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"Superconductor-ization" of $GaSr_2YCu_2O_7$

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Abstract

To make the $GaSr_2YCu_2O_7$ compound superconductive (or "superconductor-ize" it), the structural and superconducting properties of the $(Ga_{1-y}Cu_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_7$ system were systematically investigated. In case of x=0.0, the sample with y=0.6 exhibited superconductivity of around 10K after being annealed in a high-pressure oxygen gas. On the other hand, the samples with x>0.3 and y=0.0 showed superconductivity of 40K after sample annealing. A co-substitution technique was effective for "superconductor-ization" of the compound. The as-sintered sample with x=0.4 and y=0.2 showed superconductivity at temperatures below 40K. After annealing, T_c of this sample increased up to 50K.

1. Introduction

It has been expected that cuprates having two Cu-O_5 pyramid layers with an intermediate cationic layer between them could be capable to exhibit superconductivity at temperatures above 77K. Roth *et al.*[1] discovered $GaSr_2YCu_2O_7$, namely Ga-1212 phase (as shown in Fig.1), consisting of two Cu-O_5 pyramid layers, a single cationic layer and a Ga-O_4 tetrahedral layer (which is a new crystallographic block unit for layered cuprates). This compound was "superconductor-ized" by partially substituting Ca for Y and subsequential annealing in a high-pressure oxygen gas.[2-5] However, the reported values of T_c are scattered in the range of 30-70K.

In this paper, we report the structural and superconducting properties in the $(Ga_{1-y}Cu_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_7$ system.

2. Experimental

The ceramic samples were prepared by solid state reaction. High-purity powders of Ga_2O_3, $SrCO_3$, Y_2O_3, $CaCO_3$ and CuO were used as starting materials. The powders were mixed to the nominal compositions of $(Ga_{1-y}Cu_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_7$. The powder mixture was calcined at 900°C for 10h in air, pulverized and pressed into parallelepiped bars. The bar-shaped samples were sintered at 1000°C for 24h in flowing oxygen and then slowly cooled at a rate of 100°C/h. Annealing treatment at 1000°C for 5h in an Ar-20%O_2 gas of 1800 atm was performed for the sintered samples using a hot-isostatic-pressing (HIP) technique.

X-ray powder diffraction (XRD) was carried out using CuKα radiation for structural analyses. For

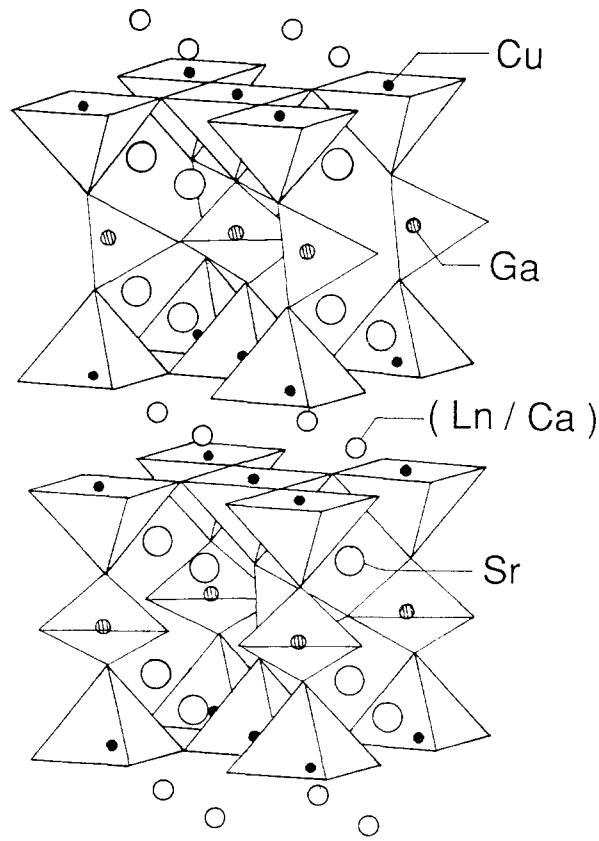

Figure 1. Crystal structure of Ga-1212 phase. Ln represents Y or one of lanthanid elements.

