Superconductivity in $(Y_{1-x}Sr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_{7-d}$ compounds

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Abstract. Careful characterization of $(Y_{0.95}Sr_{0.05})(Ba_{1.5}Sr_{0.5})Cu_3O_{7-d}$ and $Y(Ba_{1.5}Sr_{0.5})Cu_3O_{7-d}$ ceramic samples has confirmed the simultaneous substitution of Sr for both Y and Ba in the $YBa_2Cu_3O_7$ structure. The substitution at the Y site has a distinct effect on the superconducting properties of the material. The inter-grain transport properties of both samples in an external d.c. field are enhanced with respect to undoped $YBa_2Cu_3O_7$ ceramics.

Keywords. High temperature superconductors; structure; a.c. susceptibility; Sr-substitution

1. Introduction

Substitution studies have been extensively used to study the superconducting properties of $YBa_2Cu_3O_7$. Among the first substitution studies to be performed was the replacement of Ba by Sr (Veal *et al* 1987; Wada *et al* 1987). These works reported a high solubility of Sr for Ba (up to 50%) accompanied by a decrease in T_c while retaining the characteristic orthorhombic $YBa_2Cu_3O_7$ structure. Guided by a simple model using ionic size constraints (Ganguly and Sreedhar 1988), we investigated the possibility of simultaneous substitution of Sr for both Ba and Y in $YBa_2Cu_3O_7$ (Siddiqi *et al* 1989). This paper presents a careful comparison of two compounds in the $(Y_{1-x}Sr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_{7-d}$, ($x = 0, 0.05$) system in order to confirm the substitution of Sr for Y and study its effect on the superconducting properties of the material.

2. Experimental

Two samples with composition $(Y_{0.95}Sr_{0.05})(Ba_{1.5}Sr_{0.5})Cu_3O_{7-d}$ and $Y(Ba_{1.5}Sr_{0.5})Cu_3O_{7-d}$ were prepared from powders of CuO, $BaCO_3$, Y_2O_3 and $Sr(NO_3)_2$ by a standard ceramic process. The powders were ground wet (in isopropyl alcohol) and calcined at 850°C twice, followed by two further stages of wet grinding, compaction and firing in flowing O_2 at 950°C. Maximum oxygenation of the samples was ensured by slow cooling (30°C/h) to room temperature in flowing O_2 after the final firing. SEM micrographs of both samples showed a homogeneous grain diameter of roughly 2 microns, high density and no evident secondary phases at the grain boundaries. Bars of $1 \times 1.5 \times 10\text{ mm}^3$ were cut for resistivity measurements (sampling

current $0.1\text{--}1\text{ A/cm}^2$) using a Leybold closed-cycle refrigerator with Si-diode thermometry. The same bars were used for a.c. susceptibility measurements (mutual inductance bridge) in a LN_2 bath with Au-Fe thermocouple thermometry. A portion of the samples was powdered for a comparative a.c. susceptibility measurement (using a quartz capillary with internal dimension of $1 \times 1 \times 10\text{ mm}^3$ as sample holder) and powder X-ray diffraction characterization. The X-ray spectrum was digitized and fitted using the Rietveld method (Rietveld 1967, 1969; Wiles and Young 1981) to obtain cell constants. Specimens used in the TEM analysis were prepared by ion milling thin plates of the samples.

3. Results

3.1 TEM analysis

The composition of numerous grains and grain boundaries of each sample was determined by EDX. There was no significant variation of composition from grain to grain in either compound and the average composition confirmed the nominal cation ratios of the two samples. High resolution electron micrography (HREM) at representative grain boundaries of each sample is shown in figures 1 and 2. These figures show that there is no secondary phase segregation or cell distortion at the grain boundary. Preliminary analysis of the selected area electron diffraction (SAED) patterns show evidence of the twinning characteristic of the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure with no additional supercell spots.

Figure 1. HREM image of a grain boundary in $\text{Y}(\text{Ba}_{1.5}\text{Sr}_{0.5})\text{Cu}_3\text{O}_{7-d}$.

Figure 2. HREM image of a grain boundary in $(Y_{0.95}Sr_{0.05})(Ba_{1.5}Sr_{0.5})Cu_3O_{7-d}$.

3.2. X-ray diffraction

Figure 3 shows a greatly expanded portion of the X-ray diffraction spectrum of the two samples. The splitting of the peaks indicates an orthorhombic structure for both samples and the Rietveld analysis yields cell constants of $a = 3.807(2)\text{\AA}$, $b = 3.876(3)\text{\AA}$, $c = 11.624(12)\text{\AA}$ for the sample with $x = 0$ and $a = 3.812(3)\text{\AA}$, $b = 3.876(5)\text{\AA}$, $c = 11.633(20)\text{\AA}$ for the sample with $x = 0.05$. The diffraction pattern of the $x = 0.05$ sample shows a weak trace of, as yet unidentified, secondary phase (arrows in figure 3).

