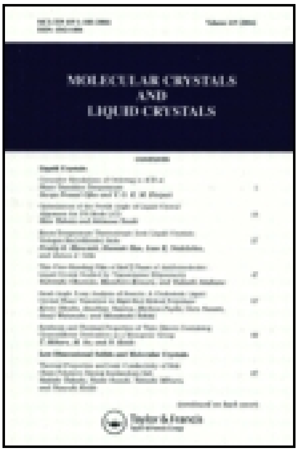

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Formation Mechanism of Bi-Based High-T_c Superconductors in the Melt-Quenching Method

Takayuki Komatsu [a], Ryuji Sato [a], Tomohiro Ohki [a] & Kazumasa Matusita [a]

[a] Department of Chemistry, Nagaoka University of Technology, Nagaoka, 940-21, Japan

Version of record first published: 22 Sep 2006.

Mol. Cryst. Liq. Cryst., 1990, vol. 184, pp. 75–79
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Printed in the United States of America

FORMATION MECHANISM OF Bi-BASED HIGH-T_c SUPERCONDUCTORS IN THE MELT-QUENCHING METHOD

TAKAYUKI KOMATSU, RYUJI SATO, TOMOHIRO OHKI and KAZUMASA MATUSITA
Department of Chemistry, Nagaoka University of Technology,
Nagaoka 940-21, Japan

Abstract Bi-based high-T_c superconductors were prepared by using the melt-quenching method. The values of critical temperature T_c and critical current density J_c for the samples of $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ (x=1.5, 1.8 and 2.0) obtained by annealing at 840°C for 250h decreased with increasing Cu content, and the glass-ceramics with x=1.5 exhibited superconductivity with a T_c(zero) of 106K and a J_c (77K, zero magnetic field) of 250A/cm^2. The formation of the high-T_c phase in the superconducting $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ ceramics was largely enhanced by the addition of a very small amount of Sb or Mo element. It was found that the lowering of the partial melting temperature at around 870°C caused by the coexistence of Pb and Sb or Mo elements was very important for the formation of the high-T_c phase.

INTRODUCTION

Since the first report on new Bi-based high-T_c superconducting ceramics with different critical temperatures of 105K (high-T_c phase) and 85K (low-T_c phase) by Maeda et al.,[1] many researchers have expended much effort to prepare pure samples of the high-T_c phase. High-T_c superconducting ceramics have usually been prepared by the conventional sintering method. Komatsu et al.[2,3] developed the melt-quenching method as a new preparation technique of Bi-based high-T_c superconducting ceramics. It has been thought that the melt-quenching method can be applied to the production of the samples with various shapes and fibers. In this paper, we report the superconducting properties of various Bi-based ceramics prepared by the melt-quenching method and discuss the formation mechanism of the high-T_c phase.

EXPERIMENTAL METHODS

The nominal compositions examined in this study are $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ (x=1.5, 1.8 and 2.0), $Bi_{1.6-x}Pb_{0.4}Sb_xSr_2Ca_2Cu_3O_y$ (x=0.1 and 0.2),

$Bi_{1.6-x}Pb_{0.4}Mo_xSr_2Ca_2Cu_3O_y$ (x=0.05 and 0.1) and $Bi_{1.6}Pb_{0.4-x}Mo_xSr_2$-$Ca_2Cu_3O_y$ (x=0.1, 0.2, 0.3 and 0.4). Commercial powders of guaranteed reagent Bi_2O_3, Pb_3O_4, $SrCO_3$, $CaCO_3$, CuO, Sb_2O_3, MoO_3 were mixed and calcined at 800-840°C for 10-12h in air. The calcined powders were melted in a platinum crucible at 1250-1300°C for 20min in an electric furnace. The melts were poured onto an iron plate and pressed quickly to a thickness of about 1.5mm. The melt-quenched samples were annealed at various conditions. Measurements of T_c and J_c were made by using a four-point probe method. The T_c measuring current was 5mA (current density 150-200mA/cm^2). Measurements of the changes in inductance for the annealed samples (bulk) were carried out by using an AC Hartshorn-type bridge, in which the frequency was 713Hz and the AC field amplitude was 0.1 Oe. Differential thermal analyses (DTA) for the melt-quenched samples were made at a heating rate of 10K/min.

