

Processing Considerations for Adding Nanometer-Scale Oxides to Enhance Flux Pinning in High-Temperature Superconductors*

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PROCESSING CONSIDERATIONS FOR ADDING NANOMETER-SCALE OXIDES TO ENHANCE FLUX PINNING IN HIGH-TEMPERATURE SUPERCONDUCTORS

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ABSTRACT

Several nanometer-scale oxide inclusions were added to $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ high-temperature superconductors to determine their effectiveness in creating intragranular flux-pinning sites. Powder pellets were fabricated and heat treated by partial-melt processing. Effects of the additives on melting response, superconducting properties, and microstructural development were examined. Al_2O_3 additions exhibited the most promise for forming stable pinning centers, ZrO_2 and SnO_2 additions were moderately promising, TiO_2 , Fe_2O_3 , and ZnO additions were less promising, and Y_2O_3 additions destroyed superconductivity.

INTRODUCTION

Nanometer-scale second phases have proved to be effective flux-pinning centers in high-temperature superconductors. Examples of improved flux pinning in the presence of second phases include Y_2BaCuO_5 in $\text{YBa}_2\text{Cu}_3\text{O}_x$,¹ carbon-rich phases in many superconductors,^{2,3} BaAl_2O_4 in $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$,⁴ and $(\text{Ca,Cu})\text{O}_x$ in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$.⁵ Bi-based superconductors are most in need of improved flux pinning⁶ at temperatures that approach 77 K, and substantial success has now been achieved with these materials.⁷⁻¹⁴

In this work, we have added nanometer-scale oxides directly to $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$. Although addition of nearly unreactive particles, such as SrZrO_3 or MgO , would be ideal,^{7,8,12,13} we have added reactive particles such as Al_2O_3 or TiO_2 . The decision to do so was based on several factors: such oxides are readily available from commercial sources at reasonable prices;^{9,15,16} they exhibit relatively tight particle-size distributions and their size can be tailored;¹⁶ and they can be obtained in nearly spherical shapes, and, therefore, exhibit minimal agglomeration.⁴ Also, Al_2O_3 or TiO_2 have previously exhibited promise in enhancing flux pinning in high-temperature superconductors.^{4,9,15} Any commercial process for flux-pinning enhancement will require that the second phase be relatively uniform in size and very well distributed within the superconductor grains. We believe that these requirements can be met by use of nanometer-scale oxides that have been grown by vapor-phase methods.^{16,17}

Phase equilibria in superconductor systems are complex, and it can be very difficult to predict reactions between superconductors and second phases. We therefore approached our work from the point of view of nanometer-scale oxide availability. Simple oxides were added to $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ and their effects on superconducting transition and microstructure were examined. Our investigations focused only on identifying promising oxide additives. Before effects on pinning can be studied meaningfully, compositions and processing methods must be optimized.

EXPERIMENTAL PROCEDURES

$\text{Bi}_{1.88}\text{Sr}_{2.11}\text{CaCu}_2\text{O}_x$ (Bi-2212) powder was synthesized from mixtures of oxides and carbonates.¹⁸ This composition was chosen because we expected Sr to react with the additives, and, in the second stage of this project, we intend to convert the Bi-2212 into $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ by addition of PbO, CaO, and CuO. X-ray diffraction (XRD) and differential thermal analysis (DTA) revealed that the Bi-2212 was virtually phase pure. All DTA studies were conducted in air at a heating rate of 300°C/h, with Al_2O_3 used for crucibles and the standard.

Nanometer-scale Al_2O_3 , TiO_2 , Fe_2O_3 , ZnO, Y_2O_3 , ZrO_2 , and SnO_2 powders were obtained from Nanophase Technologies Corporation (Burr Ridge, IL). The powders were produced by a vapor-phase reaction and consisted of nearly spherical grains.^{4,16} Each powder was mixed in a 1:4 molar ratio of oxide:Bi-2212 by vibratory milling for 1 h in isopropyl alcohol.^{4,9} Powder mixtures were then dried on a hot plate while being stirred. The dried powders were pressed into 1.5-g, 12.7-mm-diameter pellets, which were stored in a desiccator until needed.

To aid in microstructural examination, similar pellets were prepared with micrometer-scale oxide inclusions. These specimens were used to identify reaction products.

