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**High Temperature Superconductor
Materials and Applications
(5-32313)**

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Report 7-Superconducting Material Research

The laser ablation apparatus has been placed on hold because of problems with the Aluminum mirror that was being used. The last attempt to deposit thin film resulted in breakage of the mirror. The heat load produced by the laser was too great for the mirror to withstand. Therefore a specially designed mirror has been ordered that is capable of handling the heat load. In addition much effort has been expended in repairing an old sputtering system. This system will be used to study granular effects in superconducting thin films.


PREFACE

This technical report was prepared by the Resident Research Program Office of the University of Alabama in Huntsville Research Institute. This report is to serve as documentation of technical work performed under contract number NAS8-36955, Delivery Order 72. Dr. George B. Doane was principal investigator. Technical work was produced by Dr. John Golben and Mr. Curtis Banks. Dr. Eugene W. Urban, Chief of the Infrared & Cryogenic Physics Branch, Astrophysics Division, Space Sciences Laboratory, Science and Engineering, MSFC/NASA, provided technical coordination.

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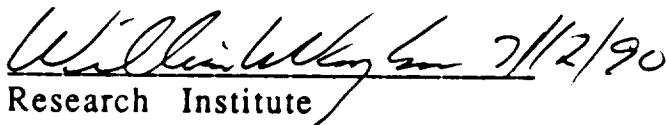

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INTRODUCTION AND OVERVIEW

The research performed during the course of this delivery order fell into two areas.

One of the areas concerned itself with the investigation of the phenomena involved in formulating and making in the laboratory new and better superconductor material with enhanced values of critical current and temperature. Of special interest were the chemistry, physical processes and environment required to attain these enhanced desirable characteristics.

The other area concerned itself with producing high temperature superconducting thin films by pulsed laser deposition techniques. Such films are potentially very useful in the detection of very low power signals. To perform this research high vacuum is required. In the course of this effort older vacuum chambers were maintained and used and in addition a new facility is being brought on line. This latter activity has been replete with the usual problems of bringing a new facility into service. Some of the problems are covered in the main body of this report.

Superconductor Material Investigations

For NASA-related applications, there are several forms of high temperature superconductors that need to be studied. Thin films have to be developed for sensors and detectors. It is very likely that the response to infra-red, optical and microwave radiation can be vastly improved by use of high Tc films. Films and single crystals are also important for various electronic applications. For many other applications, however, larger bulk superconductors have to be developed. These applications include motors and generators, power transmission, magnetic bearings, and magnetic energy storage.

Space also offers a unique environment for the study and use of these superconductors. As for any materials processing, the effects of low gravity provide insight to the optimization of these materials. The clean environment is welcome, since many of these materials are sensitive to environmental impurities. Low temperatures are desired since the "high" temperature superconductors still require a temperature far below earth ambient for superconductivity to exist. The high vacuum that is accessible, is another important property-sensitive parameter since some forms of these superconductors are severely dependent upon oxygen content. Hence, NASA has the need for the concurrent use and study of these superconductors through processing techniques.

The main purpose of the present work has been toward improving the properties and makeup of bulk high temperature superconductors, particularly the critical current, J_c , and the critical temperature, T_c . The main variable in this research has been to use different processing techniques and directions to bring about the desired properties in the superconductors.

Some of the directions toward better materials include 1. Optimizing the various forms of the superconductors (i.e. bulk, films, single crystals etc.), 2. Enhancing a particular form of the material through processing, and 3. Studying new materials. More specifically under this contract, all of the major forms have been studied to some degree. Bulk properties and structure have been enhanced using a new melt-sintering technique and arc-melting. And finally, new materials have been studied such as the systematic doping of Strontium for Barium in 1:2:3 superconductors, and the understanding and isolation of the very high temperature Bismuth-based 2:2:2:3 superconductor phase.

The high temperature superconductors presently being investigated are very anisotropic materials, i.e. their properties in one direction of the crystal lattice are quite different from the properties in another direction of the crystal lattice. This is especially true for the critical current density (J_c) which can be two orders of magnitude greater in the crystal ab plane than in the crystal c direction. Hence grain alignment of the superconducting phase is a very important factor in improving the critical current density in bulk materials.

For the so-called "1:2:3" superconductors, the starting or "nominal" elemental composition is the same as the final

composition after the correct processing treatments. Hence the grain morphology is extremely important. Melt-sintering or texturing is one method to obtain oriented grain growth. In this method, the sample is slightly melted and then slow cooled. This promotes elongated grain growth in a preferred direction. As a result, the critical current and sometimes the critical transition temperature is enhanced.

Figure 1 shows x-ray diffraction spectra for a Yb:Ba:Cu:O 1:2:3 sample in pellet (sintered surface) and powder form. The powder scan should demonstrate all of the regular reflections for this 1:2:3 compound and it does. The pellet surface on the other hand demonstrates more c-axis orientation as the (00L) peaks are enhanced. Particularly the (003) and (006) peaks are noticeably increased, while the (110)/(013)/(103) peak is significantly reduced. SEM studies show that the grain growth is elongated and enlarged. Figure 2 shows that the transition temperature is enhanced from about 83K to 90K due to cycling of the melt-sintering process.

The success of the melt-sintering process is actually dependent upon quite a few factors. Figure 3 is a graph of two of these factors, the Melt-sintering Time and Peak Temperature for a sample of Y:Ba:Cu:O. The graph demonstrates the major orientation peak intensity (x-ray diffraction) as a function of of these factors. As might be expected, less time is required to obtain a melt-sintering effect as the temperature is raised above the melting point of the compound. However the slope and other information for this type of graph is sample-dependent. The conditions are varied for samples of different 1. Dimensions, 2. Density, and 3. Preheated Purity. Other specific conditions in the processing are also critical, including the 1. Heat Rate, 2. Cooling Rate, 3. Step Temperatures, and 4. Annealing.

The results for bulk materials is encouraging. Figure 4 shows two x-ray diffraction spectra, one for single crystal Y:Ba:Cu:O and one for melt-sintered Y:Ba:Cu:O. For the single crystal, we would expect to see only the c-axis reflections, (00L)'s, since this is the preferred plane for the plate-like morphology of the crystals when mounted. Hence the single crystal spectra is an excellent measure of the success of the melt-sintering process since we can compare the degree of orientation that is obtained in bulk materials. Indeed the melt-sintered spectra is very similar to the spectra obtained for the single crystal. Except for a small peak near $2\theta=32$ degrees (which would be the major peak in the associated powder scan), the sample surface is predominantly c-axis oriented. Relative intensities of the reflections for both the single crystal and the melt-sintered samples are similar, affirming structural similarity. The significance of this success lies with the fact that the bulk sample is much larger and extensive than any crystals than can presently be made. The value of J_c associated with these oriented samples is a factor of several times that associated with the corresponding sintered sample.

