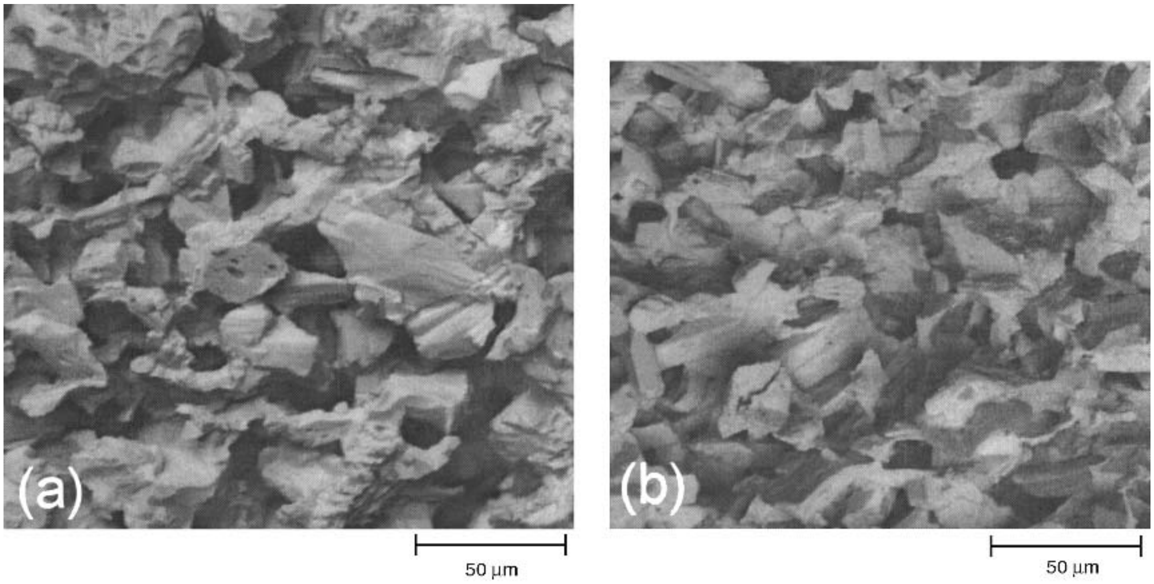

Fig. 5 The SEM image for (**a**) Sm_2CuO_4 and (**b**) $Sm_{1.95}Fe_{0.05}CuO_4$

small percentage of Y or Fe ions. Hence, one can account for the change of sign of α from positive to negative and for the decreased log ρ values for substituted samples relative to the base compound. The change of sign of α in substituted sample is due to the following:

1) The increase of negative charge carriers in CuO_2 planes.
2) The change of the character of bonds from ionocovalent in the base compound to a nearly ionic bond for Y/Fe-altered compounds due to the increase of the a-parameter.
3) The increase in mobility due to the change of sign of α from positive to negative. This result is attributed to the increase in the stability of the Y/Fe compounds. Meanwhile, the increase in the number of electrons in CuO_2 relative to the base compound explains the decrease of log ρ. Sattar et al.[15] reported that log ρ was increased and α was positive for $La_{1.95}R_{0.05}CuO_4$ (R = Y and Fe). This indicates that the substitution was not suitable in relieving the stress and charge imbalance for p-type samples because r(Y) and r(Fe) < r(La).

It is expected that the decrease in log ρ for the Fe-containing sample is greater than that for the Y-containing sample. The a-lattice parameter of the Fe-sample is greater than that of the a-lattice parameter for the Y-sample (Table 1). This promotes an increase in the reduction reaction for the Fe-sample compared with the Y-sample (i.e., the number of electrons in CuO_2 is greater than that in the Y-sample). This actually occurred for $T > 247$ K, but when $T < 247$ K log ρ for Fe-sample was greater than that for the Y-sample. Figure 6 shows log ρ as a function of ionic radius at T = 125 K and T = 250 K. To account for the increase of log ρ for the Fe-substituted sample compared with the Y-sample at $T < 250$ K, the formation of Fe^{2+} must be considered during compound preparation.[16] Here r (Fe^{2+}) = 0.76 Å > r (Cu^{2+}) = 0.69 Å, and it is expected that Fe^{2+} will move into the $[SmCuO_2]^+$ layers to relieve tension in these layers. These ions cause an anisotropy field, and, hence, the mobility of the charge carriers decreases. This accounts for the increase of log ρ for the Fe-altered compound relative to the Y-altered compound for $T < 247$ K. Such localization may also account for undetected α for Fe-altered compound at very low temperatures (Fig. 4b). For $T > 247$ K, the anisotropy field decreases, and, consequently, log ρ decreases for the Fe-altered compound relative to the Y-altered compound (Fig. 6). This means that the decrease of log ρ for the Fe-sample is due to the increase of the number of negative charge carriers, as discussed before, and to the presence of Fe^{2+} ions. For Fe-altered com-

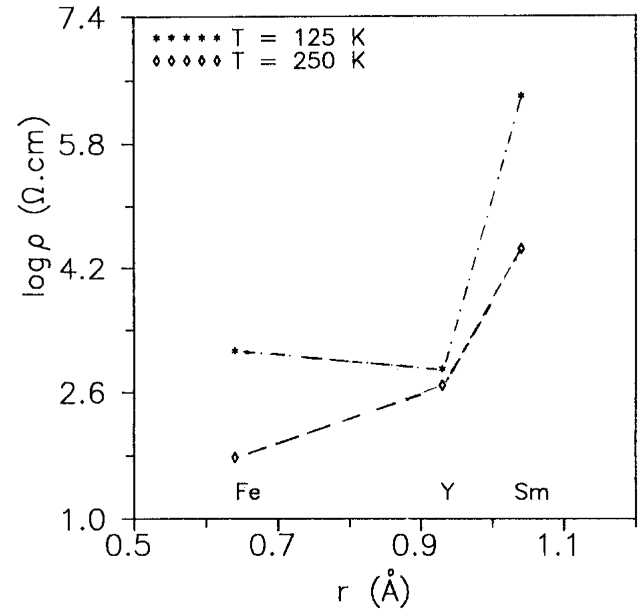

Fig. 6 The dependence of log ρ on ionic radii of Sm, Y, and Fe at different temperatures

pounds, it seems that (Fig. 2c) the anisotropy field, due to the presence of Fe^{2+} ions, begins at lower temperatures, cannot be measured, and vanishes at 200 K with a behavior similar to that of the base compound. The disappearance of the anisotropy field causes the liberation of charge carriers and may account for the rapid decrease of log ρ and the changes in α at ≈205 K (Fig. 4a and b). One notices that a change in the amount of heat absorbed occurs at ≈288 K and 256 K, respectively, for Y- and Fe-substituted samples (Fig. 2b and c). Moreover, both log ρ and α showed a change at 278 K and 255 K for these samples. The changes in DSC, log ρ, and α for substituted samples are similar to those observed in the base compound at 290 K and, as such, can be attributed to the magnetic phase transition.

4. Conclusion

The electrical resistivity decreased for substituted samples. In addition, the sign of thermoelectric power changed for substituted samples. The a-lattice parameter, reduction reaction, and, consequently, the stability of substituted samples increased relative to the unaltered one.

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