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Synthesis of Pb-doped Bi-2223 from Pb-doped Bi-2212 via partial melting

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Abstract

Nearly 100% Pb-doped Bi-2223 was synthesized from Pb-doped Bi-2212, Ca_2CuO_3 and CuO. The partially melted materials show a lamellar structure whose extent correlates with the amount of Bi-2223 phase. The fluid-like movement is attributed to the breaking of the Bi–O bonds and the rapid formation of the Bi-2223 phase attributed to the activation of the structure that enhances intercalation.

Keywords: Pb-doped Bi-2223; Bi-2212; Partial melting; Intercalation

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1. Introduction

Bi-2223 has the highest critical temperature among the bismuth cuprate family of superconductors and therefore attracts the most attention for superconductor applications. It has, however, a very sluggish rate of formation [1,2] and a very narrow range of temperature stability. Although the addition of Pb increases Bi-2223 volume fraction, the phase can be synthesized only after long sintering times and seldom in good enough phase purity. Furthermore, the role of Pb is still an issue to be resolved. The synthesis of the Bi-2223 phase continues to be a challenge to materials scientists and engineers.

Over the years much knowledge has been gained about the characteristics of Bi-2223 formation. For example, it is known that Bi-2212 precedes the formation of Bi-2223 [3] in a powder mixture consisting of the usual oxide and carbonate precursors. This implies that the oxides and carbonate precursors transform to Bi-2212 prior to becoming Bi-2223. Also, the improvement of volume fraction is commonly accompanied by some partial melting or involvement of a liquid phase [4–10].

This paper investigates the synthesis of Pb-doped Bi-2223 from Pb-doped Bi-2212. This pathway is alluded to by the intercalation models [1,11], eliminating the intermediate step of forming Bi-2212 in the case of oxide and carbonate precursors that prolong the reaction process. To further enhance the reaction, the Bi-2212 phase is brought to partial melting.

2. Methodology

Pb-doped Bi-2212 with stoichiometric composition $Bi_{1.7}Pb_{0.3}Sr_2CaCu_2O_y$, Ca_2CuO_3 and CuO were used as precursors to synthesize Pb-doped Bi-2223. The Pb-doped Bi-2212 was fabricated via the standard solid-state reaction technique using oxides and carbonates. The powder was sintered at 830 °C in air in pellet form for 100 h. X-ray investigation of the Pb-doped material shows that it is of the Bi-2212 phase. Ca_2CuO_3 was synthesized from $CaCO_3$ and CuO in stoichiometric amounts and sintered at 900 °C for 100 h in air.

Stoichiometric amounts of Pb-doped Bi-2212, Ca_2CuO_3 and CuO were mixed and formed into pellets. The pellets were sintered at various temperatures between 830 and 850 °C from 25 to 150 h. The partial melting process was done by sintering the samples at temperature just below the melting point of the Pb-doped Bi-2212. Samples that are partially melted usually exhibit warping otherwise if the tem-

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perature is too high the pellet liquefies. The samples were investigated using XRD and SEM. Superconductivity was verified via AC susceptibility.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples sintered at various temperatures for 50 h. Partial melting was observed to occur starting at around 840 °C evidenced by the warping of the pellet. The occurrence of partial melting coincides with the appearance of the Bi-2223 phase in significant amounts. The sample sintered at 830 °C did not show partial melting nor did it show any other extraneous phases. There is very little of the Bi-2223 phase. At 850 °C, the XRD pattern shows almost completely Bi-2223 phase. This is remarkable since the reaction is almost completed within only 50 h. Samples sintered above 850 °C was completely melted. Rough evaluation indicated that melted samples are decomposed Bi-2212. No further investigations were carried out for these samples. Increasing the sintering time up to 150 h does not give significant improvement to the volume fraction of Bi-2223 phase sintered at 850 °C and only moderately for samples sintered at 840 °C. The effect of sintering time at 830 °C is very small.

