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EFFECT OF MELTING ON SUPERCONDUCTING PARAMETERS OF Bi-BASED THICK FILMS*

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Evaluation of the characteristic data of superconducting properties belonging to the samples prepared by different heat treatments demonstrates their strong dependence on the annealing process. It shows that the melting causes much higher superconducting parameters as compared to those produced only by long time solid state sintering even in the case of the same nominal composition.

Introduction

The fundamental starting components of the preparation of high-T_c superconducting samples consist of the initial chemicals, their mixtures and the heat treatments applied. Consequences of the heat treatment with and without melting with respect to the superconducting properties of Bi-based films are summarized in this paper in order to demonstrate the strong effect of the annealing process on characteristic parameters.

The research of the influence of heat treatment on the superconducting properties of high-T_c thick films is motivated generally, on the one hand, by the arguments of fundamental research and, on the other hand, by the points of view of technical applications. Referring to the first, the study of the given problem can result in the revelation of the relationship between the starting conditions and characteristic superconducting parameters. As far as the practical employment is concerned, the experiences of this investigation can lead to elaborating the methods of the improvement of the quality of specimens for different kinds of application.

Characterization of samples

The experimental data are based on measurements carried out on samples prepared by an oxalate route using screen printing method [1]. The films had the nominal composition $Bi_{1.8}Pb_{0.4}Sr_{1.9}Ca_{2.1}Cu_{3.2}O_{10}$, where Pb plays a role of stabilization. According to the basic idea of the study, the main steps of the long

* Dedicated to Professor István Kovács on his eightieth birthday

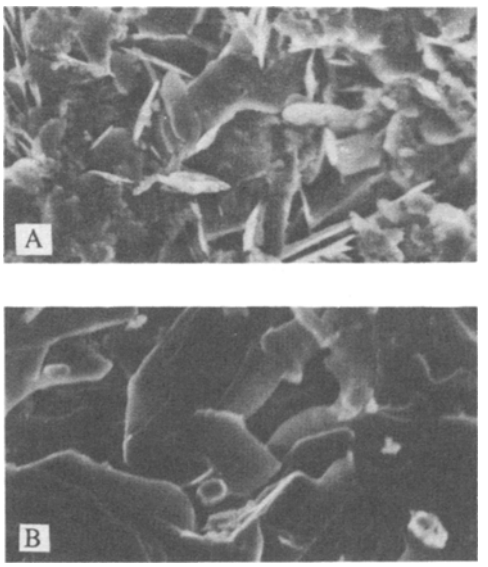

Fig. 1. SEM micrographs demonstrating the difference between samples A and B

and complicated preparation process were the same for both kinds of specimens except the melting of the last heat treatment procedure. Thus, the heat treatment of ready films type A consisted of only a long time solid state sintering at 852 °C for 80 h, while films type B had a melting at 891–895 °C for 3 min and after this a long heat annealing at 852 °C for 80 h, too.

Scanning electron microscopy (SEM) investigation already showed unambiguously different microstructures of films A and B as is demonstrated in Fig. 1. Heat treatment without melting results in randomly arranged microcrystals of small sizes in the order of 1 μm with sharp contours of highly porous structure, while the melting and the long time heat annealing lead together to a compact structure of highly textured microcrystals with sizes in the order of 10 μm.

On the basis of X-ray diffraction, both of samples A and B have majority superconducting (2,2,2,3) phase, which is supplemented by a small amount of (2,2,0,2) phase in specimens A and (2,2,0,1) and (2,2,1,2) phases in samples B (see Fig. 2).

The transmission electron microscopy (TEM) hints at a certain peculiarity of the microstructure of films B, inasmuch as the SAED patterns intensive satellite reflections (Fig. 3a) and the HRTEM micrographs demonstrate the coexistence of different lattice parameters (Fig. 3b). The meaning of the former is to indicate a superstructure in specimens B, while of the latter one is to determine the type of it, which is an interspecification of (2,2,2,3) and (2,2,1,2) phases.

