

Physical and chemical effects of silver additions to $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$

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Silver in the form of silver peroxide has been added prior to the sintering step in the preparation of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$. X-ray diffraction analysis and microscopic examination show no evidence for chemical reaction between the silver and the ceramic superconductors. However, the presence of the silver can affect the phase purity of the final product—the amount of the three-layered high- T_c (100-K) phase can either be increased or decreased depending on the sintering conditions and the starting composition. No evidence can be seen in the x-ray spectra to indicate that the silver is going into either phase. The only effect of the silver is on the thermodynamics and kinetics of the sintering process.

INTRODUCTION

Recent reports on the effects of silver added to $\text{YBa}_2\text{Cu}_3\text{O}_7$ have claimed increased flexibility and strength, as well as increased flux pinning and enhanced critical current.^{1,2} The newer layered bismuth- and thallium-based superconductors offer many advantages over $\text{YBa}_2\text{Cu}_3\text{O}_7$. These materials are receiving increased attention as candidates for wires and other high-current conductors. This is particularly true of the high- T_c phases of the bismuth family of compounds, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ with two Cu-O layers ($T_c = 80$ K), and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ with three Cu-O layers ($T_c = 110$ K). These materials do not have the environmental hazards associated with the thallium materials, and they are processed in air at $\approx 100^\circ\text{C}$ less than $\text{YBa}_2\text{Cu}_3\text{O}_7$. These considerations have provided the motivation for the present work. This Brief Report summarizes our results on some of the physical and chemical properties resulting from the addition of silver to these two phases of the bismuth-based superconductor. The electronic properties, particularly the critical current, of the silver-modified materials are in the process of being measured and will be reported later.

SAMPLE PREPARATION

All chemicals were obtained from Aesar and used as received. The minimum purities were as follows: Bi_2O_3 , 99.9998%; CaCO_3 , 99.9995%; CuO , 99.999%; SrCO_3 , 99.999%; PbO , 99.999%, and Ag_2O_2 , 99.9%. These compounds were weighed out to make three batches of materials with nominal Bi:Pb:Sr:Ca:Cu ratios of 4:0:3:3:6, 2:0:2:1:2, and 1.6:0.4:2:3:4. The mixed powders were ground and then calcined at 840°C for 36 h, followed by a slow cool ($4^\circ\text{C}/\text{min}$) to room temperature. The calcined materials were reground and processed at 848°C for 96, 40, and 144 h for the 4:0:3:3:6, 2:0:2:1:2, and 1.6:0.4:2:3:4 batches, respectively. The resulting materials were then mixed with an appropriate amount of Ag_2O_2 to produce samples with 0, 2.5, or 5% by weight silver. These mixtures were ground finely and pressed into pellets. The 4:0:3:3:6 samples were then sintered at 848°C for 18 h, the 2:0:2:1:2 samples at 848°C for 1 h, and the

1.6:0.4:2:3:4 samples at either 848°C or 840°C for 1 h. After a subsequent cool down at $1^\circ\text{C}/\text{min}$ to 800°C , the furnace was turned off and allowed to cool slowly to room temperature. All of the furnace processing described above was done with the samples in air.

After processing, the pellets were tested for bulk silver content by dissolving approximately 0.25 g in 1.5 ml concentrated HNO_3 , adjusting the pH to 4.3, and diluting to 25 ml. The solutions were tested for silver content using a standard addition technique by monitoring the potential of a Ag/AgCl electrode, measured versus a saturated calomel electrode. In all cases, the experimentally determined silver content agreed with the nominal silver percentage.

EXPERIMENTAL RESULTS

One difficulty in the interpretation of measurements on high- T_c superconducting materials is that the phase purity and phase composition are either unknown or unreported. This is very important for the bismuth- and thallium-based superconductors because they can exist in many phases. In this study, x-ray diffraction has been used to follow the phase purity of the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ family of crystal structures, when $n=2$ or 3. All of the x-ray data used in this paper were acquired with a Rigaku Rotaflex RU-200B x-ray diffractometer using copper $K\alpha$ radiation.

