



# Nucleation and texture formation of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ grains on $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_x$ plates in the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_{2.1}\text{O}_x/\text{Ag}$ system

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## Abstract

During the partial melt-growth in the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_{2.1}\text{O}_x/\text{Ag}$  system, a  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  (Bi-2212) phase formed via a reaction between a liquid and an  $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_x$  (14:24) phase. The Bi-2212 grains nucleated and grew with a  $c$ -axis perpendicular to the interface of the 14:24 grains. A texture of Bi-2212 superconducting grains, having a  $c$ -axis perpendicular to silver sheaths, formed via two steps: the alignment of the textured Bi-free grains on the silver-oxide compact interface and the formation of the textured Bi-2212 grains on the 14:24 phase with the same crystallographic orientation. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Because of its high critical current density at high magnetic fields at low temperature, and its rapid phase formation and good phase stability, the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  (Bi-2212)/Ag superconductor has become one of the most promising candidates for magnet application. To enhance the critical current density of bulk ceramic superconductors, the texture formation of superconducting grains and a uniform distribution of small second-phase particles are needed [1,2]. For the Bi-2212 system, a  $c$ -axis tex-

ture can be easily obtained by the partial melt growth (PMG) technique with Ag sheaths [3]. Recently, a high critical current density ( $J_c$ ) of  $> 500,000$  A/cm<sup>2</sup> at 4.2 K was obtained in a Bi-2212/Ag multilayer tape with a highly oriented texture [4]. However, the formation mechanism of the  $c$ -axis texture has not yet appeared to be clearly understood.

The possibility of the Bi-free phase as a nucleation site for the Bi-2212 superconducting phase has been suggested in a number of investigations [5–7], because the Bi-free phase, the superconducting Bi-2212 phase and the Bi-2223 phase are on the  $22(n-1)n$  tie line of the quaternary Bi-system [8,9]. With in situ optical microscopy, Hasebe et al. [5] observed that a  $c$ -axis textured Bi-2212 superconducting phase developed right after the disappearance of a Bi-free 1:1 phase. They, however, were not able to clearly

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identify the transformation process of the Bi-free phase to the Bi-2212 superconducting phase because of the resolution limit of optical microscopy. Siegrist et al. [6] and Xu et al. [7] also suggested that the crystal structure of 1:1 and 2:1 could be the mother structures for the Bi-2212 phase because the Bi-free phase has a similar crystal structure and has a low lattice misfit with the Bi-2212 phase. This suggestion, however, was made without enough information about the microstructure.

The purpose of the present investigation is to understand the nucleation and texture formation of the Bi-2212 phase near the Bi-free phases via microstructural observation. To this end, a model experiment with thick pellets was carried out, unlike previous investigations where thin tapes were used. To observe more distinctly, the reaction between the liquid phase and the Bi-free phases, pellets with a Cu-rich off-stoichiometric composition were partially-melted at a high partial melting temperature of 920°C.

## 2. Experimental procedure

Precursor powders with a 2 Bi/2 Sr/1 Ca/2.1 Cu cation ratio were prepared in a solid state reaction of Bi<sub>2</sub>O<sub>3</sub>, SrCO<sub>3</sub>, CaCO<sub>3</sub>, and CuO powders. The proportioned powders were ball-milled for 20 h in ethyl alcohol and then dried at 70°C for 10 h. The dried powder was calcined at 800°C for 20 h in air. The calcination was interrupted five times to grind the powder to improve its homogeneity.

The calcined powder was compressed into pellets 10 mm in diameter and 7 mm in height at 192 MPa. The powder compacts were placed between two Ag plates with no additional pressure. The thickness of the Ag plates was about 1 mm. Compared with a thin sample of the powder in tube (PIT) or the doctor blade method, this thick sample has the advantage of allowing easy observation of the microstructural development along the thickness direction during heat treatment.

