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Relation of starting precursors to the resulting high-T_c phases in the Pb and Sb doped Bi–Sr–Ca–Cu–O system

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The introduction of more reactive precursors for Pb and Sr (oxalates), as well as Ca (citrate) and the use of a Bi nitrate decomposition route, has increased the percentage of the high-T_c (2223) phase in the Bi–Sr–Ca–Cu–O (BSCCO) system. Partial substitution of Bi(Pb) with Sb gives an almost single (2223) phase sample. In addition, a single (2212) phase sample is obtained when high purity Bi_2O_3 is used as a precursor, whereas Bi acetate leads to semiconducting behavior. The morphology of the samples is studied with a scanning electron microscope (SEM), the stoichiometry with energy-dispersive x-ray analysis (EDAX), and the structure with x-ray diffraction (XRD), while the superconducting properties are investigated by dc-resistivity, ac-susceptibility, and SQUID magnetometry techniques.

I. INTRODUCTION

The $Bi_2Sr_2Ca_2Cu_3O_x$ (BSCCO) high T_c phase, which has a critical temperature as high as 110 K, is quite difficult to prepare, and it also requires additional stabilizing elements (e.g., Pb, Sb) and long annealing times.[1–4] Numerous studies are concerned with the improvement of the reaction kinetics and their role in the preparation of the samples.[6–8] Although a lot of work has been done on this subject, and an appropriate "step sintering" process, as well as the optimum percentage of Pb have indeed been found, the actual mechanism of the reaction has not been clarified yet.

In this work, samples of the Bi(2223) high T_c superconductor are synthesized using oxalates, citrates, acetates, and nitrates as starting materials. It has been proven that oxalates,[9] citrates,[10,11] and acetates[12] lead to very sinterable powders. Also, because they have lower decomposition temperatures than the corresponding carbonates, they allow for much less sintering time to be used than in the already known procedures.

The goal of the present study is the determination of the relationship between starting powders and existing phases in the resulting products, with special attention paid to the well-known superconducting phases (2201) ($T_c = 10$ K), (2212) ($T_c = 85$ K), and (2223) ($T_c = 110$ K). SEM and EDAX characterization studies of the prereacted precursors will be presented in a future paper.[13]

II. EXPERIMENTAL

Four samples of the BSCCO system are prepared using Pb and Sr oxalates and Ca nitrate as starting materials. Samples 1, 3, and 4 have the nominal composition $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_x$, while sample 2 has the nominal composition $Bi_{1.7}Pb_{0.2}Sb_{0.1}Sr_2Ca_2Cu_3O_x$. Bi is introduced into the samples as Bi nitrate in samples 1 and 2, Bi acetate in sample 3, and Bi_2O_3 of high purity in sample 4.

