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A STUDY OF ENHANCING CRITICAL CURRENT DENSITIES (J_c) AND CRITICAL TEMPERATURE (T_c) OF HIGH-TEMPERATURE SUPERCONDUCTORS

CENTER DIRECTOR's DISCRETIONARY FUND FINAL REPORT (PROJECT 90-N26)

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Space Science Laboratory
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The development of pure phase 123 and Bi-based 2223 superconductors has been optimized. The pre-heat processing appears to be a very important parameter in achieving optimal physical properties. The synthesis of pure phases in the Bi-based system involves effects due to oxygen partial pressure, time, and temperature. Orientation/melt-sintering effects include the extreme c-axis orientation of Yttrium 123 and the Bismuth 2223, 2212, and 2201 phases. This orientation is conducive to increasing critical currents. A procedure was established to substitute Sr for Ba in Y-123 single crystals.

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TECHNICAL MEMORANDUM

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INTRODUCTION

The discovery of the new high-temperature superconducting materials ($T_c \approx 80$-125 K) has generated much interest for major practical applications of these materials. Many of these applications depend on the ability of such superconductors to carry relatively high current densities (J_c) at high magnetic fields ($J_c \approx 10^5$ A/cm^2 at 77 K in fields greater than 1 Tesla.) However, inherent material and microstructural problems has prevented the realization of such high critical currents. The problem of such low J_c (20-100 A/cm^2) for bulk ceramic superconductors has to be solved before any practical use can be made of these revolutionary materials.

The objectives of this research were to carry out a detailed study of methods such as melt-texturing and Ag-composite formation for improving the critical current densities of polycrystalline bulk high-temperature superconductors realizing that a significant improvement in J_c would result in a major step toward the use of such materials in NASA-specific ground and space applications.

APPROACH

The study was separated into four specific tasks which will lead to the fulfillment of our objectives. These are:

(1) Prepare and characterize pure high-T_c superconducting materials;

(2) Process these materials using one or both of the chosen techniques;

(3) Study microstructure, critical currents (J_c), and critical temperature (T_c) of the processed materials;

(4) Correlate process parameters to improvement of J_c and T_c.

ACCOMPLISHMENTS

The transport properties of superconductors are at their optimal values in near-perfect single crystals. A method was chosen in the preparation of bulk ceramic samples which would promote elongated grain growth in a preferred direction, which best approaches single crystal character. This method is melt-sintering or texturing, involving near-melting of the sample and then slow cooling, and careful control of the process parameters.

The results of this technique for bulk materials are very encouraging. The x-ray diffraction spectra for single crystal $YBa_2Cu_3O_7$ and for melt-sintered $YBa_2Cu_3O_7$ are extremely similar. As can be expected from the plate-like single crystal only c-axis reflections (00ℓ) are present. The single-crystal nature of the melt-sintered sample is a good measure of the success of the melt-sintering process. The value of J_c associated with these oriented samples is several times greater than that of the corresponding sintered samples [1,2].

Concurrently, the growth of single crystals of the $YBa_2Cu_3O_7$ and $Y(Ba,Sr)_2Cu_3O_7$ compounds has been done from flux at high temperatures. This seems to be the only way to obtain single crystals of these materials since growth from the melt is not possible. Large single crystal plates (0.5 cm in width) have been obtained. These crystals are extremely important in the study of fundamental properties of the high-temperature superconducting materials and for future technological use in device development.

The high-temperature superconductors presently being investigated are highly anisotropic materials (their properties are dependent on the direction in the crystal in which they are measured). This anisotropy is particularly pronounced for the critical current density (J_c) which

can be 2 to 3 orders of magnitude greater in the (ab)-plane of the crystal than in the c-direction. Hence, grain alignment in the bulk superconducting material is a very important factor in improving the critical current density.

Melt-sintering or texturing is the primary method for producing bulk ceramic materials of Y-123 having elongated grain growth in the preferred direction.

The success of the melt-sintered process is dependent on a number of factors. Two of the most important parameters are the melt-sintering time and peak temperature. These conditions will, of course, vary slightly as the sample may vary in dimensions, density, and purity. The critical current of high-T_c superconductors increases as the temperature decreases below the T_c. As a result, the higher the T_c the higher would be the J_c at LN_2 temperatures. A logical means of raising the J_c would then be to obtain superconducting materials with higher T_c. Such is the case of the Bi-based system which has a compositional phase $Bi_2Ca_2Sr_2Cu_3O_{10}$ (Bi-2223) with a T_c of approximately 110 K. Much higher than the 90 K of Y-123. One of our goals was then to isolate the pure 2223-phase and prepare oriented samples having enhanced properties. The major problem encountered in this system was the existence of several other phases thermodynamically more stable than (2223), which made its isolation very difficult.

During the synthesis of the (2223) ceramic material, several important observations were made: (1) sintering temperature range was very narrow (few degrees), (2) sintering temperature range was compositionally dependent, and (3) the addition of Pb helped to stabilize this high-T_c phase. Finally, we observed that the formation of this phase was dependent on the oxygen partial pressure of the reaction environment. We proceeded, therefore, to investigate this oxygen dependence.

Figure 1 of reference 3 shows the influence of oxygen content (% O_2) in the argon flow gas. The reaction range is reduced as oxygen content is reduced. The upper part of the range (2 to 3 degrees, thick region of bar) is where 95% or more of the 110 K phase was formed. It can be concluded then that the sintering range is oxygen content dependent for a particular composi-

tion and that a reduced oxygen content in the reaction environment helps in preventing the formation of Pb secondary oxide phases. It is possible that metallic Pb acts as a flux and aids the formation and stability of the Bi-2223 phase.

The density of the Bi-based superconductors is found to be rather low and thus reduces the current path area and prevents good grain connectivity. The arc-melting technique was used in a number of experiments to enhance the material density and thus improve the physical properties. A marked improvement was observed in the overall properties of the material due to the densification by arc-melting.

The system $Y(Ba_{2-x}Sr_x)Cu_3O_7$ ($0 \leq x \leq 0.8$) was also studied in order to improve the properties of the existing material. The substitution of Ba by Sr was successful in producing single-phase bulk compounds. This represents the first success in synthesizing this material with $x > 0.6$. Figure 1 of reference 4 shows the dependence of the sintering temperature on the composition (value of x) and explains why it was difficult to obtain material with $x > 0.6$ if no appropriate change in the processing temperature was made. This material is of importance since it allows us to study the effect of reduced atomic distances (Sr has a smaller ionic size than Ba) on the superconducting properties.

A number of samples of Y-123 and Bi-based material were preformed in the laboratory and processed by the melt-sintering technique on the KC-135 during parabolic flight. Identical samples were also processed on the ground under the same conditions. Unfortunately only several samples survived intact the severe conditions of the processing. The flight and ground processed samples were characterized by XRD and magnetization measurements. The as-processed sampleds (μg and 1g) are found to be non-superconducting and composed primarily of Y_2BaCuO_5 (211-phase). Both types of samples were annealed at 927 °C under O_2 and converted to the superconducting Y-123 phase. The XRD and magnetization results do not indicate any major differences between μg and 1g samples and no firm conclusions can be drawn.

CONCLUSION

Several major objectives have been attained in this work. Optimization of the melt-sintering technique for bulk Y-123 samples has resulted in well-oriented samples with higher J_c values. Isolation of pure Bi-2223 high-temperature phase and the sintering process oxygen dependence was determined. The densification of these samples has also resulted in better structural characteristics and properties. Finally, substitution of Ba by Sr in the Y-123 series was obtained for x up to 80%, and the 100% substituted phase has been observed for the first time.