Since the critical current increases with decreasing temperature for high T_c superconductors, one 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 has a phase (the "2:2:2:3" phase) with a transition at about 107K, significantly higher than the "90K" transition for 1:2:3 materials. But since this system contains several superconducting phases with similar structures, there has been a problem in isolating the very high temperature phase from these other phases. Phase mixtures and/or intergrowths appear in most samples of this system. There have been several reports, sometimes conflicting, in the literature as to how to isolate the "2:2:2:3" phase. One focus of this contract was to understand the isolation of the high temperature phase and if successful, continue work toward orienting these samples toward better properties.

Figure 5 demonstrates the ranges for observation of the Meissner effect at liquid nitrogen temperature, as a function of nominal composition and sintering temperature. The composition ratio refers to (Bi,Pb):Sr:Ca:Cu. One important observation is that the sintering temperature range is very small (a few degrees centigrade). Hence, an unstable furnace with temperature swings of more than a few degrees centigrade would not produce these superconductors with high T_c 's. Also it is noted that these sintering ranges are very compositionally dependent. Finally, the addition of Pb on Bi sites helps to stabilize the high temperature phase; lessening the time needed to sinter the samples and increasing the margin for error in the sintering temperature. The problem with Pb is that it readily oxidizes in the 700C to 800C temperature range. As a result, there was a report that a 1% O_2 environment was needed to isolate the 2:2:2:3 phase. The Bismuth superconductor system also might have a slight oxygen dependence in the stoichiometry, similar to but not as extensive as the oxygen-dependence of the Y 1:2:3 system. For these reasons, the oxygen dependence of the formation of the 2:2:2:3 phase was studied.

Figure 6 shows these results. As the oxygen content in the flow is reduced during sintering, the actual sintering range in which the 2:2:2:3 phase is formed at all is reduced. The upper two or three degrees of these ranges (thicker regions on graph) are the areas where the 2:2:2:3 phase is formed 95% or better. Several observations can be made. One, the extent of the possible sintering range is maximized for oxygen content above 4% in the flow. Two, the highest possible sintering temperature is obtained in this particular composition at about 868K. Above this temperature, the sample melts. Three, the sintering temperature is reduced for reduced oxygen content. And finally, the extent of the range where the 2:2:2:3 phase is best formed remains approximately constant for all levels of O_2 flow. (However the phase cannot be formed under 100% Argon) In conclusion, the best conditions can be found for any content in the flow and a specific O_2 content is not required. One consequence of reduced O_2 content (other than reducing the Pb oxidation) is that if the 2:2:2:3 phase is formed at all, it will be formed in a high percentage amount.

Isolating the 2:2:2:3 phase or any phase in the Bi system is important towards enhancing the properties, or proceeding further toward making new compounds by substitutions. Figure 7 demonstrates the isolation of the 85K "2:2:1:2" phase (top x-ray diffraction spectra) and the isolation of the 110K "2:2:2:3" phase (middle diffraction spectra). These samples have also been compacted and as a result are extremely c-axis oriented. The bottom x-ray diffraction spectra shows an overlap of these two spectra. This is similar to what is usually observed for Bi-based samples; an intermixing of the phases. Note that the (002) peak is shifted to the left in the spectra for the 110K sample as compared to the spectra for the 85K sample. This is evidence for the increased cell size of the former sample. The cell is large because there is an extra CaCuO₂ layer in this phase. The extra layer also aids in the superconducting properties.

For bulk samples of Bi-based superconductors, density is a major problem. These samples are often very porous, thereby reducing the current path area and grain connectivity. Hence several samples were Arc-melted to obtain maximum density, and then annealed to enhance the high temperature phase. As a result the transition temperature for most of the sample rested at about 110K (Figure 8). The sensitivity of this measurement is very good, hence a foot structure in the resistivity can be observed between about 95K and 110K. This structure may be due to several possible factors including a small presence of the 85K phase in the sample or a small critical current for Bi samples resulting in a return to the normal state for large measuring currents. This latter factor is less likely since the measurement appears to be unchanged for different values of the measuring current. Nevertheless, an improvement in the overall properties of the sample is observed due to densification by arc-melting.

Much effort has been expended elsewhere to obtain a 1:2:3 superconductor without Ba. 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 better properties. Hence it is important to try to substitute Sr for Ba in the Y:Ba:Cu:O 1:2:3 superconductor series. One report (although seemingly irreproducible) had the observance of room-temperature superconductivity in a Y:(Ba,Sr):Cu:O sample.

Nominal compositions $Y_1(Ba_{2-x}Sr_x)Cu_3O_{7-\delta}$ ($0 \leq x \leq 0.8$) have resulted in single phase bulk compounds. This study represents the first success at synthesizing these compounds in the bulk form with $x > 0.6$. Part of this success can be explained by Figure 9. The sintering temperature range is compositionally dependent. If a systematic study of these substitutions only involves one sintering temperature (say 930C), only compositions up to about $x = 0.5$ can be made. These results also are dependent upon the preheating conditions. The desired phase must be eased into formation such that decomposition into other phases does not take place. The full substitution of Sr for Ba in the 1:2:3 compound was successful since this structure was observed in a sample that had no Ba in the starting constituents. However this phase was only observed on the