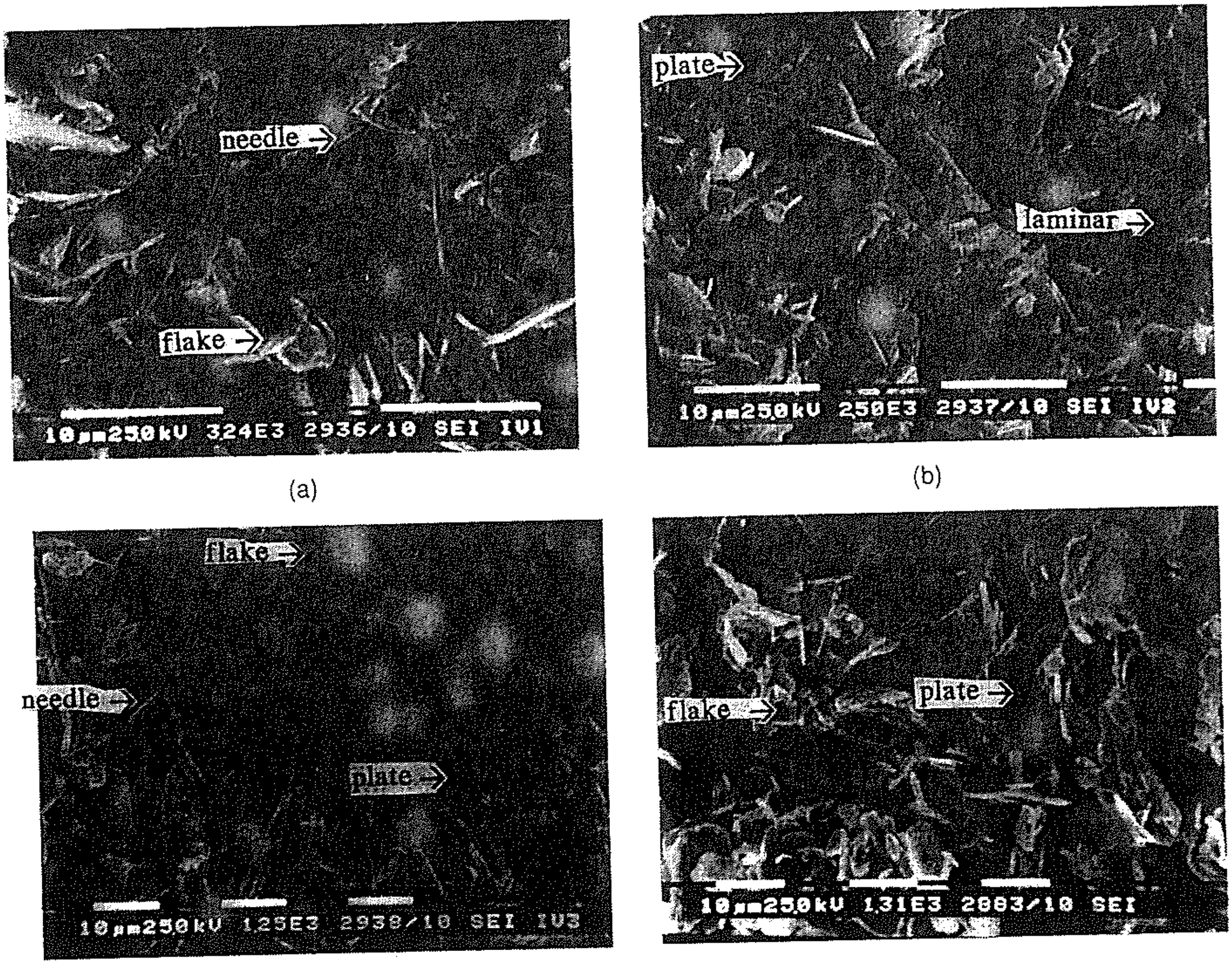
The starting materials are weighed, ball-milled with ethyl-alcohol, dried for 4 h, and allowed to decompose at 850 °C for 2 h. The resulting samples are reground and annealed at 800 °C for 7 h. Subsequently, they are pressed into pellets and sintered for 24 h at 740 °C followed by additional annealing at 840 °C for 129 h. During the last annealing period three intermediate regrindings are made.

The morphology and structure of the samples are studied with scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDAX), and x-ray diffraction (XRD). The transition temperatures are determined by dc-resistivity, ac-susceptibility, and SQUID magnetometry techniques.

III. RESULTS AND DISCUSSION

Figure 1 shows the scanning electron micrographs (SEM) of the sintered pellets, and the energy dispersive x-ray results are presented in Table I. In sample 1 [Fig. 1(a)], plate-like, needle-like, and flake-like crystals coexist in a disordered packing. Plate-like crystals are identified as the Cu-rich (2212) phase, whereas needle- and flake-like crystals have a composition close to 2:2:2:3 (the first being rich in Cu, the other poor in Ca). Sample 2 [Fig. 1(b)] mainly consists of needle- and flake-like crystals corresponding to the high T_c (2223) phase, but acicular crystals having a composition close to 2:2:2:4 also exist at a smaller volume fraction. On the other hand, sample 3 [Fig. 1(c)] has very low porosity and consists only of laminar crystals of the (2201) phase. Sample 4 [Fig. 1(d)] consists almost entirely of the high T_c (2212) phase, the (2223) being absent in it.

