The Occurrence of 1212-Type Phase in the Pb-Sb-Sr-Ca-Y-Cu-O System

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Abstract

Samples of nominal composition $Pb_{1-x}Sb_xSr_2Ca_{1-y}Y_yCu_2O_{7-\delta}$ with $0 \leq x, y \leq 1$, synthesized at 900 °C in air, argon and oxygen, have been investigated. None of the samples sintered in air or in oxygen was superconducting. Some of the samples which were prepared in argon exhibited superconductivity. The superconducting signal was not due to the "1212-phase", but probably due to a "2213-phase".

1 Introduction

Superconductors of the 12(n-1)(n) structure family ($1 \leq n \leq 4$) differ from the 22(n-1)(n) family in the smaller distance between successive groups of CuO_2-layers. This should lead to a reduction of the anisotropy which in turn might improve the ability of flux pinning and thus increase the critical current density. In a highly anisotropic superconductor with interlayer distances larger than the coherence length, the flux lines decouple into independent "pancakes" which are weakly pinned [1, 2]. A lower degree of anisotropy may cause the flux lines to interact as a whole with the pinning sites. This has been observed *e.g.* in Tl-based 1212 and 1223 compounds [3]. In an attempt to avoid the highly toxic Tl, we have studied the occurrence of 1212-type phases in the system $Pb_{1-x}M_xSr_2Ca_{1-y}Y_yCu_2O_{7-\delta}$. Superconductivity is already known for M = In [4], Cu [5], Sr [6], Ca [7] and Cd [8]. We report results of investigations where M = Sb in the range $0 \leq x, y \leq 1$. The influence of different sintering atmospheres (air, argon, oxygen) will be discussed.

2 Experimental

2.1 Sample preparation

Ceramic samples of nominal composition $Pb_{1-x}Sb_x$-$Sr_2Ca_{1-y}Y_yCu_2O_{7-\delta}$ were prepared by solid state reaction using a precursor route. High purity powders (> 99.9%) of $SrCO_3$, $CaCO_3$, Y_2O_3 and CuO were mixed and subsequently calcined at 970 °C for 18 h. After addition of PbO and Sb_2O_3 in appropriate proportions, these mixtures were ground and pressed into pellets (10 mm in diameter, about 3 mm in thickness) using a pressure of about 0.3 GPa. The pellets were then sintered at 900 °C for 12 h either in air or oxygen or in argon and furnace-cooled at a rate of about 2 °C/min.

2.2 Phase identification

The phases occurring were investigated by X-ray powder diffraction on a Seifert XRD 3000 P diffractometer using Cu K_α radiation. Further characterization was done by optical metallography and scanning electron microscopy.

2.3 Resistivity and T_c determination

Four-probe ac resistivity measurements were carried out at a frequency of 20 Hz and an applied current of about 4 mA. Contacts were made by fine copper wires attached with conductive silver paint. Susceptibility data were obtained by ac-susceptibility measurements and by SQUID measurements.

3 Results and Discussion

The powder X-ray patterns of the samples $Pb_{1-x}Sb_x$-$Sr_2Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ prepared in air are shown for $x = 0$ in Fig. 1a and $x = 0.1$ in Fig. 1b. The peaks of the 1212-phase marked (•) in the Figure could be indexed using the space-group P4/mmm and lattice constants of $a \simeq 3.82$ Å and $c \simeq 11.8$ Å. The ratio of the amount of the 1212-phase to the impurity phases as determined from integrated X-ray intensities is shown in Fig. 2 for the samples with $y = 0.5$ and $0 \leq x \leq 0.7$. The maximum at $x = 0.1$ could also be seen at different values of y for samples prepared in air. This maximum indicates that Sb is incorporated into the 1212-phase improving phase stability, or that the presence of Sb may increase the speed of 1212-phase formation under the present preparation conditions. Fig. 3 shows the change of lattice constants for the samples $y = 0.5$ and $0.0 \leq x \leq 0.7$. The a lattice parameter is nearly constant, while the c lattice parameter (and also the volume of the unit cell) shows a maximum for $x = 0.1$.
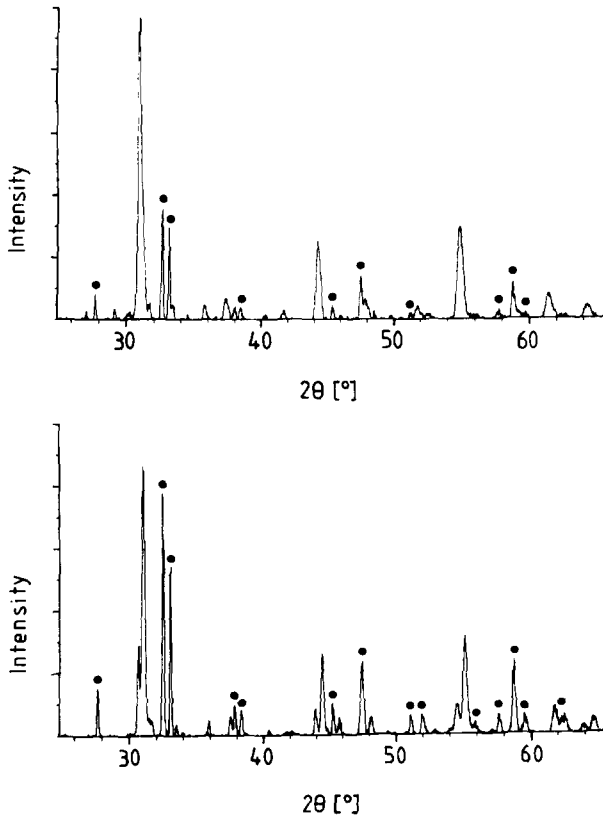
Fig. 1. Powder X-ray patterns of samples with nominal composition $PbSr_2Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ (upper panel) and $Pb_{0.9}Sb_{0.1}Sr_2Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ (lower panel). Peaks marked ● belong to the 1212-type phase.