The details of this work have been published in references 3 and 4 found in the appendex.

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APPENDIX

STUDY OF BULK AND SINGLE CRYSTAL $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ SUPERCONDUCTING MATERIALS

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Abstract. A detailed study of the substitution of Sr for Ba in the system $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ has been carried out, both for bulk and single crystal material. Successful substitution, in bulk samples, up to 80% (x = 1.6) was accomplished. This substitution is seen to have an adverse progressive effect on the value of T_c. All bulk Sr-substituted compounds were superconducting with values of T_c of at least 73 K. The 100% Sr-substituted sample $YSr_2Cu_3O_{7-\delta}$ has been observed, but only in very small amounts. Single crystals of $Y(Ba,Sr)_2Cu_3O_{7-\delta}$ with Sr/Ba substitution of up to 30% (x = 0.6) have also been synthesized and characterized by XRD and SEM.

1. Introduction

Much effort has been expended elsewhere to obtain a 1:2:3 superconductor without Ba. There are many good reasons why this type of study is important. Any time a major constituent in the composition is changed, a new realm of compositional directions is opened up. Some of these directions may prove to be fruitful in the search for superconductors with enhanced properties. For example, the 1:2:3 phase with 50% Sr/Ba substitution, i.e., $YBaSrCu_3O_{7-\delta}$, has been reported to be a possible room temperature superconductor [1]. Although this result has been irreproducible (the superconductivity may be due to some trace amount of impurity phase), a systematic Sr/Ba substitutional study may reveal this phase.

To date, there have been many substitutional studies made on the Yttrium 1:2:3 superconductor. Many of these studies have determined limits as to the degree that one atom can be substituted for another in the structure. Previous studies on Sr substitution have determined various limits; the highest of these being about 70% substitution [2-5]. As the Sr content is increased, the superconducting properties of the compound have been shown to diminish, especially the value of T_c. This is confirmed in the present study. Furthermore in this work, the limit of bulk substitution has been increased to 80% Sr/Ba (x = 1.6), and a fully 100% Sr/Ba (x = 2.0; % = (x/2) (100)), i.e., $YSr_2Cu_3O_{7-y}$, phase has been observed. We also report the synthesis of $YBa_{2-x}Sr_xCu_3O_{7-y}$ ($0 \leq x \leq 0.6$) single crystals.

2. Experiments and Discussion

2.1 Bulk Synthesis of $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ ($0 \leq x \leq 1.6$)

Precursor powders used in this investigation include Y_2O_3, $BaCO_3$, $SrCO_3$, and CuO, of at least 99.9% purity, and free of water contamination. The powders were weighed in amounts so as to produce a nominal stoichiometry of 1:2:3 in the final product. Before heat treatment the powders were finely ground to a consistent color, annd then pressed into pellets at 35,000 psi. The initial heating rate did not exceed 1 °C/min in the temperature range of 500 °C to 900 °C. Several progressive cycles of heat treatments were employed; each separated by grinding and pressing. An X-ray diffraction scan was taken on each sample after each heat treatment.

Nominal compositions $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ ($0 \leq x \leq 1.6$) have resulted in single phase bulk compounds. For the first time, the phase $YSr_2Cu_3O_{7-\delta}$ ($x = 2.0$) has been observed, albeit only significantly on the surface of a sample with this same nominal composition. The key to synthesizing these compounds lies with slow deliberate preheats. We have found that it is very important to heat the initial stoichiometric composition very slowly through the temperature range of 600 to 900 °C. This is partly due to the decomposition of the carbonates, and possibly to facilitating the formation of the solid solution of the Ba/Sr component. The preheat to a temperature just below 900 °C also takes advantage of the fact that the 1:2:3 phase can begin to form at these relatively low temperatures, while certain undesired stable impurity phases, such as $SrCuO_2$, do not.

When several slow preheats are conducted to temperatures near 900 °C, it is likely that enough homogeneity has been established in the samples such that a single phase can then be obtained. However, the actual final sintering temperature for each composition of Sr substitution is different. Figure 1 shows the ideal sintering temperatures for each nominal composition $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ ($0 \leq x \leq 2.0$), after two slow preheats to 900 °C have been conducted. There is a primary temperature range for compositions up to x = 1.6, where a bulk single phase compound can be synthesized. The allowable error in the temperature stabilization is 23 °C for 10% Sr/Ba (x = 0.2) substitution and only 2 °C for 80% Sr/Ba (x = 1.6) substitution. Thin lines on the graph represent the range where a 90% single phase sample can be produced.

Figure 1 demonstrates the solution to a basic problem with these types of substitutional studies. Each level of substitution represents a new composition and as a result it requires individual changes in the synthesis process. In this case, the most determining factor lies in the final sintering temperature. For example, if for consistency, only one sintering temperature (say 930 °C) were employed for all compositions, then a conclusion might be that Sr could only be substituted up to 40% (see Figure 1). Such a conclusion would obviously be wrong.

2.2 The $YSr_2Cu_3O_{7-\delta}$ Phase

Figure 1 reveals that a predominantly 1:2:3 phase with 100 % Sr (x = 2.0) substitution was observed, but only more significantly on the surface of the sample. A bulk powder diffraction scan of this latter sample appears in Figure 2. The most likely phases involving the

constituents Y, Sr, and Cu are compared with a 1:2:3 phase consisting of these elements. Many significant lines could only be identified with the 1:2:3 phase. In keeping with the nominal composition of $YSr_2Cu_3O_{7-\delta}$, and assuming a rough 3:1 ratio of $YSr_2Cu_3O_{7-\delta}$ to $SrCuO_2$ in the final product, a cursory combination of phases in this sample can be surmized:

$$11\ YSr_2Cu_3O_{7-\delta}\ \text{(nominal)} \rightarrow 9\ YSr_2Cu_3O_{7-\delta}\ \text{(phase)} + 3\ SrCuO_2 + Y_2SrO_4 + 3\ CuO$$

The fact that the $YSr_2Cu_3O_{7-\delta}$ phase can be observed, lends hope to obtaining this compound in single phase form in the future. This bulk multi-phase sample was measured on the Vibrating Sample Magnetometer (VSM) for a possible critical transition temperature, but any observed signal was too close to the noise level to be conclusive. A higher percentage of this phase was observed on the surface of this sample, but not enough quantity could be obtained to measure its properties.

Observing that the $SrCuO_2$ phase was the main impurity phase in this compound, as it was in all the compositions of Sr substituting for Ba, attempts were made to synthesize the $YSr_2Cu_3O_{7-\delta}$ compound using various Sr:Cu:O precursors, such as $SrCuO_2$, Sr_2CuO_3, and $SrCu_2O_2$. All subsequent attempts to synthesize $YSr_2Cu_3O_{7-\delta}$ using each of these precursors individually and/or together failed. The $SrCuO_2$ phase proved to be particularly resilient in the sintering temperature range between 900 °C and 1000 °C. It became evident that once the $SrCuO_2$ phase had formed, attempts to form other phases, such as the 1:2:3 phase, would fail.

This finding was consistent with the ideas expressed earlier about the importance of comparatively low-temperature preheats to avoid forming this phase before the Ba/Sr solid solution was established.

