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PHASE FORMATION AND SUPERCONDUCTIVITY IN PIT-TYPE (Bi,Pb)-1212*

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It was shown via powder-in-tube (PIT) processing that the (Bi,Pb)-1212 phase readily forms inside a silver sheath at 920°C in air. Composition, oxygen pressure, time, and temperature were all varied to study their effects on (Bi,Pb)-1212 phase purity and superconductivity.

1. INTRODUCTION

Ehmann et al. reported the existence of a superconducting 1212 compound in the Bi-Sr-Y-Cu-O system in 1992 (1) and found that doping Ca for Y and Pb for Bi could increase the critical temperature in the Bi-1212 system.

Conflicting results have been reported, however, regarding the existence and source of superconductivity in the Bi-1212 system. Some (1-4) attributed the superconductivity in their bulk "Bi-1212" samples to the 1212 phase. Others (5,6) attributed the presence of superconductivity to trace amounts of 2212 in their samples and found phase-pure 1212 to be non-superconducting.

The goal of this work was to create a high purity 1212 phase in a Ag-sheathed tape form. Samples were formed inside a silver sheath to help in controlling the evaporation of lead from the samples. The Y:Ca ratio was varied to study its effect on phase purity and superconductivity. Time, temperature, and oxygen partial pressure were also varied to determine their influence on phase formation.

2. EXPERIMENTAL

Samples were prepared from Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, Y_2O_3, and CuO. Appropriate amounts of the starting powders were mixed to form a composition of $(Bi_{0.30}Pb_{0.50})$-$Sr_{2.13}$-(Ca_xY_{1-x})-$Cu_{2.20}$-O_z, where x=0.15, 0.50, 0.85. This powder was calcined at 900°C for 16h in air. The calcined powder was packed into Ag tubes (OD 6.35 mm and ID 4.35 mm), with a packing density of 25%, and were heated at 720°C for 3h in 2.5 torr of 100% oxygen to remove adsorbed species. The composites were drawn into wires, rolled into tapes with a thickness of 0.25 mm, and cut to 2.54 cm long samples. The tapes were subjected to heat treatments of varying temperatures and atmospheres. The phases and phase assemblages were analyzed by means of SEM, EDS and XRD. The superconducting transition temperature (T_c) was determined by magnetization measurements.

3. RESULTS AND DISCUSSION

In an atmosphere of 1%O_2/bal. Ar, no Bi-1212 phase was formed. However, in atmospheres of both 8%O_2/bal. N_2 and CO_2-free air, Bi-1212 formed quickly and homogeneously.

The influence of temperature on phase formation was studied by varying the temperature (920°C to 940°C) while holding the time and atmosphere constant (24 hr, Air). The study showed that the Bi-1212 phase readily formed in the range of 920° to 940°C.

Additionally, it was discovered that the Bi-1212 phase forms in as little as 6 hours at 920°C in CO_2-free air. However, SEM depicted that a longer dwell is preferred for producing a grain colony microstructure.

Figure 1 shows a SEM micrograph of a 1212 tape (x=0.15) that had been processed in air for 24 hours at 920°C. The gray regions, approximately 80% of the sample area, are the 1212 phase. Other phases present were $Sr_4Bi_3Y_3O_z$ (white areas), and $YSr_2Cu_3O_z$ (black areas). Additionally, x-ray analysis of this sample indicated enhancement of the (00*l*) reflections suggesting a preferred c-axis orientation (Fig. 2). Clearly, 1212 can be processed within a silver sheath.

In this study, samples with Y:Ca ratios of (1-x):x, where x ≥ 0.50, showed superconducting transitions with $T_{c,onset}$ as high as 80K. Samples with x < 0.50 were found to be nonsuperconducting.

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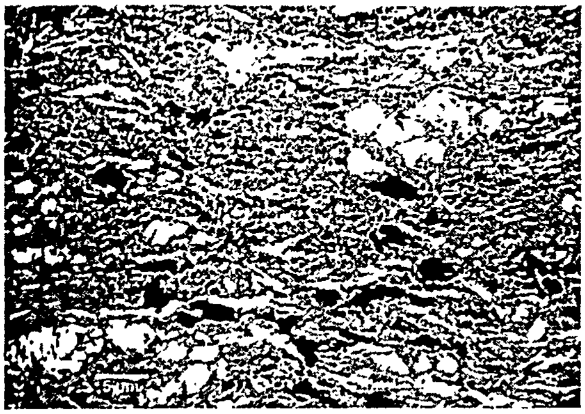

Figure 1: 920°C, 24 hours, Air

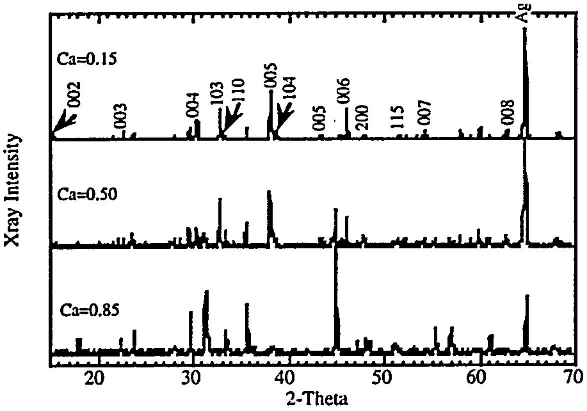

Figure 2: X-ray diffraction of 1212 tapes

We observed the presence of a 2212 phase in samples where superconductivity was detected. Additionally, we have estimated a superconducting volume of ~12%, which closely corresponds to the estimated volume fraction of the 2212 phase in our samples that were superconducting. Bauer (2), Frank (3), and Ritschel (4) also observed superconducting transitions for samples with Ca-content greater than 0.30. Frank's (3) measured effects were attributed to the 1212 phase, as it was the dominant phase, but it was stated that the presence of the 2212 phase could not be excluded as a source of the superconductivity results. Ritschel (4) also noted the presence of 2212 in their samples.

High volume fractions of 1212 were produced, and the amount of 2212 was minimized, only for samples with low Ca-contents ($x < 0.50$). This is consistent with the studies of Bauer (2) and Ritschel (4). XRD patterns of our samples with a Y:Ca ratio of 0.85:0.15 indicate a (nearly) single phase 1212 material (Fig. 2). However, as the Ca-content increased, the amount of second phases, primarily 2212, increased. This development was also noted by Ritschel, Bauer, Kaesche (5) and Schneider (7), who observed an increase in the Bi-1212 phase fraction when the Ca-content was decreased.

4. SUMMARY AND CONCLUSIONS

We have shown that high volume fractions of 1212 can be formed in a silver sheath. It was found that the 1212 phase formed in under 12 hours in an atmosphere of 8%-21% oxygen at a temperature as low as 920°C. We have also studied the effect of the Y:Ca ratio on 1212 phase purity as well as superconductivity. As the Ca-content increased, the amount of 2212 phase increased; at higher Ca-contents ($x \geq 0.50$), the samples exhibited weak superconducting transitions. The presence of the 2212 phase, and the fact that the superconducting volume closely corresponds to the 2212 phase fraction, leads us to believe that 2212, and not 1212, is responsible for the observed superconductivity of our samples.

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