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EFFECTS OF LOW-LEVEL Ag DOPING ON $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ *

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Effects of Low-Level Ag Doping on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$

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$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ has been doped with silver, up to to 10,000 ppm, in three ways: excess additions, substitution of Ag for Bi, and substitution of Ag for Sr. Effects of doping on the c-axis lattice parameter and critical temperature (T_C) were measured. Effects from doping were only observed in slow-cooled [$10^\circ/\text{hr}$] oxygen equilibrated samples. Doping by excess additions caused a small decrease in T_C and an increase in the c-axis length of the lattice. Doping by substitution, compared to excess Ag additions, caused a larger decrease in T_C and higher c-axis values for doping levels up to 1,000 ppm. Doping by substitution at higher levels (1,000-10,000 ppm) caused T_C to increase and the c-axis to decrease. Samples with similar substitutional doping levels exhibited comparable T_C values and samples with Ag substituted for Sr consistently exhibited higher c-axis values than samples that had equivalent amounts of Ag substituted for Bi.

High-critical-temperature superconducting wires are being produced for electric power generation, transmission, storage, motors, transportation, medical technology and other applications.¹ The desired properties for these applications include high T_C , high critical current density (J_C), high stability in the presence of magnetic fields and good mechanical properties.² The most promising approach for producing high- T_C superconducting wires is the powder-in-tube (PIT) process,³ in which a silver tube is packed with an oxide powder, swaged, drawn and rolled to produce a tape, that is then treated thermomechanically.³ Wire development has mainly used two phases of the Bi-Sr-Ca-Cu-O (BSCCO) system: Pb-doped Bi-2223 ($\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, $T_C \approx 110$ K), and Bi-2212 ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, $T_C \approx 90$ K) compounds as the superconducting oxide core of PIT wires.⁴ Silver is used as the metal sheathing for these wires because of its oxidation resistance and favorable mechanical, thermal, and electrical properties.⁴ Silver is also known to affect the properties of BSCCO superconductors, but currently there is little agreement on what these effects are.

Silver is known to lower the melting temperature of BSCCO superconductors,^{5,6} enhance texture,⁷⁻⁹ and alter reactions within the ceramic core during heat treatments.⁵⁻¹¹ Due to the highly anisotropic properties of BSCCO ceramics, the texture of superconducting grains within the wires has a strong effect on current-carrying capacity. Several studies indicate that the interfacial area between the superconducting ceramic and Ag sheathing, where the texture is highest, controls the current carrying capacity of a high- T_C wire.¹²⁻¹⁷ Wires are also being made with Ag added to the BSCCO ceramic core to enhance mechanical properties.^{18,19} These studies indicate that the interaction of the Ag with BSCCO has an important influence on the final properties of superconducting wires.

The reported effects of Ag additions to BSCCO on T_C and J_C are mixed.¹⁸⁻²⁴ Silver is reported to both increase and decrease T_C ^{20-22,25,26} or to have no effect on T_C .^{23,24} J_C is also reported to both increase²³ and decrease^{24,25} with Ag additions. Typically in these studies, Ag or Ag_2O is added in excess of 10 wt.% to Bi-2223 or Bi-2212 powders, sintered and observed for changes in properties with respect to undoped samples. It is

difficult to interpret the results when both the amount of Ag and the extent of interaction are unknown. Diffusion studies of Ag in BSCCO performed by Fang and Routbort²⁵ concluded that Ag diffuses on Bi and/or Sr sites. This is in contrast to the Y-Ba-Cu-O system, in which Ag is known to substitute for Cu.²⁸ Others have studied the Ag/BSCCO interface with photoemission studies.²⁹⁻³¹ Hwu²⁹ reported that Ag replaces Bi in the Bi-2212 phase in addition to causing a shift in the kinetic energy of the Bi 5d electrons. Hwu²⁹ also reported that the presence of Ag caused shifts in the spectrum of the Sr 3d electrons, but does not seem to alter the spectrum of the Cu 3p electrons. In contrast, Meyer³⁰ and Lindberg³¹ reported that Cu valency was reduced by the presence of Ag; this conclusion was based on observed changes to the Cu 2p spectrum.