The temperatures for partial melting and stabilization were taken to be 920°C and 860°C, respectively, because the partial melting temperature of the prepared powder was found to be 877°C by DTA and TG analyses. The high temperature of 920°C is thought to be beneficial for rapid and homogeneous

phase formation during the partial melting and hence allows the development of a distinctive microstructure during subsequent heat treatment. All the processing was done in air. Some samples were partially melted at 920°C for 10 min and water-quenched. Others were held at 920°C for 10 min, cooled to 860°C at different cooling rates and then heat-treated for 1 h. The heat-treated samples were then water-quenched.

After the partial melting and heat-treatment, the tablet-shaped samples were horizontally cut and polished. The polished samples were etched in a solution of 95 vol.% 2-butoxy-ethanol and 5 vol.% perchloric acid (60% dilute). The microstructures were observed under a scanning electron microscope (SEM; Model 515, Philips, Holland). The cation compositions of the phases present in the samples were identified by Energy Dispersive X-ray Spectroscopy (EDS). The samples for transmission electron microscope (TEM; JEM-3010, JEOL, Tokyo, Japan) were prepared by the conventional carbon replica method where the thickness of the carbon replica was 50 nm. Selected surfaces of samples were etched in a solution of 80 vol.% 2-butoxy-ethanol and 20 vol.% perchloric acid (60% dilute) before carbon deposition.

## 3. Results and discussion

After the partial melting and heat treatment, all the samples consisted mostly of Bi-2212, Bi-free phases, and a matrix which had been liquid at 920°C. Fig. 1a shows the shape of the Bi-free plates present around a pore of the sample partially-melted at 920°C for 10 min, cooled down to 860°C at a rate of 45 K/h, annealed at 860°C for 1 h, and then water-quenched. All the Bi-free plates were found to be the 14:24 phase by EDS analysis. The Bi-free phase has an elongated plate shape. Fig. 1b shows the shape of the Bi-free plates formed at the interface between the Ag sheath and oxide compact in the sample partially-melted at 920°C for 10 min and water-quenched. Almost all the Bi-free phases were 14:24. Several cross-sectional images revealed that the shape of these 14:24 plates was just the same as that shown in Fig. 1a. Compared to Fig. 1a, the 14:24 plates in Fig. 1b had a *c*-axis perpendicular to the surface of the Ag sheath.



Fig. 1. SEM micrographs showing the shape of  $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_x$  plates formed (a) around a pore in the sample partially-melted at  $920^\circ\text{C}$  for 10 min, cooled down to  $860^\circ\text{C}$  at a rate of 45 K/h, annealed at  $860^\circ\text{C}$  for 1 h and then water-quenched and (b) at the interface between the Ag sheath and oxide compact in the sample partially-melted at  $920^\circ\text{C}$  for 10 min and water-quenched.

In the sample shown in Fig. 1b, a small number of Bi-free phases with a  $(\text{Sr,Ca})/\text{Cu}$  cation ratio of 1:1 was also detected together with the 14:24 phase. According to the phase equilibria studies done by MacManus-Driscoll et al. [10] and Hasegawa et al. [11], with increasing temperature, the stable Bi-free phase changes from 2:1 to 1:1, and further to 14:24. Since the overall composition of our samples was Cu-rich and the temperatures for partial melting and heat treatment were as high as  $920^\circ\text{C}$  and  $860^\circ\text{C}$ , a 14:24 phase was the major Bi-free phase in our samples.

When a sample was heat-treated following the typical PMG method with a slow cooling rate, the nucleation behavior of the Bi-2212 superconducting

phase was able to be characterized via microstructural observation. Because the microstructure of all the samples was inhomogeneous along the thickness direction from the Ag sheath, microstructural change was observed along this direction after grinding several times each sample parallel to the Ag sheath by  $100\ \mu\text{m}$ . Fig. 2 shows a region about 1 mm away from an Ag sheath in the sample partially-melted at  $920^\circ\text{C}$  for 10 min, cooled down to  $860^\circ\text{C}$  at a rate of 45 K/h, held for 1 h, and then water-quenched. Fig. 2a was taken on a plane parallel to the Ag sheath. 14:24 plates are also aligned with the  $c$ -axis normal to the Ag sheath, similar to the case shown in Fig. 1b. Bi-2212 grains appear to nucleate on 14:24 plates and grow around the plates as indicated by arrows. In other regions, however, no Bi-2212 phase was