All heat treatments were conducted in air, with the pellets placed in Ag crucibles. Each heat treatment consisted of rapid heating to a temperature $\approx 20^\circ\text{C}$ greater than the onset of melting indicated by DTA, holding at temperature for 0.2–1.0 h, and then cooling either by an air quench, or slowly, to nucleate and grow the Bi-2212 phase.^{9,19} (Bulk $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ superconductors are invariably partial-melt-processed to achieve high transport J_c values.^{19,20}) DTA revealed that, in general, the oxide additions induced a slight broadening of the melting endotherm (Fig. 1). Approximate onset temperatures of significant melting (T_m) for each powder are listed in Table 1.

A commercial SQUID magnetometer was used to measure the superconducting transition temperature (T_c) of the slowly cooled samples. The samples were examined by XRD, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) for microstructural analysis.

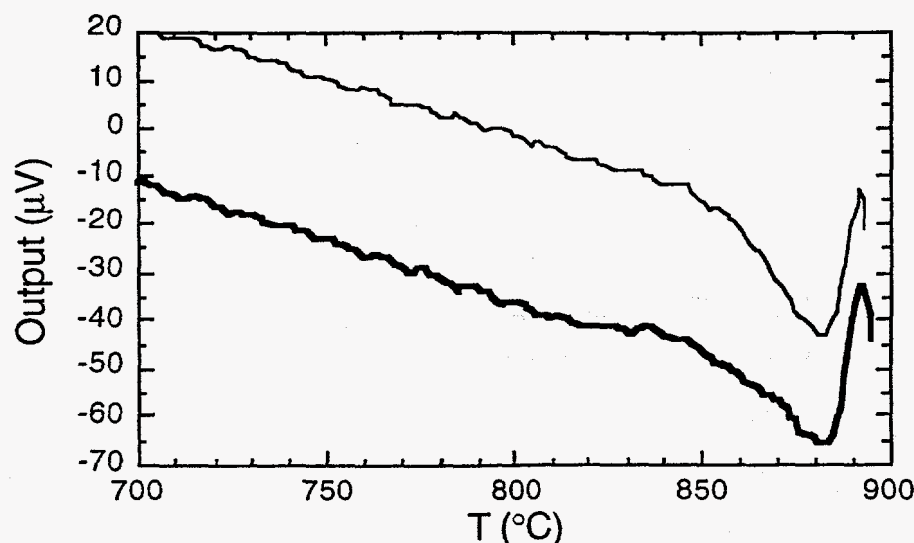


Figure 1. Representative DTA data for Bi-2212 (fine line) and Bi-2212 + Al_2O_3 (bold line).

Table 1. Onset of melting in air as determined by DTA.

Composition	T_m (°C)
Bi-2212	854
Bi-2212 + Al ₂ O ₃	846
Bi-2212 + TiO ₂	845
Bi-2212 + Fe ₂ O ₃	854
Bi-2212 + ZnO	852
Bi-2212 + Y ₂ O ₃	854*
Bi-2212 + ZrO ₂	864
Bi-2212 + SnO ₂	869

*The first melt was small and did not appear to correspond to substantial melting of the Bi-2212 phase.

RESULTS AND DISCUSSION

Rapid heating to a partial-melt temperature, followed by slow cooling to grow superconductor grains in which nanometer-scale oxides are enveloped, has proved to be successful in creating stable flux-pinning centers in YBa₂Cu₃O_x and TlBa₂Ca₂Cu₃O_x.^{4,9,15} Key features of the microstructural-development sequence are (a) suppression of a eutectic reaction by rapid heating to a melt, (b) rapid reaction in the melt with Ba to form a stable oxide such as BaTiO₃ or BaAl₂O₄, (c) avoidance of coarsening of the second phase, and (d) incorporation of the nanometer-scale phase into growing superconductor grains during cooling. Because the molar concentration of any additive is high, it is imperative that the oxide additive not exhibit a strong tendency to substitute directly into the superconductor lattice. If it does, overdoping and reduced superconducting properties are generally the result.