The x-ray spectra for single-phase³ $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2:0:2:1:2 batch) and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (1.6:0.4:2:3:4 batch)^{4,5} are shown in Fig. 1 with and without the addition of silver. For simplicity, only the most relevant portions of the spectra are shown. In parts (a) and (c), the region near the (002) peak is shown to give a succinct overview of the phase distribution between the $n=2$ and 3 structures. The $n=2$ structure has the (002) reflection near $2\theta=5.8^\circ$ and the $n=3$ structure near $2\theta=4.8^\circ$, where 2θ is the x-ray scattering angle. In parts (b) and (d), the portion of the spectra containing the primary peak for elemental silver is shown, near $2\theta=38.3^\circ$. The figure shows the phase composition starting with the pure material, and then with 2.5% and 5.0% by weight silver. Note that for the 2:2:1:2 ($n=2$) phase, parts (a) and (b)

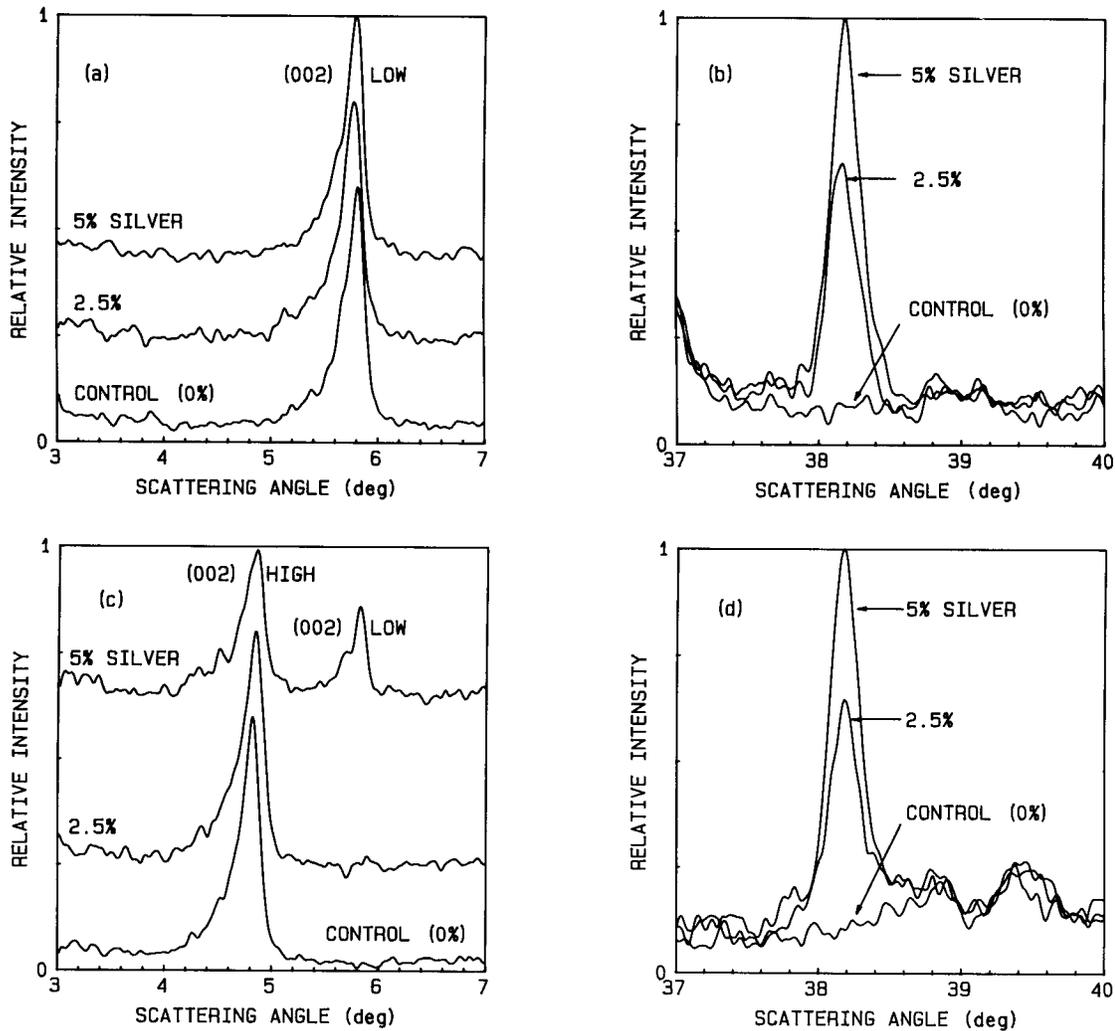


FIG. 1. The x-ray intensity vs scattering angle 2θ showing (a) the (002) peak of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ for samples with 0, 2.5, and 5% silver by weight (the data have been adjusted vertically for clarity), (b) the primary peak for elemental silver for the same samples as in (a), (c) the (002) peak of $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ for samples with 0, 2.5, and 5% silver by weight (adjusted vertically for clarity), and (d) the peak for elemental silver for the same samples as in (c). The labels "low" and "high" refer to the low- T_c (80 K) and high- T_c (110 K) phase, respectively.