This appears counterintuitive, if the atomic or ionic radii are considered and the smaller Sb substitutes on

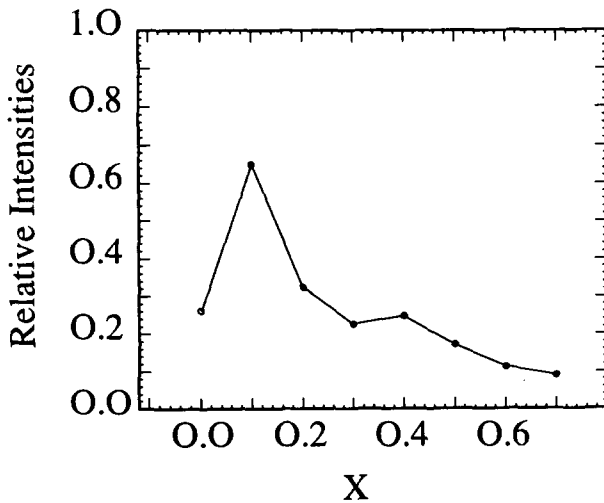Fig. 2. Ratio of the amount of 1212-type phase to the amount of impurity phases for $Pb_{1-x}Sb_xSr_2Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ with $0 \leq x \leq 0.7$, determined from integrated X-ray intensities.
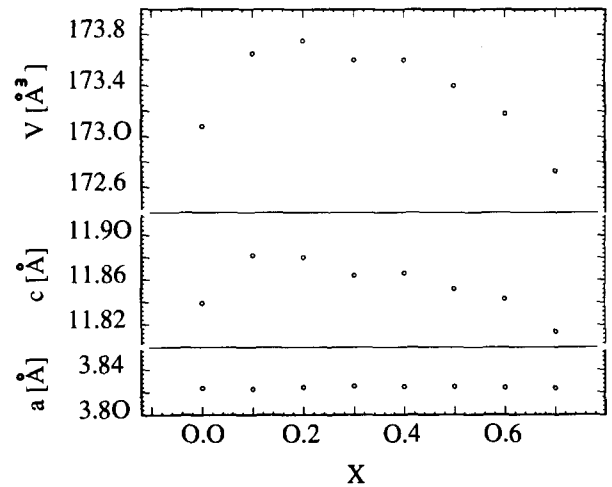

Fig. 3. a and c lattice parameters and unit-cell volume V for $Pb_{1-x}Sb_xSr_2Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ ($0 \leq x \leq 0.7$).

the Pb lattice site. However, at present the degree of site disorder is not known. As long as the samples are not single phase, the fact that the lattice parameters vary in a systematic way with nominal Sb content shows that the phase composition varies, but not necessarily the Sb content; it does not prove that Sb is incorporated into the structure.

It is remarkable that the sample with $x = 0.1$ shows the smallest resistivity (see Fig. 4). None of the samples prepared in air or in oxygen as described above is superconducting. Their resistivities show semiconducting behaviour.

Samples prepared in argon have non-monotonic resistivity. Fig. 5 presents the resistivity measurement as a function of temperature for the sample $Pb_{0.7}Sb_{0.3}Sr_2Ca_{0.3}Y_{0.7}Cu_2O_{7-\delta}$ prepared in argon. The local maximum in the resistivity curve marks the
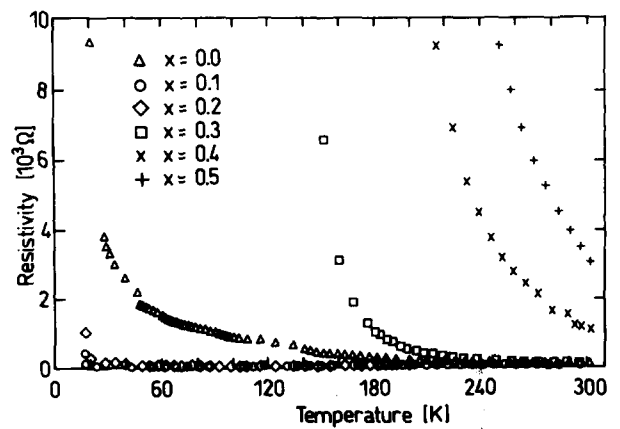

