Synthesis of Pb-doped Bi-2223 from Pb-doped Bi-2212, Ca_2CuO_3, and CuO Above the Glass Transition Temperature of Bi-2212

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ABSTRACT

Synthesis of Pb-doped Bi-2223 from Pb-doped Bi-2212 (Pb=0.3), Ca_2CuO_3, and CuO was done by sintering at the glass-phase temperature of Pb-doped Bi-2212. The sample sintered at 850°C possesses nearly 100% Pb-doped Bi-2223, as revealed from the XRD pattern and magnetic susceptibility data. The presence of holes, terrace-like features, and magma-like flow features in the SEM micrographs of the sample strongly support a glass-state Pb-doped Bi-2223 formation.

Key words: Pb-doped Bi-2223, glass transition temperature

INTRODUCTION

Bi-2223 has the highest critical temperature (110K) among the superconducting phases of the Bi-Sr-Ca-Cu-O system, but it is the most difficult to synthesize (Khaled et al., 1996; Murayama et al., 1988; Shimojima et al., 1989). The difficulty of preparing Bi-2223 lies in the complexity of its structure and its narrow phase stability. Considerable effort has been made in order to synthesize single-phase Bi-2223 (Zhu et al., 1999). Methods of increasing the volume fraction of Bi-2223 includes long sintering time (Yu et al., 1996; Hadano et al., 1988), reduced oxygen partial pressure (Oka et al., 1989; Hadano et al., 1988), control of composition (Endo et al., 1989; Hadano et al., 1988), and Pb-doping (Hadano et al., 1988). Although Bi-2223 in pure form is quite difficult to achieve, substitution of lead enhances its formation, and it is the most common way to increase the volume fraction of Bi-2223. The role of lead in the formation of Bi-2223, however, is still obscure.

Studies on Bi-2223 revealed that: (1) Bi-2212 precedes the formation of Bi-2223 (Holesinger et al., 1996); and (2) the presence of a liquid phase (Ono, 1988) and the occurrence of partial melting (Hadano et al., 1988; Oka et al., 1989) enhances its formation. Intercalation models take into account that Bi-2223 comes from Bi-2212 via insertion of Ca-Cu-O units. One variation of this model states that CuO_2/Ca bilayers are inserted into the CuO_2/Ca/CuO_2 blocks of Bi-2212 to form Bi-2223 (Garnier et al., 2000). Another states that insertion of $CaCuO_2$ slab into Bi-2212 results in the formation of Bi-2223 (Zhu et al., 1999). Nucleation and growth models are about the involvement of a liquid phase in Bi-2223

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formation. Dissolution precipitation, low-level mobile liquid droplet, partial molten-phase precipitation, and two-dimensional nucleation growth describe the role of the liquid in Bi-2223 formation (Garnier et al., 2000).

Since it was observed that Bi-2212 precedes Bi-2223 formation, using Bi-2212 as the starting material would offer easier reaction since it would readily transform to Bi-2223, as opposed to using carbonate and oxides as precursors. The observed fluid-like movement that is associated with increased Bi-2223 formation could be Bi-2212 in its glassy phase. We use the term “glassy phase” to describe the state in which a substance retains some degree of crystallinity but possesses fluid-like mobility. Glass state occurs above the glass transition temperature and below the melting point. We expect that a substance is more mobile in glassy phase, which gives them the ability for faster reaction, than in solid phase. The melting point of Bi-2212 (for certain Pb-doped level) is below the melting point of Bi-2223, so it is possible to synthesize Bi-2223 at the glassy state of Bi-2212. Differential thermal analysis (DTA) curves of Bi-2212 is presented in the works of Liu et al. (1988). Other substances which precedes Bi-2223 formation, such as those belonging to the CaO-CuO system, have melting points higher than that of the Bi-2223 system. The phase diagram of the CaO-CuO system is presented in the works of Risold et al. (1995).