2.3 Single Crystal $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ ($0 \leq x \leq 1.6$)

Single crystals with up to 30% Sr/Ba (x = 0.6) substitution were synthesized using flux growth. The most successful method of crystal growth began with the sintered composition of $Y(Ba,Sr)_2Cu_3O_{7-\delta}$, and utilized a flux of $BaCuO_2$ and CuO in a (1:2:3)/$BaCuO_2$/CuO molar ratio of 1:7:20. $SrCuO_2$ was sometimes used in addition or in place of $BaCuO_2$ with little or no success. A slightly higher temperature (ΔT = 5-15 °C) was used as the Sr content in the 1:2:3 component was increased. Although $Y(Ba,Sr)_2Cu_3O_{7-\delta}$ compositions with up to 80% Sr substitution were used, the resulting crystals had a maximum of only 30% Sr substitution (Table 1). However, each increase in the Sr content of the $Y(Ba,Sr)_2Cu_3O_{7-\delta}$ component resulted in an increase in the Sr content of the corresponding single crystal. The crystals were characterized by SEM elemental analysis. In attempts to form single crystal $YSr_2Cu_3O_{7-\delta}$, other flux combinations with no Ba present were also tried, but again with no apparent success.

2.4 Sr Content vs. Lattice Constants

The lattice constants for all Sr/Ba compositions have been determined and are displayed in Figure 3. It is well known that the crystal structure in 1:2:3 compounds is very dependent upon the oxygen content and hence it is hard to compare Sr substituted samples without specifically knowing the oxygen content of each sample. However, since all of the samples were annealed in the same way (550 °C in flowing oxygen), it is hypothesized that the oxygen contents in these samples also were similar. Hence, the Sr content is believed to be the most important factor involved in the decrease of the cell parameters.

Figure 3 demonstrates that there is a general reduction in the a, b, and c parameters with Sr substitution for Ba. This can be expected since the Sr^{+2} ion is significantly smaller in size than the Ba^{+2} ion. Table 2 lists the values of T_c measured for these superconductors through use of the Vibrating Sample Magnetometer. In general, there is a marked decrease in the value of T_c as the Sr content is increased. However, even the 80% Sr (x = 1.6) sample had a value of T_c that was significantly high. In earlier 1:2:3 oxygenation studies T_c has been observed to correlate dramatically with cell size and/or electronic changes, both resulting from changes in the oxygen content. In the present study, marked changes in cell size result from the substitution of the smaller Sr^{+2} ion for the larger Ba^{+2}. This predominantly structural change has a small but progressive influence on the value of T_c.

2.5 Single Crystal Characterization

As mentioned earlier in this paper, our single crystals were characterized through differential elemental analysis. Since the crystals preferentially grow as very thin platelets in the ab plane, it was easy to characterize the crystals in the c-axis direction through x-ray diffraction. The crystals were aligned such that only (00ℓ) lines were observed. From these scans the c-parameters were calculated and the results are plotted in Figure 4 along with bulk values for the same level of Sr substitution. Apart from a slight offset, magnified by the scale chosen for this figure, it can be seen that the actual Sr composition found in the crystal can be empirically correlated with the c-parameter. The present data does not take into account the difference in oxygen content between the crystals and the bulk samples that is bound to exist, and therefore susceptible to influence the value of the c-parameter. These different oxygenation levels might explain the observed offset between both types of samples. Future efforts to synthesize single crystals with more than 30% Sr substitution, might first use this empirical method to initially obtain a qualitative characterization of the Sr content. Although the area in some of these crystals sometimes approached 5mm x 5mm, the crystals were so thin and deformable so as to make magnetic or electrical characterization very difficult. To date, all attempted measurements have revealed nothing about the possible superconductivity of these crystals.

3. Conclusion

In conclusion, bulk substitution of Sr for Ba in $YBa_2Cu_3O_{7-\delta}$ has been successful up to 80% (x = 1.6). The increased substitution of Sr for Ba seems to have an adverse progressive effect on the value of T_c. All bulk Sr-substituted compounds were superconducting with values of T_c of at least 73 K. The 100% Sr-substituted sample, $YSr_2Cu_3O_{7-\delta}$, has been observed, however only in amounts too small for its properties to be measured. Single crystals of $Y(Ba,Sr)_2Cu_3O_{7-\delta}$ with Sr/Ba substitution of up to 30% (x = 0.6) have also been synthesized and characterized by X-ray diffraction and SEM analysis.

Acknowledgements

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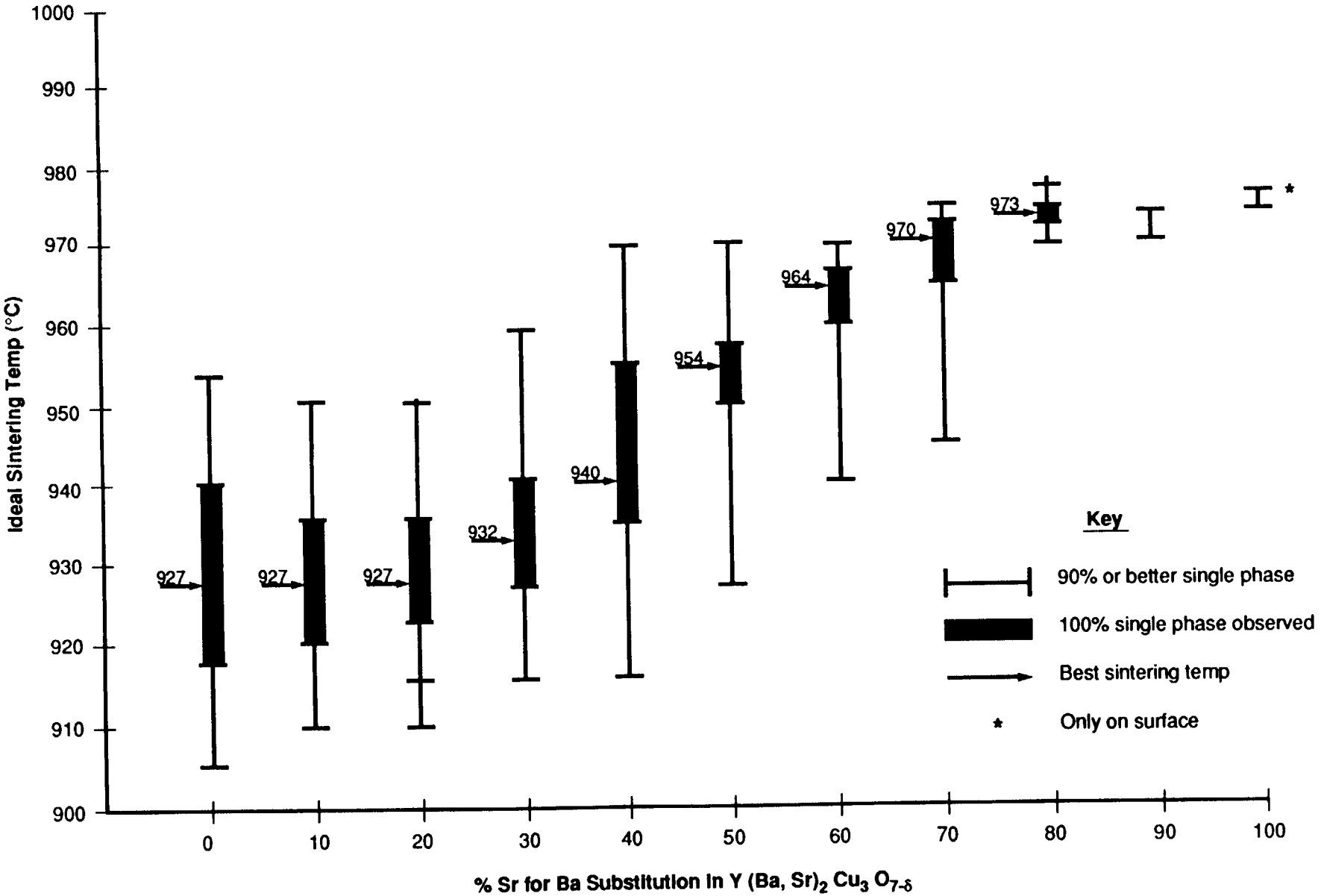
Figure Captions

