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LEAD-RICH PHASES IN PARTIALLY PROCESSED Ag/Bi-2223 COMPOSITE CONDUCTORS*

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Abstract

The occurrence, composition, and melting behavior of lead-rich phases detected during the thermal processing of Ag/Bi-2223 composite conductors have been investigated by a combination of transmission electron microscopy (TEM), energy dispersive analysis (EDS), x-ray diffraction, differential thermal analysis, and Raman spectroscopy. A (Bi,Pb)-Sr-Ca-Cu-O composition with "4112" metal atom stoichiometry and $Pb \approx Bi$ was detected during TEM/EDS examinations of partially processed/quenched Ag/Bi-2223 composites. An as-synthesized oxide mix with this stoichiometry was found to melt at a temperature <700°C. The lead-rich "3221" phase was found to have a wide range of compositional stability in terms of Pb/Bi ratio and Bi + Pb stoichiometry. Evidence was seen for the co-existence of this phase with $(Ca,Sr)_2PbO_4$ in partially processed Ag/Bi-2223 composites that were cooled slowly through the 800 to 600°C range.

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Introduction

There is a considerable body of evidence(1-10) suggesting that lead-rich phases play a significant role in the phase evolution and microstructure development that occurs during thermomechanical processing of silver-sheathed/$(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Ag/Bi-2223) composite conductors. Whereas the occurrence of plumbates, i.e., $(Ca,Sr)_2PbO_4$, is well established, two other phases -- a lead-rich "liquid" phase(1-3) and a lead-rich $(Bi,Pb)_3Sr_2Ca_2CuO_y$ (3221) phase(8,11-15) -- have been implicated but not thoroughly characterized. In a prior paper[2] we reported the observation by transmission electron microscopy (TEM) of a lead-rich amorphous phase in Ag/Bi-2223 composite specimens that were quenched during the early stages ($\leq$1500 minutes) of heat treatment. Calibrated energy dispersive spectroscopy (EDS), done in conjunction with the TEM measurements, was used to determine the approximate composition of this amorphous phase, but its melting temperature was not determined. We have now completed a more detailed study of this amorphous phase and, in addition, have investigated by x-ray diffraction (XRD) and Raman spectroscopy the lead-rich "3221" and plumbate phases that appear during processing of Ag/Bi-2223 composites.

Experimental Procedures

The procedures employed to fabricate and heat treat the Ag/Bi-2223 composite conductor examined in this study have been reported elsewhere.(2,16-18) The TEM/EDS measurements were performed using a Philips CM-30 (operated at 300 kV) equipped with a Noran EDS detector. The DTA scans were made with a Netzsch STA 409. XRD patterns were recorded on peeled specimens using a Philips XRG-3100 with a Cu Kα source. Raman spectra were obtained with a Renishaw System 2000 instrument using 633 nm radiation from an He-Ne laser. The methodology used to prepare samples for the Raman measurements is described in a recently submitted paper by Wu et al.(19)

Results and Discussion

The "4112" composition

In two previous papers(2,20) we reported the observation of amorphous phases in Ag/Bi-2223 composite specimens that were heat treated at near-optimum conditions of temperature (~825°C) and oxygen pressure (0.075 atm O_2) for periods ranging from 10 to 1500 minutes, then rapidly quenched to ambient temperature by dropping them into an oil bath. By quenching these samples in a partially processed state, we were able to lock in the phases present during the early to middle stages of the Bi-2223 formation reaction. It is in these stages that one expects to find the ubiquitous "liquid" phase whose demonstrable presence was highlighted in the work of Morgan et al.(1) Typical examples of the manifestations of this "liquid" phase in our prior work on partially processed Ag/Bi-2223 composites are shown in Fig. 1 for a monofilament specimen that was heat treated at 825°C in 0.075 atm O_2 for 1500 minutes prior to quenching.(2) At this stage, where the Bi-2223 formation reaction is at most 50% complete, there are numerous evidences in our TEM results for pockets of amorphous phase (as in Fig. 1a) and streaks of amorphous material (as in Fig. 1b).