of the figure, for all levels of silver dopant shown, the phase composition of the sample does not change, nor do the lattice parameters, as the relative height of the silver peak increases. This offers convincing evidence that the silver does not go into the superconductor's structure. The corresponding results for the 2:2:2:3 ($n=3$) phase are shown in parts (c) and (d) of the figure. For the 2:2:2:3 material under these conditions, unlike for the 2:2:1:2, once the silver concentration reaches approximately 5% (by weight), the phase composition changes. These samples were sintered at 848°C . Some 2:2:1:2 phase material is now present in the sample which started as x ray pure 2:2:2:3 phase material. However, just as with the 2:2:1:2 sample, the silver peak's height grows proportionately with silver dopant level.

Samples of nominal composition $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_6\text{O}_x$ were also prepared with 0 and 2.5% (by weight) silver added. This starting composition yielded mostly the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ phase. However, long sintering times produced increasing amounts of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ as well. No lead

was added to any of these samples. The effect of the addition of 2.5% silver by weight to such a sample showing no $n=3$ phase is illustrated in Fig. 2. As in Fig. 1, the (002) peaks are shown in Figs. 2(a) and 2(c). In addition, the (115) peak region is also shown here in Figs. 2(b) and 2(d). The (115) peak region is actually the most sensitive part of the spectrum to observe small amounts of either 2:2:1:2 or 2:2:2:3 which may be present as a minor phase. The spectra in parts (a) and (b) of Fig. 2 are for the control sample with no silver. This sample is all 2:2:1:2 phase material. The effect of adding silver is shown in parts (c) and (d). In Fig. 2(c), a small 2:2:2:3 phase (002) peak is visible. Growth of the 2:2:2:3 phase is more clearly seen in Fig. 2(d), where the 2:2:2:3 phase (115) peak at $2\theta=26.0^\circ$ is unmistakable. From the x-ray data, the amount of 2:2:2:3 phase is estimated to be less than 10% by volume based on the relative size of the peak.

The x-ray spectra of Fig. 2 are consistent with the electrical transport measurements made on these samples shown. The resistive transition, for the silver-doped sam-