RESULTS AND DISCUSSION

We first examined the effects of Cu content on the glass formation for the melt-quenched samples with the compositions of $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ and on the superconducting properties for the annealed samples. It was found from X-ray powder diffraction (XRD) and DTA analyses that the composition with x=1.5 had a tendency to form a glass and $Bi_2Sr_2CuO_y$ crystals tended to precipitate easily during the rapid quenching of melts in the compositions with x=1.8 and 2.0. The temperature dependence of the resistivity for the samples annealed at 840°C for 250h (air-cooled after annealing) is shown in Figure 1. It is seen that the value of T_c increases with decreasing Cu content and the value of normal-state resistivity decreases. The obtained values of T_c and J_c (77K, zero magnetic field) are summarized in Figure 2. It is clear that an excess amount of Cu element, which is estimated as a deviation from the nominal composition of the high-T_c phase, causes a degradation in the superconducting properties. It is supposed that the origin of the degradation in the superconducting properties is due to the precipitation of CuO, though the formation of the high-T_c phase is enhanced by the addition of the excess amount of Cu element. The furnace-cooled sample after annealing at 840°C for 250h exhibited the superconductivity with T_c=106K and J_c=250A/cm^2.

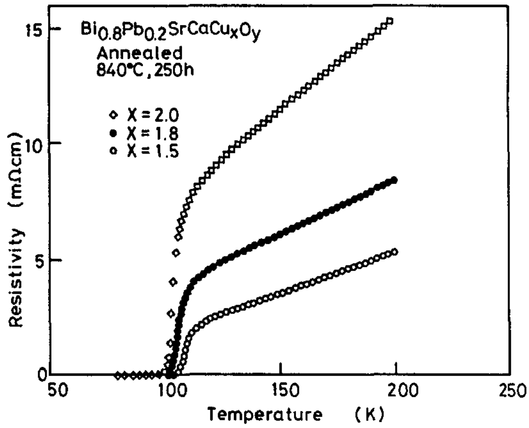

FIGURE 1 Temperature dependence of the resistivity for the air-cooled samples after annealing at 840°C for 250h in air.

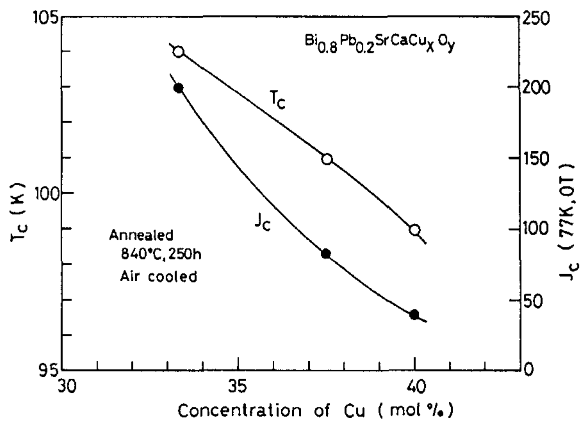

FIGURE 2 Values of critical temperature T_c and critical current density J_c for the annealed samples of $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$.

In the DTA curve for the melt-quenched sample of $Bi_{0.8}Pb_{0.2}SrCa-Cu_{1.5}O_y$, a very broad exothermic peak and an endothermic peak are observed at around 800°C and at 861°C, respectively. The XRD patterns for the samples annealed at 770°C, 800°C and 820°C for 1h are mainly assigned to the low-Tc phase, indicating that the exothermic peak at around 800°C is closely related to the formation of the low-T_c phase. As the annealing temperature increased from 820°C to 860°C, the intensities of peaks due to the low-T_c phase became weak and new peaks attributable to $Bi_2Sr_2CuO_x$ appeared. Furthermore, it was found from XRD analyses and the changes in inductance that the volume fraction of the high-T_c phase was increased with increasing annealing time at around 840°C.