We presumed at the time of this earlier work that the amorphous phase had been a liquid at the heat treatment temperature and that the streaks in Fig. 1b were caused by wetting-induced flow of amorphous pockets like the one in Fig. 1a. An EDS examination of the amorphous patch in

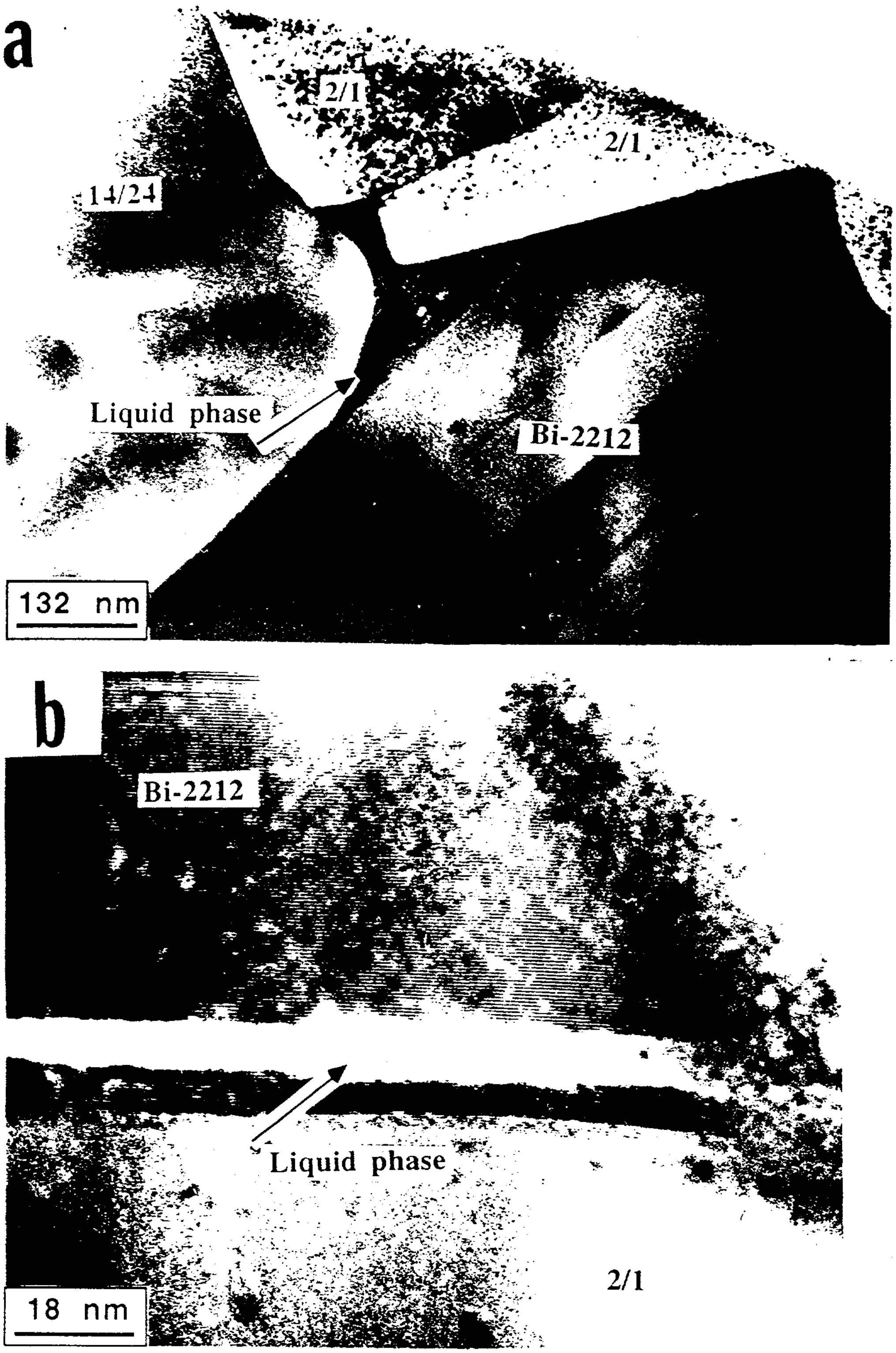

Figure 1. Transmission electron micrographs of an Ag/Bi-2223 composite heat treated at 825°C in 0.075 atm O_2 for 1500 minutes then quenched. Image (a) shows amorphous ("liquid") pocket in multiphase grain cluster. Image (b) shows amorphous ("liquid") streaks between Bi-2212 planes.