The phase purity of the samples was verified by AC magnetic susceptibility as shown in Fig. 2. The samples sintered at 840 and 850 °C show a sharp diamagnetic transition at around 105 K due to the presence of the Bi-2223 phase. A second transition in the sample sintered at 840 °C is due to the presence of Bi-2212 phase. The sample sintered at 830 °C shows only the Bi-2212 transition. This indicates that the method of partial melting greatly enhances the formation of Bi-2223. The sample sintered at 850 °C for 50 h shows only the Bi-2223 phase. Due to the inherent dependence on the sample volume and geometry of the signals detected by the susceptibility apparatus, it was difficult to make a definite estimate on the improvement on the volume fraction from sintering time. Data, however, do not indicate any dramatic improvement.

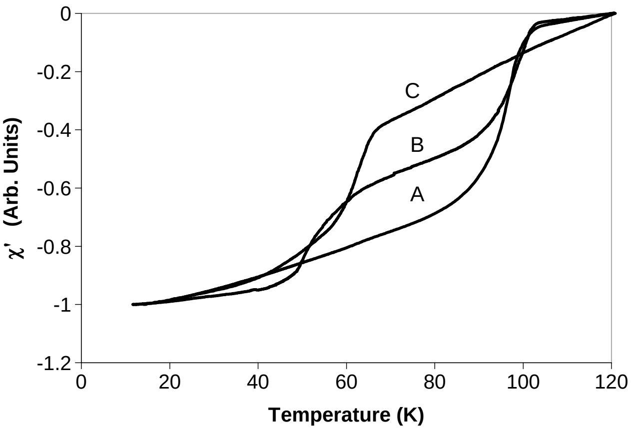

Fig. 2. AC magnetic susceptibility vs. temperature of sample sintered for 50 h at (A) 850 °C, (B) 840 °C and (C) 830 °C.

The SEM images in Fig. 3 show that samples sintered at 840 and 850 °C have considerable inter-granular fusion that is not seen in the sample sintered at 830 °C. This fusion is evidence of partial melting that the sample underwent. A closer view of the partially melted sample is shown in Fig. 4. The terrace-like structure is very obvious in the figure. This structure indicates a lamellar type of flow. The more extensive this type of structure is, as in the sample sintered at 850 °C, the more enhanced the Bi-2223 phase.

Starting with the Pb-doped Bi-2212 phase, the Pb-doped Bi-2223 phase may be formed by a simple intercalation of Ca_2CuO_3 and CuO. It is reasonable that this reaction may be enhanced if the intercalating materials are in a fluid-like state for increased mobility. The lamellar structure in the data shows that the materials are not completely liquid. This is possible in the Bi-2212 structure due to the weak Bi–O bonds that dissociate at high temperature while keeping the rest of the structure relatively intact. The breaking of the Bi–O bonds contribute to the fluid-like character of the re-

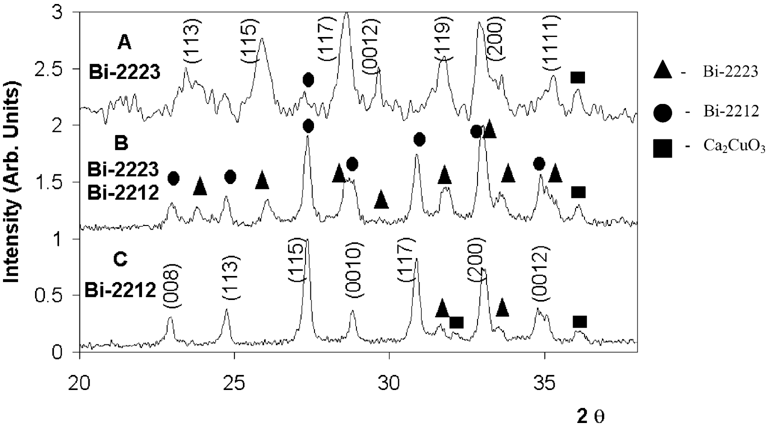

Fig. 1. XRD pattern of samples sintered for 50 h at (A) 850 °C (indices are for Bi-2223), (B) 840 °C and (C) 830 °C (indices are for Bi-2212). (▲) Bi-2223; (●) Bi-2212; (■) Ca_2CuO_3.