The possibility of having a glassy state in Bi-2212 lies in its structural anisotropy. The a,b plane of the superconducting phases of the Bi-Sr-Ca-Cu-O system (Bi-2212 and Bi-2223) are weakly bonded between the neighboring BiO layers (Majewski, 2000). The weaker bonding of a,b planes are dissociated at a lower temperature (glass transition temperature) than the bonding at other directions (that dissociates at the melting point). When the bonding between the BiO layer are dissociated, the a,b plane layers can move more freely. There is still crystallinity within a layer since the bonding between the b,c planes and a,c planes are still present.

The concept previously stated indicates that to facilitate the formation of Bi-2223, it is necessary to sinter the sample at a temperature just below the melting point where the glassy state is expected and has optimum effect. For Pb-doped Bi-2223 (Pb=0.3), the candidate sintering temperature for a fast-forming Bi-2223 would be at 850°C. This temperature corresponds to the position of the pre-peak of Bi-2212 endothermic curve (Liu et al., 1998), which also corresponds to melting.

In this paper, Pb-doped Bi-2223 was synthesized from Pb-doped Bi-2212 via partial melting in the glass state. By avoiding decomposition, results indicate that Bi-2223 formation becomes faster and more homogeneous. Magnetic Susceptibility measurements suggest that conversion of Bi-2212 phase to the Bi-2223 is almost 100% complete.

METHODOLOGY

Stoichiometric amounts of oxide/carbonate precursor powder were used to prepare Pb-doped Bi-2212 (Pb=0.3) and Ca_2CuO_3 via solid state reaction. These were used as precursors for the formation of Pb-doped Bi-2223. These were mixed with CuO to achieve a stoichiometric amount of Bi-2223. The mixture was then sintered at 830°C, 840°C, and 850°C for 50 to 150 hours.

The presence of Bi-2223 was detected using x-ray diffraction (XRD) and was verified using Magnetic Susceptibility. Confirmation using susceptibility measurements was preferred over resistivity since the former does not rely on granular connectivity to manifest a signal. The samples were observed using a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Our success in producing Bi-2223 from Bi-2212 (Pb=0.3), Ca_2CuO_3, and CuO is verified by the magnetic susceptibility data (Fig. 1) and the XRD patterns (Fig. 2). From the magnetic susceptibility measurements (Fig. 1B), the sample sintered at 850°C shows an almost single phase Bi-2223, with a critical temperature of 103K.

The sample sintered at 830°C shows small amounts of Bi-2223 (Fig. 2A). The sample is composed of unreacted Bi-2212. Increasing the sintering time up to 150 hours does not show any significant increase in Bi-2223 volume fraction. Fig. 2B shows the XRD pattern of the sample sintered at 840°C, which shows

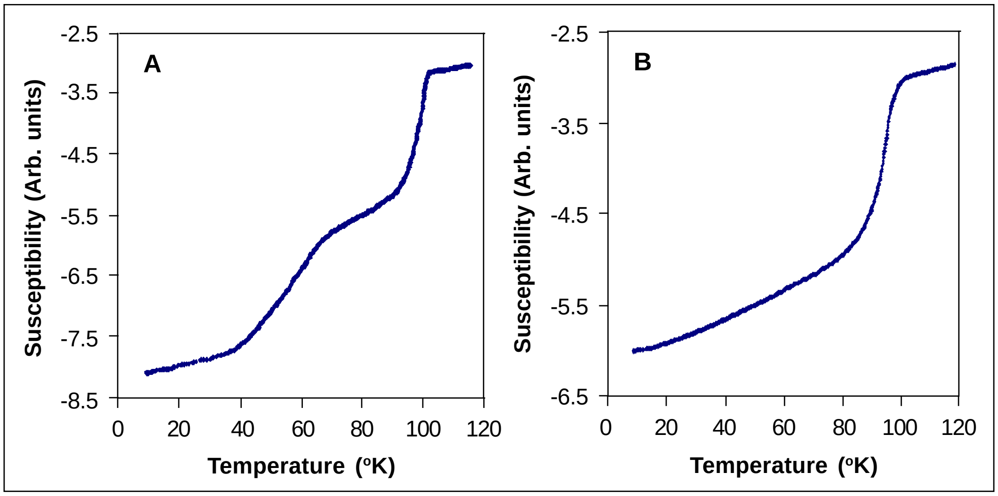

Fig. 1. Magnetic Susceptibility of samples sintered for 50 hrs at (A) 840°C and (B) 850°C.

