Relation between Inhomogeneous Structure and Transport Properties for Superconductor-Insulator Transitions

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Abstract. In the study of superconductor-insulator transitions of high-$T_c$ cuprates complicated behaviors in transport properties were observed for example quasi-reentrant behaviors. In this study we report that the relation between microscopic structure and transport properties for Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$ crystal with substitution of Ca by Y. From the energy dispersive X-ray spectroscopy it was estimated that samples contain almost 45% Y when the starting composition was only 10% Y. Also the values of $c$-axis length were almost constant and shorter than those of Y free samples. However there were various $\rho(T)$ behaviors dependent on sample: localized, quasi-reentrant, broad superconducting transition etc. All sheet resistances defined per CuO$_2$ bilayer in the normal state were much larger than the quantum resistance $h/4e^2$, or 6450 Ω. We were able to observe the inhomogeneous distribution of Y using a combination of electron energy loss spectroscopy and a high-angle annular dark-field technique in a scanning transmission electron microscope. The Y rich region formed the belt with about 20 nm width. This inhomogeneous structure seems to be the origin of various transport properties.

1. Introduction

The superconductor-insulator transition (SIT) has been intensively studied in homogeneously disordered two-dimensional (2D) thin films since the late 1980s [1]. A lot of attention has been directed towards a clear separation between superconducting and insulating in a sequence of films of different sheet resistances. Experimental works have been investigated about the critical sheet resistances which were compared with the quantum resistance $h/4e^2$, or 6450 Ω.

High-$T_c$ cuprates are a quasi-2D system, and the SIT of them has been reported on many kinds of samples. These reports indicate the existence of a threshold sheet resistance. However not all the threshold sheet resistances were close to the quantum resistance. Furthermore several methods to calculate a sheet resistance were used: the sheet resistance per a CuO$_2$ bilayer, per individual CuO$_2$ plane etc. Sometimes complicated transport properties were observed for example quasi-reentrant behaviors. There still remain problems about sample and material dependence.

Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$ (Bi2212) crystals with substitution of Ca by Y are one of suitable material to study the doping-controlled SIT. In this paper we report that the relation between microscopic structure and transport properties for Y-substituted Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+y}$ crystals (Y-Bi2212).
2. Experimental

Y-Bi2212 single crystals were grown using a self-flux method in Al2O3 crucibles [2, 3]. Starting materials for the crystal growth were powder Bi2O3, SrCO3, CaCO3, Y2O3 and CuO, and were weighted out to yield an atomic ratio Bi:Sr:Ca:Y:Cu=2.4:2:0.9:0.1:2. 10% Ca was displaced with Y for starting materials. Excess Bi2O3 acts as a flux for the crystal growth. Those materials was mixed and fired at 900°C for 40 h except Bi2O3. The product were added Bi2O3 and melted at 1100°C for 5 h, then cooled down slowly to 940-840°C at a rate 1°C/h, followed by a furnace cooling down to room temperature. The crystals were removed after breaking the crucible. Typical dimensions were 2mm × 4mm. To study the efficacy of oxygen content, some crystals were annealed in an Ar atmosphere at 450°C 48 h. The c-axis parameter was measured by X-ray-diffraction (XRD). The Kα radiation from a copper anode was selected. The temperature dependence of resistivity was measured by dc four-probe method. The composition and surface structure were studied by energy-dispersive X-ray spectroscopy (EDS) and the combination of a high-angle annular dark-field (HA-ADF) technique in the scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS).

3. Results and discussion

The dispersion of the c lattice constant determined from XRD is less than 0.1 Å. It was reported that the c axis changed linearly with Y content [4]. Therefore the Y distribution seems to be homogeneous from XRD results. However 4 types of ρ(T) characteristics were measured as shown in figure 1: localized behavior (yellow), quasi-reentrant behavior (light blue), broad superconducting transition (green) and two-step superconducting transition (blue). Annealing procedure made the transition sharp and Tc slightly increase (correspond to red line in figure 1). It is also found that the sheet resistances per CuO2 bilayer in the normal state are much larger than the quantum resistance.

It can be seen that the quasi-reentrant samples show abrupt decrease of ρ due to local superconductor near the Tc of global superconductors. The emergence of a superconducting transition from an insulating temperature dependence, which we call quasi-reentrant behavior, has been observed in granular superconductors, where superconducting islands are embedded in an insulating background. These results suggest inhomogeneous of Y distribution in our samples.

As previously stated, the c lattice constants of samples in figure 1 are very close as shown in table 1. It seems that the averaged Y component did not change from XRD. The EDS was performed to determine stoichiometry, dopant incorporation and sample homogeneity. The Bi:Sr ratio tends to be stoichiometric for Y-Bi2212 in contrast to Bi2212 (nonstoichiometric) as reported in the literature[6]. The composition of Cu for Y-Bi2212 was smaller than that for
Table 1. c lattice constant of four samples in figure 1.

| sample (color in figure 1) | c lattice constant (Å) |
|---------------------------|------------------------|
| yellow                    | 30.49                  |
| light blue                | 30.51                  |
| green                     | 30.43                  |
| blue                      | 30.52                  |

Figure 2. HA-ADF STEM image of Y-Bi2212. The dark region corresponds to Y-rich region. The bright region to Ca rich region.

Figure 3. Example of EEL spectrum in the dark region (red line) and the bright region (black line).

Bi-2212. The ratio of $[Y]/[Y + Ca]$ is about 45%, and there is no evidence of inhomogeneity.

However there is a possibility that the size of inhomogeneity is smaller than the space resolution of EDS ($\sim$ several µm). The combination method of HA-ADF STEM and EELS was used to observe the inhomogeneous distribution of Y with a high accuracy [7]. The HA-ADF image of Y-Bi2212 crystal was shown in figure 2. Based on the Z-contrast mechanism in incoherent HA-ADF imaging and EELS results, we can associate the dark region to Y-rich region, and the bright region corresponds to Ca-rich region (see figure 3). The Y-rich region formed the belt with about 20 nm width. The Ca rich region was surrounded with Y-rich region. It is expected that the inhomogeneous distribution changes $\rho(T)$ characteristics: localized behavior when the major of the sample is Y-rich region, quasi-reentrant behavior when Ca-rich region is surrounded with Y-rich region, broad transition which maybe relate to oxygen distribution and two-step transition due to composition segregation. The area observed by the STEM is too small to investigate the inhomogeneous distribution in a whole sample. Therefore we could not confirmed the relation between the inhomogeneous distribution and $\rho(T)$ properties. However, it expects that microscopic inhomogeneity is the origin of complicated behaviors in $\rho(T)$, science the sample dependence of averaged Y content was not observed.

In summary, we present the microscopic inhomogeneity in Y-Bi2212 crystals. The dimension of inhomogeneity is smaller than the space resolution of EDS. The microscopic structure seems
to relate with transport properties.

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