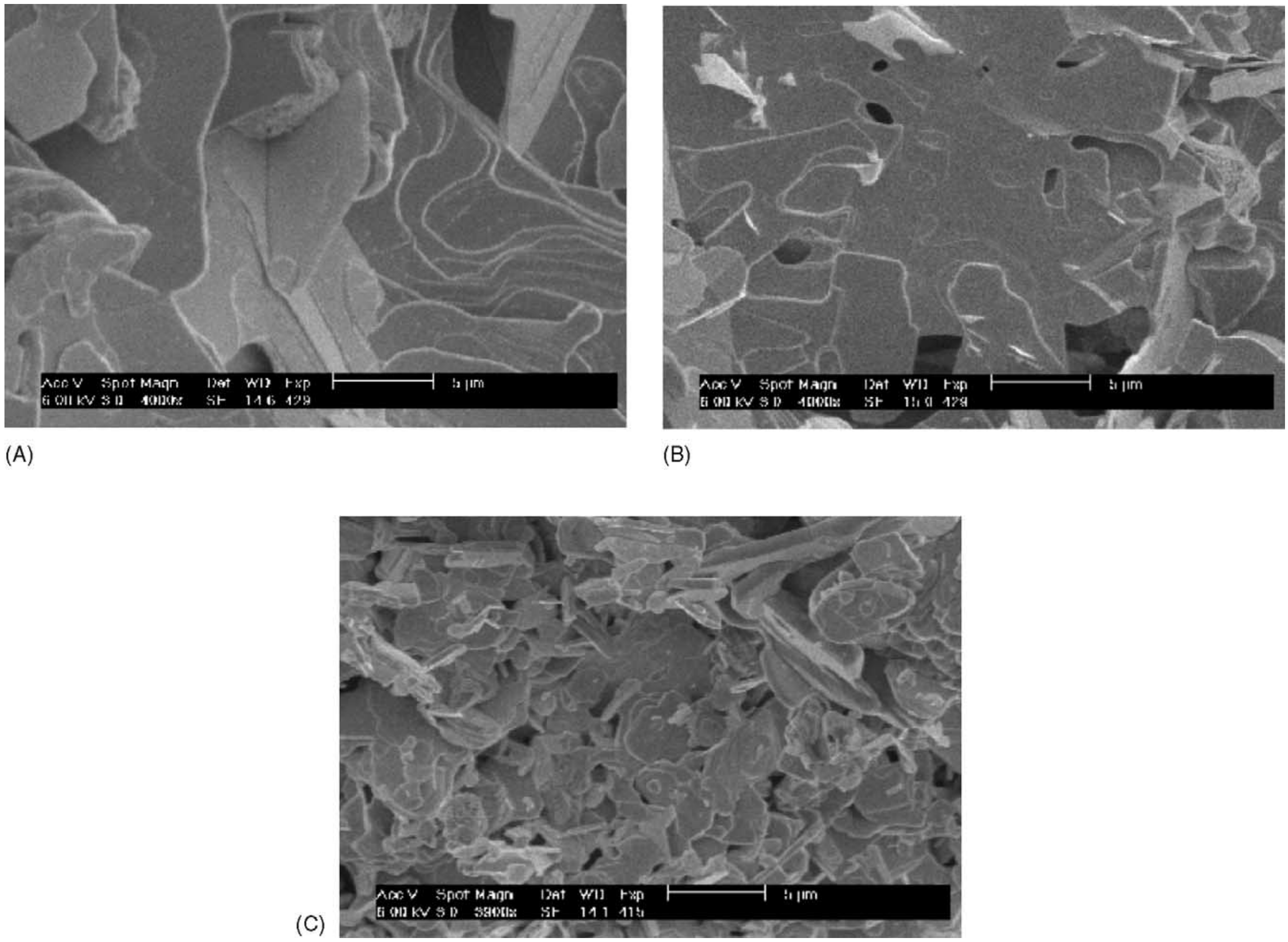

Fig. 3. SEM images of samples sintered for 50 h at (A) 850 °C, (B) 840 °C and (C) 830 °C.