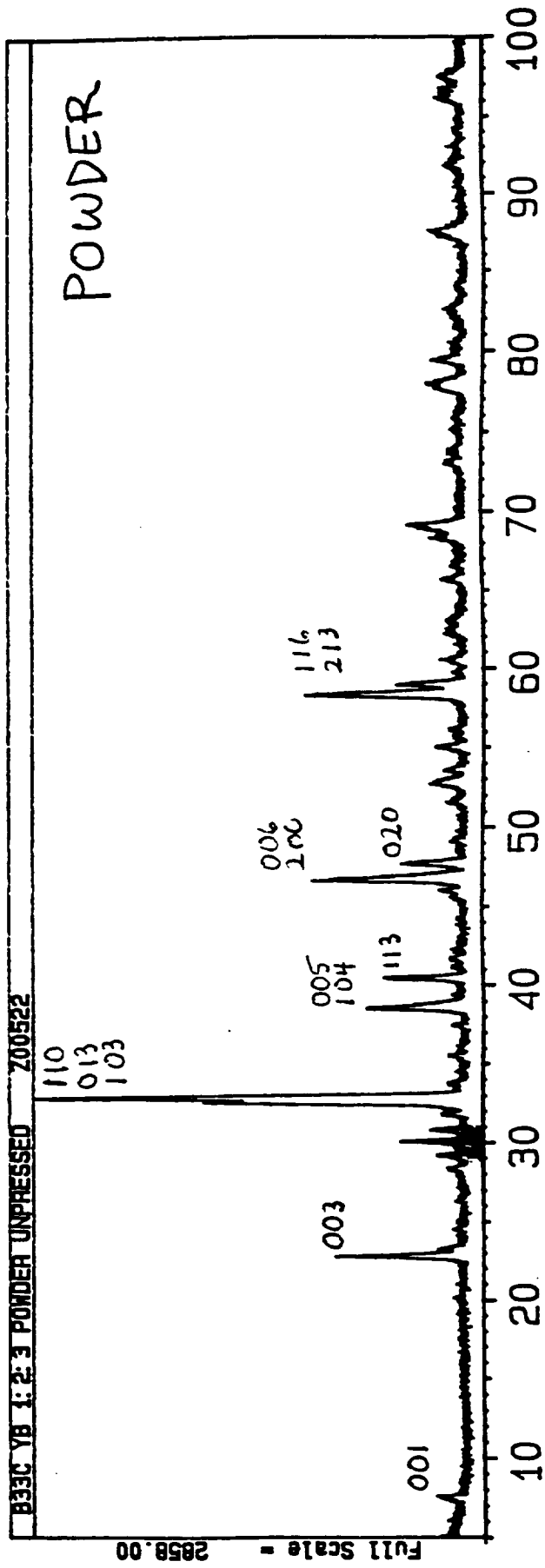
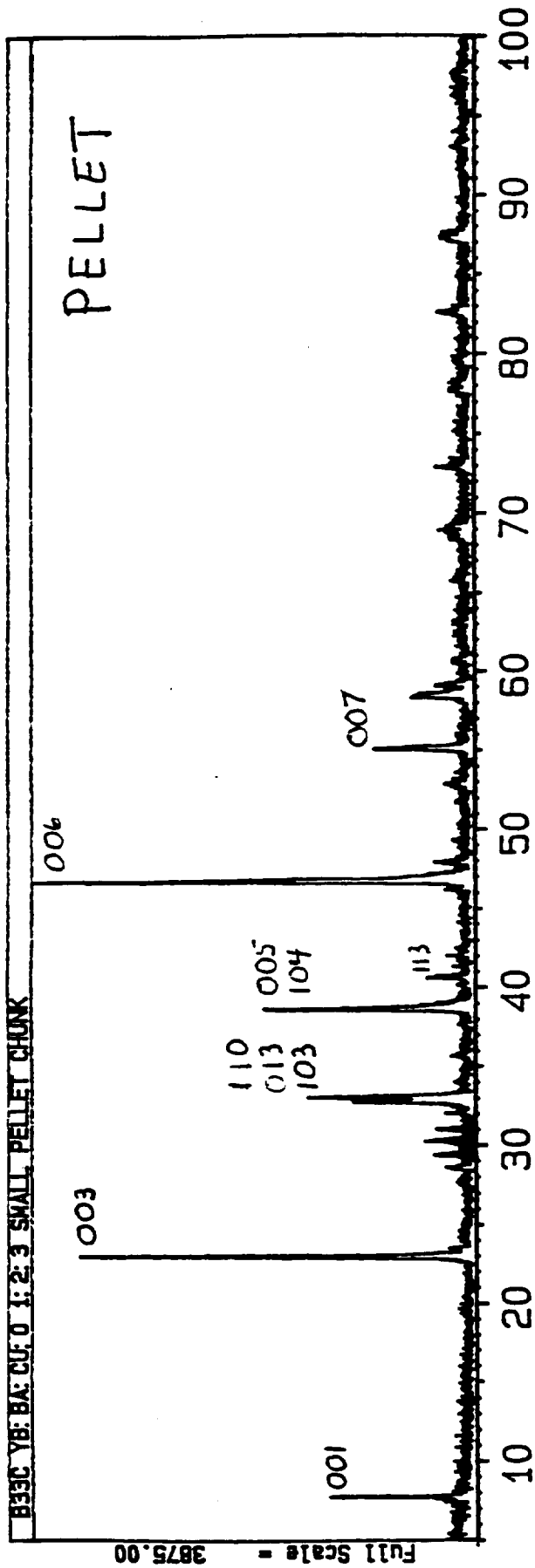
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surface of particular samples and not in the bulk of these samples. It is emphasized then that the 1:2:3 phase without Ba can be made, but to date not enough quantity can be made to isolate and observe the properties of this phase.

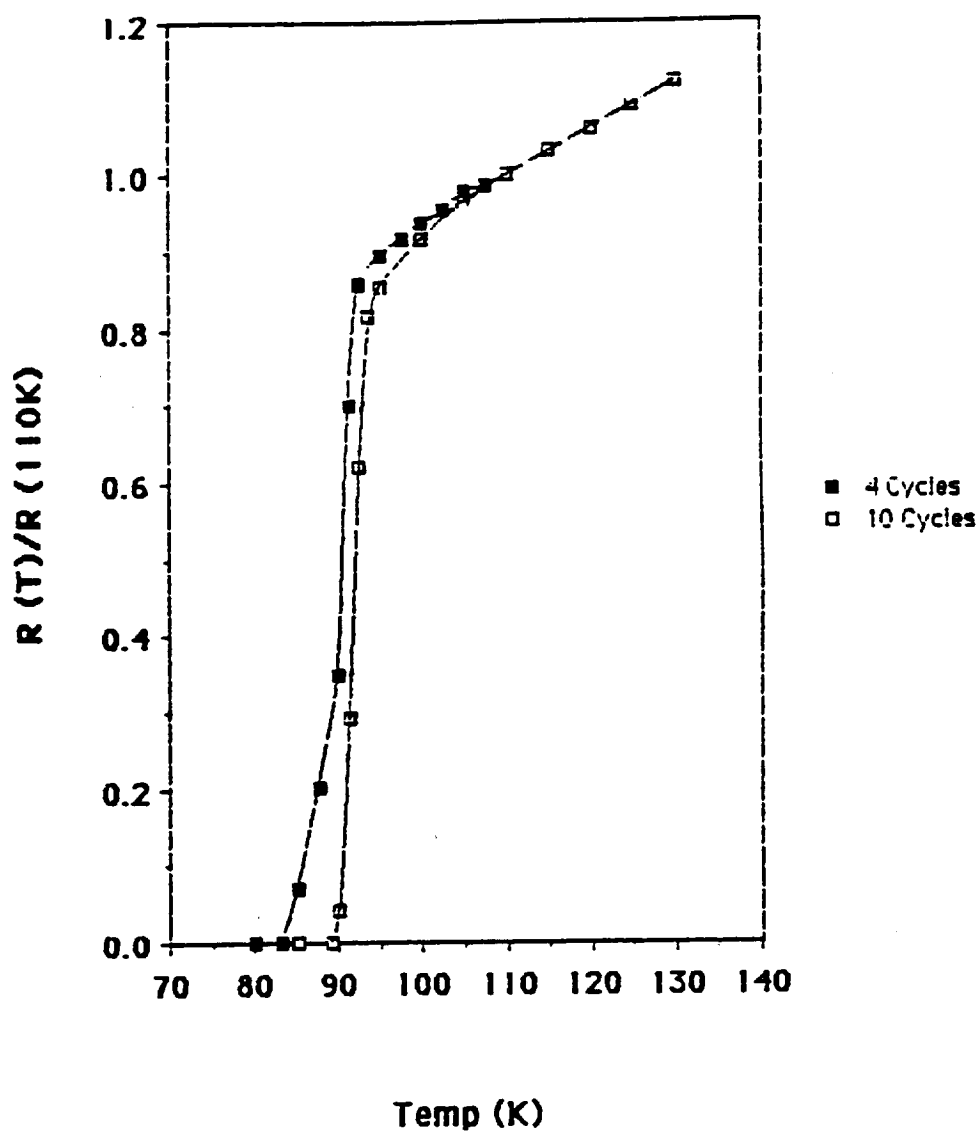
The lattice constants for all Sr for Ba compositions can be determined and are displayed in Figure 10. In general, there is a reduction in the a,b, and c parameters with Sr substitution. This can be expected since the Sr atom is significantly smaller in size as compared to the Ba atom. Other studies have shown that the superconducting properties in 1:2:3 compounds can be empirically linked to the Cu-O distance in the c-axis direction. In this case, a reduction in the Cu-O distance would tend to destroy superconductivity. Preliminary observations on these samples seem to confirm this.