Fig. 1a (calibrated against an analyzed Bi-2212 specimen) gave a metal atom composition (normalized to Cu = 2.0) of $Bi_{2.2}Pb_{1.6}Sr_{1.3}Ca_{1.0}Cu_{2.0}$. (Hereafter we shall refer to this composition as "4112".) Similar pockets with much the same metal atom stoichiometry were detected in other regions of the same specimen and in other partially reacted Ag/Bi-2223 composite specimens as well. Therefore, it seemed appropriate to examine the melting characteristics of an oxide mix having this same stoichiometry.

To explore this "4112" composition further, a $Bi_{2.2}Pb_{1.6}Sr_{1.3}Ca_{1.0}Cu_{2.0}O_x$ mix was prepared from an aqueous nitrate precursor solution by aerosol spray pyrolysis. Figure 2 shows the results of a DTA measurement on this as-synthesized "4112" powder composition. A melting endotherm is observed starting near 650°C. Examination of the powder specimen after a similar DTA scan terminated at 750°C showed that it had fused together almost completely, indicating melting of nearly all of the sample. Repeated cycling between 500°C and 800°C in the DTA apparatus eventually caused the endotherm in Fig. 2 to broaden out and disappear. Also, the endotherm shown in Fig. 2 was the one obtained for the second cycle, meaning that the sample had already been to 800°C at least once. We believe this result constitutes convincing evidence that there are compositions in the lead-rich region of the Bi-Pb-Sr-Ca-Cu-O phase field with melting points below 700°C. It is not tenuous to surmise from this result that a much broader range of liquidus compositions is possible at temperatures above 800°C.

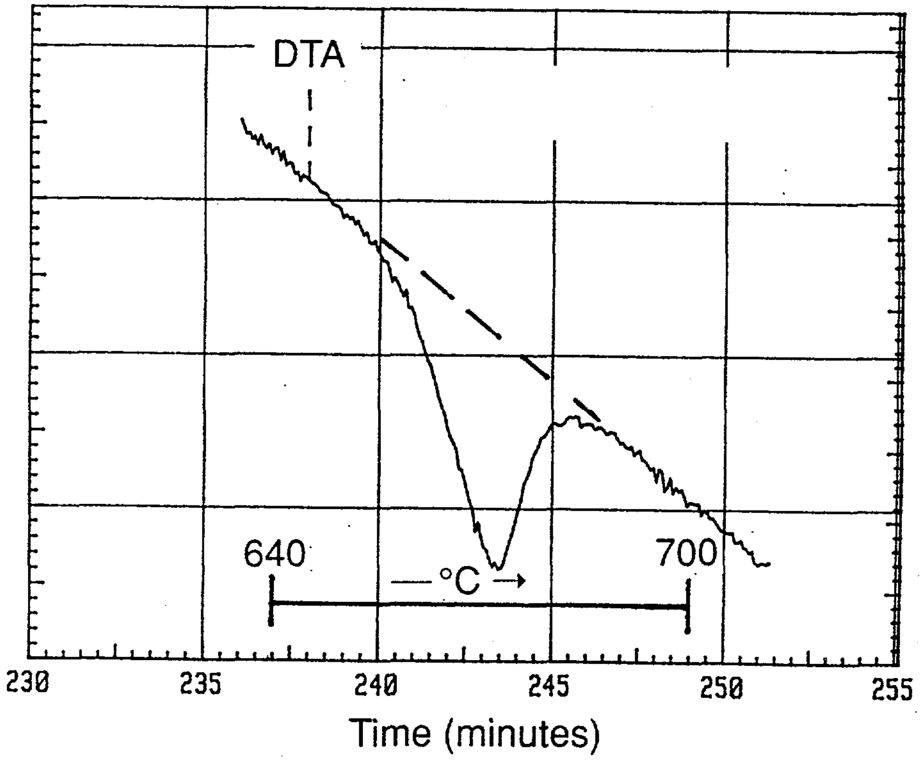

Figure 2. DTA curve for $Bi_{2.2}Pb_{1.6}Sr_{1.3}Ca_{1.0}Cu_{2.0}O_x$ powder mix after first cycling to 800°C then back to 500°C.