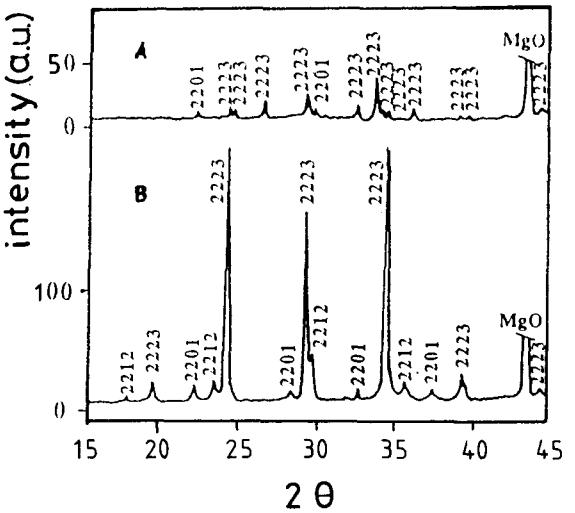

Fig. 2. X-ray diffractograms of films A and B representing the existence of impurity phases, too

Superconducting properties

Based on our earlier experimental investigations [2], the importance of the role of heat treatment in the development of superconducting parameters of Bi(Pb)–Sr–Ca–Cu–O thick films can be demonstrated. Summarizing their main results, conclusions on the relationship among the preparation, microstructure and superconductivity can be drawn.

Electrical (resistivity–temperature, R–T) and magnetic (magnetic hysteresis–magnetic field, M–H and magnetization–temperature, M–T) measurements provide very different curves for unmelted and melted samples, representing the effect of unlike heat treatments.

Function of R–T represents semiconducting character, wide transition and low critical temperature T_c for films A and metallic behaviour, narrow transition and high T_c for films B (see Fig. 4). The resistivity of unmelted specimens A has an increasing tendency with decreasing temperature with an onset value $T_0 = 112$ K and zero resistance at $T_c = 43$ K, while melted samples B can be characterized by decreasing resistance until $T_0 = 11$ K and a sharp drop with $T_c = 105$ K. The room temperature specific resistivities of both kinds of films differ strongly from each other, having a value of 17.37 mΩcm and 0.12 mΩcm, respectively.

As far as the magnetic properties are concerned, magnetic hysteresis measurements provide values of lower critical magnetic field H_{c1} and the upper one H_{c2} can be measured by the four-point method and extrapolate to the zero temperature by

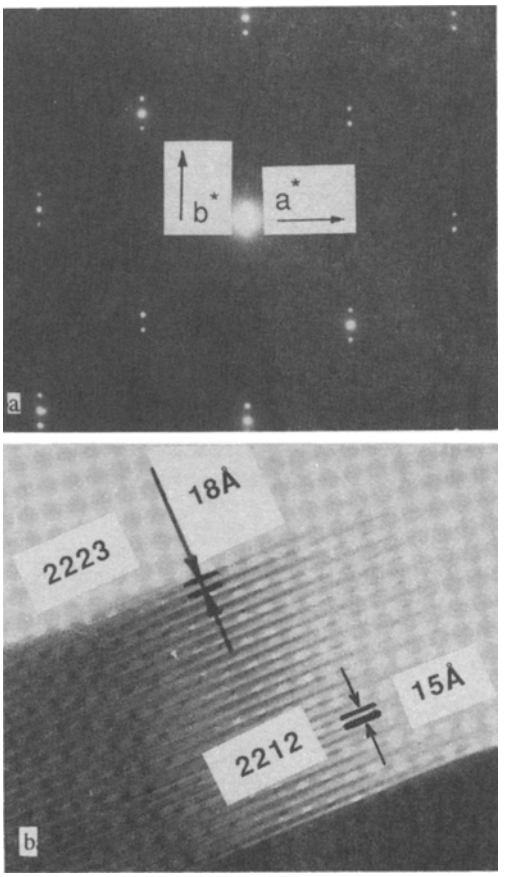

Fig. 3. SAED and HRTEM microscopy hint at the specification of specimens B

HWH theory [3].

The difference in the properties of samples A and B is reflected by the hysteresis curves of Fig. 5, but both of them represent the highest value of susceptibility in the interval of type I superconductivity (linear part of M–H characteristics). The average values of $H_{c1}(0)$ are 79.6 mT and 49.9 mT for specimens A and B. As is seen, the trapped magnetic flux can also be determined from the curves causing the irreversibility of the magnetization process.