Single crystals grown from these compositions have shown substitution of Sr for Ba within the structure. Further study of these crystals will offer systematic evidence of the range of superconductivity as a result of doping in these materials.

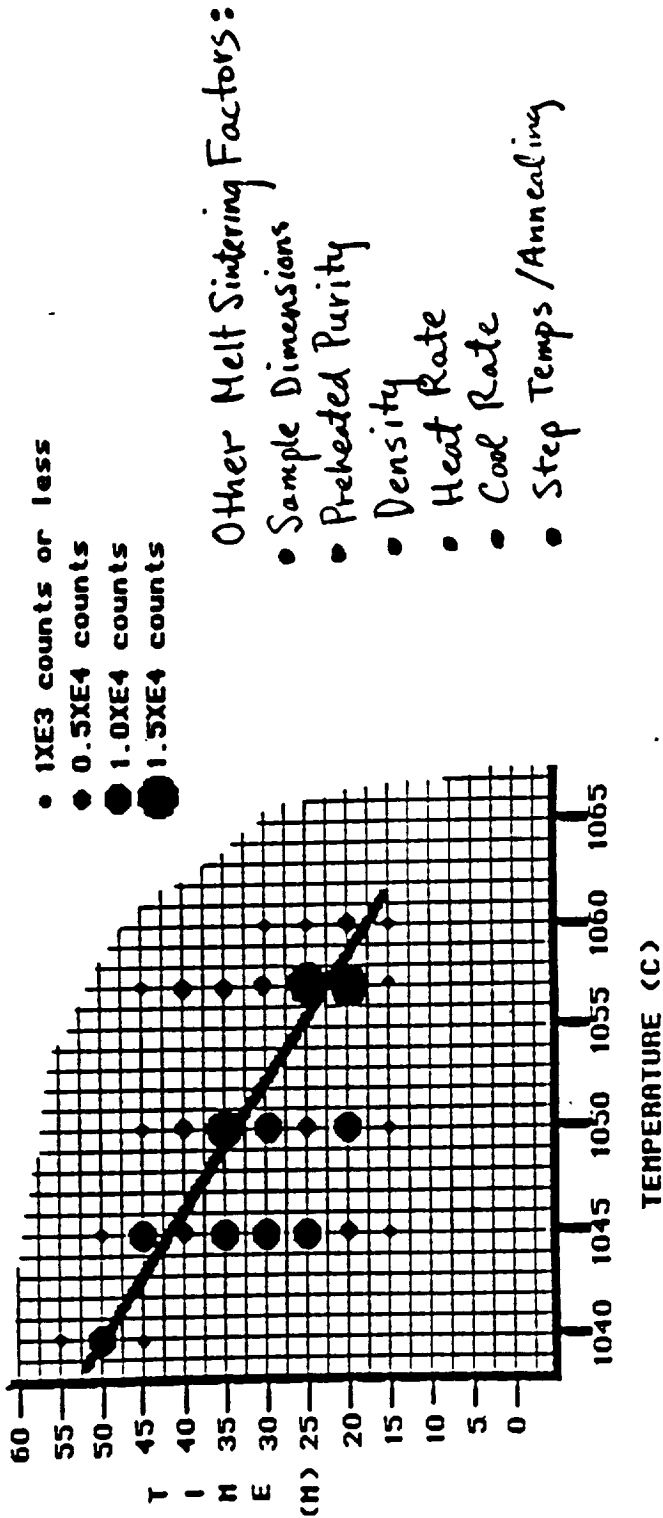
In conclusion, several major objectives have been obtained with the present work. Optimization of the melt-sintering technique for bulk 1:2:3 samples has resulted in highly oriented samples with higher values of J_c . This process optimization should be continued to apply to even larger bulk samples. Isolation of the high temperature Bi phase and the sintering oxygen dependence of this phase has been performed. Compaction and densification processes on these samples have also resulted in better structural characteristics and better properties. Finally, Sr for Ba substitution in the 1:2:3 series can be obtained in bulk samples up to 80%, and the 100% substituted phase has been observed for the first time. This may open up new avenues for substitutional directions.