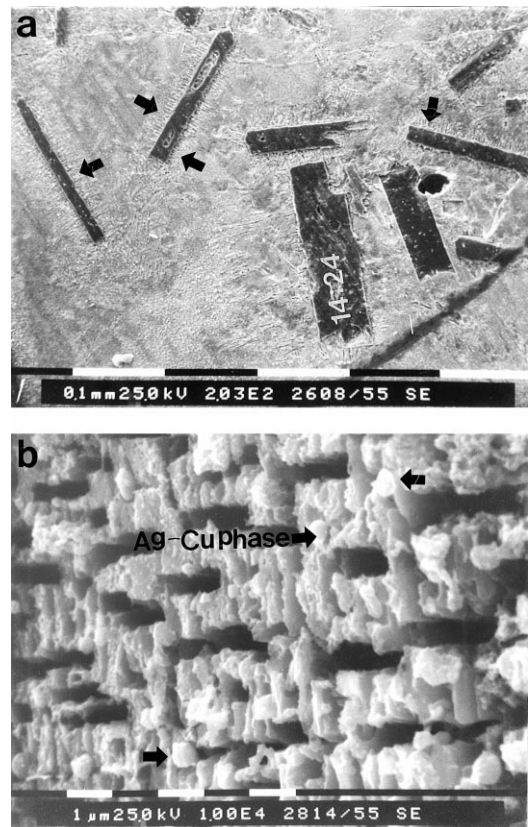


Fig. 2. SEM micrographs showing the nucleation of Bi-2212 grains on 14:24 plates in region 1 mm away from Ag sheath in the sample partially-melted at  $920^\circ\text{C}$  for 10 min, cooled down to  $860^\circ\text{C}$  at a rate of 45 K/h, held for 1 h, and then water-quenched: (a) low magnification image and (b) high magnification image.

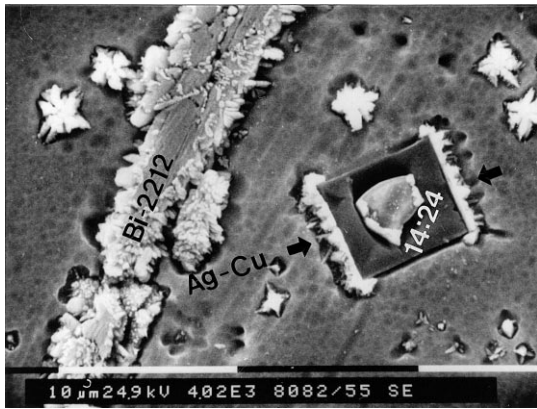


Fig. 3. A SEM micrograph showing selective growth of Bi-2212 superconducting grains on a  $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_x$  plate in a region 2 mm away from the Ag sheath in the same sample shown in Fig. 2.

formed. Fig. 2a implies that the 14:24 Bi-free plates are the major nucleation sites for the Bi-2212 phase. A magnified image of the Bi-2212 grains near a 14:24 plate, Fig. 2b, clearly shows the shape of a nucleated superconducting phase with its orientation relationship. Small and plate-like Bi-2212 grains nucleated perpendicularly on the 14:24 plate surface. The shape of the grains suggests that the  $c$ -axes of the two phases have the same crystallographic orientation. This result, shown in Fig. 2, indicates that a reaction between 14:24 and liquid is the major one in the formation of the Bi-2212 superconducting phase and the 14:24 plates act as preferential nucleation sites.

The white spheres, indicated by arrows in Fig. 2b, were an Ag–Cu phase. They were always present near 14:24 plates and between superconducting grains [13,14]. The distribution of Ag–Cu spheres was inhomogeneous. They formed at the interface between the Ag sheath and oxide compact at the initial stage of partial melting and also in the central region of the compact with increasing partial melting treatment time [14]. The formation of the Ag–Cu phase is thought to be a result of the Bi-2212 formation via the peritectic reaction between the 14:24 and the liquid phases. Considering the liquid composition reported by Margulies et al. [15], the Cu content in the liquid may increase due to the peritectic reaction. It seems that the increased Cu precipitates as the Ag–Cu spheres shown in Fig. 2b.