Fig. 1: Sintering Temperatures to Obtain Single Phase $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ ($0 \leq x \leq 2.0$); %Sr = (x/2) (100)

Fig. 2: Powder X-Ray Diffraction Pattern (CuK_α) of $YSr_2Cu_3O_{7-\delta}$

Fig. 3: Lattice Parameters of Bulk Ceramic $YBa_{2-x}Sr_xCu_3O_{7-\delta}$

Fig. 4: The Lattice Paramter c/3 of Bulk Material and Single Crystals as a Function of Sr Content (%Sr = (x/2) (100))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932
940
954
964
970
973
*
Key
90% or better single phase
100% single phase observed
Best sintering temp
* Only on surface
0
10
20
30
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70
80
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% Sr for Ba Substitution in Y (Ba, Sr)2 Cu3 O7-δ

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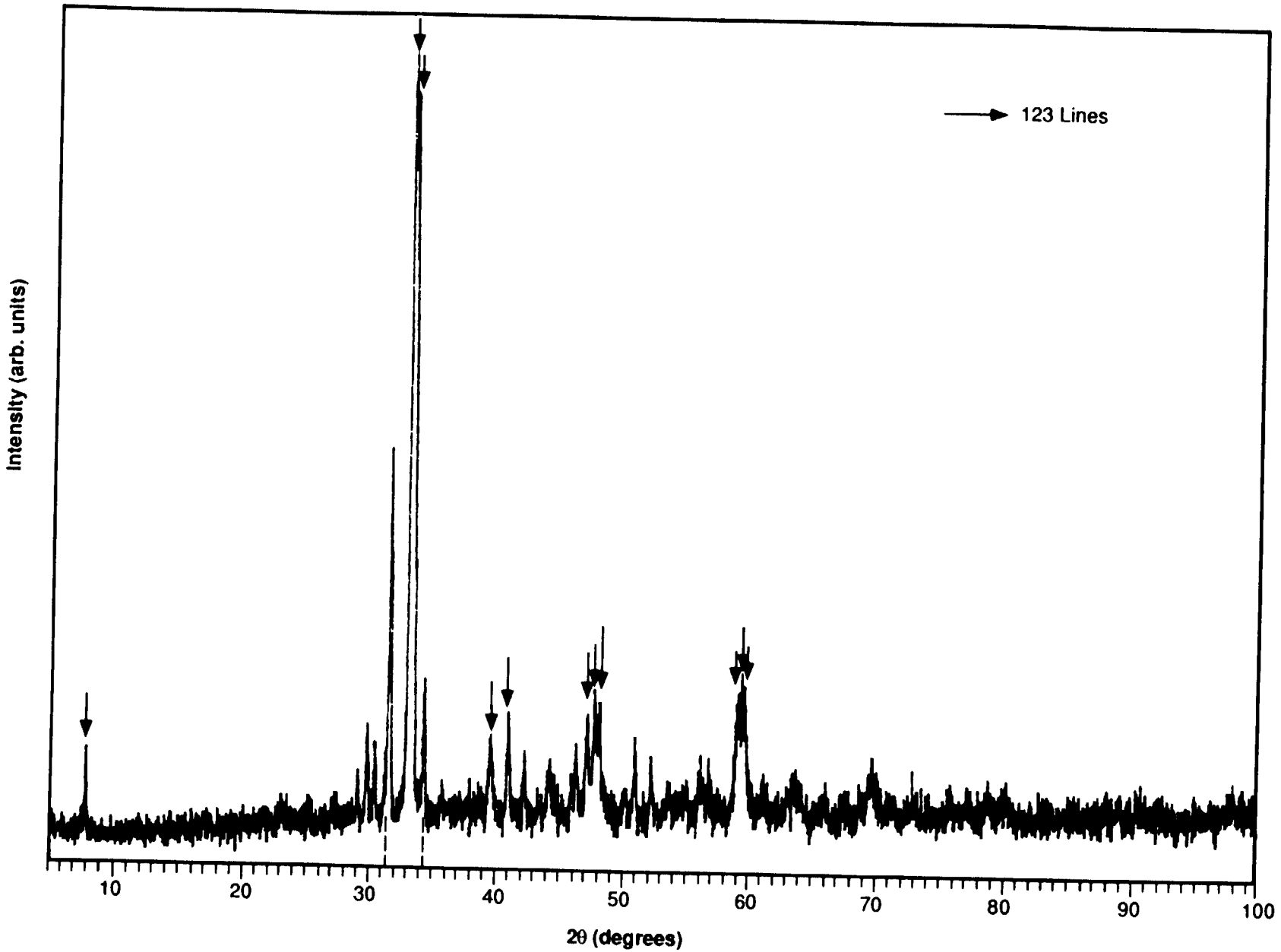
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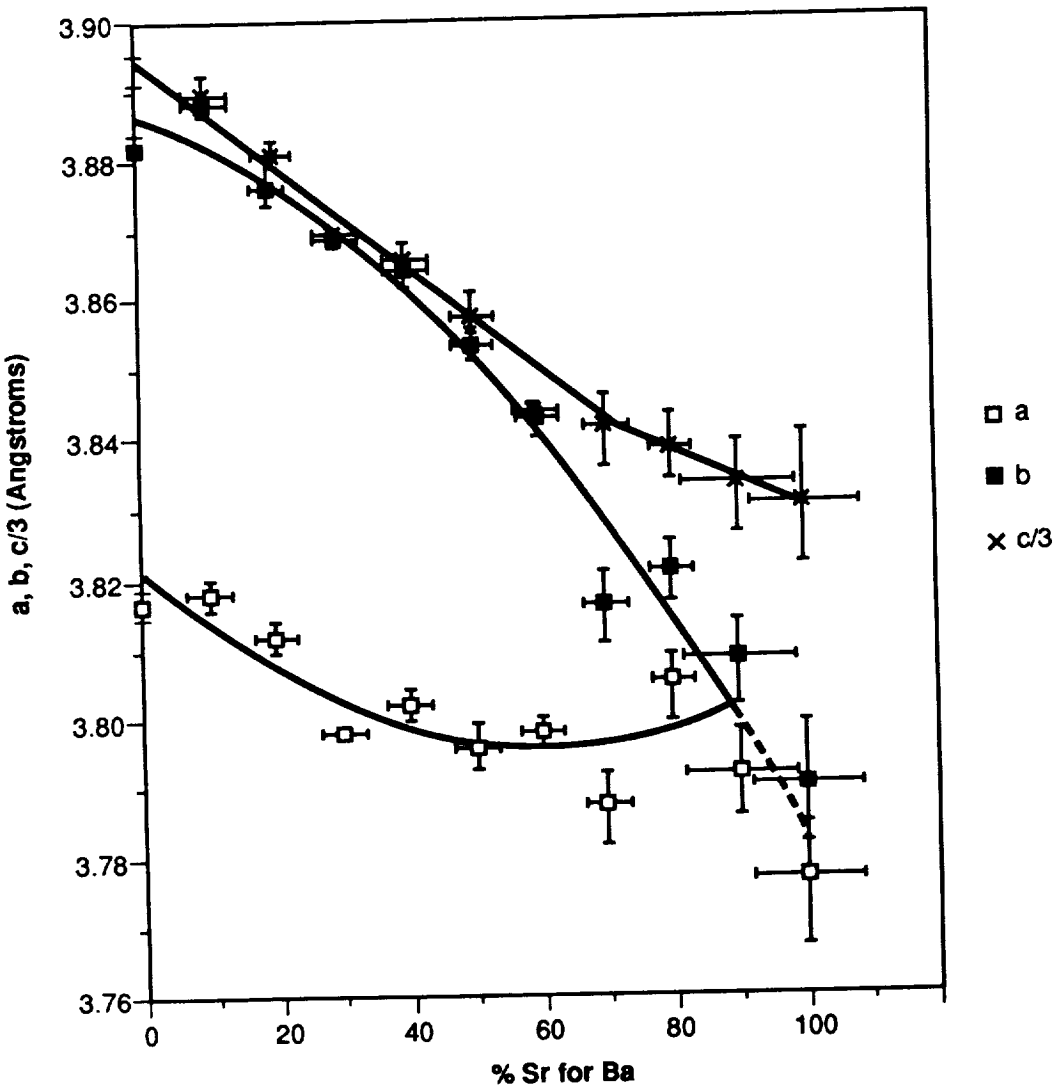
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3.84
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80
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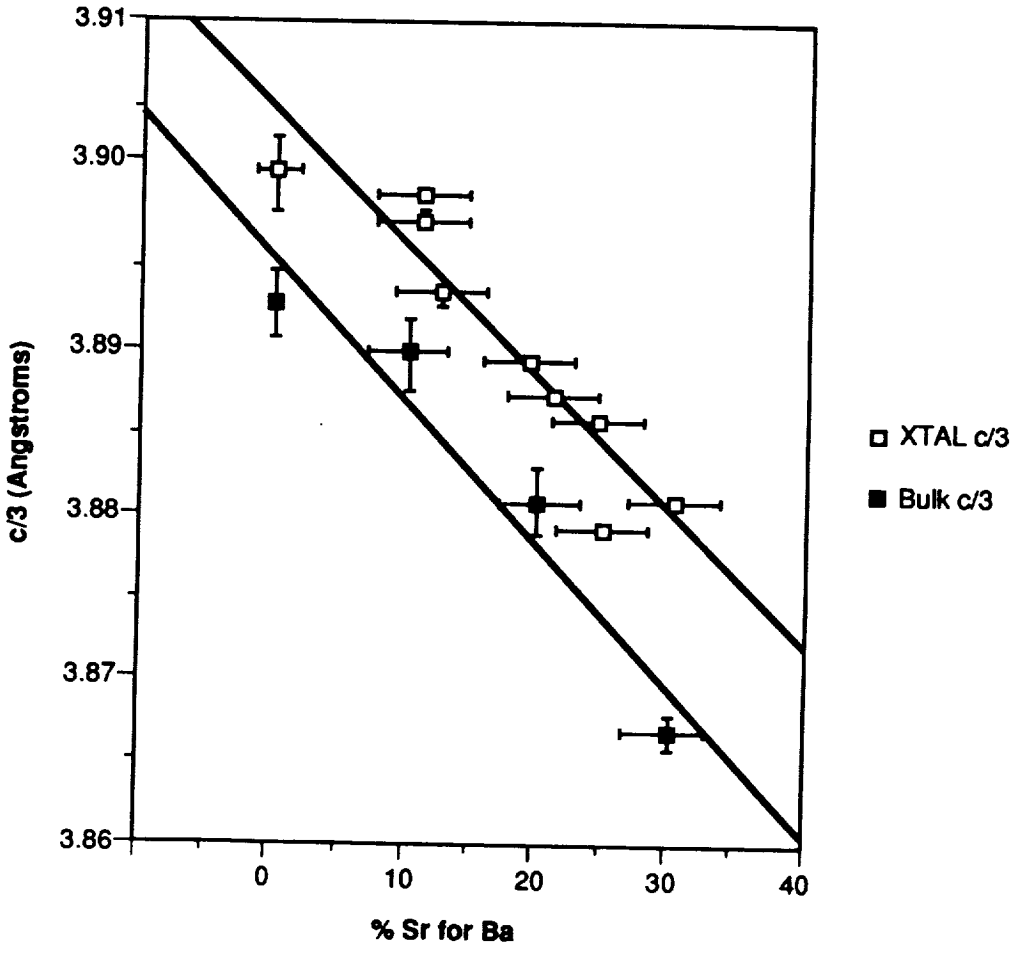
% Sr for Ba
a
b
c/3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3.89
3.88
3.87
3.86
c/3 (Angstroms)
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10
20
30
40
% Sr for Ba
XTAL c/3
Bulk c/3