Figure 2 shows the x-ray diffraction patterns for all samples. In sample 1 [Fig. 2(a)], the (2223) and (2212) are the primary phases, but it also contains small amounts of the (2201) and Ca_2PbO_4 phases. Sample 2 [Fig. 2(b)] consists mainly of the (2223) orthorhombic (c = 37.10 A) phase, but a small amount of the (2212) (c = 30.90 A) phase is also present. There is no evidence of the (2201) phase in this sample. Sample 3 [Fig. 2(c)] is found to consist of the (2201) phase. It seems that prolonged annealing time causes steady decomposition of the (2223) phase on behalf of the matrix phase (2201) and of the secondary phases Ca_2CuO_3 and CuO. Another phase, which could not be indexed and which exhibits strong semiconducting behavior, is also present in this sample. A more accurate investigation of



(a)

(b)

(c)

(d)

FIG. 1. SEM micrographs of BSCCO sintered pellets: (a) sample 1 (×3000); (b) sample 2 (×2000); (c) sample 3 (×1200); (d) sample 4 (×1200).

TABLE I. Summary of scanning electron microscopy results for the BSCCO samples 1, 2, 3, and 4.

Sample	Compound	Composition ratio Bi + Pb + Sb : Sr : Ca : Cu	Identified phase and observations
1	Needle-like crystal	2 : 2.17 : 1.83 : 3.3	2223 (Cu-rich)
	Flake-like crystal	2 : 1.85 : 1.65 : 2.95	2223 (Ca-poor)
	Plate-like crystal	2 : 1.86 : 1.25 : 2.67	2212 (Cu-rich)
2	Needle- and flake-like crystals	2 : 2 : 1.90 : 3.27	2223 (Cu-rich)
	Plate-like crystals	2 : 2.29 : 2.21 : 4.2	2224 (Bi-poor and Cu-rich)
3	Small laminar crystal	2 : 1.50 : 0.1 : 1.10	2201 (Sr-poor)
	Large laminar crystal	2 : 1.48 : 0.1 : 1.07	2201 (Sr-poor)
4	Flake-like crystal	2 : 1.82 : 1.20 : 2.25	2212
	Plate-like crystal	2 : 1.78 : 1.25 : 2.17	2212

the specific mechanisms that occur in sample 3, which has a distinct behavior among our sample, is in progress. Sample 4 [Fig. 2(d)] consists of the (2212) phase only.

It is also worth mentioning that the *c*-axis of the (2223) phase in the Sb-free sample (sample 1) is a little longer than that in the Sb-doped one (sample 2). This can be