The "3221" Phase

The numerous observations(8,11-15) of a lead-rich "3221" phase, particularly prevalent in Ag/Bi-2223 composites cooled slowly from typical heat treatment temperatures, deserves further exploration. Four samples of this phase with varying Pb/Bi ratios (2 to 8) and Bi + Pb stoichiometries (2.5 to 3.5), prepared by other groups of investigators, were characterized by XRD and Raman spectroscopy. The four compositions were:

(1) $Bi_{1.0}Pb_{2.0}Sr_{2.0}Ca_{2.0}Cu_{1.0}O_x$ (Bi + Pb = 3.0, Pb/Bi = 2)

(2) $Bi_{0.5}Pb_{2.0}Sr_{2.2}Ca_{1.8}Cu_{1.0}O_x$ (Bi + Pb = 2.5, Pb/Bi = 4)

(3) $Bi_{0.4}Pb_{2.5}Sr_{2.0}Ca_{2.0}Cu_{1.0}O_x$ (Bi + Pb = 2.9, Pb/Bi = 6)

(4) $Bi_{0.4}Pb_{3.1}Sr_{2.1}Ca_{2.0}Cu_{1.0}O_x$ (Bi + Pb = 3.5, Pb/Bi = 8)

Composition (1) was prepared at Los Alamos National Laboratory, composition (2) at American Superconductor Corporation, and compositions (3) and (4) at Argonne National Laboratory. XRD patterns of two of the four compositions are shown in Fig. 3. These two patterns are, for all practical purposes, indistinguishable from one another and from the pattern of the other two compositions (not shown). In essence, all four patterns look the same.

Figure 4 shows Raman spectra of the same four compositions, and here again the differences are minor. From these XRD and Raman data we have concluded that the "3221" phase exists over a wide range of Pb/Bi values (possibly wider than the 2 to 8 range of the four compositions studied here) and a sizable range of Pb + Bi values, i.e., "(2.5)221" to "(3.5)221." DTA measurements on these four compositions indicated a melting point $\geq$830°C in all cases, which is well above the <700°C value for the "4112" composition, but not much above typical Ag/Bi-2223 heat treatment temperatures.

We have also observed the "3221" phase in Ag/Bi-2223 composite specimens that were furnace cooled (~5°C/min) from heat treatment temperatures >800°C and in other specimens that were slowly heated (first cycle) from room temperature to temperatures in the 650 to 750°C range, then quenched. (Raman microspectroscopy was particularly helpful in making these observations.) We have deduced from these and other related studies that the conditions for prevalence of the "3221" phase are nominal temperatures of 650 to 750°C (possibly even to 600°C on the lower end and to 790°C on the upper end) and nominal oxygen pressures $\leq$0.08 atm. We have also noted that it is possible to misinterpret $(Ca,Sr)_2PbO_4$ for the "3221" phase (and vice versa) from XRD data, as will be discussed below.

The Plumbate Phase

The plumbate phase in calcined Bi-2223 precursor powders, usually described as being Ca_2PbO_4, is most probably a partially strontium-substituted phase, which we shall refer to as $(Ca,Sr)_2PbO_4$. It is almost always present in Bi-2223 precursor powders (even after calcination) and often persists during part of the Bi-2223 conversion process. Higher oxygen pressures (0.20 atm and above) tend to stabilize $(Ca,Sr)_2PbO_4$ relative to the lead-doped (orthorhombic) Bi-2212 phase, quite possibly because the higher oxygen pressures tend to favor the Pb^{4+} state