Table 1. Tc Values for Bulk $YBa_{2-x}Sr_xCu_3O_{7-\delta}$

% Sr	x	Tc(K)
0	0	91.0
10	0.2	86.0
20	0.4	82.5
30	0.6	82.5
40	0.8	76.5
50	1.0	80.0
60	1.2	76.0
70	1.4	77.0
80	1.6	73.0

Table 2. Single Crystal Composition of $YBa_{2-x}Sr_xCu_3O_{7-\delta}$

Nominal %Sr in 1:2:3 Flux Component	Obs. %Sr in Crystal (±3.5%)
0	0
10	11.0
20	11.1
30	12.4
40	19.2
50	21.0
60	24.3
70	25.0
80	30.5

PROCESS OPTIMIZATION FOR THE Pb AND Sb-SUBSTITUTED Bi-BASED 2:2:2:3 BULK CERAMIC SUPERCONDUCTORS

by

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Abstract. The synthesis and superconducting properties of Pb and Sb substituted Bi-2:2:2:3 materials have been investigated. The preparation conditions for the formation of the pure 2:2:2:3 phase have been optimized. Actual Sb-substitution into the Bi-system 2:2:2:3 phase was successful as indicated by the XRD study. The transport measurements revealed no significant enhancement of the critical temperature as was reported previously for the Sb-substituted phase. However, an enhanced melt-sintering orientation effect was observed in samples containing unreacted Sb_2O_3.

Introduction

Since the critical current increases with decreasing temperature for high T_c superconductors, one possible direction towards raising the critical current is to synthesize and/or isolate a superconducting phase with a higher critical transition temperature. The Bismuth-based superconductor system [1] has a phase (the "2:2:2:3" phase) with a transition at about 110K, significantly higher than the "90K" transition for 1:2:3 materials.

The Bi-based superconductor system actually consists of three high temperature superconducting phases with very similar crystal structures. The general chemical formula for these phases can be written as $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$, n=1,2,3 corresponding to the 22K (2:2:0:1), 85K (2:2:1:2) and 110K (2:2:2:3) phases, respectively. Because of the similarity of their structures and formation thermodynamics, all three phases can be present to some degree in the average sample. Only careful control of the processing conditions for these samples would permit formation of any one of these phases in pure form. There have been several reports in the literature, at times conflicting, as to how to isolate the 2:2:2:3 phase [2-7]. One focus of the present work is to understand the process for isolating the high temperature phase and if successful, study methods of orienting this material toward better properties.