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the detection of superconductivity, electrical resistivity was measured by a standard four-probe method and the d.c. magnetic susceptibility was monitored using a SQUID magnetometer in the "field-cooling" mode employing a field of 10 Oe.

3. Results and discussion

3.1. Cu substitution into the Ga site

Samples with x=0.0 and various y were prepared. Figure 2 shows the XRD pattern for the as-sintered sample with y=0.0. The sample was single-phase of the Ga-1212 structure having an orthorhombic symmetry (noncentrosymmetric space group of Ima2) with the lattice parameters: a=2.2788nm b=0.5474nm c=0.5388nm. Single-phase samples were obtained for the range of y=0.0-0.6. The unit cells for samples with y=0.0-0.2 were orthorhombic and those for the samples with y=0.3-0.6 tetragonal. The samples with y>0.6 were of multi-phases. With increasing y, the stacking period of mono-layer Ga-(Cu)-O increased and the Cu-Cu distance in the Cu-O2 sheet decreased. Electrical resistivity for the as-sintered sample decreased with increasing y. The annealed samples

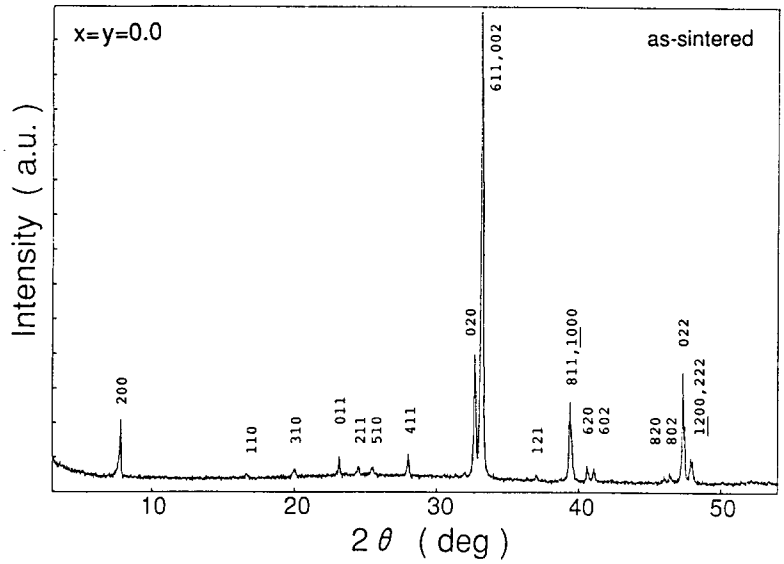

Figure 2. XRD pattern for as-sintered sample with x=y=0.0.

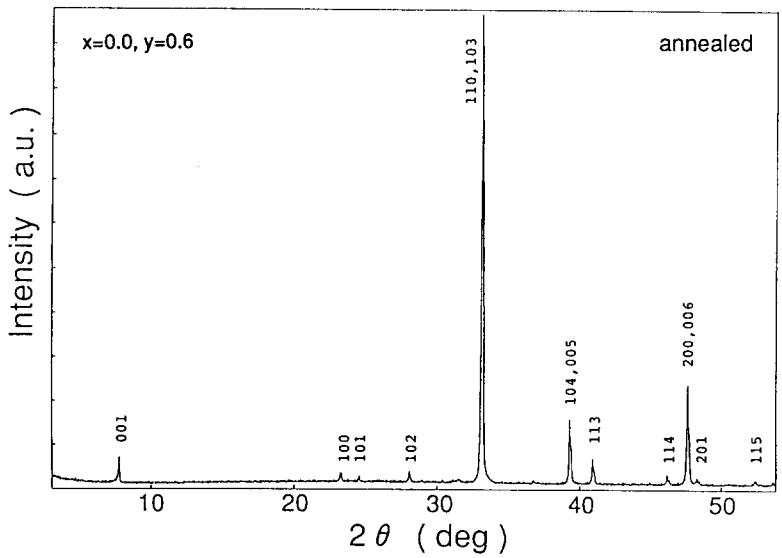

Figure 3. XRD pattern for annealed sample with x=0.0, y=0.6.