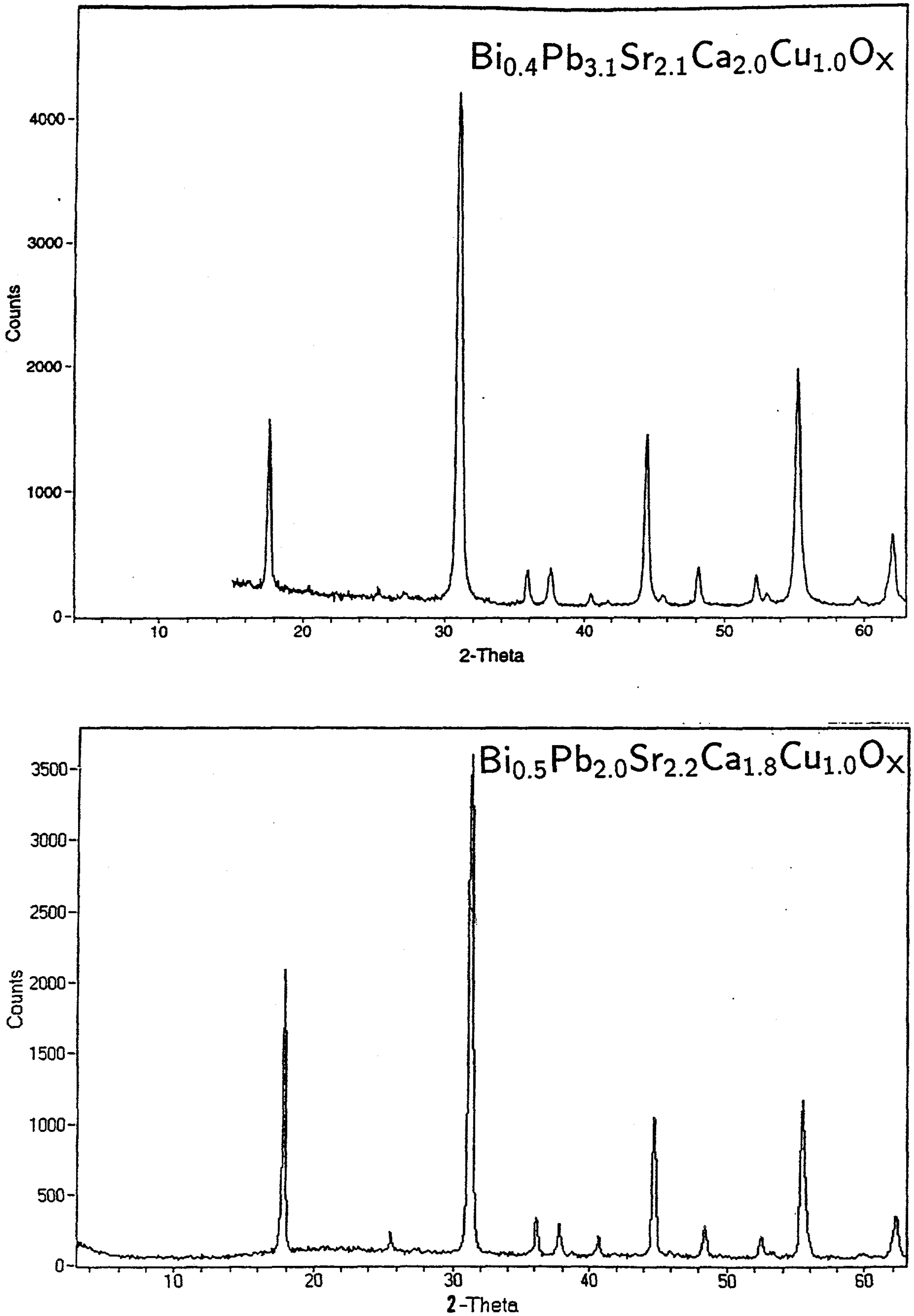

Figure 3. XRD patterns for two "3221" compositions as indicated in the figure.