Fig. 4. Temperature dependence of the resistivity of $Pb_{1-x}Sb_xSr_2Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ samples with $0 \leq x \leq 0.5$.
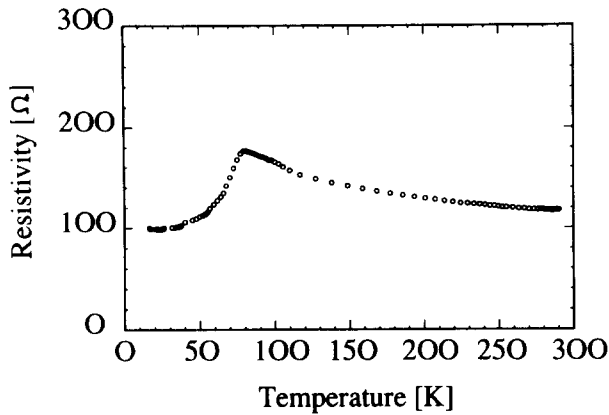
Fig. 5. Resistivity versus temperature for the sample with nominal composition $Pb_{0.7}Sb_{0.3}Sr_2Ca_{0.3}Y_{0.7}Cu_2O_{7-\delta}$.

onset of a superconducting transition as is confirmed by the SQUID-magnetometer (see Fig. 6). The rise of the resistivity with decreasing temperature below the local minimum reveals that there is no continuous superconducting path. Fig. 6 shows the SQUID measurement for the sample of Fig. 5. The field-cooled curve is displayed ($B = 0.03$ T). The onset of the superconducting transition is at about 52 K. The X-ray powder diffraction diagram of this sample is shown in Fig. 7. There are no traces of the 1212-phase, instead peaks of a 2213-phase, labeled •, are observed. These peaks are indexed within the space group Cmmm with lattice constants of $a = 5.39Å, b = 5.42Å$ and $c = 15.75Å$.
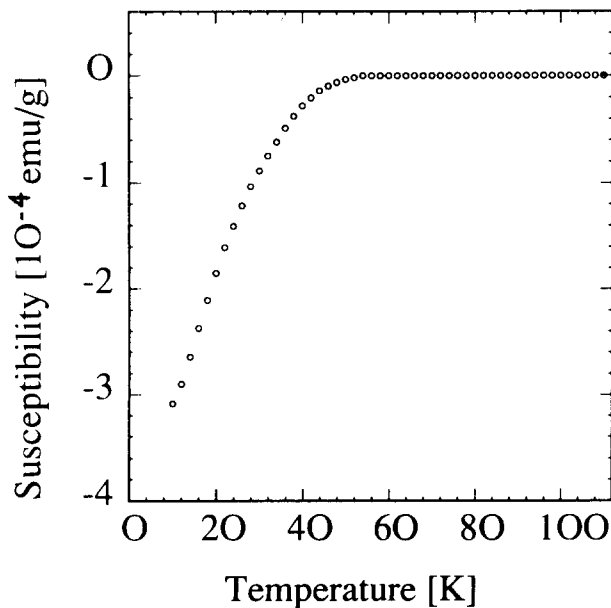

Fig. 6. Susceptibility of the sample with nominal composition $Pb_{0.7}Sb_{0.3}Sr_2Ca_{0.3}Y_{0.7}Cu_2O_{7-\delta}$ as determined with the SQUID magnetometer.
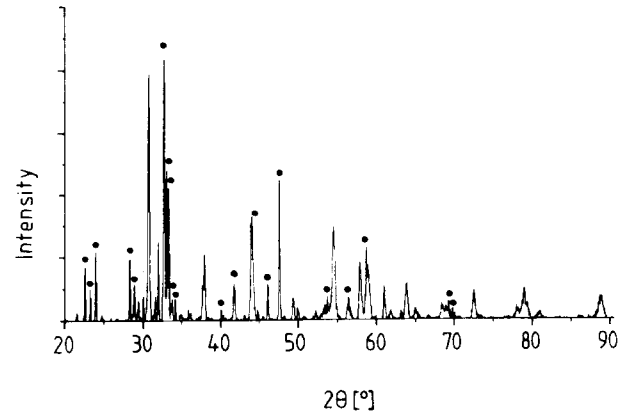

Fig. 7. Powder X-ray pattern of the sample of fig. 6. (•) peaks of 2213-type phase.

The impurity phases could not be identified. Since we did not obtain single-phase samples, it is not clear whether Sb is incorporated into this 2213-phase or not. Further investigations are needed to clarify this point.

4 Conclusions

Under our preparation conditions, the 1212-phase is formed over a wide range of nominal composition when sintered in air or in oxygen. The addition of Sb appears to favour 1212-phase formation; however, since no single-phase samples were obtained, it remains unclear whether Sb enters the phase. None of the 1212-phases is superconducting. Under argon atmosphere, the 1212-type structure is not stable against the formation of a 2213-type compound. Samples containing 2213-phase exhibit traces of superconductivity.

Acknowledgments

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