

Bi cuprates of type 1212 - a new family of superconductors in the Bi series

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Abstract

Studies of the influence of chemical composition and post-treatment on the superconducting properties of the new superconducting family Bi-1212 indicate that the superconducting transition temperatures as well as the superconducting volume fraction are dependent on both parameters. The highest $T_c = 84\text{K}$ is obtained for Bi:Pb:Sr:Y:Cu = 0.4:0.3:2:0.6:2.1 after post-annealing in flowing Ar (600°C/50h). From the uniform observation of an increase of the superconducting volume fraction after post-annealing at moderate temperatures (500-700°C) follows the important correlation between a certain crystalline order and the development of superconductivity; actually values up to a Meissner fraction of about 10% are obtained.

1. Introduction

Bi cuprates of type 1212 are members of a new family of superconductors in the Bi series [1]. Their crystal structure is composed of superconducting perovskite slabs with two CuO_2 planes separated by a single rocksalt-like layer containing the Bi ions (Fig. 1). Consequently, in comparison with the Bi-2212 type, characterized by the wellknown extreme two-dimensionality of the flux line lattice, for Bi-1212 the coupling between the superconducting slabs should be enforced owing to the thinner rocksalt-like spacer. In fact, YBCO-123 is an analog and special form of the 1212 structure (Fig. 1) with the only difference that the single rocksalt-like layer in 1212 is replaced by CuO chains in 123. This replacement decreases the crystal symmetry from tetragonal (space group $P4/mmm$; 1212) to orthorhombic ($Pmmm$; 123). As a result of its higher crystal symmetry 1212 is superior to 123 due to the absence of a structural transformation from a non-superconducting, tetragonal high-temperature material into an orthorhombic superconductor.

In the present study the influence of chemical composition and post-treatment on the superconducting properties is investigated. It is shown that both parameters influence the superconducting transition temperature. The highest value is situated at 84K for a sample of nominal Bi:Pb:Sr:Y:Cu ratio of 0.4:0.3:2:0.6:2.1 after post-annealing in flowing Ar at 600°C/50h. The

superconducting volume fraction is likewise highly sensitive to both parameters. Actually, values up to about 10% are obtained after post-treatment at moderate temperatures of 500-700°C. From the significant temperature reduction of more than 200°C between the post-treatment and the preparation temperature (960-990°C) follows that the development of a certain crystalline order is most probably responsible for the improvement of superconductivity.

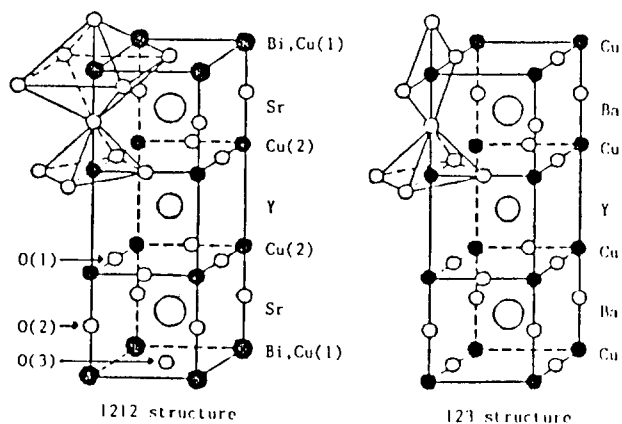


Figure 1. Crystal structure of Bi-1212 ($(\text{Bi}_{0.5}\text{Cu}_{0.5})\text{-Sr}_2\text{YCu}_2\text{O}_7$ [1]) in comparison with the orthorhombic 123-structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$.