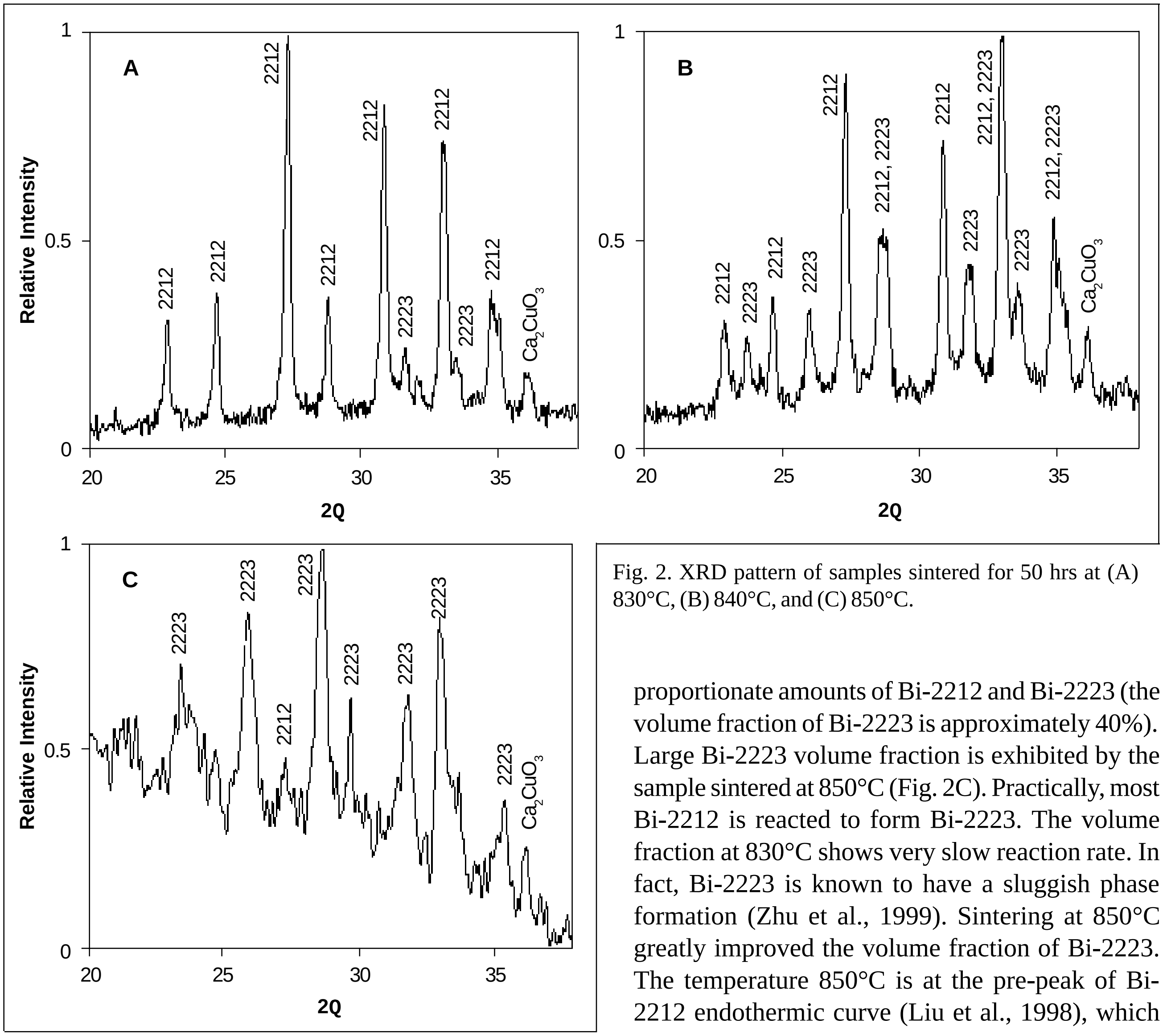

Fig. 2. XRD pattern of samples sintered for 50 hrs at (A) 830°C, (B) 840°C, and (C) 850°C.