If the value of the magnetic field in hysteresis experiments is much lower than the formerly mentioned values of H_{c1}, the low-field hysteresis data (Fig. 6) refer to the current paths between the grains, across the intergrain material. From the results of these measurements the intergrain critical current density can be evaluated

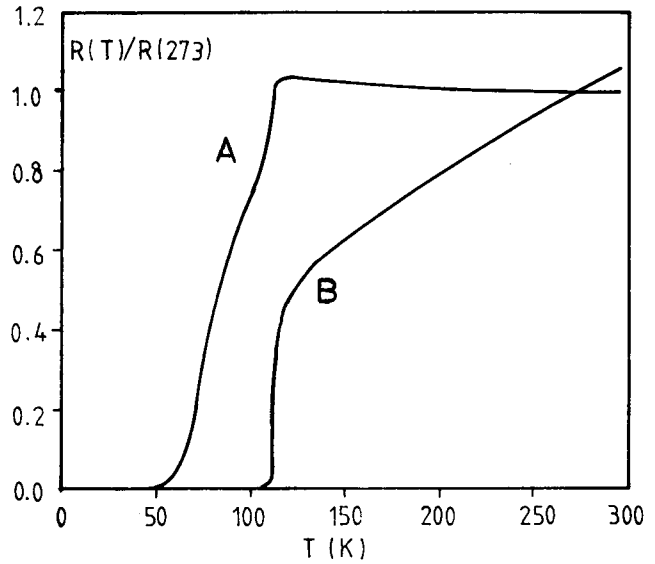

Fig. 4. R–T curves of films A and B having semiconducting and metallic character, respectively

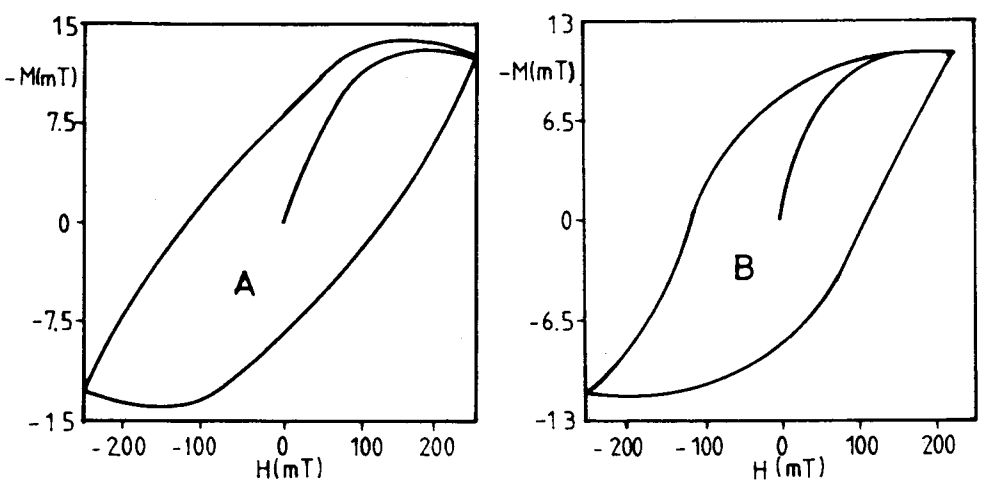

Fig. 5. High field hysteresis curves of samples A and B

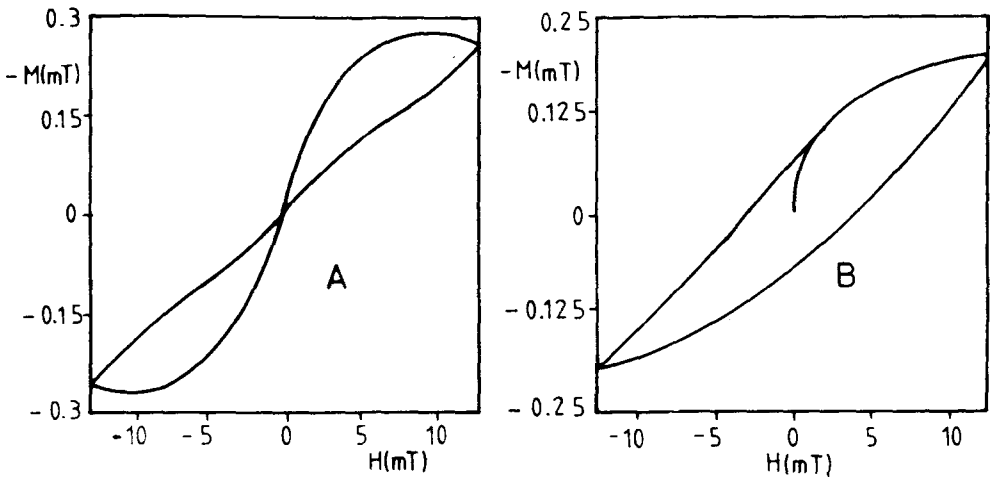

Fig. 6. Low field hysteresis curves giving a possibility to calculate the intergrain critical current