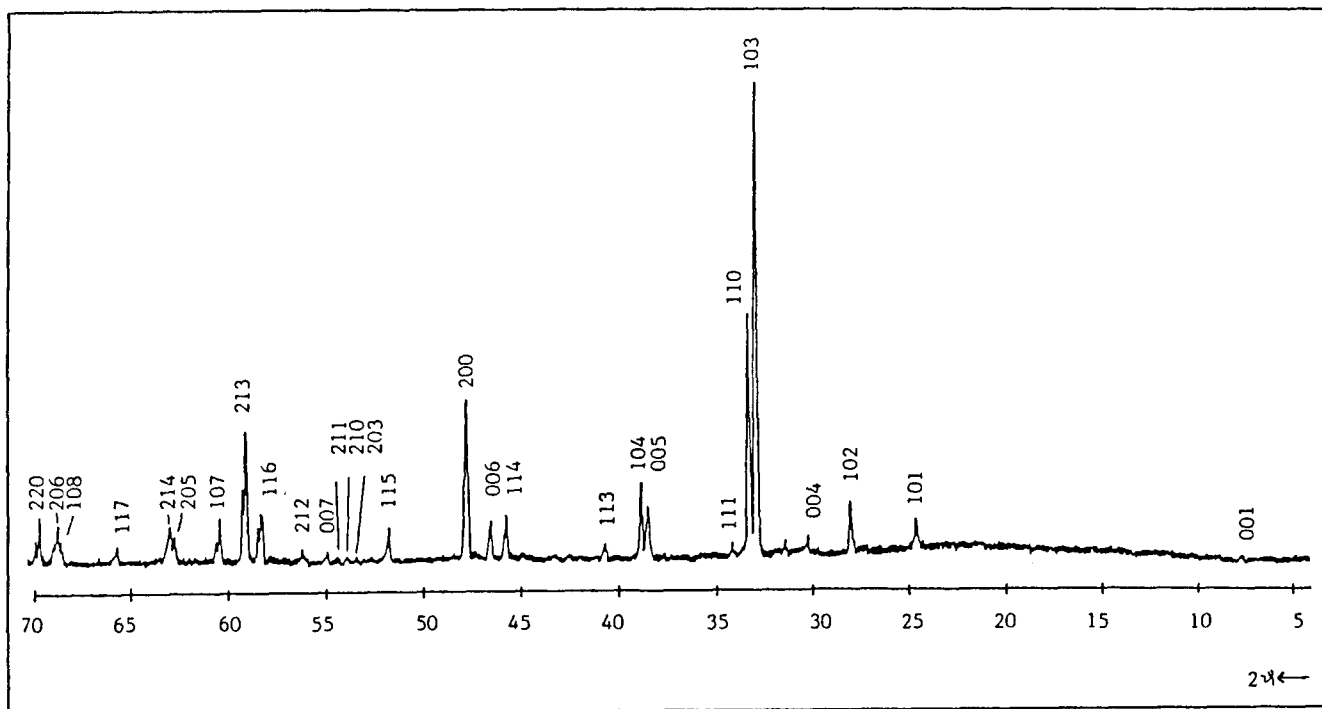


Figure 2. Section of the XRD pattern of a powder of Bi:Sr:Y:Cu ratio of 0.4:2.0:1.0:2.5; the 1212 reflections are indicated (lattice constants of the tetragonal unit cell : $a = 3.815(5)$; $c = 11.73(1)\text{\AA}$).

2. Experimental

Samples of nominal composition $(\text{Bi}_{1-v-w}\text{Pb}_v\text{Cu}_w)\text{-Sr}_{2-x}\text{M}_x(\text{Y}_{1-y}\text{M}_y)\text{Cu}_2\text{O}_{7-z}$ ($M = \text{Ba}, \text{Sr}, \text{Ca}, \text{Cu}$) were prepared via a solid state reaction from $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (DAB6; Merck), PbO , $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, CaCO_3 (all p.A.; Merck), CuO (puriss.p.A.; Fluka) and Y_2O_3 (99.99%; Rhône Poulenc). After an initial decomposition of the nitrates at $\approx 700^\circ\text{C}$ (1h) the materials were ground in an agate mortar and heated in corundum crucibles in air at $960 - 990^\circ\text{C}$ for several times with intermittent regrindings and X-ray analysis (Philips powder diffractometer, $\text{CuK}\alpha$ radiation, Au standard). The reaction was stopped after no further change was detected in the XRD. This stage was reached after a total firing time of 25-120h. All samples were air quenched. Aliquots of these as-prepared materials were subsequently submitted to several post-treatments. The samples were characterized by XRD, neutron powder diffraction, analytical and DC susceptibility (SQUID) measurements.