were also single-phase of the 1212 structure. Figure 3 shows the XRD pattern for the annealed sample with y=0.6. This pattern indicated that the tetragonal (Ga/Cu)-1212 phase was obtained. Sample annealing resulted in further decrease in resistivity. The resistivity data for the sample with y=0.6 before and after the annealing are shown in Fig.4. The annealed sample ehxibited a sharp resistive-drop around 10K. The Meissner signal for the samples was detected at 10K, as shown in Fig.5 (triangls). It was confirmed that the observed resistive-drop was due to superconductivity. Recently, Den *et al.*[7] reported a superconductor of T_c=21K by fine tuning of the value of y (=0.65) in a similar system.

3.2. Ca substitution into the Y site

Samples with various values of x and y=0.0 were prepared. The samples with x<0.4 were nearly single-phase of the orthorhombic Ga-1212 structure. The Ca-doping up to x=0.4 resulted in a decrease in resistivity. However, no superconductivity was observed in the as-sintered samples. Further decrease in resistivity by annealing was observed in this case. The resistivity data for the samples with x=0.4 before and after annealing are shown in Fig.6. The annealed sample showed superconductivity of around 40K (Figs.6 and 5 (solid circles)). Any increase in T_c was not observed by further doping.

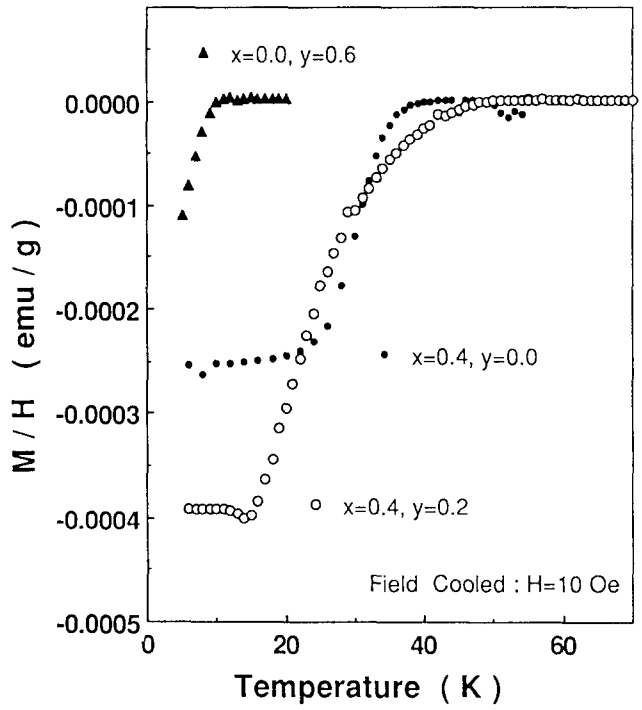

Figure 5. d.c. susceptibility data for samples with (x, y)=(0.0, 0.6), (0.4, 0.0) and (0.4, 0.2).

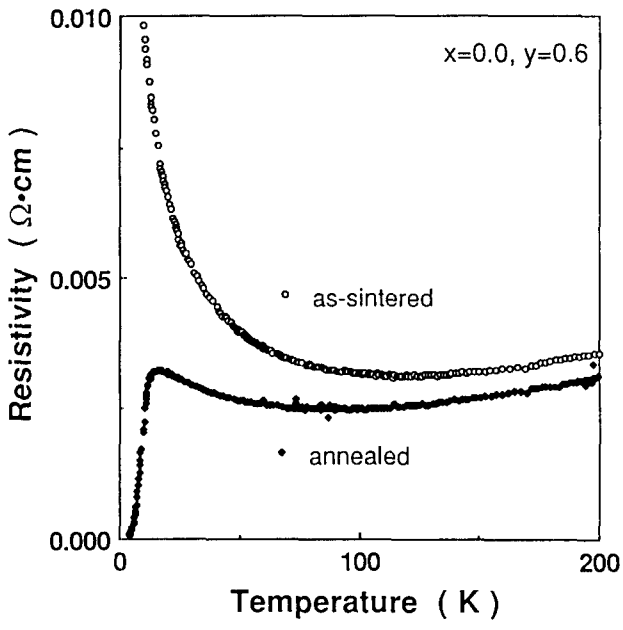

Figure 4. Electrical resistivity for sample with x=0.0, y=0.6 before and after annealing.

