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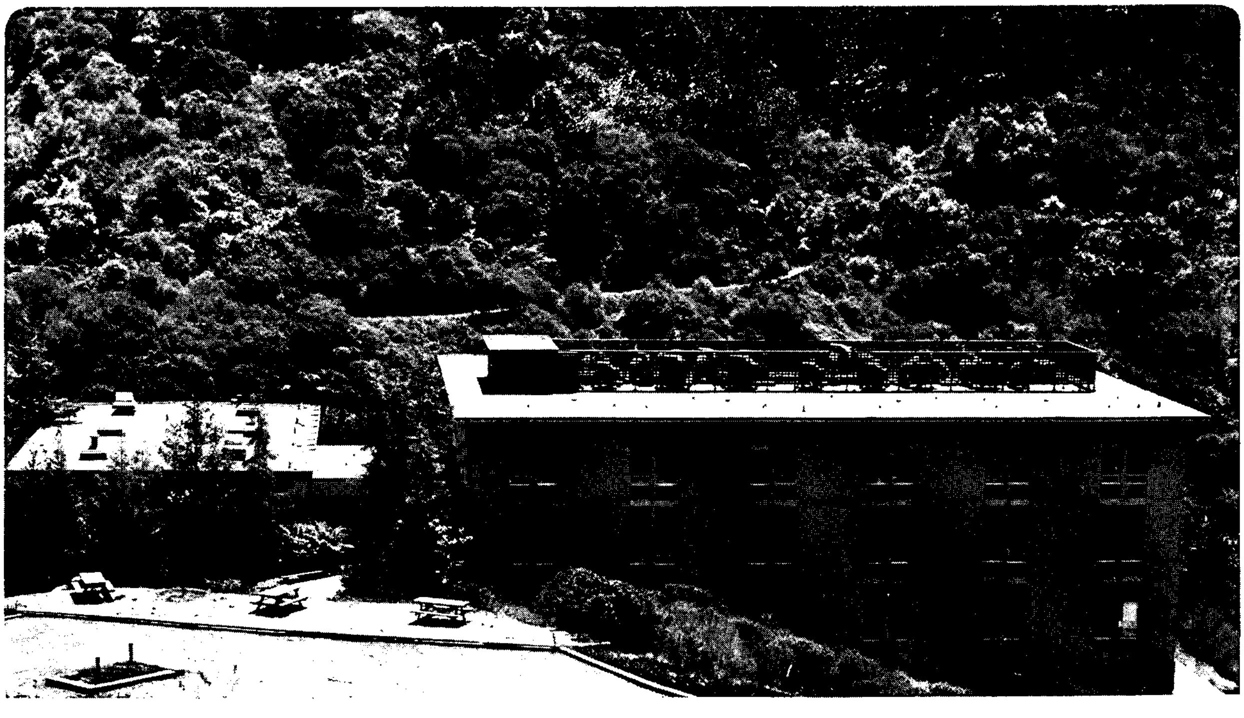

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MASS TRANSPORT AND CHEMICAL DEMIXING OF Y-Ba-Cu-O COMPOUNDS DURING SINTERING IN TEMPERATURE GRADIENTS

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ABSTRACT

A thin cylindrical powder compact (3mm diameter by 20mm) with a nominal composition of $YBa_2Cu_3O_x$ was sintered in a static temperature gradient of 25^oC/mm in air for 12 hours. The temperature at the hot end of the sample was maintained at 940 ± 5^oC. Considerable mass transport and chemical demixing occurred along the length of the sample. The results are consistent with the formation of a liquid phase at the hot end of the sample, transport of the liquid down the temperature gradient and the formation different eutectic compositions along the length of the sample. The implications for processing high T_c superconductors in the system Y-Ba-Cu-O are discussed.

I. INTRODUCTION

High temperature superconductivity at temperatures in the range of $30^{0}K$ was first observed by Bednorz and Muller[1] in the La-Ba-Cu-O compound system. The superconductivity in this system was later confirmed and attributed to a ternary compound with the general formula $La_{2-x}Ba_xCu\ O_4$, which has the tetragonal K_2NiF_4- type structure.[2,3] Subsequently, a variety of closely related compounds exhibiting superconductivity with transition temperatures up to $40^{0}K$ have been reported.[4,5] Superconductivity in the Y-Ba-Cu-O system with a superconducting transition temperature in the range of $90^{0}K$ was first found by Chu,[6] and reported by Hor, et al.[7] and later by several groups of researchers.[8-10] The superconductivity was attributed to the $Y\ Ba_2Cu_3O_{6+\delta}$ phase, with a crystal structure based on a distorted oxygen-deficient perovskite.[10-13]