Yb1Ba2Cu3O7 Melt Sintering



Melt Sintering Time vs. Peak Temp



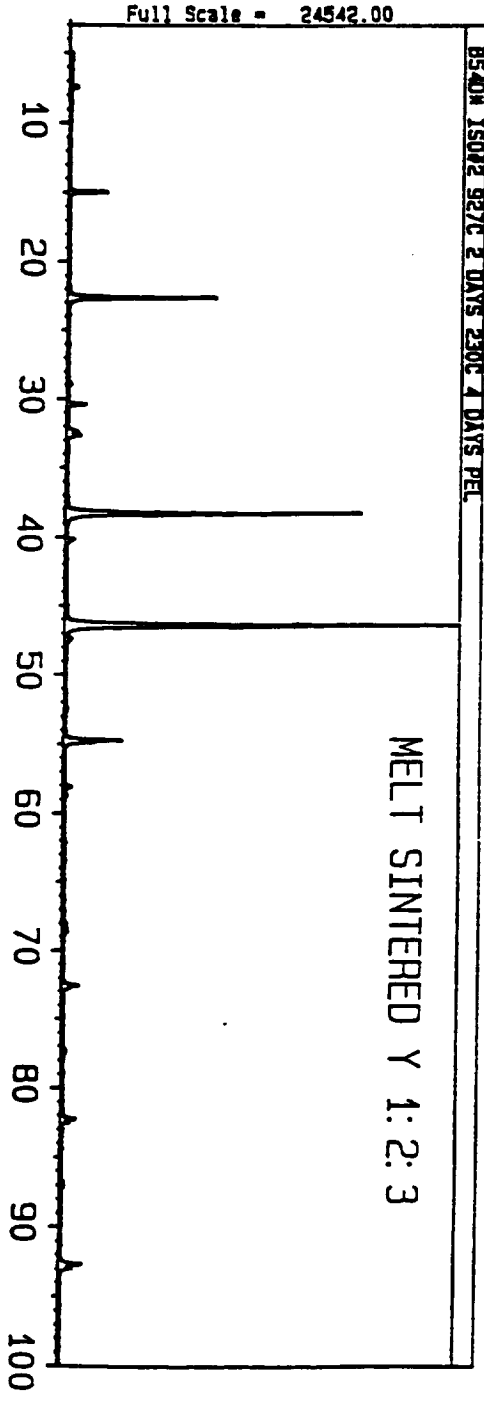
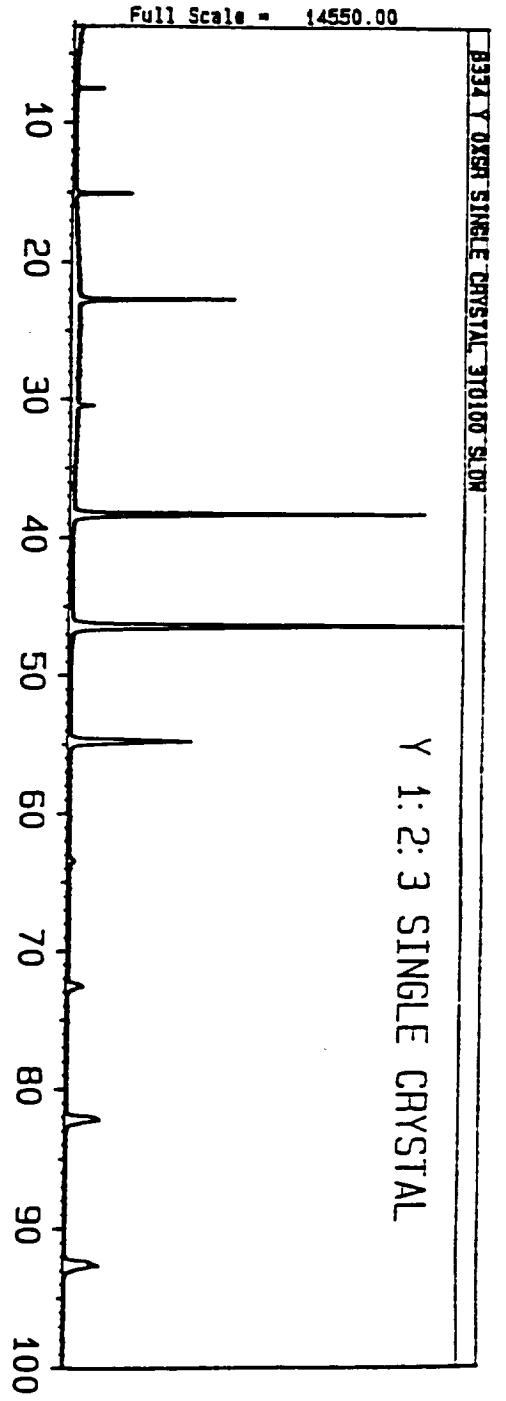
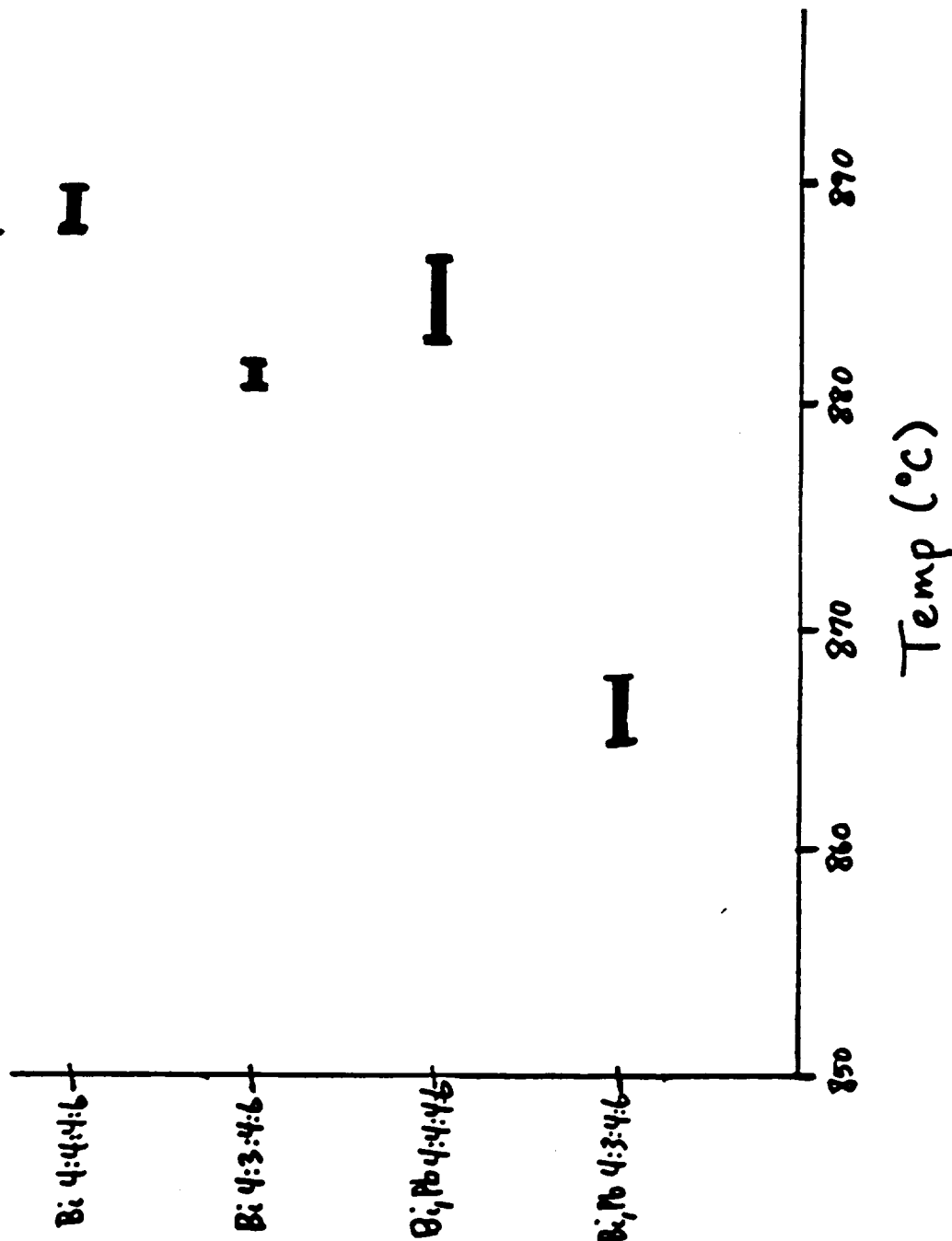