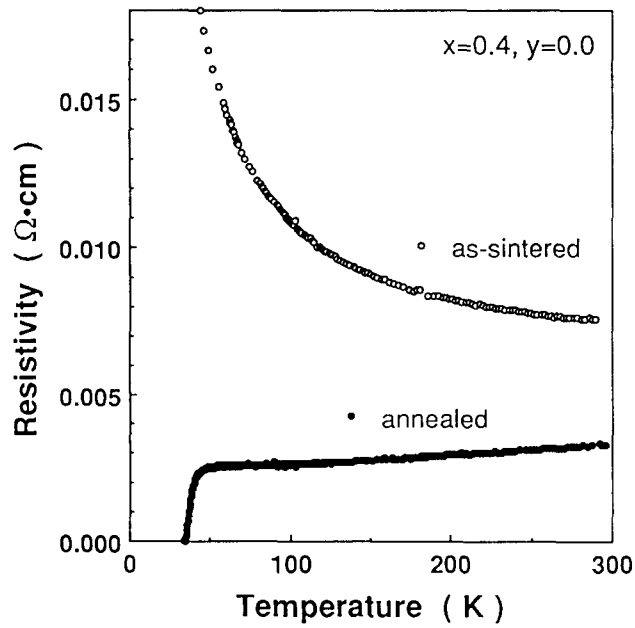

Figure 6. Electrical resistivity for sample with x=0.4, y=0.0 before and after annealing.

3.3. *Simultaneous substitution*

The co-substitutions of Ga by Cu and of Y by Ca were attempted. Figure 7 shows the electrical resistivity for the sample with x=0.4 and y=0.2. The as-sintered sample showed a superconducting transition around 40K. It was found that such co-substitutions were effective for the "superconductor-ization" of Ga-1212 phase without annealing in high-pressure oxygen. The superconducting properties were improved by annealing (Figs.7 and 5(open circles)). The T_c increased up to 50K. However, the 70-K superconductivity reported by Dabrowski *et al.*[5] was not observed throughout the present investigation.

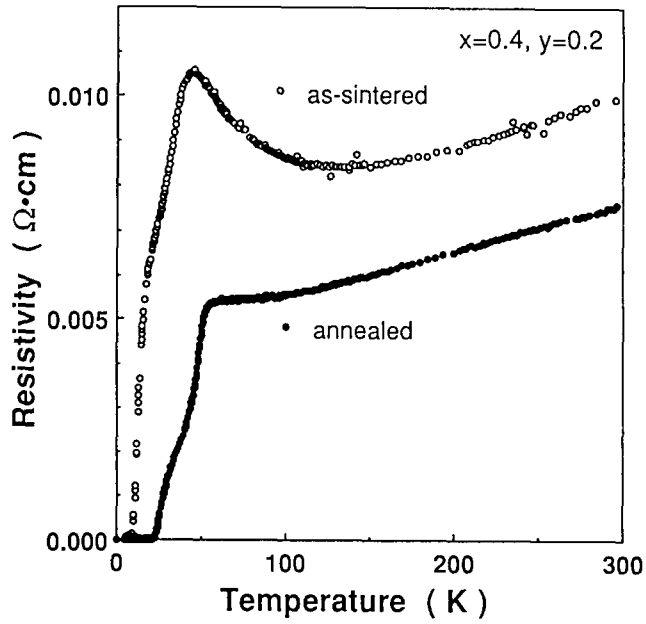

Figure 7. Electrical resistivity for sample with x=0.4, y=0.2 before and after annealing.

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