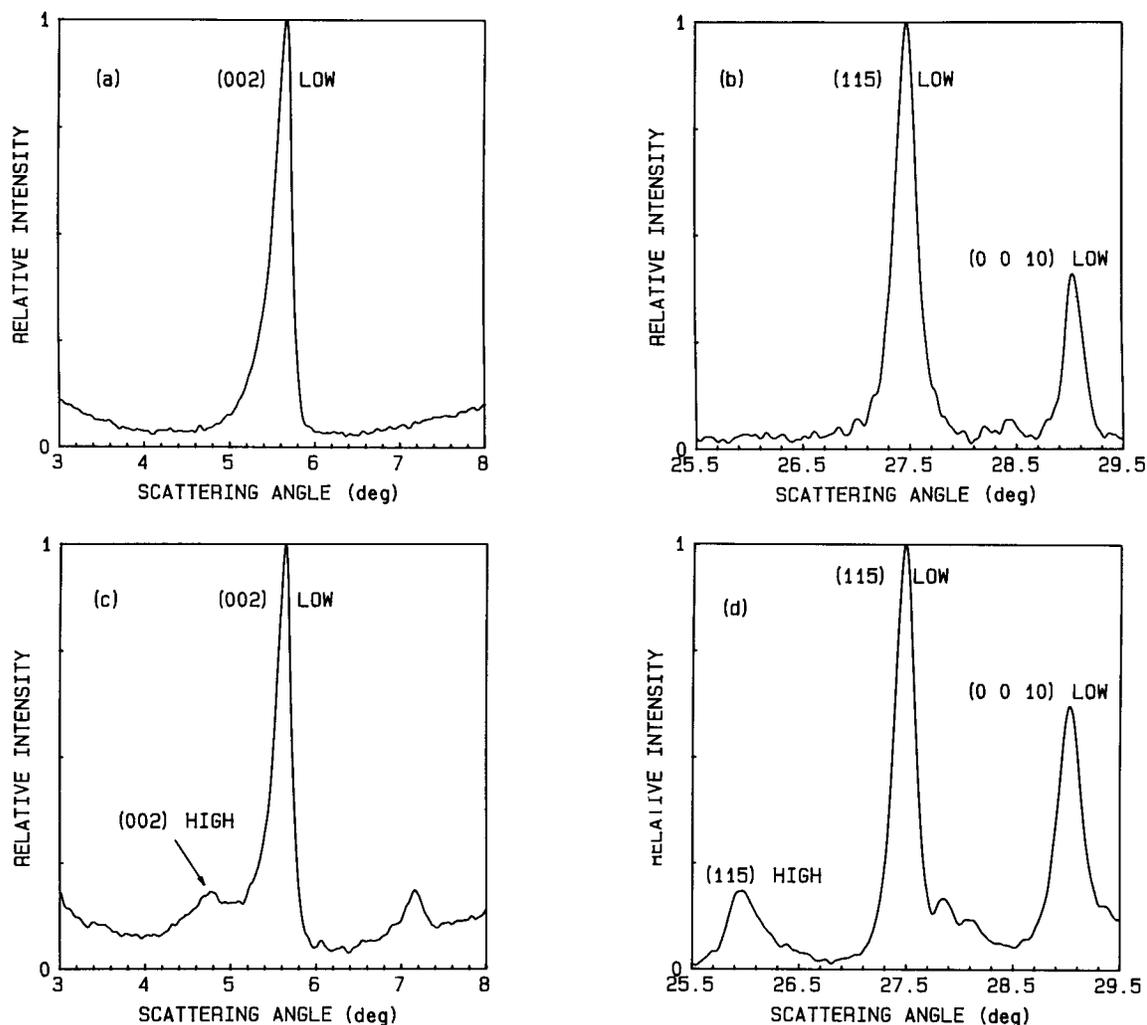


FIG. 2. The x-ray intensity vs scattering angle 2θ for samples with a starting nominal composition of $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_6\text{O}_x$ showing (a) the (002) peak of pure phase $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, (b) the (115) peak showing the pure 2:2:1:2 nature of the sample, (c) the (002) peak for the same sample with 2.5% silver showing the growth of some $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ material [the peak near $2\theta = 7.2^\circ$ is due to some 2:2:0:1 ($n=1$) phase produced], and (d) the same silver doped sample as in (c) showing the (115) peak region as additional evidence of the growth of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$. The labels "low" and "high" refer to the low- T_c (80 K) and high- T_c (110 K) phases, respectively.

ple of Fig. 2(d), is illustrated in Fig. 3. Note that this sample has a large drop in resistance near 110 K, but the resistance does not go to zero until about 80 K. This shows that there is no percolation path through the sample due to the 2:2:2:3 phase. That is, the volume fraction of 2:2:2:3 phase is less than about 15%. This is consistent with the x-ray data described above. For comparison, the resistive transitions for the $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_6\text{O}_x$ control with no silver (mostly 2:2:1:2 phase) and for a sample showing a good 2:2:2:3 transition are also shown in Fig. 3.

Finally, the effect of lowering the process temperature for silver-doped $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ material is shown in Figs. 4(a) and 4(b). The low-angle spectral region of a single-phase 2:2:2:3 sample before adding silver is displayed in Fig. 4(a). Five percent silver by weight was added to this sample, which was then sintered at 840°C . The resulting spectrum is shown in Fig. 4(b). Clearly, under these conditions, the phase purity of the starting material is preserved. These results should be contrasted

with Figs. 1(c) and 1(d), where the higher temperature (848°C vs 840°C) produced material with some lower- T_c phase.