To date, the method most often used to prepare ceramic superconductors in the Y-Ba-Cu-O system involves the solid state reaction between Y_2O_3, CuO and $BaCO_3$. The limitations of solid state reaction between powder particles for producing phase-pure compositions and for achieving complete reaction are well known. Indeed, earlier researchers[9-13] obtained more than one phase in their attempts to synthesize $YBa_2Cu_3O_{6+\delta}$ by the solid state reaction techniques. The presence of secondary phases can lead to severe problems in the densification of ceramic superconducting powders; these problems include incongruent melting, chemical demixing, transport of matter (especially liquid phases) in temperature gradients, formation of undesirable eutectics, and segregation of phases.

In the present study, compacts of ceramic superconducting powders with a nominal composition of $Y_2Ba_3CuO_{6+\delta}$ were sintered in a temperature gradient of ~25°C/mm, with the hotter end of the sample maintained at 940±5°C. While the primary objective of the research was to stimulate preferential grain growth and grain alignment under the influence of the temperature gradient, a number of very interesting effects relevant to the processing of ceramic superconductors were observed.

II. EXPERIMENTAL

A furnace for providing a relatively steep temperature gradient was constructed by winding a resistance wire (Kanthal, 0.8mm diameter) on a quartz tube (7.5mm internal diameter and 1mm wall thickness) using ~ 4 turns per cm. The coils were more closely spaced near the ends of the furnace (compared to near the center), and a closely fitting, thin Inconel tube was placed inside the quartz tube to maximize the temperature gradient. The furnace was well insulated and power was provided by a variable transformer. The temperature profile of the furnace was calibrated by placing a Chromel-Alumel thermocouple at known distances inside the furnace.

Powders of the ceramic superconducting compound with a nominal composition of $YBa_2Cu_3O_{6+\delta}$ (δ undetermined) were prepared by solid state reaction between Y_2O_3,[*], CuO[+], and $BaCO_3$[#], at 850°C, for 24h. These powders were milled while dispersed in toluene, in a polyethylene container, using high purity zirconia balls[**] as a milling medium. The calcination at 850°C

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[*] Sigma Chemical Co., St. Louis, MO 63178. Y_2O_3: No. Y-3375; purity: 99.999%.

[+] Aldrich Chemical Co., Milwaukee, WI 53231. CuO: 20,313-0 (1317-38-0); purity: 99.999+%.

[#] Noah Chemical, Farmingdale, NY 18229; $BaCO_3$: purity: 99.999%.

[**] Toya Soda, USA, Inc., 1700 Water Place, Suite 204, Atlanta, GA 30339.

produced a very friable powder that was easily ground with a mortar and pestle. X-ray examination of the calcined powder showed it to be single phase $YBa_2Cu_3O_{6+\delta}$ to within the detection limit (~ 1%). The resulting powder (~1μm average particle size) was dried and stored in a vacuum desiccator prior to use. Thin cylindrical powder compacts (~3mm diameter by 20mm) with a relative green density of ~0.65 were prepared by cold isostatic pressing at ~400MPa.

After the temperature in the gradient furnace had reached equilibrium, the sample was quickly inserted and positioned so that the temperature at its hotter end was 940°C; the temperature at the other end of the sample was 350-400°C depending on the exact length of the sample. Typically, the gradient sintering was carried out for ~12h. After removal from the furnace, the cylindrical surface of the sample was ground on silicon carbide paper and then polished using diamond paste and non-aqueous lubricants. Density variations, as manifested by microstructure and phase composition gradients, were evident in scanning electron microscope observations. Phase compositions were obtained by energy dispersive x-ray analysis (EDAX). For the EDAX studies, a spot size of $0.25mm^2$ was used, and data were collected every 0.5mm along the length of the sample.

III. RESULTS AND DISCUSSION

The temperature profile along part of the length of the furnace is shown in Fig. 1. It is seen that the temperature gradient experienced by the sample was 25-30°C/mm.

Figure 2 shows a sample, originally of uniform diameter, after sintering in the temperature gradient for 12h. A length of 5mm was cut off from the cold end of the sintered sample to ensure that it was not too long to be manipulated in the scanning electron microscope. The sintered sample has four distinct regions, denoted A,B,C and D in Fig. 2, along its length. A rather unusual feature is the pronounced ridge that developed at region C. The temperature at the mid-point of the ridge was $\sim 720^{\circ}$C during the sintering.