Figure 5

Formation of $> 1K$ Superconductor
vs. Composition and Temp



Formation of "2223" Phase as a Function of Temperature and O₂ content in Flow

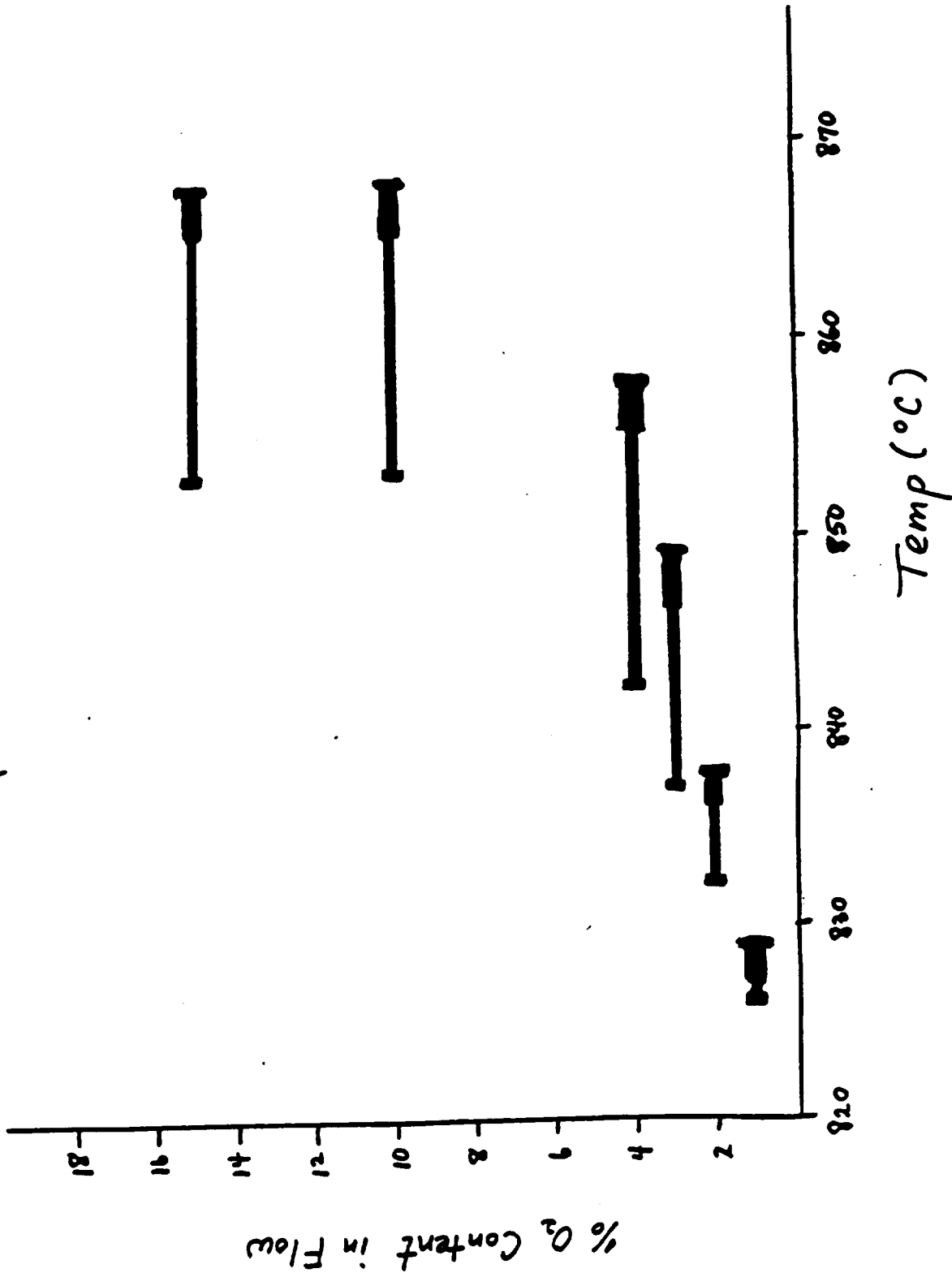


Figure 7