We are looking for an oxide that when added to Bi-2212 will react as, for example, Al₂O₃ reacts with TlBa₂Ca₂Cu₃O_x.⁴ Goals for the additive are that it alter peritectic-melt and crystal-growth responses minimally, have little deleterious effect on T_c , and form a stable phase, probably by reaction with Sr or Ca. Of the oxides selected, only Y₂O₃ failed to achieve any of the goals. Minor substitution of Y into the Bi-2212 lattice can enhance flux pinning.²¹ However, our method of addition caused a complete change of the melting characteristics, with most of the melting being driven to a higher temperature, suppression of Bi-2212 crystallization after melting, and complete loss of superconductivity at $T \geq 4.2$ K. All other oxide additions merited closer examination.

T_c values of the slowly cooled pellets are shown in Table 2. No attempt was made to optimize T_c by changing oxygen stoichiometry. Although ZrO₂ and SnO₂ had no appreciable effect on the onset T_c , Al₂O₃ induced a slight decrease in T_c , and TiO₂, Fe₂O₃, and ZnO decreased T_c and broadened the transition width significantly. Based on T_c values only, Al₂O₃, ZrO₂, and SnO₂ nanometer-scale additions appear to hold promise as additives to Bi-2212 for partial-melt processing.

SEM/EDS studies revealed clear differences for the effects of the various oxide additives on microstructural development. Representative microstructures of specimens with micrometer-scale oxides that were air quenched after 0.25 h at the partial melt temperature are shown in Fig. 2.

Table 2. T_c values for melt-processed pellets that were cooled slowly from a partial melt.

Composition	$T_{c, \text{onset}}$ (K)	$T_{c, \text{midpoint}}$ (K)
Bi-2212	88	84
Bi-2212 + Al ₂ O ₃	82	73
Bi-2212 + TiO ₂	74	52
Bi-2212 + Fe ₂ O ₃	45	29
Bi-2212 + ZnO	74	58
Bi-2212 + Y ₂ O ₃	Not superconducting	—
Bi-2212 + ZrO ₂	88	78
Bi-2212 + SnO ₂	88	82

