‘Maturization’ of high-\(T_c\) precursor powders for use in superconducting tapes

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Abstract

In recent years, the focus of research on high-\(T_c\) superconductors has shifted towards the use of these materials in practical applications. Superconducting tapes and wires have the potential for use in power transmission. After fabrication, the tapes are subjected to mechanical and thermal treatments, causing changes in the phase assemblage to occur within. It is therefore of paramount importance to understand the behaviour of the precursor powders under different heat treatment schedules. In this paper, we present our studies on precursor powders with the nominal starting composition \(\text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{1.8}\text{Ca}_{2.2}\text{Cu}_{3.2}\text{O}_y\) synthesized by spray pyrolysis. By a combination of X-ray diffraction and magnetization studies, we have identified a ‘mature’ heating schedule, by which we can control the Pb content in the (Bi,Pb)-2212 precursor powders, which we take as the schedule for optimum conversion to the (Bi,Pb)-2223 phase.

1. Introduction

Since the discovery of high-\(T_c\) superconductivity in \(\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}\) [1], intense research activity has led to the discovery of several new phases in this system. While most of the subset members seem to be non-superconducting, the \(n = 1, 2\) and \(3\) members (also known as 2201, 2212 and 2223) show superconductivity with transition temperatures (\(T_c\)) around 6, 85 and 110 K respectively [2]. The Bi–Sr–Ca–Cu–O system possesses a very complex phase diagram and synthesis of single-phase members with higher values of \(T_c\) is difficult due to the problem of intergrowths. The phase field is further complicated due to the addition of an extra element, Pb, which is necessary to stabilize the \(n = 3\) member of the above-mentioned series [3].

From the point of view of practical applications, power transmission with negligible loss is an area where high-\(T_c\) superconductors have a great potential. The proposed devices are tapes and wires, which are usually manufactured by the powder-in-tube method where the precursor powder is densely filled into Ag tubes and drawn into the necessary shape. The products are then subjected to different mechanical and thermal processes.

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The \( n = 3 \) member, i.e., the \((\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y\) phase, is of choice due to its high \( T_c \) and \( J_c \) values. However, synthesis of this composition in single phase is difficult. Different phases in the phase diagram coexist at different temperatures and it is very important to understand the influence of the fabrication conditions on the phase assemblages; such knowledge would help in optimizing the phase of choice while minimizing additional phases. Since the tapes and wires are subjected to various heat treatments in the fabrication process, it is desirable to start with a suitable precursor powder and let it convert to the \((\text{Bi,Pb})\)-2223 phase inside the tape or wire.

This study aims at understanding the effect of different processing conditions on the precursor powders towards conversion to 2223. In the first step, we had undertaken a comparative study of the different synthesis methods [4] and concluded that the powders prepared by the method of spray pyrolysis are most suitable for conversion to the \((\text{Bi,Pb})\)-2223 phase. In this paper, we report heat-treatment studies on the phase \( \text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{1.8}\text{Ca}_{2.2}\text{Cu}_{3.2}\text{O}_y \) and suggest a ‘mature’ heating schedule, which we take as the schedule for optimum conversion to the \((\text{Bi,Pb})\)-2223 phase.

### 2. Experimental

The precursor powder with the nominal composition \( \text{Bi}_{1.7}\text{Pb}_{0.4}\text{Sr}_{1.8}\text{Ca}_{2.2}\text{Cu}_{3.2}\text{O}_y \) was synthesized by the method of spray pyrolysis [4] at Merck KGaA. Different batches of the powders obtained from the spray pyrolysis unit were subjected to an initial heat treatment, after which they were heated at 800 °C for 24 h each and then at 810 °C for 12 h with intermediate grindings. Following this, they were heated at 820 °C for varying durations. For conversion to the \((\text{Bi,Pb})\)-2223 phase, the powders were heated at 842 °C for 12, 24, 48 and 72 h. Powder X-ray diffraction (XRD) patterns were recorded after each heat treatment on a Scintag D1 powder diffractometer. The diamagnetic behaviour was studied by means of DC magnetic susceptibility, measured on a SQUID magnetometer (quantum design).

### 3. Results and discussion

Fig. 1 shows the powder XRD patterns of the sample after treatments at 800 °C for 24 h and at 810 °C for 12 h. After the initial treatment, the sample consists mostly of the 2201 phase, with \( \text{Ca}_2\text{PbO}_4 \) (CP) present as the major secondary phase. After the treatments at 800 and 810 °C, the 2212 phase evolves as the majority phase, with CP as the secondary phase. Following the treatment at 810 °C, the powders were heated at 820 °C for 12, 24 and 36 h, followed by treatments at 842 °C for varying durations. The treatment at 842 °C is for the conversion to the \((\text{Bi,Pb})\)-2223 phase.

Fig. 2 shows the low-angle (002) reflection in the XRD patterns of the powders after treatments at 800, 810 and 820 °C. As can be seen, there is a shift to lower 2θ with increasing temperature and time, indicating that the larger \( \text{Pb}^{2+} \) ion substitutes the smaller \( \text{Bi}^{3+} \) site [5]. Our heat treatment schedule thus offers a method of controlling the amount of Pb in the \((\text{Bi,Pb})\)-2212 precursor pow-
der, which may be an important factor in the optimum conversion to the 2223 phase.

Fig. 3 shows the XRD patterns of the powders after treatment at 820 °C for 12, 24 and 36 h, followed by heating at 842 °C for 72 h (three treatments each of 24 h with intermediate grindings). It can be seen that when the powder is heated for a longer duration at 820 °C, the XRD pattern shows extra reflections (indicated by arrows in the figure) indicating the appearance of impurity phases. Thus, we find that a shorter duration of treatment at 820 °C for 12 h is ideal.

In the process of conversion to the 2223 phase, samples heated for durations of 24 h or less show the presence of the 2212 phase and hence a longer duration of heating is necessary. Samples heated at 820 °C for 12 h followed by treatments at 842 °C for 72 h show nearly single phase 2223, with CP as the minor secondary phase.

Fig. 4 shows the temperature variation of magnetization for the samples treated for different durations at 820 and 842 °C. The samples for susceptibility measurements were carefully weighed and nearly the same mass of the sample was used for each run so that the magnitude of the signal is proportional to the superconducting
volume fraction. It can be seen from Fig. 4 that with increasing duration at 820 °C, the strength of the diamagnetic signal decreases, showing a decrease in the superconducting volume fraction, which is probably due to the appearance of an impurity phase. This is in agreement with the result obtained from the XRD study.

The two curves on the right side of the Fig. 4 are after conversion to the (Bi,Pb)-2223 phase. Again, it can be seen that the magnitude of the signal is larger for the powder heated for 72 h at 842 °C, showing that a combination of lower heating times at 820 °C and longer durations at 842 °C is favourable for optimum conversion.

In conclusion, we find that for the precursor powder with the composition used in the present study, treatments at 800, 810 and 820 °C, followed by heating at 842 °C is suitable for conversion to the (Bi,Pb)-2223 phase. We suggest this schedule as the 'mature' schedule for precursor powders with the composition used in the present study.

Powders heated for longer durations at 820 °C show the growth of additional phases.

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