Experimental

In order to avoid formation of unwanted impurity phases during the preparation of the 2:2:2:3 phase, certain preheat procedures must be followed. The preheat must include a slow heat through the 600 °C to 800 °C temperature range to insure the decomposition of the carbonate precursors used. However, once the superconducting phase is formed, the time during cool down in the 800 °C to 700 °C region must be minimized to avoid the re-oxidation of the Pb that has been incorporated into the compound. The starting materials Bi_2O_3, PbO, Sb_2O_3, $CaCO_3$, and CuO were of at least 99.9% purity. These constitutents were mixed in stoichiometric amounts with the molar ratio Bi:Sr:Ca:Cu of 2:2:2:3. Pb substitution for Bi was either 10% or 15% (at.), while the Sb substitution for Bi was either 0% or 5% (at.). To increase sample homogeneity, after weighing the initial powders were mixed and coarsely ground, placed into a ball mill with ethyl alcohol and ground for several hours. The alcohol was then evaporated at 200 °C. The remaining sediment was heated in powder form to 810 °C for 12 hours, reground, and pressed into pellets under 35,000 psi. X-ray diffraction (XRD) demonstrated these preheated powders to be a mixture of 2201, 2212, and Pb and Sb-dominated phases (when the latter elements were used).

For most of the samples containing Sb that underwent subsequent melt sintering only one preheat was conducted. For the acquisition of phase-pure samples, subsequent grindings and preheats were necessary. A progressive raise in temperature of about 10 °C was possible on each subsequent preheat without causing unwanted reactions to occur within the sample. It was found that if a detrimental reaction had occurred as indicated by XRD, further process-

ing was ceased since successful formation of the higher order superconductor phases would not occur. On all secondary preheats the heating rate through the 700 °C to 800 °C range was generally greater than 10 °C/min.

Results and Discussion

Figure 1 shows the sintering conditions required to synthesize the 2:2:2:3 phase from a nominal composition of the same basic stoichiometry (and with 17.5% (at.) Pb for Bi). As the oxygen content in the flow is reduced during sintering, the actual temperature range in which the 2:2:2:3 phase is formed at all is reduced. The upper two or three degrees of these ranges (clear regions on graph) are the areas where the 2:2:2:3 phase is formed at 95% volume or better (determined by x-ray diffraction with a possible error of ±5%). Several conclusions involving bulk sintering can be drawn:

1. There is the prime sintering range (about 2 °C to 3 °C) where the 2:2:2:3 phase forms with the highest purity, and the extent of this range remains approximately constant for all levels of % O_2 in the flow. The prime sintering range is always just below the point where a portion of the sample will melt.

2. The extent of the possible sintering range (about 15 °C) is maximized for oxygen content above 4% in the flow. Below this flow rate, the conditions for synthesis of the 2:2:2:3 phase are so limited that the possible sintering range and the prime sintering range approach the same extent. At 1% O_2 flow, the two ranges are about the same.

3. The highest possible sintering temperature for the 2:2:2:3 composition is approximately 868 °C. This maximum temperature is first obtained with about 10% O_2 in the flow. If no Pb is added to the initial composition, the temperatures for the results presented in Figure 1 would all increase by about 10 °C.

4. For each nominal composition, the prime sintering temperature is reduced for reduced oxygen content in the flow. The melting point also adjusts in accordance with the adjustment of the prime sintering range, staying just above this range.

For consistency, the amount of sintering time for each sample that comprised the results of Figure 1 was one day. It is likely that a pure phase can be produced at a sintering temperature that is not within the prime temperature range, if enough time is permitted. This would explain why there have been conflicting reports regarding time requirements (ranging from a few days to a few weeks) [9-11].

To date, we have found that conditions involving time, temperature, oxygen partial pressure, and nominal composition, all contribute to the isolation of the 2:2:2:3 (110K) phase. Other factors such as heating and quenching rates and general pre-sintering conditions are also important but these factors are as yet not well-defined. Though these samples were single phased, there still seems to be a problem with connectivity through the sample as evidenced by the resistance vs. temperature plot (Figure 2). The onset is above 110K, but the eventual zero-resistance of this latter sample was 95K.

For the Bi 2:2:1:2 (85K) and 2:2:2:3 (110K) phases, it has been shown that the partial substitution of Pb for Bi in the compounds greatly reduces the time required to form the phases [4-6]. Low level substitution of Sb for Bi has not reduced the reaction time, but has improved the superconducting properties of the sample in some cases [8-10]. We therefore investigated Sb substitution in the hope that we could enhance the superconducting properties.

5% (at.) Sb for Bi Substitution in $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$ (x = 0.3)

One particular objective of this work was to form the pure 2:2:2:3 phase with Sb substitution for Bi. There had been several reports of very high transition temperatures (ranging from about 125K to 132K) in samples that contained Sb in the nominal stoichiometry but these reports did not specify which phase was actually responsible for these high transitions and it is unclear whether or not Sb was actually substituting into these phases [8-10].

Our first efforts to form this compound, using only methods that were successful with the Pb-substituted compound, failed. Through some of these samples were actually high temperature superconductors, X-ray diffraction demonstrated these samples to be multi-phased. These extra phases primarily consisted of unreacted initial constituents, including Sb_2O_3. These superconductors often showed very high onset transition temperatures (between 110K and 120K) but rarely obtained a zero resistance state above liquid nitrogen temperature. An onset transition between 110K and 120K could be attributed to a non-Sb

substituted phase and this result would be consistent with the range generally reported for the pure Bi 2:2:2:3 phase or the Pb-substituted phase.

Hence, the conditions required to produce a high temperature superconductor with Sb present, were more strict than normally required for pure Bi superconductors. It was also found that, depending upon the preheated conditions, it was sometimes impossible to form a high temperature superconductor at all. The solution to the problem of forming a Sb-substituted 2:2:2:3 phase rested mainly with the preheat treatment, i.e. several preheats conducted at progressively higher temperatures until the actual sintering temperature is approached.

The incorporation of 5% (at.) Sb for Bi in the Pb-substituted phase lowered the required sintering temperature 15 °C to 18 °C. Using the above techniques, a pure Sb-substituted 2:2:2:3 phase was finally synthesized (to the limits of x-ray diffraction). The structure and properties were very similar to that of the Pb-substituted phase. No transition onset was found above 115K as determined by transport measurements.

Melt-Sintering of Bi-System Superconductors

In attempting to form the above Sb-substituted phase, there were many failures. Most of these failures arose from improper or incomplete preheat treatments, allowing Sb_2O_3 to remain unreacted in the sample. It was found, however, that these samples with small amounts of unreacted Sb_2O_3, had unusual melt sintering properties. Under melt-sintering

conditions, these samples became very dense, glossy, and smooth on the surface. Samples without Sb_2O_3 present did not show this enhanced melt-sintering effects. X-ray diffraction scans showed that these samples were highly oriented on the surface. The intensities of the (00ℓ) peaks were one to two orders of magnitude higher than for samples without Sb_2O_3 present in the initial constituents. The effect was similar to a film of superconductor material forming on a substrate of sintered material. The high density and orientation found in these samples should lead to much improved superconducting properties.

Subsequently it was also found that the melt-sintering effect could be optimized for all Bi-based samples if the samples were ground for a specified amount of time, thereby insuring an ideal particle size in the sample. This optimum grinding time ranged from about 5 minutes to 2 hours, depending upon the particular pre-grinding synthesis of each sample. It became evident that the Sb_2O_3 had been acting as a flux (melting pt. = 655 °C), increasing the orientation of the superconductor material. An ideal particle size improved the action of the flux. The improved orientation due to the flux action of excess Sb_2O_3, might explain some of the improved properties observed in the above mentioned Sb-substitution studies. However, it should be noted that too much Sb_2O_3 present (above 0.1% by weight), was detrimental to the sample.