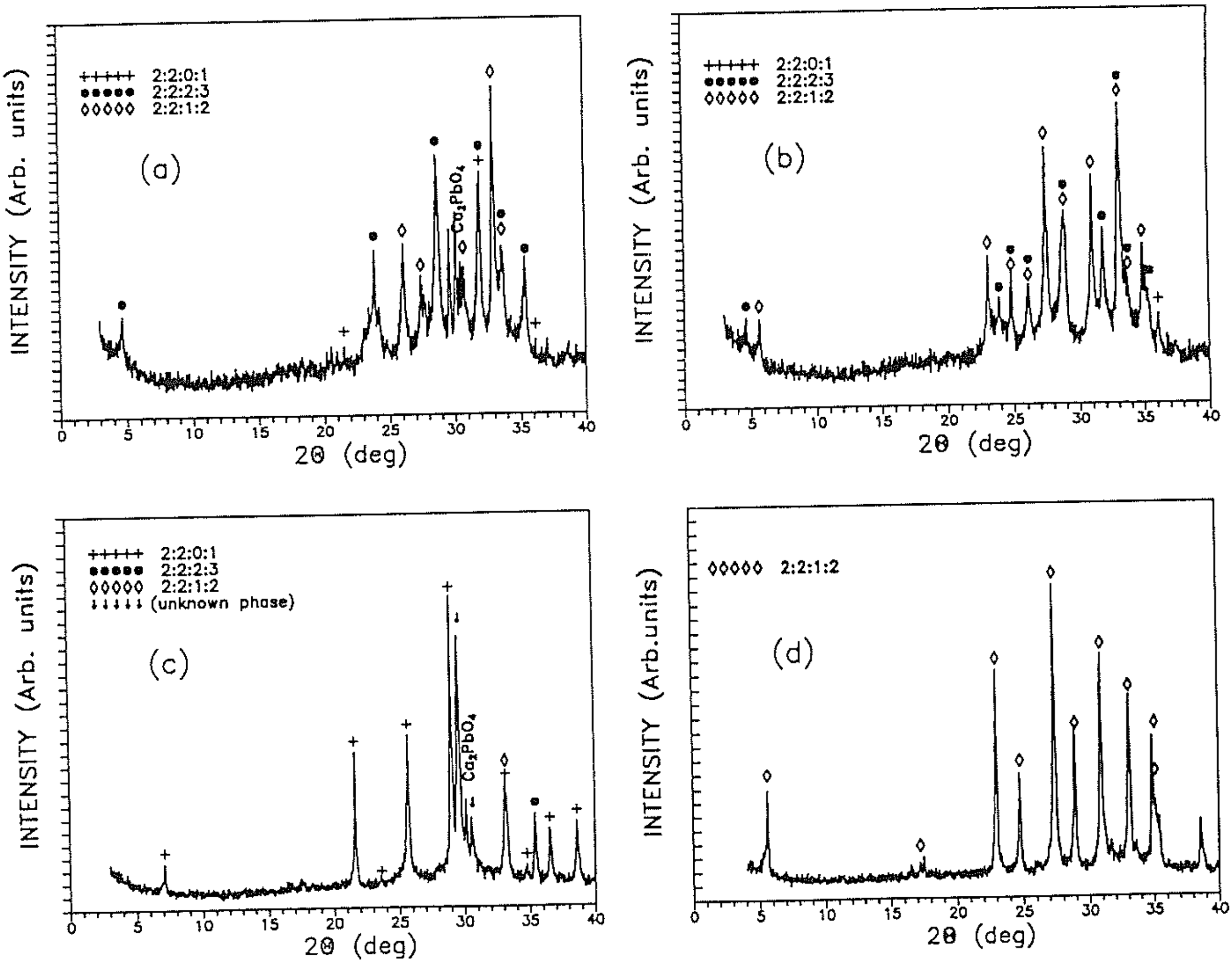


FIG. 2. X-ray diffraction patterns for BSCCO: (a) sample 1, (2223) and (2212) primary phases; (b) the (2223) orthorhombic phase, (c) (2201) phase, and (d) the (2212) phase.

explained by a possible strengthening of the interlayer bonding due to the partial substitution of Bi(Pb) by Sb in the Bi_2O_3 layers.[8]

The resistivity as a function of temperature is measured for all the sample using a conventional four probe method. Normalized data corresponding to samples 1, 2, and 4 are shown in Fig. 3. All samples are superconducting except for sample 3 which exhibits strong semiconducting behavior. The onset of superconductivity is at the temperatures 105 K, 110 K, and 80 K for the samples 1, 2, and 4, respectively, while the corresponding temperature values of the zero resistivity are 82 K, 102 K, and 72 K. The resistivity in the normal state increases linearly with temperature for all superconducting samples, indicating metallic behavior.