3. Results and discussion

3.1. XRD and neutron powder diffraction

Materials with a high crystalline purity are obtained for a nominal composition near $(\text{Bi}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_{7-z}$. As an example the XRD pattern of a sample of a Bi:Sr:Y:Cu ratio 0.4:2.0:1.0:2.5 is given in Fig. 2. From an analysis of the X-ray [1] and neutron powder diffraction data (space group $P4/mmm$) follows an occupation of the rocksalt-like plane by Bi and Cu (Fig. 1). Similar to other members of the 1212 family [2] the oxygen atom O(3) is situated in the centre of the basal plane and likewise a displacement from the ideal $1c$ site $(1/2, 1/2, 0)$ to a $4h$ site $(x, 1/2, 0)$ with $x \approx 0.3$ is present, whereas an 123-like occupation of the "chain oxygen" positions (Fig. 1) can be completely excluded. The Cu-O distances within the $\text{Cu}(2)$ pyramids fall in the usual regions ($\text{Cu}(2) - \text{O}(1)$: 1.92\AA ; $\text{Cu}(2) - \text{O}(2)$: 2.31\AA). According to TEM investigations there is no modulation in the crystal structure [3].

Since as prepared materials of nominal composition $(\text{Bi}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_{7-z}$ are non-superconducting several substitution routes were tested for the introduction of superconductivity. The main interest was concentrated on a substitution of Ba, Sr, Ca, Pb for Y or Sr and Pb for Bi. According to the larger ionic radius of Pb^{2+} (1.19Å; CN6) in comparison with Bi^{3+} (1.03Å) the parameters of the still tetragonal unit cell are expanded ($a = 3.835(5)$, $c = 11.82(1)\text{Å}$ for Bi:Pb:Sr:Y:Cu = 0.4:0.3:2:0.6:2.1 in comparison with $a = 3.815(5)$, $c = 11.73(1)\text{Å}$ for $(\text{Bi}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_{7-z}$), whereas a formal substitution of Ca^{2+} (1.00Å) for Sr^{2+} (1.18Å) results in a shrinkage of the cell dimensions ($a = 3.812(5)$, $c = 11.61(1)\text{Å}$ for Bi:Sr:Ca:Y:Cu = 0.4:1.9:0.1:0.8:2.5). Only materials with a high 1212 content were considered further and submitted additionally to several post-treatments at various temperatures in different gas atmospheres. The purity of the samples is not affected by the method of post-treatment.

3.2. Magnetic susceptibility

Whereas materials of nominal compositions near $(\text{Bi}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_{7-z}$ are non-superconducting in the as prepared state, superconductivity is introduced after post-annealing between 600 and 700°C in either air or $\text{Ar}/\text{O}_2(8\%)$, respectively. However, the superconducting volume fraction rests still below about 1%. Fortunately, some methods of increasing the Meissner fraction have been found and examples are given in Fig. 3. A decrease of the Y content

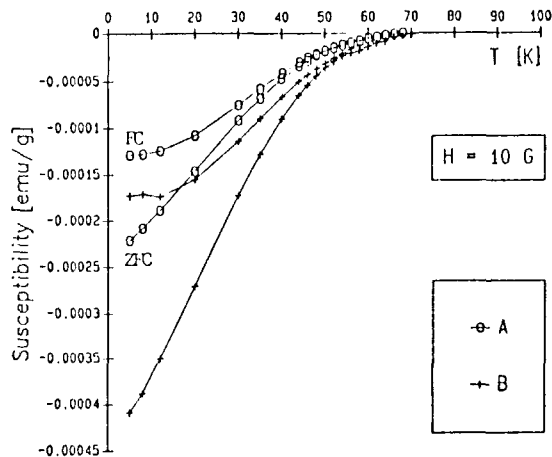


Figure 3. χ vs. T for $\text{Ar}/\text{O}_2(8\%)$ post-annealed materials with (A) Bi:Sr:Y:Cu = 0.4:2.0:0.8:2.5; 50h/600°C and (B) Bi:Sr:Ca:Y:Cu = 0.4:1.9:0.1:0.8:2.5; 12h/600°C (FC: field cooled; ZFC: zero field cooled).