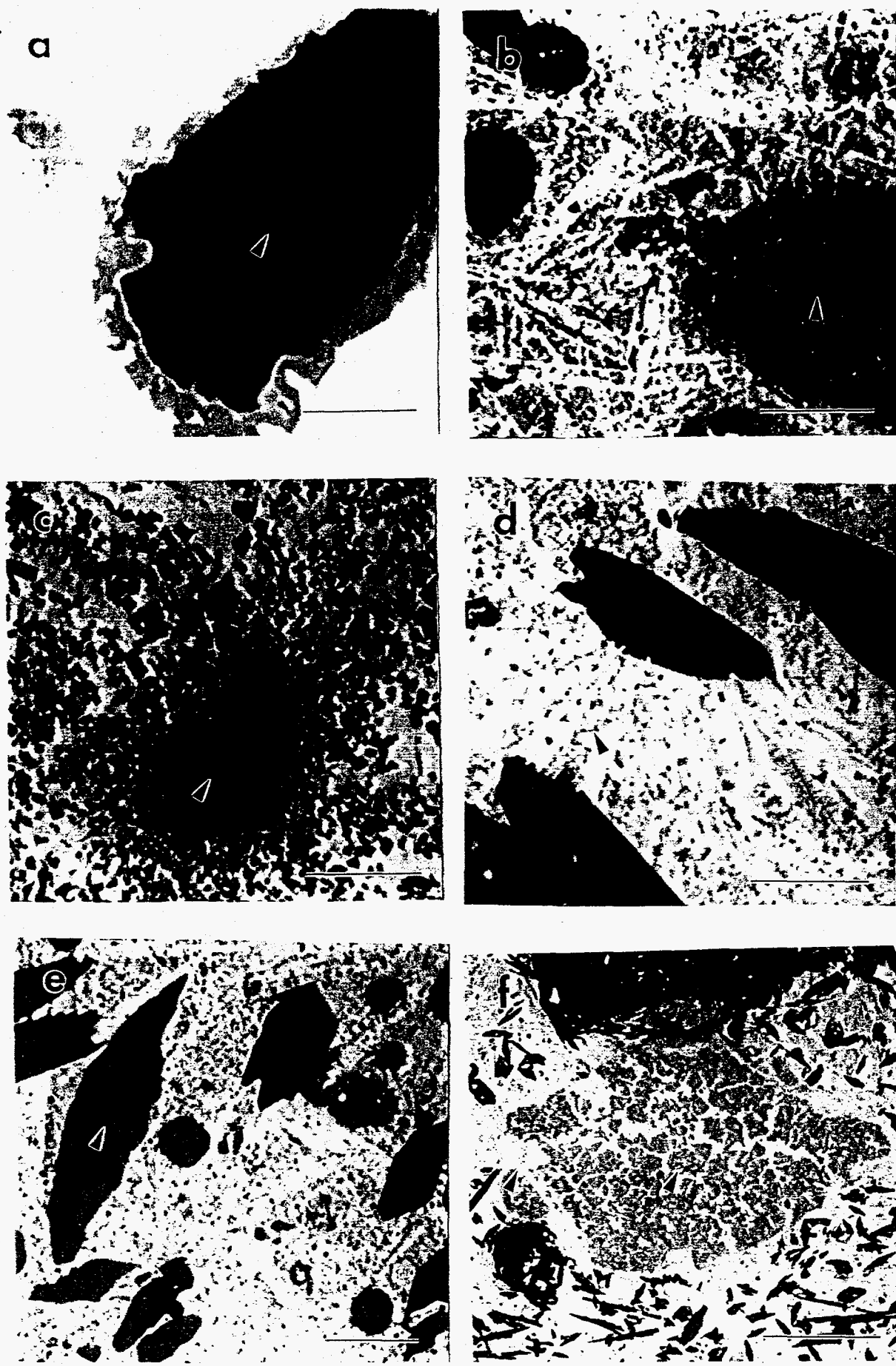


Figure 2. SEM photomicrographs of air-quenched Bi-2212 specimens that contained: (a) Al_2O_3 , (b) TiO_2 , (c) Fe_2O_3 , (d) ZnO , (e) ZrO_2 , and (f) SnO_2 . Arrows indicate the region that was richest in the additive; each bar = 10 μm , except (f), for which the bar = 100 μm .

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The Al_2O_3 -containing specimen (Fig. 2a) exhibited evidence of formation of stable reaction products. A dark ring of $(\text{Sr,Ca})_2\text{AlO}_x$ was present around each Al_2O_3 particle. In most cases, a thinner, lighter-colored, partial ring, of approximate composition $\text{Al}_{0.5}(\text{Sr,Ca})_{0.4}\text{Bi}_{0.1}\text{O}_x$, was also present. EDS analyses indicated that the concentration of Al in the matrix of the solidified melt was $\approx 1\%$. The dominant alkaline earth cuprate phase in the quenched sample was $(\text{Sr,Ca})\text{CuO}_2$. This phase was smaller than is generally observed in melt-processed Bi-2212;¹⁹ the refining effect of Al_2O_3 additions on alkaline earth cuprates in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ has been reported.²²

Heating at the maximum temperature for 1 h caused the $(\text{Sr,Ca})_2\text{AlO}_x$ phase to break up and diffuse away from the parent Al_2O_3 , rather like icebergs separating from a glacier; however, individual islands did not grow significantly. The Al_2O_3 :Bi-2212 system exhibited a response close to that desired: peritectic melting was relatively unaffected and, as a benefit, refinement of the $(\text{Sr,Ca})\text{CuO}_2$ phase occurred; the T_c value was slightly depressed, but the transition remained sharp; and, although two Al-containing phases were formed, the $(\text{Sr,Ca})_2\text{AlO}_x$ was dominant and appeared to be stable.

Given the stability of SrTiO_3 , one would expect that the TiO_2 :Bi-2212 system would be similar to the Al_2O_3 :Bi-2212 system. This did not prove to be so. Although some $(\text{Sr,Ca})\text{TiO}_x$ formed, Ti exhibited a strong tendency to dissolve into the melt (Fig. 2b). For this system, the dominant alkaline earth cuprate was approximately $(\text{Sr,Ca})_2\text{Cu}_3\text{O}_x$, with $\approx 1\%$ Ti incorporated. The quenched matrix consisted of lighter and darker regions, with the darker regions containing $\approx 5\%$ Ti. This microstructure strongly suggests that significant concentrations of Ti would be present in any Bi-2212 that formed. Small concentrations of Ti on the Bi-2212 lattice can be beneficial,²³ but our concentrations appear to be too high. T_c was strongly depressed and, in earlier work, we reported that little enhancement of flux pinning was obtained.¹³ Similar effects from overdoping have been reported by Grivel et al.²⁴ Although TiO_2 additions did not prove to be effective in these studies, it may be that, given the inherent stability of SrTiO_3 , some other set of processing conditions, for example use of a different oxygen partial pressure or perhaps Sr-rich Bi-2212 compositions, could lead to enhanced flux pinning.