The effect of the addition of Sb or Mo element on the formation of the high-T_c phase in the Bi-based superconductors was examined. The temperature dependence of the changes in inductance for the annealed (first at 850°C for 100h and then at 400°C for 10h) samples of Sb-free and Sb-doped $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ superconductors is shown in Figure 3. In the Sb-doped sample, the changes in inductance occur almost in one step at temperature around 110K, indicating that the main superconducting phase is the high-T_c phase. However, two-step transitions are clearly observed in the Sb-free sample, indicating that both the low-T_c and high-T_c phases are present. The XRD patterns at room temperature for the Mo-doped $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ superconductors are shown in Figure 4. It is seen that the main superconducting phase is the high-T_c phase. Some unidentified peaks are also observed in these Mo-doped samples. These results indicate that the formation of the high -T_c phase was largely enhanced by the coexistence of Pb and Sb or Mo elements.

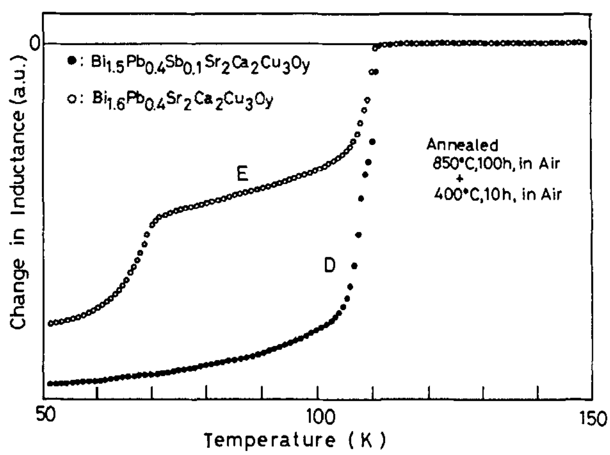

FIGURE 3 Temperature dependence of the changes in inductance for the annealed (first at 850°C for 100h and then at 400°C for 10h) samples.

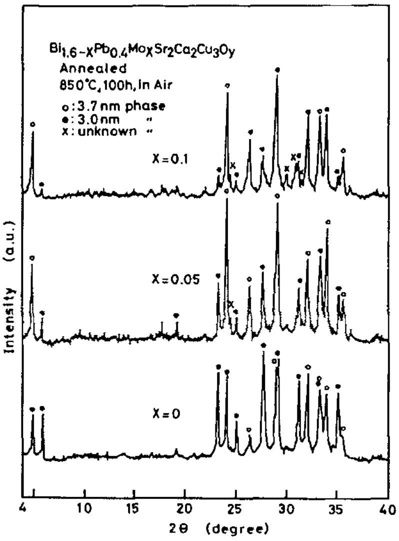

FIGURE 4 X-ray powder diffraction patterns at room temperature for the Mo-doped samples annealed at 850°C for 100h in air.

We consider the reason why the coexistence of Pb and Sb or Mo elements is effective for the formation of the high-T_c phase. The DTA analyses were performed for various melt-quenched samples, and it was found that the partial melting temperature was lowered by addition of Pb element and this lowering is enhanced by the coexistence of Pb and Sb or Mo elements. Considering that the formation of the high-T_c phase is largely enhanced in Sb- and Mo-doped $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ samples but is very difficult in $Bi_2Sr_2Ca_2Cu_3O_y$ and $Bi_{1.6}Mo_{0.6}Sr_2Ca_2Cu_3O_y$ samples, it is concluded that the lowering of partial melting temperature is very important for the enhancement of the formation of the high-T_c phase.

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