Four important conclusions can be made on the melt sintering effect for Bi-based superconductors:

1. There is a reversal in the order of phases formed in the melt sintering process as compared to a simple sintering process, when the temperature is increased. In bulk sintering (in air), the 2:2:0:1 phase will be formed in the temperature range of about 810 °C to 830 °C, the 2:2:1:2 phase will be formed in the temperature range of about 830 °C to 860 °C, and the 2:2:2:3 phase will be formed in the range of about 860 °C to 880 °C (unsubstituted phases). These temperatures are approximate since the actual values depend on the exact nominal composition. When melt-sintering conditions are applied (heating above the melting point for a prescribed time), an oriented 2:2:2:3 phase will be formed first, followed by oriented 2:2:1:2 and 2:2:0:1 phases as the temperature is increased.

This melt-sintering effect is demonstrated by the XRD patterns of Figure 3. These scans were taken from identical samples (containing Sb and Pb) that were treated at the temperatures of 853 °C (a), 873 °C (b), and 933 °C (c). The resulting c-axis oriented phases were 2:2:2:3, 2:2:1:2, and 2:2:0:1, respectively.

2. As the selected melt-sintering temperature is increased above the melting point for the sample, the allowable time required to obtain a melt sintering orientation is decreased. The extent of this inverse relationship is very compositionally dependent.

3. Very compositionally dependent is also the time period applied for melt sintering. Time periods to form a melt-sintered 2:2:2:3 phase can be on the order of seconds, while that for the 2:2:0:1 phase can be hours. The Sb_2O_3 addition increases the time necessary for the melt-sintering and, therefore, decreases possible errors.

4. Attempts at Pb and Sb substitution for Bi in the amounts specified above greatly enhances the melt-sintering orientation effect, probably due in part to the tendencies of unreacted Sb_2O_3, and possibly unreacted PbO, to act as fluxes. The intensities of the (00ℓ) peaks, especially for samples containing Sb, can be an order of magnitude higher than for melt-sintered samples without Sb.

In conclusion, synthesis conditions for the formation of the 2:2:2:3 phase were optimized. Actual Sb substitution into the Bi-system 2:2:2:3 phase was also successful, as determined to the limits of X-ray diffraction measurements. Transport measurements revealed no significant enhancement of the superconducting properties as previously reported for nominal compositions of this latter phase. Melt-sintering results indicate that enhanced properties of samples containing Sb_2O_3, may be due to the orientation of the superconductor phases caused by the flux action of this constituent.

Acknowledgements

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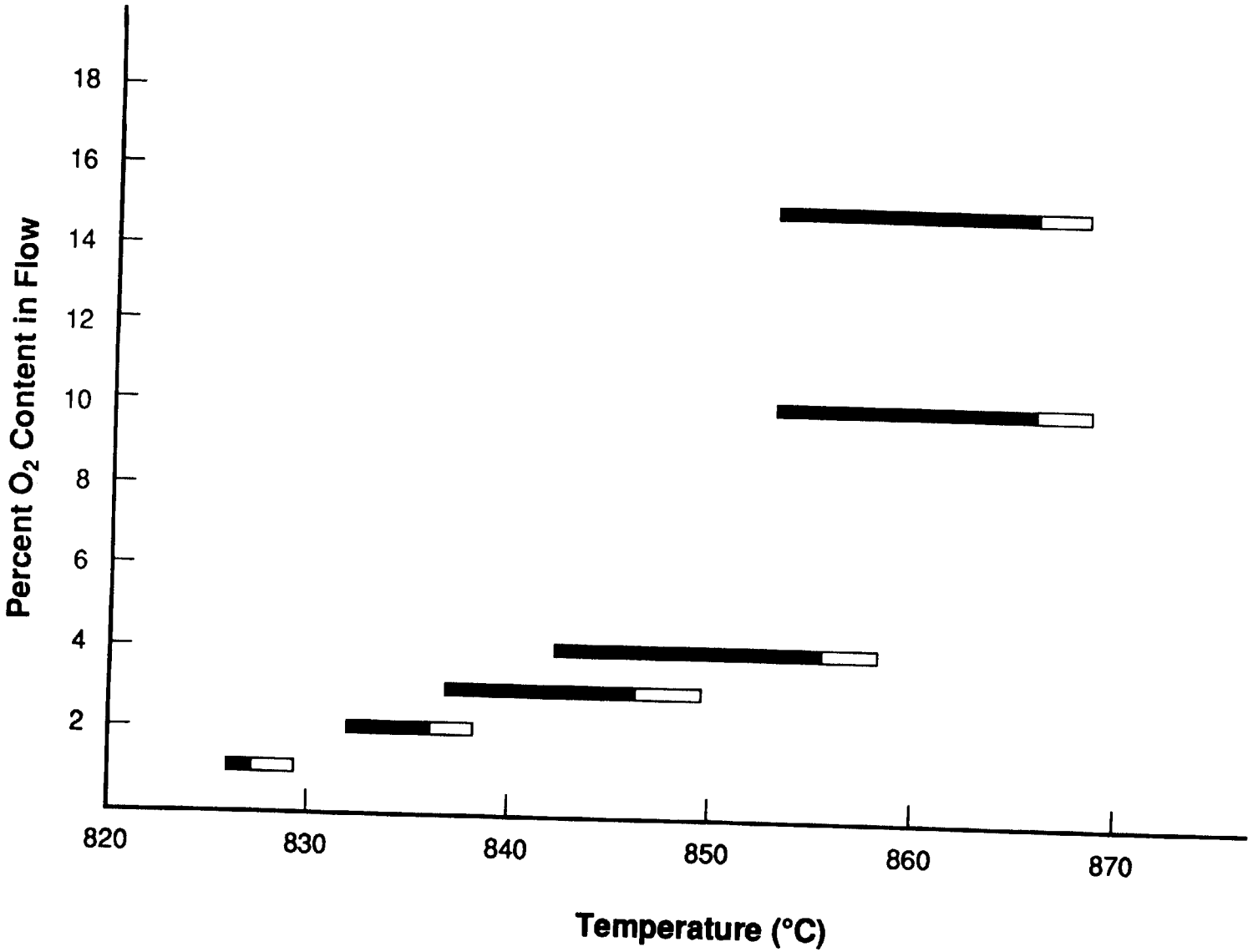
Figure Captions