proportionate amounts of Bi-2212 and Bi-2223 (the volume fraction of Bi-2223 is approximately 40%). Large Bi-2223 volume fraction is exhibited by the sample sintered at 850°C (Fig. 2C). Practically, most Bi-2212 is reacted to form Bi-2223. The volume fraction at 830°C shows very slow reaction rate. In fact, Bi-2223 is known to have a sluggish phase formation (Zhu et al., 1999). Sintering at 850°C greatly improved the volume fraction of Bi-2223. The temperature 850°C is at the pre-peak of Bi-2212 endothermic curve (Liu et al., 1998), which

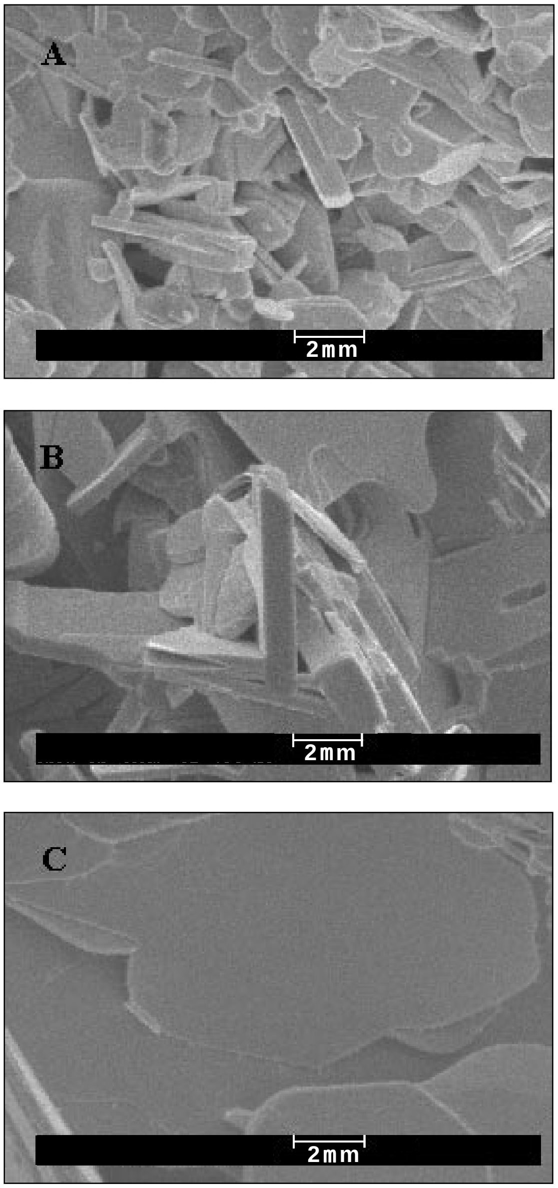

Fig. 3. SEM images of samples sintered for 50 hrs at (A) 830°C, (B) 840°C, and (C) 850°C.