Fig. 3 shows the microstructure of a region 2 mm away from an Ag sheath in the same sample as that in Fig. 2. The Bi-2212 superconducting grains and Ag–Cu spheres are only developed on two sides of a 14:24 plate, indicated by two arrows, which is unparallel to the Ag sheath. In Fig. 2a and other vertical sections of the samples, the Bi-2212 phase nucleated on the  $b$ - $c$  and  $a$ - $c$  planes of the 14:24 plates. The nucleation behavior in Fig. 3 seems reasonable, because the  $a$ - $b$  plane has a higher bonding energy compared to the  $b$ - $c$  or  $a$ - $c$  planes.

The 14:24 and Bi-2212 phases have the same Cu–O block as a structural unit.  $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$  consists of alternating stacks of the plane of the edge sharing the  $\text{CuO}_2$  chain, the (Sr,Ca) layer, and the plane including a two leg  $\text{Cu}_2\text{O}_3$  ladder [16]. The Bi-free phase, including the 14:24 phase, can transform into the Bi-2212 superconducting phase by the substitution of Bi and ordering of Sr and Ca. The Bi-free phase was thought to be a heterogeneous nucleation site for the Bi-2212 phase [6,12].

To confirm the heterogeneous nucleation of the Bi-2212 phase on the 14:24 phase, a TEM observation was made. Fig. 4 shows carbon replica image of the interface region between the 14:24 and liquid phases. The white line in Fig. 4 indicates an interface between the 14:24 and liquid phases. This micrograph together with those in Fig. 2 shows that the

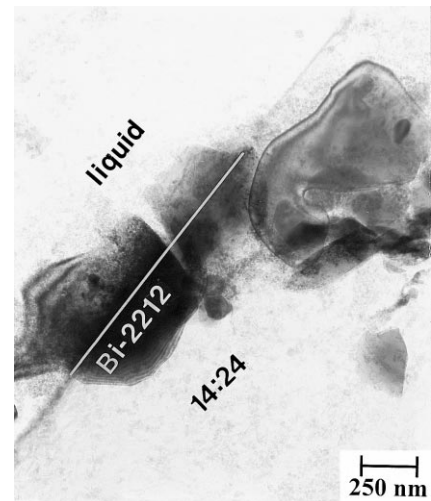


Fig. 4. A TEM micrograph showing the formation of plate-like Bi-2212 at the interface between the Bi-free 14:24 phase and the liquid.

Bi-2212 phase forms at the interface and  $a$ – $b$  plane of the Bi-2212 plate is parallel to  $a$ – $b$  plane of the 14:24 phase. In our experimental conditions of Cu-rich composition, high partial melting temperature and high heat-treatment temperature, 14:24 plates appear to be the only heterogeneous nucleation site for the superconducting phase.

Fig. 5 shows the growth shape of the Bi-2212 in the samples partially-melted at 920°C for 10 min, cooled down to 860°C at various cooling rates, held for 1 h, and water-quenched. All fractographs were taken at the interface between the Ag sheath and the oxide compact. As the cooling rate from 920°C to 860°C decreased, the thickness of the Bi-2212 superconducting grains decreased, but their size increased, resulting in better texturing.

The present microstructural investigation has shown that the texture formation of Bi-2212 grains occurred via two steps. First, Bi-free plates form with a  $c$ -axis perpendicular to the Ag sheath, which is similar to the observation of Ionescu et al. [9]: the alignment of the 14:24 phase along a silver sheath. Second, the Bi-2212 phase nucleates on  $a$ – $c$  or  $b$ – $c$  plane of the 14:24 Bi-free phase with the same crystallographic orientation as that of the Bi-free phase. Because the 14:24 plates are aligned with a  $c$ -axis texture at the interface, as shown in Fig. 2a, the Bi-2212 superconducting grains also have a  $c$ -axis texture near the Ag sheath, as shown in Figs. 4 and 5. In the central region of the samples, however, the Bi-2212 and 14:24 phases have random orientation and have no preferred texture, as shown in Fig. 3.