In Fig. 4, the ac-susceptibility results of samples 1, 2, and 4 are presented, which are measured in an ac field with $H_{rms} = 2$ Oe. Sample 1 has a $T_c = 106$ K, sample 2 has a $T_c = 100$ K, and for sample 4, $T_c = 60$ K. From these measurements it can be seen (small kink observed at around $T = 60$ K, of the real part χ' of the χ_{ac}) that samples 1 and 2 contain both (2223) and (2212) phases. In sample 1 the (2212) phase is about 10% of the sample's volume, while in sample 2 is about 5%.[4] The corresponding data for sample 4 in the same figure indicated that it also contains the above two phases, but the (2223) phase is also less than 5% of its volume. In Fig. 5, similar behavior is observed in the field-cooled (FC) magnetization versus temperature data (M vs T) which is obtained by using a SQUID magnetometer with an applied field $H = 20$ Oe. It can be noted that besides some deviation in the T_c's between the resistivity and the magnetic techniques (which is rather expected) the results are mutually consistent. In addition, it is obvious that the sensitivity of the magnetic techniques in detecting small amounts of superconducting phases is higher than that of the XRD method.[4]

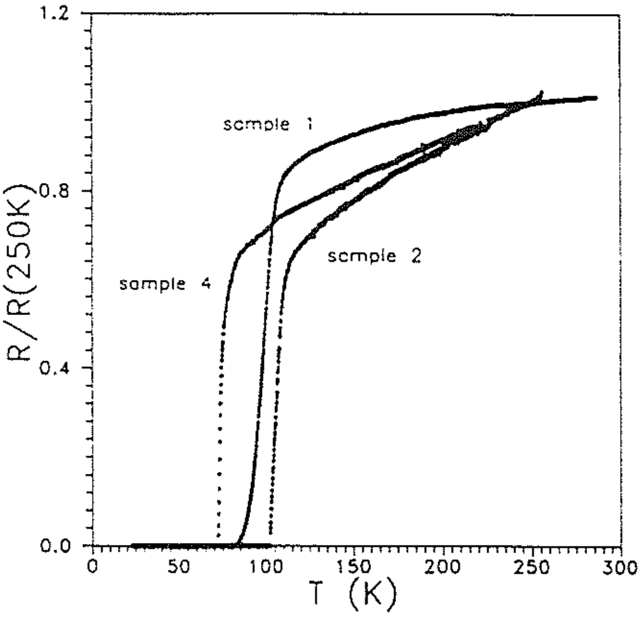


FIG. 3. Normalized resistivity measurements for the BSCCO samples 1, 2, and 4.

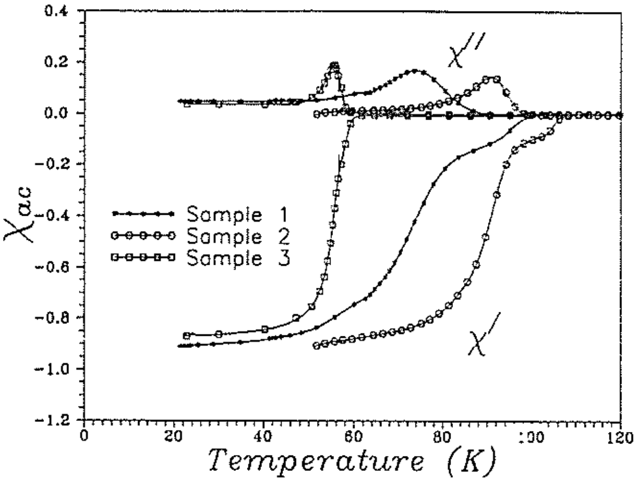


FIG. 4. Real (χ') and imaginary (χ'') part of the ac-susceptibility results for the bulk BSCCO samples 1, 2, and 4 in a field $H_{ac,rms} = 2$ Oe.

IV. CONCLUSION

High T_c superconducting ceramics are prepared by using more reactive precursors than the ones previously used: oxalates for Pb and Sr, citrate for Ca, and various precursors for Bi_2O_3 : Bi nitrate, Bi acetate, and high purity Bi_2O_3. The nominal composition in $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_x$ for all samples except one, where Bi(Pb) is partially substituted by Sb.