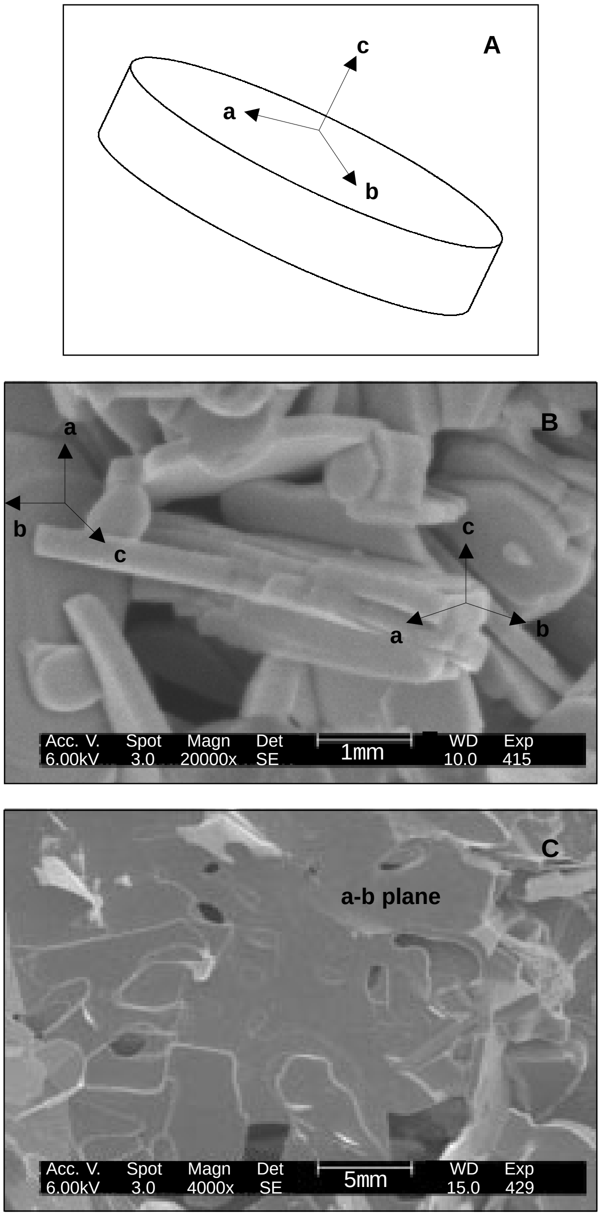

Fig. 4. (A) Crystallographic axis of Bi-Sr-Ca-Cu-O grain; (B) SEM image of grains sintered at 830°C; and (C) SEM image of grains sintered at 840°C.

corresponds to melting. In this temperature, Bi-2212 is expected to be at its glassy phase, which possesses higher mobility than the Bi-2212 in the solid phase.

The corresponding SEM images of the three samples are presented in Fig. 3. The image in Fig. 3A is the sample sintered at 830°C, showing unreacted precursors. The grains are smaller in comparison with Bi-2223 grains in the sample sintered at 850°C (Fig. 3C). The grain size of the samples sintered at 850°C is the largest since it is sintered at a higher temperature.

Owing to the anisotropy of the superconducting phases of Bi-Sr-Ca-Cu-O (Bi-2212 and Bi-2223), the rate of crystallization about the a,b planes is much faster (1000x) than in the c-direction (Majewski, 2000). Due to the slow crystallization rate, the c-direction would have the thinnest part in the grain. For comparison with

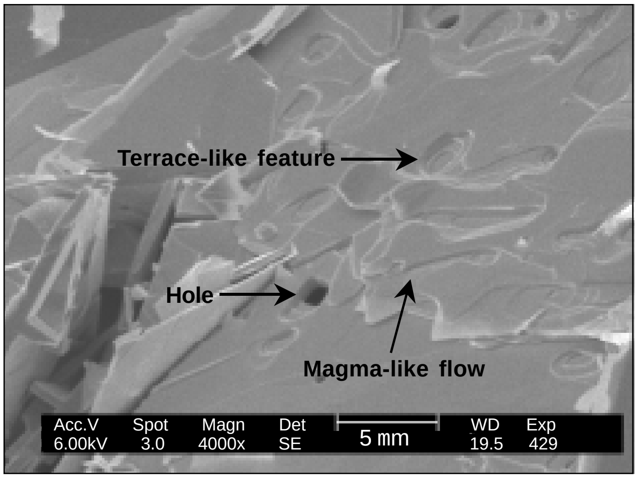

Fig. 5. SEM image of sample sintered at 840°C showing terrace-like feature, magma-like flow, and holes.