Additions of Fe_2O_3 produced several microstructural effects (Fig. 2c). Adjacent to the Fe_2O_3 particles, a phase formed with approximate composition $(\text{Sr,Ca})_{0.5}\text{Fe}_x\text{Cu}_y\text{O}_z$, where $x \approx 0.2-0.35$ and $y \approx 0.15-0.3$. This phase was not as stable as the $(\text{Sr,Ca})_2\text{AlO}_x$ phase was in the Al_2O_3 -containing specimens; none was retained in the slowly cooled specimens. Other phases present in the melt were CuO and $(\text{Sr,Ca})_2\text{Cu}_3\text{O}_x$. The solidified melt contained $\approx 4-8\%$ Fe. Fe has been shown to substitute for Cu in superconductor lattices. The depression of T_c may have been caused by such substitution.

ZnO additions produced no single identifiable Zn-rich phase (Fig. 2d). Regions of solidified melt contained 1-2% Zn (light shade) and 9-10% Zn (dark shade). $(\text{Sr,Ca})_2\text{Cu}_3\text{O}_x$ was the dominant alkaline earth cuprate. For flux pinning, ZnO additions appear to be more suitable to solid-solution alloying schemes than to the production of distinct nanometer-scale second phases.

Nanometer-scale SrZrO_3 has been reported to impart enhanced flux pinning in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$.^{7,8,25} Although we could identify a distinct $(\text{Sr,Ca,Cu})\text{ZrO}_x$ phase within the melt (Fig. 2e), it was not prevalent and the melt contained 4-8% dissolved Zr. Thus, although presence of a fine-scale alkaline earth zirconate can yield enhanced flux pinning, the processing scheme of rapid heating to a partial-melt temperature does not seem to be ideal to take advantage of the possibilities. High concentrations of Zr in a melt will probably promote coarsening of any zirconate second phase.^{4,9} Preliminary measurements of magnetic hysteresis in a set of our ZrO_2 :Bi-2212 specimens indicated no enhancement of flux pinning at temperatures to as low as 5 K.²⁶

Additions of SnO_2 to Bi-2212 induced a complex response. A phase of approximate composition $(\text{Sr,Ca})_3\text{SnO}_x$ was identified (Fig. 2f). Enhanced flux pinning in Sn-doped $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ has previously been ascribed to this phase.²⁷ Sn-doping has, however, also been correlated with broadening of the superconducting transition and with a decrease in the fraction of the high- T_c phase.²⁸ The solidified melt in our Sn-doped specimen generally contained $\approx 10\%$ Sn, with some regions containing up to $\approx 30\%$ Sn. It appears that Sn is likely to form a stable alkaline earth phase and to substitute onto the Bi-2212 lattice. As no depression in T_c was observed, additions of nanometer-scale SnO_2 may hold promise. However, as was the case with our ZrO_2 additions, preliminary

magnetic hysteresis measurements indicated no enhancement of flux pinning in our Sn-doped specimens.

When cooled slowly, all specimens other than the one that contained Y_2O_3 consisted primarily of the $Bi_2Sr_2CaCu_2O_x$ phase (Fig. 3). Of all the dopant-containing second phases, $(Sr,Ca)_2AlO_x$ was the only one that proved to be highly stable and present in large concentrations in a slowly cooled pellet. As stated previously, other processing conditions could perhaps lead to different results. For the approach taken here, nanometer-scale Al_2O_3 additions appear to offer the most promise for enhancing controlled flux pinning in melt-processed $Bi_2Sr_2CaCu_2O_x$. We have reported some success with this system.⁹ Although the other oxide additives may prove useful, processing will be complicated by the fact that, in general, the oxides appear to form second phases and substitute into the superconductor lattice.