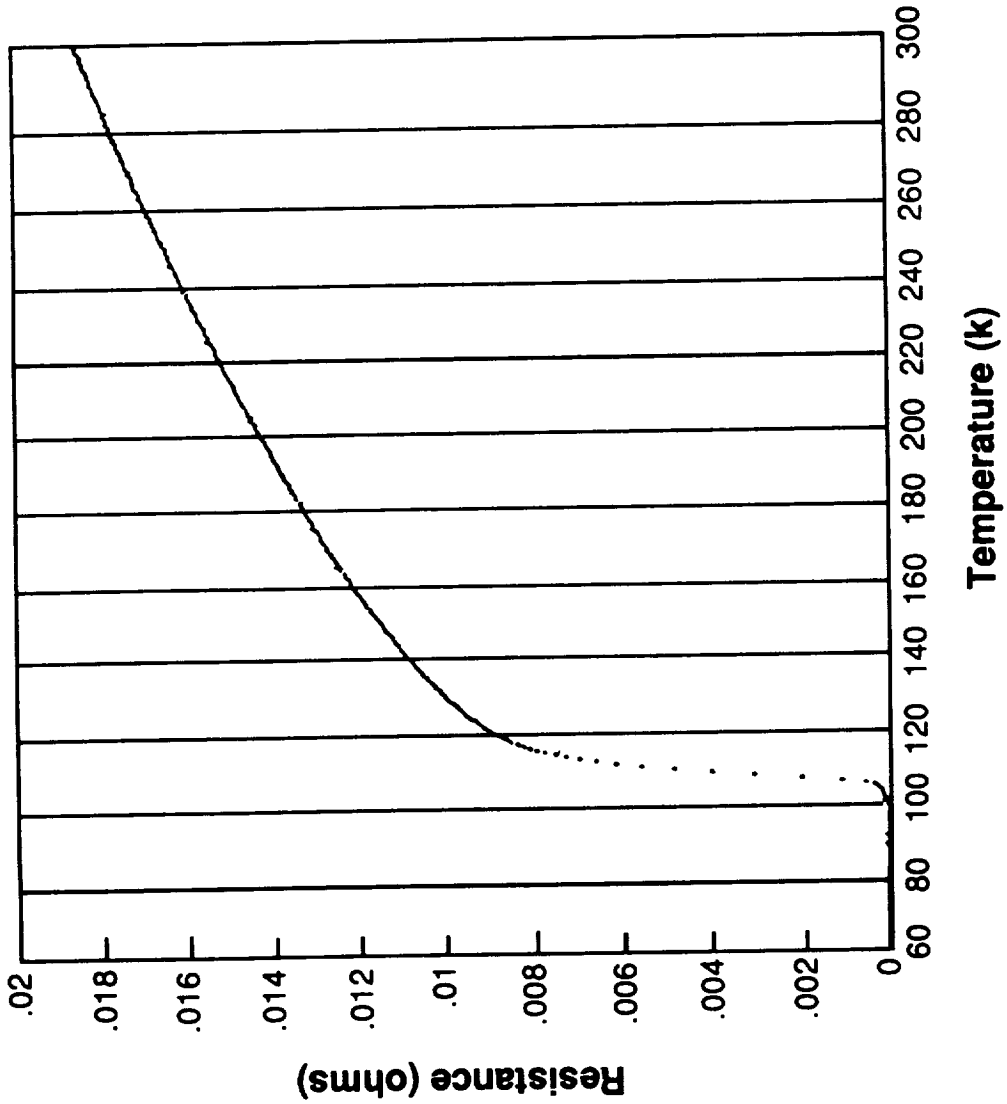
Fig. 1: Formation of the Bi 2:2:2:3 phase as a function of temperature and O_2 content in the gas flow. All samples were sintered for a period of 1 day. The bars indicate the temperatures where the phase was observed. Clear sections of the bars indicate where maximum yield was obtained.

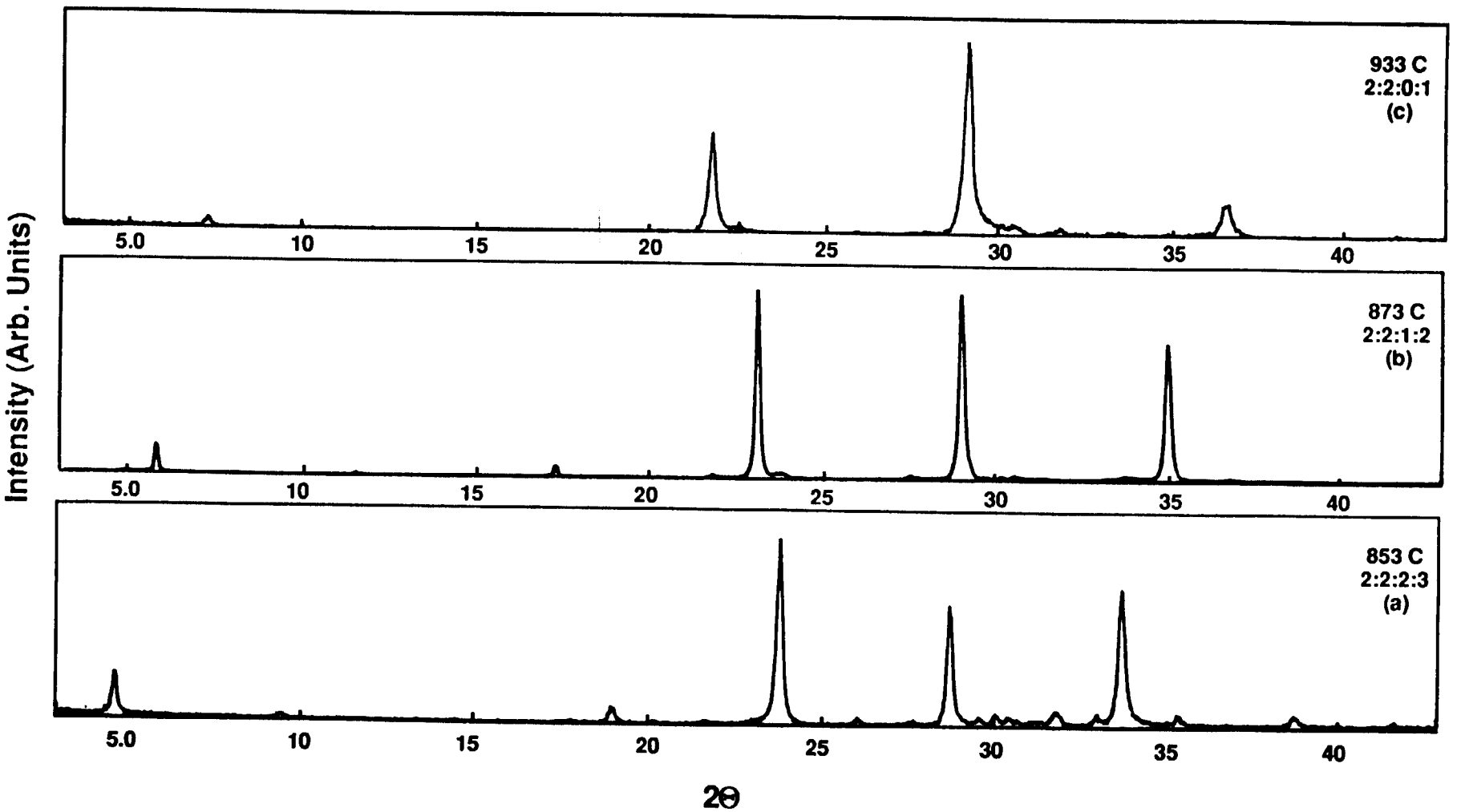
Fig. 2: Temperature dependence of the electrical resistence for a (Bi, Pb)-2:2:2:3 superconductor.

Fig. 3: XRD of melt-sintered samples of Bi-based materials showing (00ℓ) orientation effects at different temperatures.


Percent O_2 Content in Flow
18
16
14
12
10
8
6
4
2
820
830
840
850
860
870
Temperature (°C)

5-15205.2-429


Resistance (ohms)
.02
.018
.016
.014
.012
.01
.008
.006
.004
.002
0
60
80
100
120
140
160
180
200
220
240
260
280
300
Temperature (k)


933 C
2:2:0:1
(c)
873 C
2:2:1:2
(b)
853 C
2:2:2:3
(a)
5.0
10
15
20
25
30
35
40
Intensity (Arb. Units)
2Θ

5-15206-2-439

APPROVAL

A STUDY OF ENHANCING CRITICAL CURRENT DENSITIES (J_c) AND CRITICAL TEMPERATURE (T_c) OF HIGH-TEMPERATURE SUPERCONDUCTORS -- CENTER DIRECTOR'S DISCRETIONARY FUND FINAL REPORT (PROJECT NO. 90-N26)

By Marcus Vlasse

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

E. TANDBERG-HANSSEN
Acting Director
Space Science Laboratory

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