Low levels (<1 atomic %) of homogeneous Ag doping were obtained by freeze drying precursor nitrate solutions.³⁰ Samples were prepared for stoichiometric (2212), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$; (2212 + Ag), $\text{Ag}_x\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ($x = 0.002-0.02$); Ag substitution for Bi, $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{CaCu}_2\text{O}_8$ ($x = 0.0002-0.02$); and Ag substitution for Sr, $\text{Bi}_2\text{Sr}_{2-x}\text{Ag}_x\text{CaCu}_2\text{O}_8$ ($x = 0.0002-0.02$). After drying, powders were heat treated in flowing oxygen at 850°C for 50 hr with intermittent grindings. Samples were then either air quenched or slow-cooled at a rate of 10°/hr in flowing oxygen. X-ray diffraction (XRD) was used to determine phase purity and c-axis lattice parameters by scanning the (0 0 20) reflection with an internal Si reference standard. Critical temperatures were determined by a SQUID magnetometer.

Table I summarizes the stoichiometry, cooling, T_c and c-axis length of all samples. T_c vs c-axis is plotted in Figs. 1 and 2. Fig. 1 shows results for both doped and undoped samples that have been either quenched or slow-cooled (10°C/hr). All quenched samples, regardless of doping, display a linear relation between T_c and c-axis. This result is similar to that reported by others³³⁻³⁶ and represents a regime where oxygen content is a controlling factor. The oxygen content of the 2212 phase has a strong temperature dependence, displaying an increasing content with decreasing temperature.^{33,34} Although reported values vary, samples quenched from high temperatures (>800°C), exhibit high T_c

(≈ 90 K), and low excess oxygen (≈ 8.0). As cooling rates are decreased and the oxygen content is allowed to equilibrate, the oxygen content of 2212 increases to ≈ 8.3 and T_C decreases to ≈ 70 K. As shown in Fig. 2, samples doped with as little as 100 ppm (0.01 at.%) of Ag depart from this regime when slow-cooled.

Figure 2 shows T_C vs c-axis for both undoped and doped samples that were slow-cooled. As Ag is added (0-10,000 ppm), without corresponding adjustment by removing either Bi or Sr removal, there is a small decrease in T_C from 72 to 69 K and an increase in the c-axis from 30.78 to 30.81 Å. In the range of 0-100 ppm Ag substitution, with corresponding adjustment of either Bi or Sr, the trend is also an increase in c-axis and a decrease in T_C with increased doping. The change in T_C , with respect to doping level, is more pronounced when Ag is substituted for Bi or Sr than when Ag is added without a corresponding decrease in Bi or Sr. The change in c-axis is greatest when Ag is substituted for Sr. In the range of 100-1,000 ppm Ag substitution for Bi or Sr, the trend is also a decrease in T_C with increased doping, but no change in the c-axis is observed.

When Ag is substituted for Bi or Sr at levels greater than 1,000 ppm, the observed trend changes to decreased c-axis and increased T_C . Changing the doping level from 1,000 to 10,000 ppm of Ag for Sr results in a small c-axis decrease from 30.81 to 30.80 Å, but a significant increase in T_C from 60 to 70 K. Changing the doping level from 1,000 to 10,000 ppm of Ag for Bi results in a larger decrease of the c-axis from 30.80 to 30.76 Å and a comparable increase in T_C from 63 to 71 K.

Interpretation of these data is complicated for several reasons. The 2212 phase is known to have a large variability in stoichiometry,^{37,38} and the reported levels for these occurrences in stoichiometry are in excess of the doping levels used in this study. In addition, we do not fully understand what changes are occurring to the oxygen content and the sites of oxygen occupancy within this regime.