SUMMARY

Micrometer-scale and nearly spherical nanometer-scale Al_2O_3 , TiO_2 , Fe_2O_3 , ZnO , Y_2O_3 , ZrO_2 , and SnO_2 particles were added in a 1:4 molar ratio to Bi-2212. Resultant cold-pressed pellets were partial-melt processed in air and then either quenched in air or cooled slowly to form the superconducting phase. These oxide additions were selected on the basis of availability of high-quality supplies. Goals of the study were to determine whether the oxide additions formed stable second phases or substituted into the superconductor lattice, and whether the oxide additions had an effect on the superconducting transition temperature. Al_2O_3 additions, which exhibited the most promise for forming stable pinning centers, also induced a small decrease in T_c . ZrO_2 and SnO_2 appeared to form stable second phases, but also may have substituted partially into the superconductor lattice; however, T_c values were nearly unchanged by these additions. TiO_2 , Fe_2O_3 , and ZnO additions led to significant decreases in T_c , probably because of lattice substitution. Y_2O_3 additions altered the melting response of Bi-2212 significantly and prevented formation of the superconducting phase.

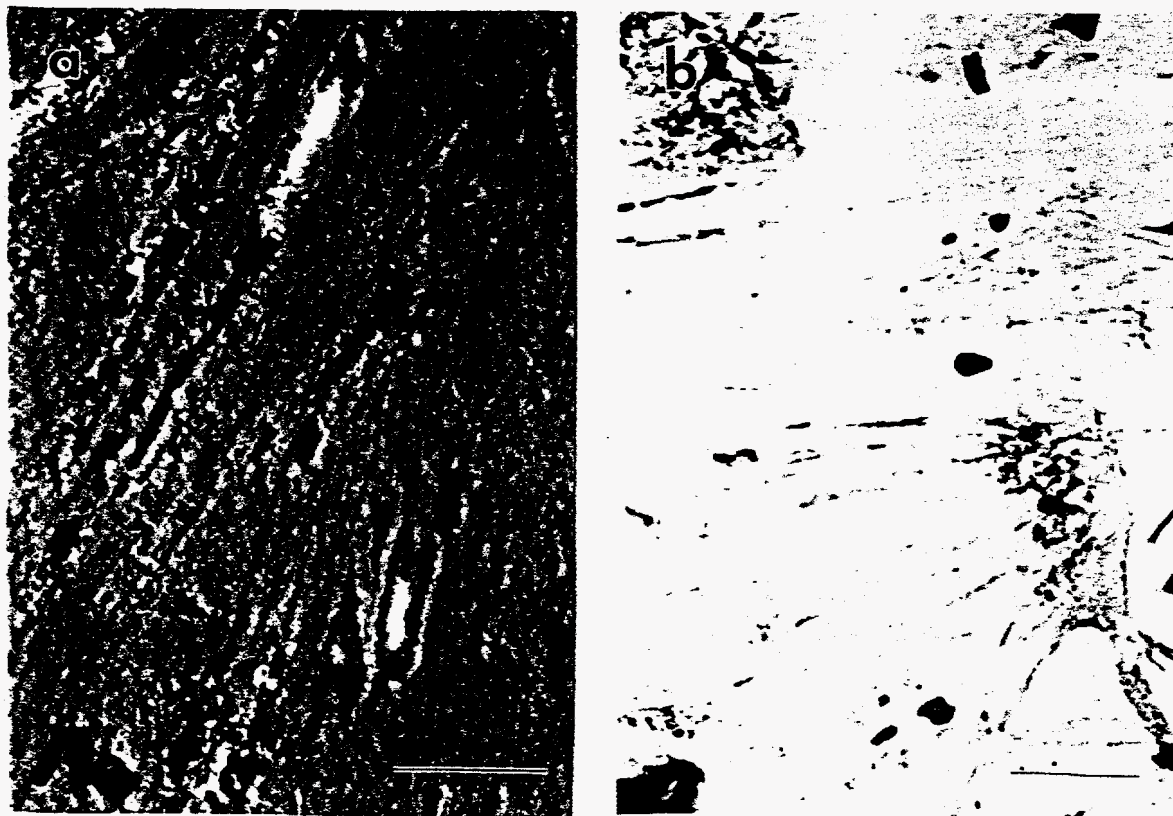


Figure 3. Representative SEM photomicrographs of slowly cooled Bi-2212 specimens that contained (a) Al_2O_3 and (b) SnO_2 . The light-colored regions are Ag, which dissolved from the crucible. Elongated Bi-2212 grains are dominant and little second phase is evident. Bars = 10 μm .

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