with the help of the Bean's model [4] modified by Chaddah et al [5]. The obtained data are 100 A/cm^2 and 150 A/cm^2 for the films A and B, respectively.

A very impressive difference manifests itself in the measurements of the transport critical current density of samples A and B, having extremely deviating values, namely 175 A/cm^2 and 23000 A/cm^2.

The upper critical magnetic field H_{c2} was determined by the shift of T_c in an external magnetic field. Zero extrapolated values of H_{c2} were 77 T and 88 T for unmelted and melted films.

By using the BCS [6] and the GLAG theories [7,8,9] microscopic parameters as the coherence length $\xi(0)$, penetration depth $\lambda(0)$ a Gl parameter κ can also be obtained from the data of macroscopic measurements. They are 21 Å, 1700 Å and 81 for specimens A and 19 Å, 2150 Å and 113 for samples B.

The measurement of the temperature dependence of d.c. magnetization by a SQuID magnetometer led to some particular results (see Fig. 7). It showed first of all, that the magnetic susceptibility of specimens A at low temperatures is significantly higher than that of specimens B. On the other hand, a few of kind B samples had a small, but finite diamagnetic susceptibility above T_c, having 100 times smaller values at high temperatures, than at liquid helium ones. This effect was measured to be a time-dependent phenomenon.

The value of the gap parameter $2\Delta/kTc$ provides very useful information on phonon coupling (where Δ is the gap). The results of low temperature electron tunneling spectroscopy (Fig. 8) hint at the values for unmelted specimens to be in strong coupling interval and those for melted ones near to the borderline between weak and strong coupling superconductivity. The actual magnitude of the gap

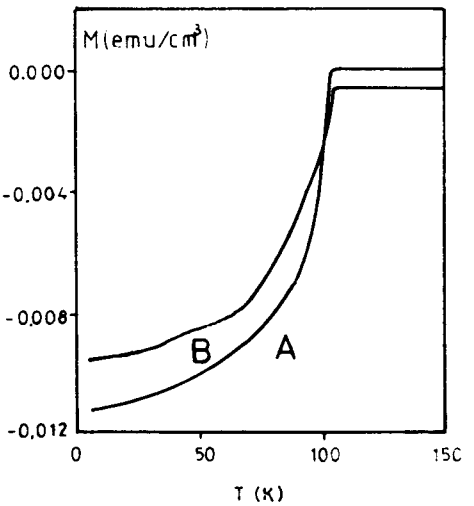

Fig. 7. Directly measured functions of magnetization vs temperature

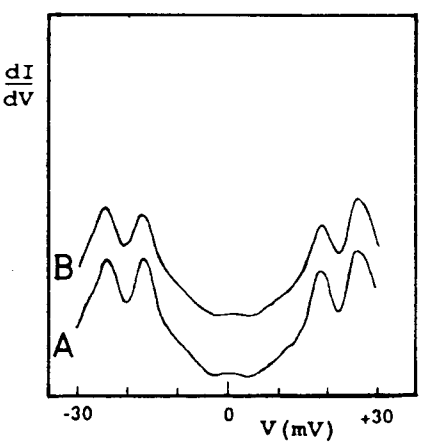

Fig. 8. Characteristics of low temperature tunneling microscopy

parameter is 3.98 for melted films and falls between 4.54 and 9.75 for unmelted ones, the uncertainty of which is originated from the shape of the curve A in Fig. 4 depending on the double-phase character of the samples.

Conclusions

Analysis of experimental results cited above leads to the most important conclusions as follows:

1. It is obviously pointed out that the melting influences the superconducting parameters to a large extent in high-T_c superconductors.

2. It brings about a lower superconducting volume fraction than that of unmelted specimens, but the superconducting parameters are much higher in the latter case.

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