SEM images, the crystallographic direction of Bi-Sr-Ca-Cu-O grains is presented in Fig. 4A. The a- and b-directions could be treated isotropically. They can be labeled arbitrarily in any direction in the plane perpendicular to c-direction.

The relative proportions of both Bi-2212 and Bi-2223 phases from samples sintered at 840°C suggest that it would be possible to observe the transformation of Bi-2212 (frozen in the sample) to Bi-2223. Since the reaction at 840°C is slower than the reaction at 850°C (because the later temperature is higher), it is possible to see remnants of Bi-2212 movements. These movements are no longer apparent in samples sintered at 850°C due to the rapid reaction rate.

By comparing the SEM images of the samples sintered at 830°C and 840°C (Fig. 4B and Fig. 4C, respectively), we could see the difference between the grains of mostly unreacted sample (sample sintered at 830°C) and those of the sample which reacted (sample sintered at 840°C). The grains of samples sintered at 830°C are unfused and stacked with other grains, while the grains of the samples sintered at 840°C are fused with other grains. These observations indicate that at 840°C the sample becomes very soft and attain fluid-like movement as compared with samples at 830°C, which are solid. This agrees with the idea that the presence of fluid enhances Bi-2223 formation (Khaled et al., 1996; Ono, 1988).

Further examination of the sample sintered at 840°C reveals the presence of terrace-like structures, fluid-like movements, and holes (Figs. 5, 6, and 7). Two important characteristics of these features include: (1) movement between planes that are manifested by the displacement of one layer with respect to other layers; and (2) there exists a degree of order within a plane as exemplified by the layered orientation of the plane. These are the features of a substance in the glassy state. Fig. 6 shows the layered structure where one layer is displaced with respect to other layers, resembling a terrace. Fig. 7 shows the presence of a magma-like flow feature (Fig. 7A) and holes (Figs. 7B, 7C, and 7D). Holes also have a structure similar to a terrace. Fig. 8 shows the possible mechanism, which happens to the Bi-2212 grains. Fig. 8A shows the initial condition of Bi-2212. The bonding in all directions is still intact. When Bi-2212 is brought above the glass transition temperature (Fig. 8B), the bonding between the Bi-O layers (a-b planes) is dissociated. When this happens, the a-b planes can move freely with respect to each other. Since the bonding in the other directions is still intact, a degree of order still exists within a plane.

The fast formation of Bi-2223 from the glassy phase of Bi-2212 could explain the relationship between the existence of fluid-like movement and large Bi-2223 volume fraction. The increase in the rate of Bi-2223 formation is a result of the higher mobility of Bi-2212, due to the freely moving a-b planes of Bi-2212 above the glass transition temperature. This allows Bi-2212 to move faster and react with other reactants to form Bi-2223. This shows the importance of fluid-like movement in Bi-2223 formation.

The above concept offers a possible explanation regarding the relationship between the increase in Bi-2223 volume fraction and the increase in Pb-doping. Likewise, it could also explain the existence of an optimum value of Pb-doping in Bi-2223. The melting point of Bi-2212 decreases with an increase in Pb-doping. DTA of Bi-2212 with different Pb-doping levels is presented in the works of Liu et al. (1998). For a sample sintered at a particular sintering temperature (below the melting point of undoped Bi-2212), increasing the amount of Pb-doping entails the glass state to be nearer the sintering temperature, which results in faster reaction. Optimum Pb-doping exists when the melting