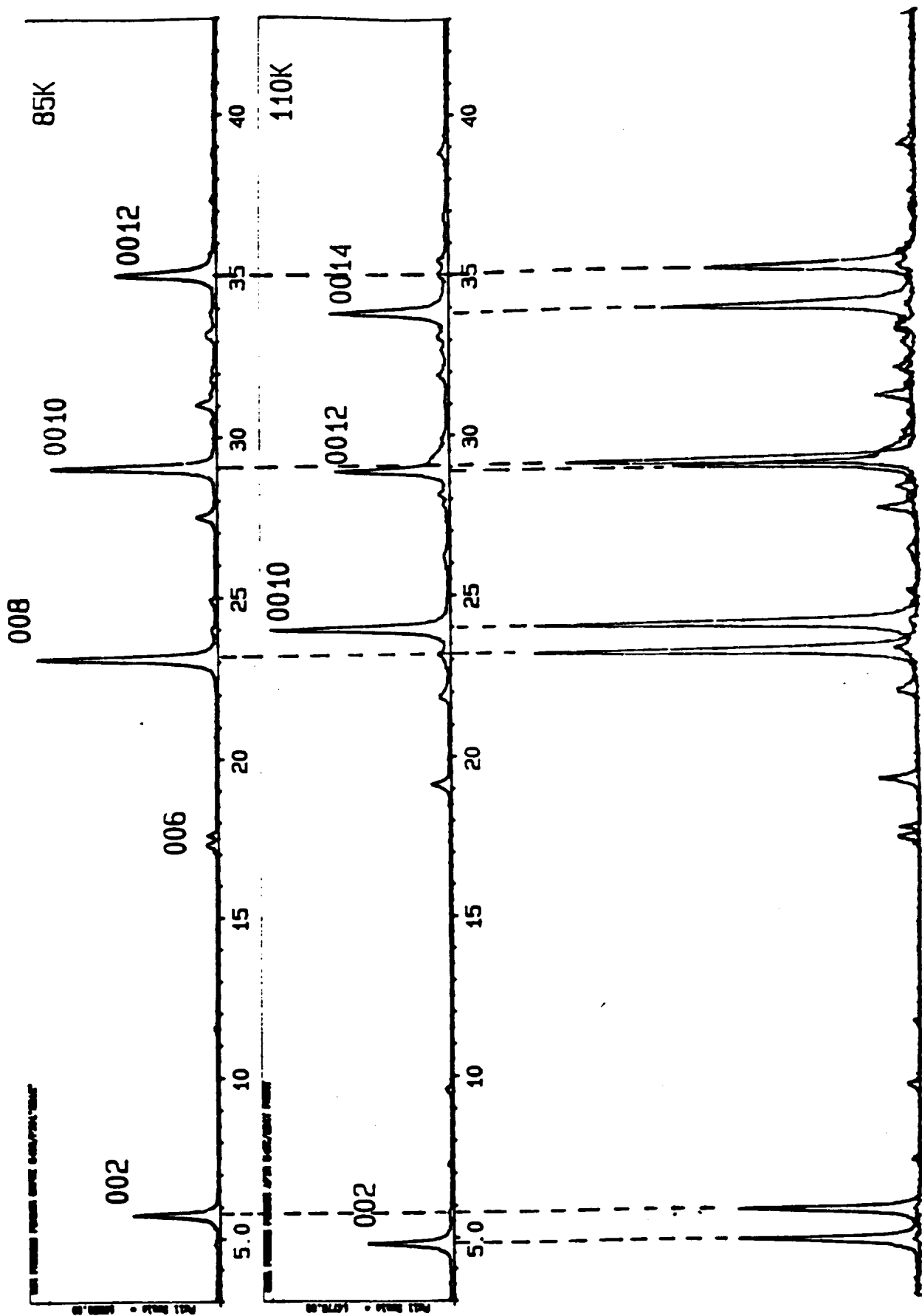


Figure 8

High Temperature Superconductivity Data Acquisition System

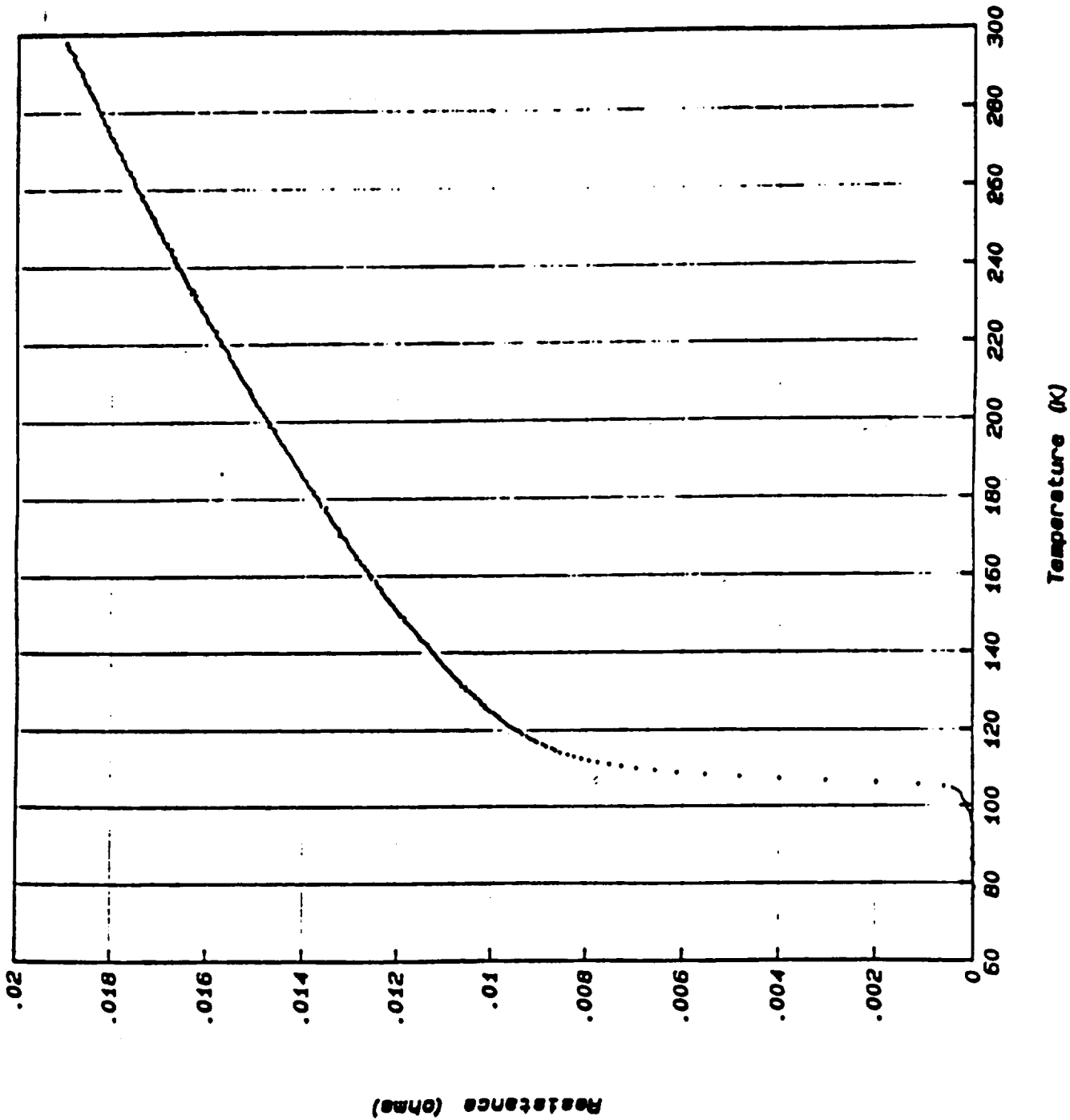
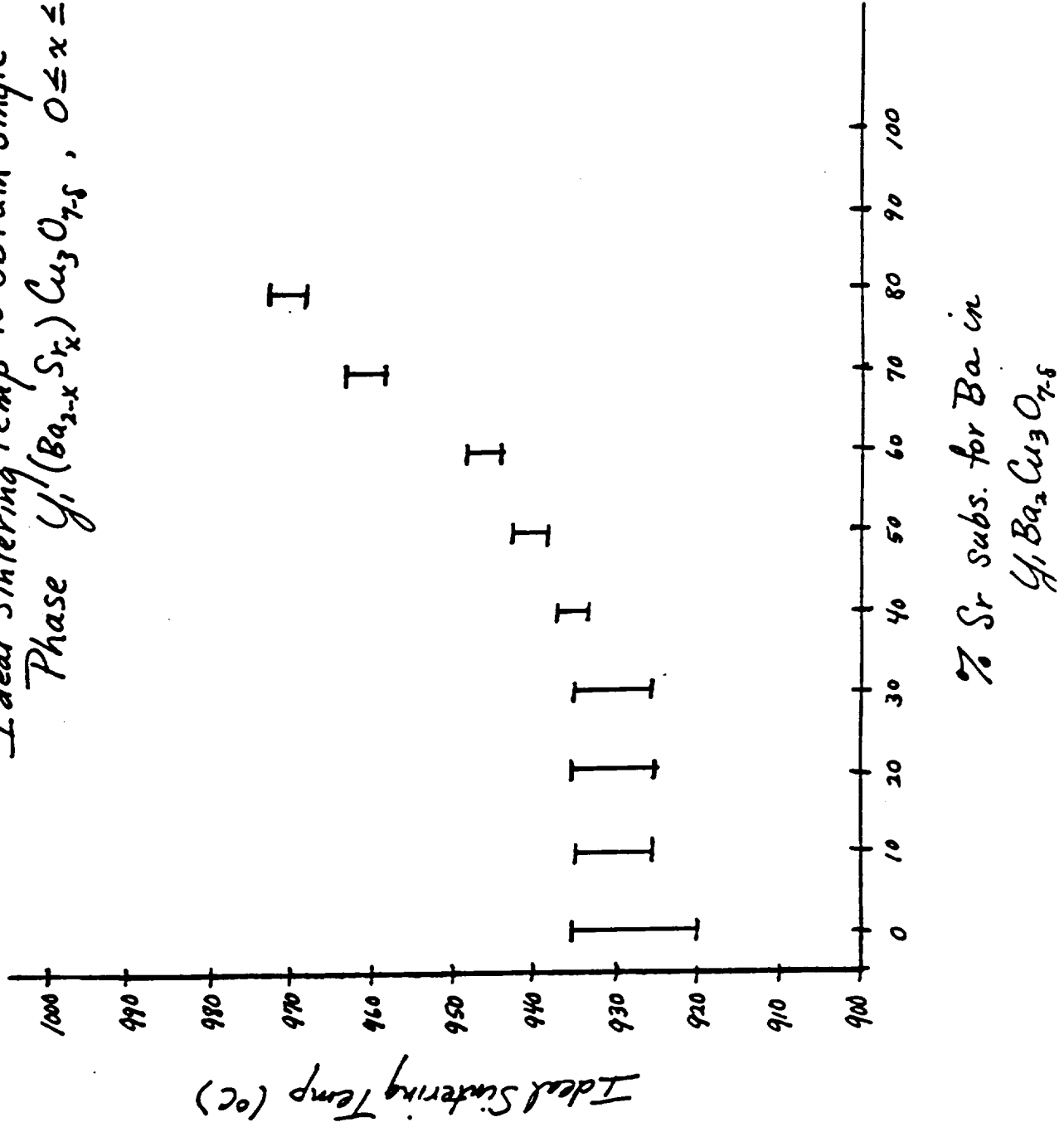
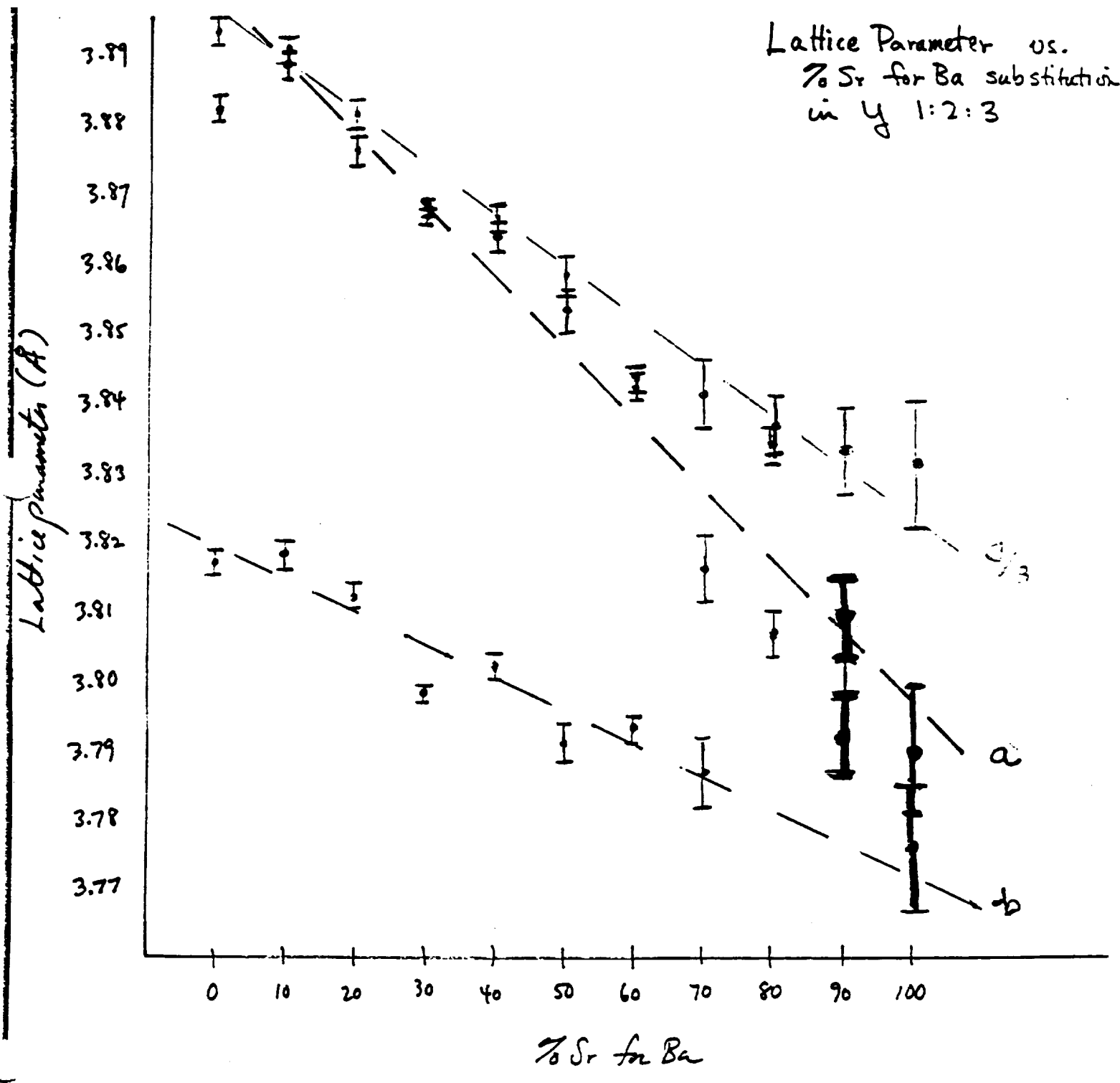