3.3 Resistivity and a.c. susceptibility

The resistivity as a function of temperature near the superconducting transition (figure 4) indicated that the $x = 0$ sample has a markedly higher and sharper T_c than the $x = 0.05$ samples (due to the precision of the thermometry and the presence of gradients through the sample and sample holder, there is an overall 1.5 K uncertainty in the temperature scale of figure 4). Both samples showed distinct metallic behaviour ($R_{300}/R_{100} = 2.2$) up to room temperature.

The real and imaginary a.c. susceptibilities of the bulk samples (figures 5 and 6) have several noteworthy features. Both the $x = 0$ and $x = 0.05$ samples show no evidence of dissipation related to the intra-grain field expulsion, consistent with the small grain size observed by SEM. A comparison of the intra-grain region of the two samples shows that in the $x = 0$ sample (figure 5) the transition is sharper, shaped differently and its

Figure 3. Powder X-ray diffraction pattern ($CuK_{\alpha 1}$ radiation) of two $(Y_{1-x}Sr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_{7-\delta}$ samples. The arrows indicate a minute quantity of secondary phase in the $x=0.05$ sample.

Figure 4. Resistivity vs temperature near the superconducting transition for two $(Y_{1-x}Sr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_{7-\delta}$ samples.

Figure 5. Real (negative) and imaginary (positive) parts of the a.c. susceptibility of $\text{Y}(\text{Ba}_{1.5}\text{Sr}_{0.5})\text{Cu}_3\text{O}_{7-\delta}$ as a function of temperature for varying external d.c. field.

Figure 6. Real (negative) and imaginary (positive) parts of the a.c. susceptibility of $(\text{Y}_{0.95}\text{Sr}_{0.05})(\text{Ba}_{1.5}\text{Sr}_{0.5})\text{Cu}_3\text{O}_{7-\delta}$ as a function of temperature for varying external d.c. field.

onset is less field-dependent than in the $x=0.05$ sample (figure 6). The inter-grain coupling in both samples is marked by dissipation in the imaginary susceptibility. The field-dependence of this dissipation is relatively small for both samples (screening occurs within a few degrees of the intra-grain onset even for d.c. fields of 50 Gauss). The

Figure 7. Screened fraction (calculated as described in text) for powdered samples of $(Y_{1-x}Sr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_{7-d}$ as a function of external d.c. field.

$x = 0$ sample shows a larger field dependence than the $x = 0.05$ sample in this intra-grain transition, and by 50 Gauss applied d.c. field the dissipation occurs at the same temperature for both samples. In order to get a quantitative measure of the volume of superconducting material, the a.c. susceptibility of powdered samples with the same dimensions (but lower density) was measured. After correction for the different densities, the size of the diamagnetic signal of the powders at $T = 0.9 T_{Conset}$ (for each value of applied field) was divided by the zero-field diamagnetic signal of the bar at 77 K. The resulting percentages (figure 7) give an approximate indication of the superconducting volume fraction as a function of applied d.c. field at the same reduced temperature. These data indicate that the $x = 0.05$ sample has a smaller superconducting fraction than the $x = 0$ sample at all fields.

4. Discussion and conclusions

The TEM and X-ray diffraction data show that the two samples are essentially single-phase and that Sr is indeed able to substitute for Y when Ba is being simultaneously replaced by Sr. The increased a -axis in the $x = 0.05$ sample is consistent with the larger Sr substituting for Y in an 8-fold coordinated site. The b -axis, being constrained by the Cu-O chains, remains unchanged, while the c -axis shows a small expansion, again consistent with a larger Sr ion. The presence of this small quantity of divalent Sr replacing trivalent Y has a distinct effect on the superconducting properties of the material. The lower and broader intra-grain transition, as well as the lower superconducting volume fraction imply that the Sr may do local damage to the structure or electronic properties within the grains. This damage, however, appears to have little effect on the inter-grain coupling. The small (as compared to pure

YBa₂Cu₃O₇ prepared under the same conditions) temperature difference between the onset of superconductivity and the inter-grain screening (in the $x = 0.05$ sample particularly) indicate a relatively steep J_c vs T curve and not a very pronounced degradation of J_c in small external fields.

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References

- Ganguly P and Sreedhar K 1988 in *Progress in high temperature superconductivity* (ed) C N R Rao (Singapore: World Scientific) 7 134
- Rietveld H M 1967 *Acta Crystallogr.* **22** 151
- Rietveld H M 1969 *J. Appl. Crystallogr.* **2** 65
- Siddiqi S A, Sreedhar K, Drobac D, Infante C, Maticotta F C and Ganguly P 1989 *Proc. Third European Conf. on low-dimensional conductors and superconductors, Dubrovnik* (to appear)
- Veal B W, Kwak W K, Umezawa A, Crabtree G W, Jorgensen J D, Downey J W, Nowicki L J, Mitchell A W, Paulikas A P and Sowers C H 1987 *Appl. Phys. Lett.* **51** 279
- Wada T, Adachi S, Mihara T and Inaba R 1987 *Jpn J. Appl. Phys.* **26** L706
- Wiles D B and Young R A 1981 *J. Appl. Crystallogr.* **14** 149