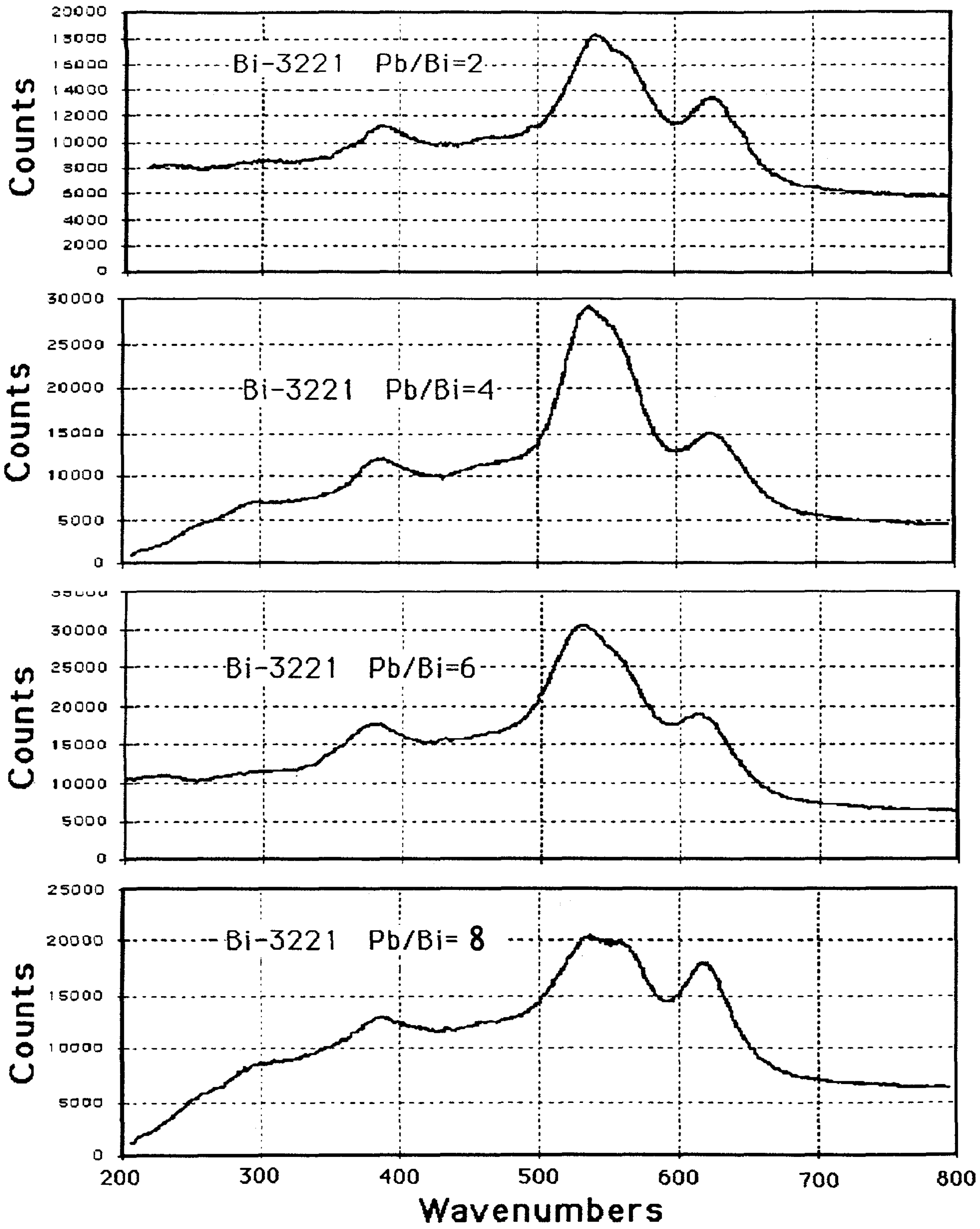

Figure 4. Raman spectra of four "3221" compositions as indicated in the figure.

relative to the Pb^{2+} state. It is also interesting to note that a one mole plus one mole combination of the Bi-2201 phase and Ca_2PbO_4 (1020) would produce a lead-rich "3221" of the type discussed above. Since Bi-2201 and Ca_2PbO_4 are commonly observed constituents of calcined Bi-2223 precursor powders, the possibility exists that reaction of Bi-2201 with Ca_2PbO_4 is one of the pathways to "3221" phase formation.

The XRD results presented in Fig. 5a represent what we have interpreted as evidence for the co-existence of $(Ca,Sr)_2PbO_4$ and the "3221" phase in an Ag/Bi-2223 composite that was heated to 700°C and quenched under conditions that should stabilize Ca_2PbO_4. The Cu Kα-based XRD line used by most investigators to establish the presence of Ca_2PbO_4 is the one at a 2θ value of 17.79°. This same diffraction line is located at 16.84° in Sr_2PbO_4, and Kitaguchi et al.(21) have shown that there is a monotonic shift of this line between the two values as Sr substitutes for Ca. There is also a prominent "3221" line in this same 2θ range at 17.87°. Since we know that the latter line is relatively insensitive to composition changes (e.g., Fig. 3), we interpret that the two lines in Fig. 5a are due to a slightly Sr-doped Ca_2PbO_4 and "3221", which is consistent with the fact that the sample in Fig. 5a was processed to stabilized Ca_2PbO_4 and the lead-free (tetragonal) form of Bi-2212 in accord with the method of Jeremie et al.(5)