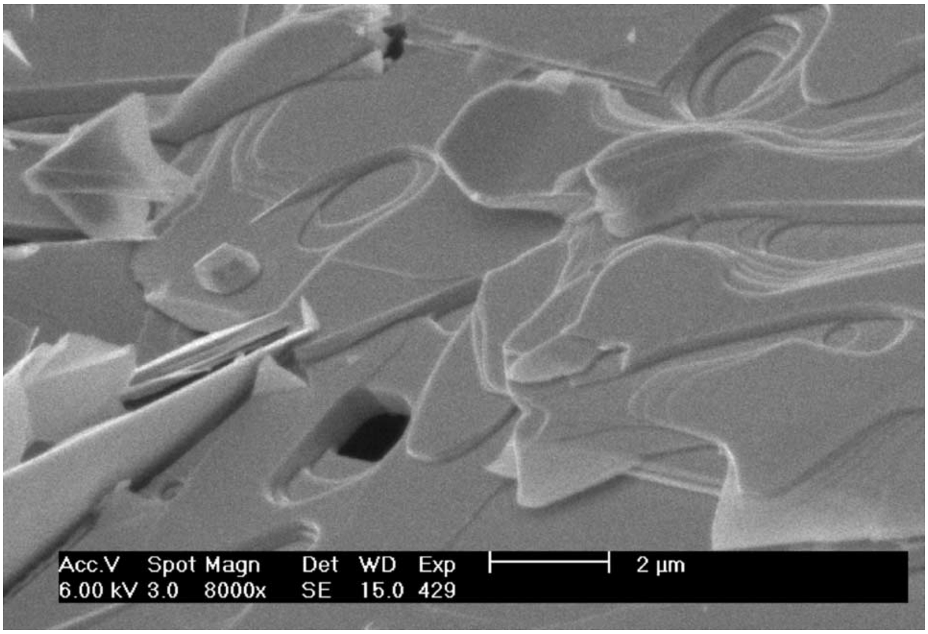

Fig. 4. SEM images of the partial melted sample.

actants. Although the rest of the Bi-2212 structure is intact, they are nevertheless extremely activated in the sense that a small increase in the temperature brings decomposition. This activated state of the Pb-doped Bi-2212 allows for enhanced intercalation of the Ca_2CuO_3 and CuO into the structure to form Pb-doped Bi-2223. This type of reaction is supported by the present data as evidenced from the enhancement of the Bi-2223 phase just below complete melting of the Pb-doped Bi-2212. At 830 °C, the Bi–O bonds are still intact, so there is no fluid-like movement and very little Bi-2223 phase is formed, if at all. At 840 °C, the Bi–O bonds are dissociated giving some fluid-like movement. But since the energy is "quite low", the reaction is still slow. After 50 h, a significant amount of the Bi-2212 phase is left unreacted. Increasing the time does not improve the volume fraction because the Pb-doped Bi-2212 structure is not yet optimally activated. At 850 °C the dissociated lamellae become more mobile and the higher temperature encourages intercalation more readily, completing in 50 h, since at this temperature the Pb-doped Bi-2212 structure is now optimally activated. It is interesting to note that the Pb-doped Bi-2212 could remain in the activated mode for an extended temperature range. This appears to be the role Pb plays in the bismuth cuprate family of superconductors. Pb seems to be the agent that expands the intercalation-ready state of the Bi-2212.

4. Summary and conclusion

Synthesis of nearly 100% Pb-doped Bi-2223 was achieved, for as short as 50 h, by sintering stoichiometric amounts of Pb-doped Bi-2212, Ca_2CaO_3 and CuO very close to the melting point of Pb-doped Bi-2212. The closer the material is brought to melting the more readily the Pb-doped Bi-2223 phase forms. The fluid-like character of the reaction is attributed to the breaking of the Bi–O bonds in the Bi-2212 phase. The fluidity allowed for better mixing of the reactants and because the material is activated very close to melting, intercalation reaction is made favorable. The extent of the stability of the activated state of the Bi-2212 phase is due to the incorporation of Pb in the Bi-2212.

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