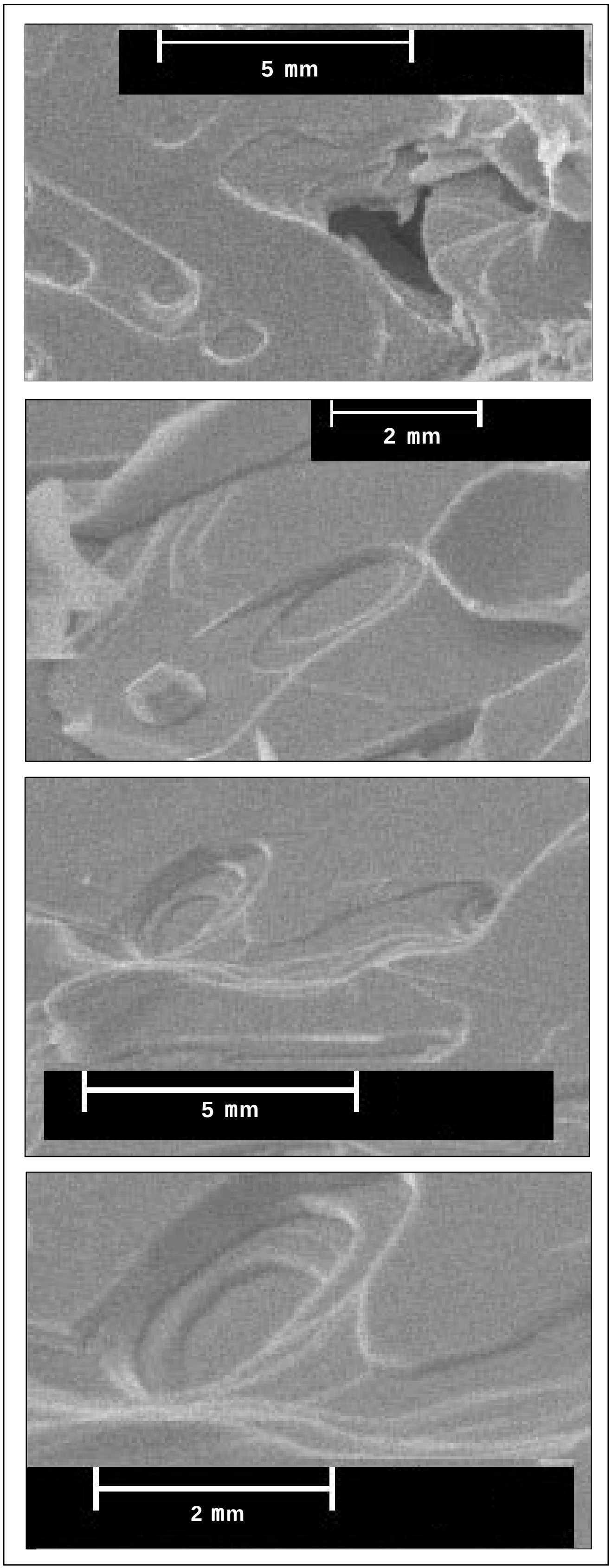

Fig 6. SEM image of sample sintered at 840°C showing terrace-like feature.

temperature of Pb-doped Bi-2212 is just below the sintering temperature. Further increase in the amount of Pb will result in the melting of the sample.

SUMMARY AND CONCLUSION

Pb-doped Bi-2223 (Pb=0.3) from Pb-doped Bi-2212 (Pb=0.3), Ca_2CuO_3, and CuO, at the glassy phase of Bi-2212, was successfully prepared. The Bi-2212 phase dominates the samples sintered at 830°C. At 840°C, Bi-2212 and Bi-2223 phases coexist at almost equal proportions. At 850°C, Bi-2223 dominates such that the presence of Bi-2212 is no longer discernible from the susceptibility measurements. SEM investigation reveals the presence of frozen, fluid-like movement in the material, which is attributed to the formation of a glassy phase of the sample sintered at 840°C and above. This glassy phase is responsible for the enhancement of Bi-2223 formation because Bi-2212 can move freely to react with Ca_2CuO_3 and CuO.