Two effects of adding silver to these samples appear to be faster kinetics and improved sintering, which are probably due to a suppression of the melting temperature. To check this hypothesis, the sample of Fig. 4(a)—pure 2:2:2:3 phase material—was heated to 1000°C for 5 min to melt it. The result is shown in Fig. 4(c) and clearly shows that the melted sample resolidifies in the 2:2:1:2 phase. Similarly, the 2:2:1:2 phase appears when silver is added to the high- T_c phase and the sample is processed at the normal processing temperature (848°C), as previously shown in Fig. 1(c).

CONCLUSIONS

Measurements to determine the effects of silver additions up to 5% by weight in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $(\text{Bi,Pb})_2$

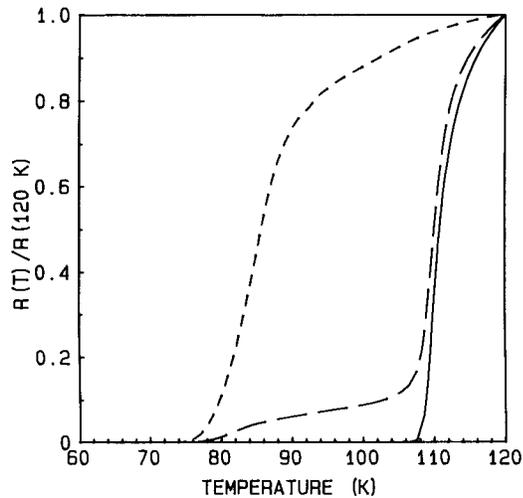


FIG. 3. The resistance R , normalized to the value at 120 K, vs the temperature T , for the $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_6\text{O}_x$ control sample with no silver—mostly 2:2:1:2 phase (small dashes), for the mixed-phase silver-doped $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_6\text{O}_x$ sample of Fig. 2 (large dashes) and, for reference, a sample which shows a complete 2:2:2:3 transition (solid line).

$\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ have shown that there is no discernible reaction with the superconductors and that the silver does not appear to enter the crystal structure. However, the presence of the silver has a thermodynamic and/or kinetic effect on the sintering—both the proper sintering temperatures and times are reduced. It was shown that, depending on the sintering conditions and the starting composition, these effects can either enhance or reduce the growth of the higher- T_c phase relative to the lower- T_c phase.

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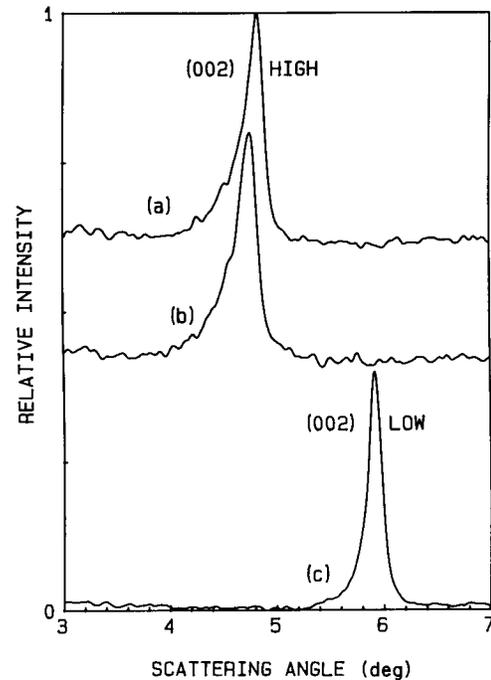


FIG. 4. (a) The (002) peak for a sample of single phase $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ material. (b) The same sample as in (a) but with 5% by weight silver added and sintered at 840°C . (c) The result of taking the sample shown in (a) and heating it to 1000°C for 5 min—a complete return to the 2:2:1:2 structure. The labels “low” and “high” refer to the low- T_c (80 K) and high- T_c (110 K) phases, respectively; the data have been adjusted vertically for clarity.

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³Single phase, as used here, refers to the x-ray purity of the sample with respect to all the possible phases of $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$, where $n=1, 2$, or 3 . Since the single-phase 2:2:1:2 material is prepared from stoichiometric amounts of each element, the samples are chemically pure as well. That is, there are few detectable impurities and nonreacted by-products of the synthesis. This is not the case for the 2:2:2:3 material, however, as it is prepared from the off-stoichiometric 2:2:3:4 starting composition. Detectable amounts of various cuprate by-products of the synthesis can be seen in the x rays and in energy dispersive x-ray analysis. However, no significant amount of the other superconducting phases is seen in the x-ray spectra.

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