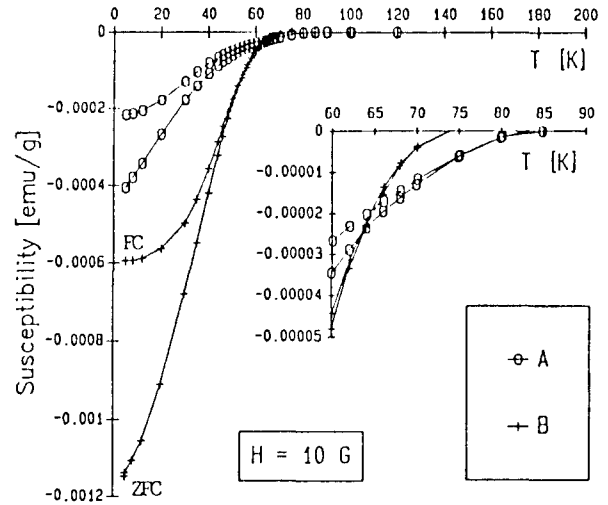


Figure 4. χ vs. T for a material with Bi:Pb:Sr:Y:Cu = 0.4:0.3:2.0:0.6:2.1 after post-treatment in (A) flowing Ar (50h/600°C) and (B) O_2 (6h/550°C); the inset gives an enlargement of the section between 60 and 90 K (FC: field cooled; ZFC: zero field cooled).

(Bi:Sr:Y:Cu = 0.4:2.0:0.8:2.5) and post-treatment in $\text{Ar}/\text{O}_2(8\%)$ for 50h/600°C increases the Meissner fraction to about 1.5%. Furthermore, this value can be practically doubled by a nominal $\text{Ca} \rightarrow \text{Sr}$ substitution (Bi:Sr:Ca:Y:Cu = 0.4:1.9:0.1:0.8:2.5; post annealed in $\text{Ar}/\text{O}_2(8\%)$ for 12h/600°C, Fig. 3). For both materials T_c is situated at about 70K. From the observed sluggish transition to superconductivity follows most probably the presence of inhomogeneities in the ionic distribution of both materials.

Partial substitution $\text{Pb} \rightarrow \text{Bi}$ introduces superconductivity in the as prepared state for cases with simultaneously adjusted overall cation content. E.g. for the as prepared, air quenched material with Bi:Pb:Sr:Y:Cu = 0.4:0.3:2:0.6:2.1 the Meissner fraction is about 5% and improves by a factor of about two after post-treatment at moderate temperatures. Interestingly, in the temperature region between 500 and 700°C the surrounding gas atmosphere (O_2 , air, $\text{Ar}/\text{O}_2(8\%)$) does not meaningful influence the superconducting volume fraction. However, the position of T_c strongly depends on the oxygen content of the gas environment (Fig. 4) and increases with decreasing oxygen amount from 74K ($\text{O}_2/500^\circ\text{C}$) via 75K (air/500°C), 79K (air/600°C), and 80K ($\text{Ar}/\text{O}_2(8\%)/700^\circ\text{C}$ to 84K ($\text{Ar}/600^\circ\text{C}$).

the Pb substituted Bi-2212 system [4], thus pointing to the existence of a similar mechanism for the development of superconductivity. Its origin is still not fully understood but most likely correlated with the development of a certain crystalline order. Actually, we are concerned with experiments of further optimizing the superconducting volume fraction as well as the transition temperature with the intention to reach a value of about 100K, typical for the isostructural Tl-based 1212 materials [5].

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