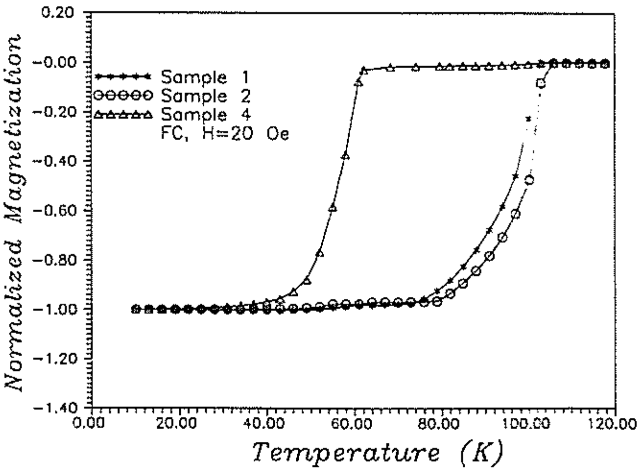


FIG. 5. Field-cooled magnetization versus temperature data for the samples 1, 2, and 4, obtained in a field of 20 Oe by using a SQUID magnetometer.

It is found that after a short sintering time and a four-step annealing treatment, the best samples [i.e., containing the highest portion of the (2223) phase] have been obtained by the nitrate decomposition route. In addition, partial substitution of Bi(Pb) with Sb leads to an almost pure (2223) phase sample exhibiting zero resistance at 102 K. On the other hand, the use of Bi acetate results in an increase in the fraction of the (2201) phase, while another unknown phase also appears, which exhibits strong semiconducting behavior. In the same annealing conditions, incorporation of ultrapure Bi_2O_3 induces (2212) almost single phase sample.

In addition, it is found that the required sintering time for achieving the high-T_c (2223) phase in the Pb- and Sb-doped BSCCO system is shorter than that required through the conventional ceramic method, due to the higher reactivity of our precursors.

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REFERENCES

1. S. M. Green, C. Jiang, Y. Mei, H. L. Luo, and C. Politis, Phys. Rev. **38**, 5016 (1988).
2. M. Takano, J. Takada, K. Oda, H. Kitaguchi, Y. Miura, Y. Ikeda, Y. Momii, and H. Mazaki, Jpn. J. Appl. Phys. **27**, L1041 (1988).
3. U. Endo, S. Koyama, and T. Kawai, Jpn. J. Appl. Phys. **27**, L1476 (1988).
4. M. Pissas, G. K. Nikolaides, V. Psycharis, and D. Niarchos, Physica C **196**, 157 (1992).
5. M. Pissas, D. Niarchos, C. Christides, and M. Anagnostou, Supercond. Sci. Technol. **3**, 128 (1990).
6. D. A. Gardwell, J. M. Cockbaum, and A. W. Whatmore, Supercond. Sci. Technol. **2**, 132 (1991).
7. A. Castro, R. Enjabert, D. Esparza, J. Galy, I. Resinas, and M. L. Rovetto, Physica C **185–189**, 457 (1991).
8. G. F. de la Fuente *et al.*, Physica C **185–189**, 509 (1991).
9. F. H. Chen, H. S. Koo, T. Y. Tseng, R. S. Liu, and P. T. Wu, Mater. Lett. **8**, 228 (1989).
10. H. H. Wang, C. M. Wang, H. C. I. Kao, D. C. Ling, H. C. Ku, and K. H. Lii, Jpn. J. Appl. Phys. **28**, 1505 (1989).
11. S. K. Sinha, S. C. Gadkari, S. C. Subharwal, L. C. Gupta, and M. K. Gubta, Physica C **185**, 499 (1991).
12. K. Tanaka, A. Nozue, and K. Kamiya, Jpn. J. Appl. Phys. **28**, L934 (1989).
13. F. Vasiliou, F. Constantinescou, and C. Bunescou, Mater. Lett. (1993, in press).