Figure 9

Ideal Sintering Temp to Obtain Single
Phase $Y_1(Ba_{2-x}Sr_x)Cu_3O_{7.5}$, $0 \leq x \leq 1.6$





Superconducting Thin Film Deposition

Objective: To deposit high temperature superconducting thin films utilizing pulsed Laser deposition. This technique, once optimized, will be used to make superconducting quantum interference devices (SQUIDS), and aid in the fabrication of bolometers.

Over the past six months various developmental problems arose that hampered and delayed our efforts to deposit high temperature superconducting thin films using pulsed Laser deposition. Failures in the past few days included a mirror that absorbed too much heat. The resulting over heating led to a breakage of the mirror. However, much effort and time has been devoted to designing, fabricating and assembling components used in the deposition system.

The upper-half of the chamber was setup. Various flanges, turbo pumps, mechanical pumps, and gate valves were attached. Cooling water, electrical and ventilation connections were made. The excimer laser was installed. Personnel from Lambda Physik came on site to evaluate the Laser operations and also to train potential users.

The lower half of the chamber had to be re-designed and some fabrication became necessary. The original design was found to be inappropriate. The ejected material that came from the target did not have a cosine distribution as thought. Rather, the material comes off as a vertical plume.

The optical feed-thru was originally designed to be outside of the chamber. The target material rested on a copper block, at the center of the lower half of the chamber, coupled to a shaft that was at a 45° from the vertical.

In order to accommodate the vertical plume, the optic feed-through was placed inside the lower-half of the chamber. The lens was mounted in a lens holder designed and fabricated on site. The sample holder, with its necessary flanges, was redesigned and mounted from the bottom $3/4$ " off center.

The substrate holder, a component that is housed in the upper half of the chamber, has been designed and was fabricated. This component has to withstand 1000° C in an oxidizing atmosphere. Therefore, AL₂O₃ was found to be too brittle for close tolerances. Boron nitride is now being suggested for use since it will withstand these temperatures in such an environment.

Finally, although all the necessary component are not completed at this time, the effort to show pulsed Laser film deposition will continue. The proper mirror will be ordered soon. Once all these action are completed the desired deposition process should be accomplished.

CONCLUSIONS

As covered in the report new knowledge was gained in the quest to understand and produce new and better superconducting materials. Also considerable progress was made in furthering the technology and capabilities needed to produce thin superconducting films by laser deposition techniques.

All concerned at UAH look forward to continuing to work in these exciting areas in the coming months.

