Zero resistance states in modified Y–Ba–Cu–O system with transition temperatures above 135 K

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Abstract. Superconducting transition of minor-dispersed phase in modified $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples is found to occur at around 140 K. The amount of this minor phase is enough to provide zero resistivity above 135 K. The measurements of the electrical resistivity indicated that the material is stable, thermally recyclable and reproducible. X-ray analysis of the sample with the highest T_c shows a major phase with perovskite-like structure with $a = 3.820(1) \text{ \AA}$; $b = 3.873(1) \text{ \AA}$ and $c = 11.659(2) \text{ \AA}$ along with several unidentified weak peaks. Magnetic measurements confirmed the mixed-phase nature with diamagnetic transition temperatures at 137, 91 and 86 K. The minor phase responsible for superconductivity with zero resistivity above 135 K is about 0.4% of the bulk and its nature is still unidentified. The details of the preparation and chemical modification process and the results are presented.

Keywords. High T_c superconductivity; chemical modification; 123 compounds; YBaCuO sulphide; magnetic susceptibility.

1. Introduction

The discovery of high T_c superconducting oxides (Bednorz and Muller 1986; Wu *et al* 1987) has initiated intensive research activities aimed not only to understand the nature of high temperature superconductivity (Bardeen 1988), but further to develop new techniques for their production in useful and reproducible forms for technological applications (Jin *et al* 1987; Togano *et al* 1988; Gross *et al* 1988) and to raise the superconducting critical temperature (Maeda *et al* 1988; Chu *et al* 1988).

A number of sulphur additions to the Y–Ba–Cu oxides have been studied. The results of these sulphur modifications were not consistent and highly dependent on the starting material and the preparation conditions. An improvement of T_c with zero resistance at 108 K (Taylor *et al* 1987) was noticed when sulphur was added as CuS , but the material was unstable on repeated cycling and degraded when left in air at room temperature. On the other hand, lowering of T_c was reported (Matsubara *et al* 1988) when sulphur was added as CuS or Cu_2S . Modification using sulphur in vacuum reduced the superconducting properties (Amador *et al* 1988), but sputtering S simultaneously with Y–Ba–Cu oxide ceramic produced modified materials having higher transition temperature (Tanaka 1989). Transition temperature at 135 K and zero resistance at 112 K have also been reported for these materials (Imai and Kurokawa 1989).

In this paper we present the results of the substitution effect (modification) of few percentage of BaS for BaO of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and preparation conditions on superconductivity transition temperature, lattice constants and magnetic properties.

2. Experimental procedure

Samples of the modified 123 system Y–Ba–Cu–S–O ceramics were prepared from Y_2O_3 , BaO containing few percentage of BaS (up to 3%) and CuO powders. These powders were intimately ground, mixed and pressed into 13 mm diameter pellets of 0.4 to 0.7 mm thickness. The pellets were subjected to heat treatment for 5 h at $875 \pm 5^\circ\text{C}$ in ceramic crucibles and cooled slowly to room temperature with an average rate of $2^\circ\text{C}/\text{min}$. The annealing as well as cooling processes took place in a stream of O_2 0.4 to 0.6 lit/min flow rate. The ceramic crucibles used in preparation were preheated at the same temperature in O_2 atmosphere for 2 h. No apparent reaction took place at the pellet-crucible interface.

3. Results

3.1 Electrical resistivity

The superconducting transition temperature for prepared pellets was measured by four-point probe technique using silver paint for electrical contacts. All the modified materials showed an improvement in T_c . The resistivity versus temperature curve for one of the modified materials with the highest T_c is shown in figure 1. Above 150 K one can see a purely metallic behaviour with a faint knee around 183 K. The onset of superconductivity as manifested by a sharp drop in the resistivity starts at approximately 140 K. The resistivity reaches zero resistance state at 137 K in one step. Measurements taken using different values of current densities (10–100 mA) below 137 K confirmed the zero resistance state within the detection limit of 10^{-8} V. The measurements of the electrical resistivity indicated that the material is stable, thermally recyclable and reproducible.

3.2 X-ray analysis

X-ray powder diffraction (figure 2) shows that the resulting metallic pellets of nominal composition $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{S}_x$ are not single phase. The material was found to contain

Figure 1. Electrical resistivity as a function of temperature of the modified 123 material.

Figure 2. X-ray powder diffraction pattern of modified 123 material.

Figure 3. Magnetic properties of modified 123 material as a function of temperature.

a major orthorhombic phase with refined lattice parameters $a = 3.820(1) \text{ \AA}$; $b = 3.873(1) \text{ \AA}$; $c = 11.659(2) \text{ \AA}$ and $V = 172.50(5) \text{ \AA}^3$. Extra weak peaks corresponding to a few per cent of a second unidentified phase were also found. Increasing sulphur doping leads to an increase in the intensity of these weak peaks. Their reliable refinement is in progress.

3.3 Magnetic properties

A special SQUID magnetometer was used to measure the magnetic properties of the prepared materials to determine if diamagnetic contributions associated with zero resistance could be detected. The zero-field cooled magnetization (ZFC) curve shown in figure 3a for the sample with the highest T_c indicates a weak diamagnetic-like deviation from paramagnetic background at about 137 K. The (ZFC) curve shown in figure 3b contains two diamagnetic deviations, a moderate one at about 91 K and a major one at about 86 K. The minor diamagnetic deviation at 137 K corresponds to about 0.4% of the bulk. The major diamagnetic contribution of 86 K corresponds to about 95% of the total material. The strong temperature correlation of the weak diamagnetic signal at 137 K to the electrical resistance results may provide an evidence for the onset of superconductivity in the studied samples at about 140 K. The diamagnetic response is also in agreement with the mixed-phase nature indicated by X-ray diffraction analysis.

4. Conclusion

Thermally recyclable zero-resistance states with improved superconducting transition temperature as high as 140 K are observed in the 123 compounds partially modified by sulphur. The one-step preparation conditions reported in this study for the first time seems to be adequate for the preparation of high T_c superconductors. The highest temperature diamagnetic deviation was found to occur at the same temperature as the superconducting transition.

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