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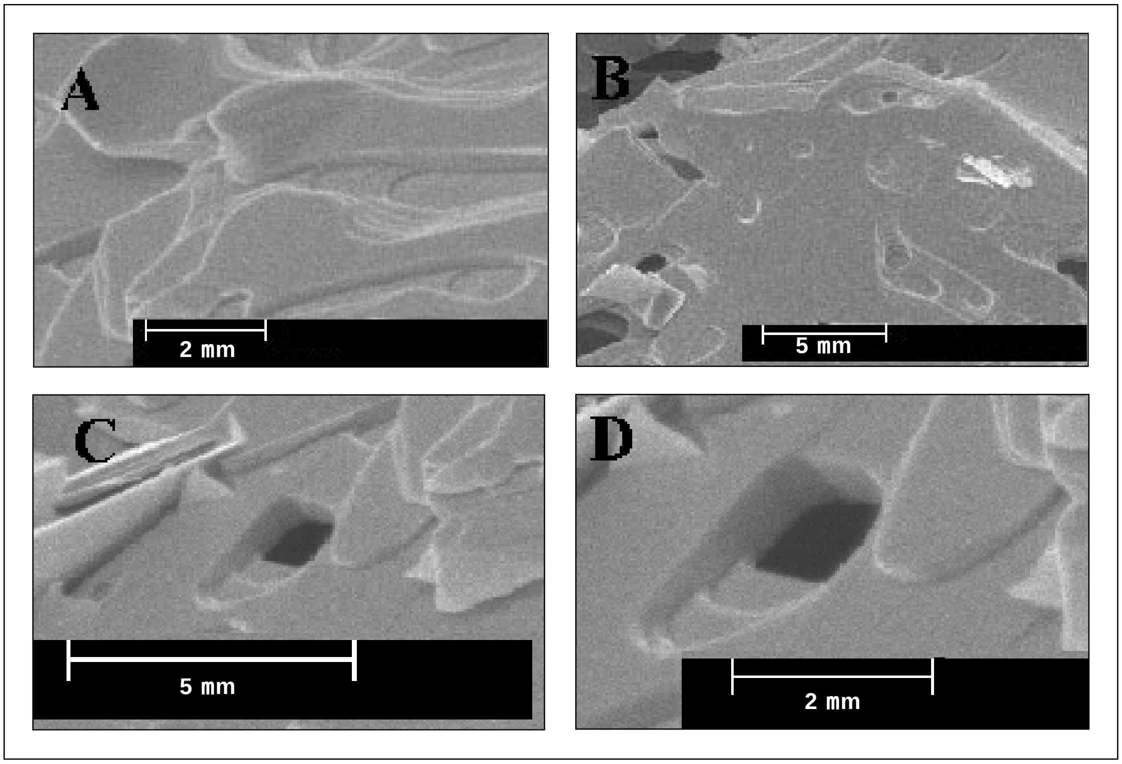

Fig 7. SEM image of sample sintered at 840°C showing magma-like flow feature (A) and holes (B-D).

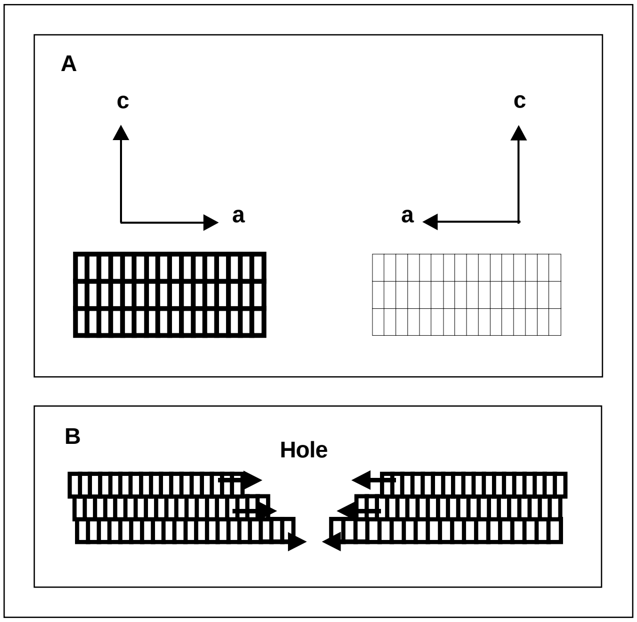

Fig 8. (A) Bi-2212 grains below glass transition temperature; and (B) movement of Bi-2212 above the glass transition temperature.

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