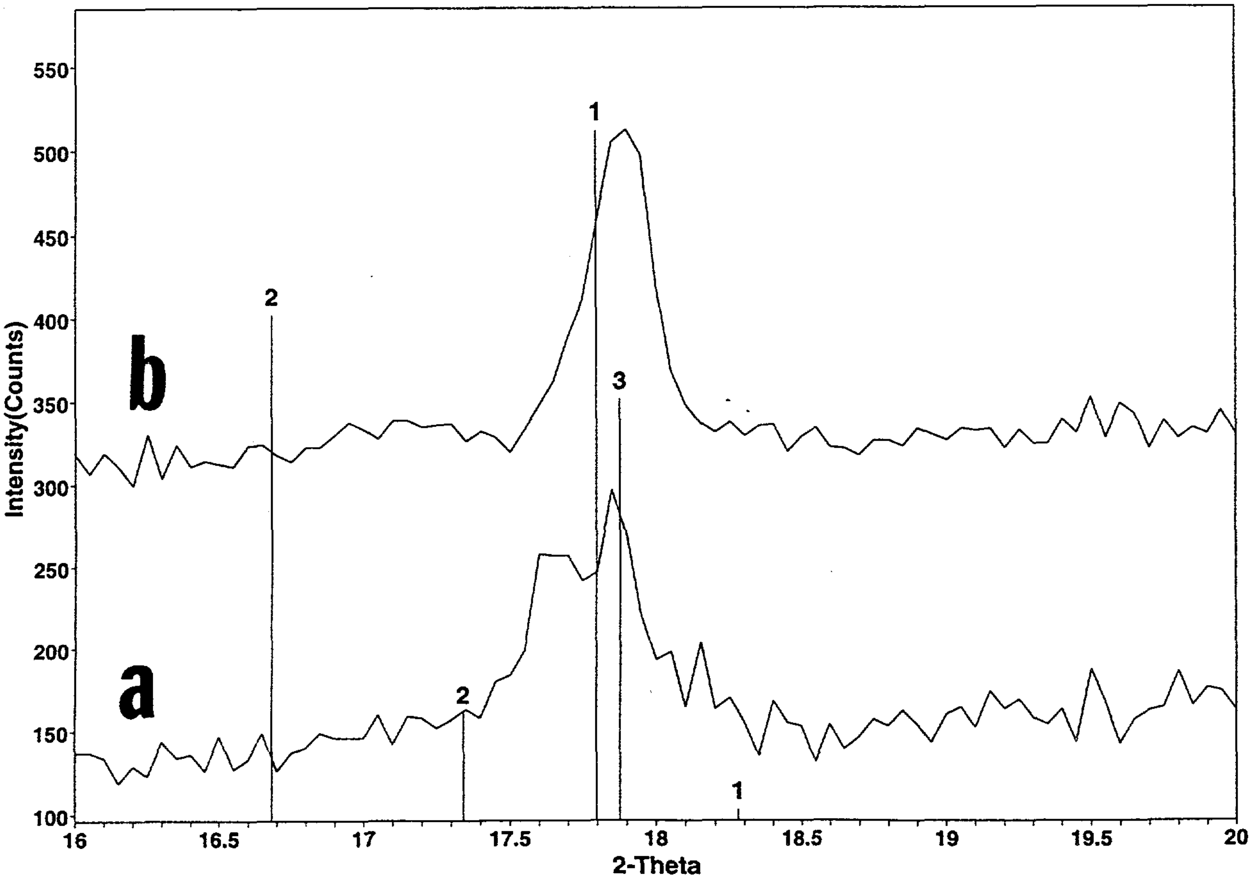

Figure 5. XRD patterns for Bi-2223 precursor powders containing (a) tetragonal Bi-2212 and (b) orthorhombic Bi-2212. (1) = Ca_2PbO_4, (2) = Sr_2PbO_4, and (3) = "3221".

In contrast to Fig. 5a, the sample in Fig. 5b was processed to stabilize the lead-doped (orthorhombic) form of Bi-2212 and destabilize Ca_2PbO_4. In the case of Fig. 5b, only the "3221" phase appears to be present. These conclusions were confirmed by Raman spectroscopy, as will be reported in a subsequent publication.(19) Some caution needs to be exercised in interpreting XRD data for Bi-2223 samples that spent any significant time in the 600 to 800°C temperature range prior to cooling to room temperature. Even 20 to 30 minutes in this range might be enough time to generate detectable quantities of "3221" and/or $(Ca,Sr)_2PbO_4$, especially if some "liquid" phase was still present when cool down started.

Acknowledgments

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