Despite the difficulties in establishing a defect model for this behavior, several points are clear. Low-level Ag doping (<1 at.%) in Bi-2212 does not significantly alter T_C in metastable quenched samples. In this regime, T_C is controlled by the unequilibrated

oxygen content, which is strongly temperature-dependent. However, oxygen-equilibrated samples have properties (T_C , c-axis) that are influenced by the presence of Ag. These effects are observable at levels as low as 100 ppm. Samples with similar doping levels have comparable T_C values, but different c-axis values; those with Ag substituted for Sr consistently had higher c-axis values than did samples with Ag substituted for Bi.

Based on previous diffusion and photoemission studies, it is assumed that Ag occupies Bi sites within the lattice. In addition, it is well known that Bi can substitute for Sr within the 2212 lattice.^{39,40} This leads to the possibility that the difference between substitutionally doped samples is the amount of Bi occupying Sr sites, assuming Bi replaces the decreased Sr content. Samples with Ag substituted for Sr will then have more Bi on Sr sites, but equal amounts of Ag on Bi sites compared to samples with Ag substituted for Bi. Because Bi ions are larger than Sr ions this could explain the higher c-axis values when Ag is substituted for Sr compared to those of the Bi-substituted samples. It is tempting to conclude that the level of doping controls the T_C value, while the different ratios of cations control the c-axis lattice parameter. The greatest difference in T_C values is seen at a doping level of 1,000 ppm. The Ag substituted for Bi sample exhibited a T_C of 63 K, while the Ag substituted for Sr sample had a T_C of 60 K. Further work is needed to clarify these points.

Work is in progress to further understand the effects of both Ag and Ag doping on BSCCO. These effects have important implications on the properties of Ag-clad superconducting wires now being produced for applications.

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TABLE I. Stoichiometry, cooling and characterization data for samples 1-17

Sample	Stoichiometry	Cooling from 850°C	T _c (K)	c-axis (Å)	Label
1	Bi-2212	air quenched	86	30.848	2212
2	Bi-2212	10°C/hr	72	30.766	2212
3	Bi-2212	10°C/hr	72	30.780	2212
4	Bi-2212 1,000 ppm Ag addition	10°C/hr	70	30.794	P1K
5	Bi-2212 10,000 ppm Ag addition	10°C/hr	68	30.810	P10K
6	Bi-2212 100 ppm Ag for Sr	air quenched	89	30.864	100Sr
7	Bi-2212 100 ppm Ag for Sr	air quenched	81	30.822	100Sr
8	Bi-2212 100 ppm Ag for Sr	air quenched	78	30.816	100Sr
9	Bi-2212 100 ppm Ag for Sr	10°C/hr	66	30.810	100Sr
10	Bi-2212 100 ppm Ag for Sr	10°C/hr	65	30.810	100Sr
11	Bi-2212 100 ppm Ag for Bi	air quenched	80	30.820	100Bi
12	Bi-2212 100 ppm Ag for Bi	10°C/hr	65	30.802	100Bi
13	Bi-2212 100 ppm Ag for Bi	10°C/hr	65	30.798	100Bi
14	Bi-2212 1,000 ppm Ag for Sr	10°C/hr	60	30.808	1KSr
15	Bi-2212 1,000 ppm Ag for Bi	10°C/hr	63	30.802	1KBi
16	Bi-2212 10,000 ppm Ag for Sr	10°C/hr	70	30.798	10KSr
17	Bi-2212 10,000 ppm Ag for Bi	10°C/hr	71	30.762	10KBi

Figure Captions

Fig. 1. Plot of T_C vs. c-axis for both undoped and Ag-doped 2212 samples that were either quenched or slow-cooled.

Fig. 2. Plot of T_C vs. c-axis for both undoped and Ag-doped 2212 samples that were slow-cooled.