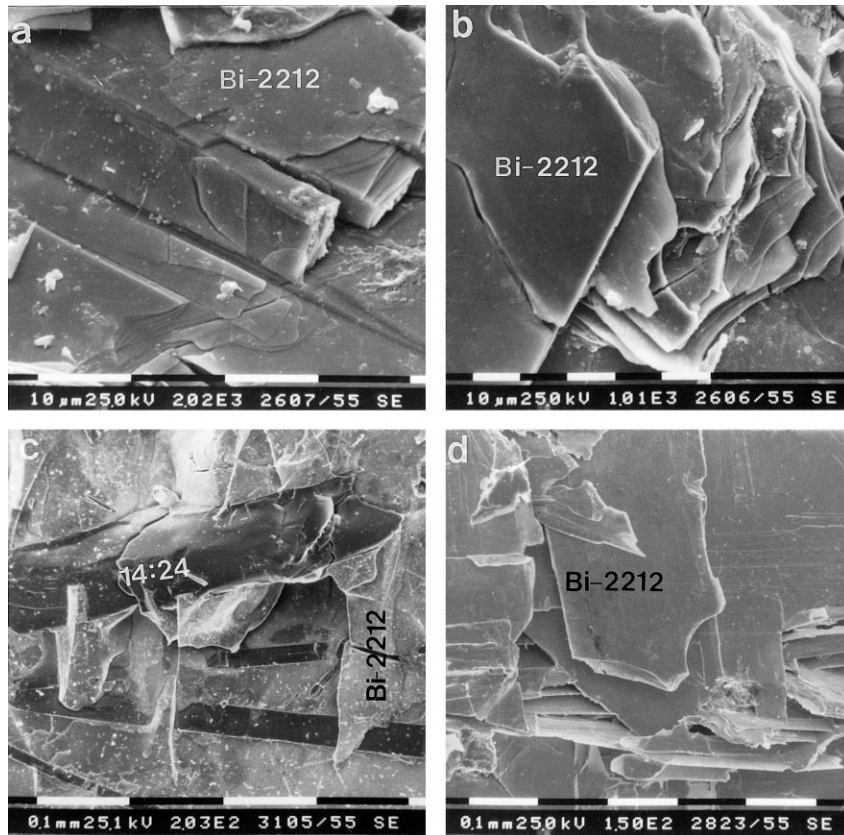


Fig. 5. Micrographs showing Bi-2212 superconducting grains at the interface between the Ag sheath and oxide compact in the samples partially-melted at 920°C for 10 min, cooled down to 860°C at rates of (a) 180 K/h, (b) 45 K/h, (c) 20 K/h, (d) 5 K/h, held for 1 h, and then water-quenched.

#### 4. Conclusions

The nucleation and texture formation of Bi-2212 grains on 14:24 Bi-free plates have been investigated via microstructural observation in the Bi<sub>2</sub>Sr<sub>2</sub>-CaCu<sub>2.1</sub>O<sub>x</sub>/Ag system with a Cu-rich composition. A superconducting Bi-2212 phase formed on cooling from 920°C to 860°C and stabilizing at 860°C through a reaction between the 14:24 and liquid phases. When the cooling rate was slow, the Bi-2212 superconducting grains nucleated perpendicularly on the Bi-free 14:24 plates. The directions of the *c*-axes of the superconducting Bi-2212 grains and 14:24 plates were parallel. A textured microstructure formed through the alignment of the 14:24 plates at the interface between the Ag sheath and oxide compact and then the formation of Bi-2212 superconducting grains with a *c*-axis perpendicular to the Ag sheath and 14:24 plates.

The present investigation may suggest that a key process for obtaining highly textured Bi-2212 grains is the alignment of the 14:24 plates at the interface between the Ag sheath and oxide compact. When the 14:24 plates were not aligned in the same direction as that of the Ag sheath, the resultant Bi-2212 superconducting grains also did not have a *c*-axis texture. For the microstructural optimization of the Bi-2212/Ag system, further investigation on the alignment of the Bi-free plates at the Ag/oxide compact interface may be needed.

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