Differences in color and texture between regions A through D were readily apparent. For example, region A appeared black after polishing, but quickly turned green upon reaction with moisture in the atmosphere. Figures 3(a) through (d) show scanning electron micrographs of regions A through D, respectively. The differences in microstructure are very striking. Region A is extremely porous and contains large holes; region B is less porous and the porosity is also of a smaller scale. In contrast, Fig. 3(c) shows that the ridge of region C is very dense. Finally, region D is fine-grained and the microstructure is not very different from that of the green compact. It is clear from Figs. 3(a) through (d) that a quite pronounced and unusual mass transport has been produced by the temperature gradient.

It is interesting to correlate the density variations of Figs. 3(a) through (d) with the data for phase composition shown in Fig. 4, where the normalized atomic percent of yttrium, barium and copper are plotted as a function of distance from the hot end of the sample. The data of Fig. 4 also seem to fall into four regions corresponding to the four different regions of Fig. 2. Compared to the superconducting $YBa_2Cu_3O_x$ compound, region A is yttrium-rich (and consequently deficient in barium and copper); region B is slightly barium-rich; region C is extremely rich in copper;

while region D has a composition similar to $YBa_2Cu_3O_x$. The differences in phase compositions in the four different regions of the sample are shown in a more striking manner in Fig. 5, where the atomic percentages of barium and copper are plotted relative to that of yttrium. The yttrium-rich region, A, and the copper rich region, C, are very well defined. The compositional path resulting from the decomposition is shown in the ternary diagram, Fig. 6. Initially, in region A, the overall compositon follows the 211-$BaCuO_2$ Alkemade line, indicating eutectic activity in that pseudo-binary. Then, in region B, the compositional path is along a 132-CuO tieline, suggesting a compositional compatibility triangle below about 850 C that is not in the present phase diagrams.[14]

Although it is possible that the unsintered powder (produced by solid state reaction) initially contained small amounts of undesirable phases, it is emphasized that the strong effects described in this study were produced entirely by the relatively steep temperature gradient. A sample of the same size sintered at a uniform temperature of 930°C showed none of the striking variations in density and phase composition observed for the sample sintered in the temperature gradient even on a microscopic scale.

The results suggest that during sintering in the temperature gradient, liquid phases form at the hot end of the sample and travel down the temperature gradient. These liquid phases are copper-rich (and possibly slightly barium- rich) and their passage along the sample causes further chemical reaction and the formation of different eutectic compositions. Most of the mass transported down the temperature gradient is deposited in a narrow region of the sample (region C in Fig. 2). Initially, the chemical potential gradient of the components, caused by the gradient in temperature, can produce the onset of decomposition.[15,16] Chemical reactions and oxygen compositional differences may possibly assist the migration of the liquid phases. In addition, temperature gradient induced interface and surface tension gradients may cause liquid flow (Marangoni effect).

The results of the present work have important consequences for the fabrication of ceramic superconductors, especially in the production of large samples and long wires or fibers that need to be zone-sintered. During heat-up to the sintering temperature, thermal impedance causes the surface of the sample to be generally at a higher temperature than the interior of the sample. In-zone sintering, the samples are fed into the furnace at some rate, with inherent temperature gradients. If the gradient becomes steep enough, then any liquid phases formed in the hotter regions may travel into the cooler regions, thereby producing phases other than the superconducting $YBa_2Cu_3O_{6+\delta}$ phase. The need for phase purity of the unsintered powder is also emphasized if the mass transport and chemical demixing effects are to be minimized.

The superconducting properties of the different regions of the sample sintered in the temperature gradient have not yet been measured. Recent work by Dong, et al.[17] has suggested that the optimum composition for superconductivity is $YBa_{2.3}Cu_{3.3}O_x$. It is interesting to note that this composition corresponds closely to that of region B of the sample sintered in the temperature gradient.

IV. CONCLUSIONS

Thin cylindrical powder compacts of the superconducting compound $YBa_2Cu_3O_{6+\delta}$ (δ undetermined) prepared by solid state reaction and isostatic compaction, showed considerable mass transport and chemical demixing when sintered in a relatively steep temperature gradient of 25-30^{o}C/mm. For a sample sintered in air with one end at 940$\pm$5^{o}C and the other end at 370$\pm$5^{o}C, the data are consistent with the formation of a copper- rich liquid phase at the hotter end, transport of liquid down the gradient, chemical reaction leading to the formation of different eutectic phases, and finally the deposition of copper- rich material in a narrow, dense ridge. The results emphasize the need for improved processing and phase purity of powders used for the fabrication of dense ceramic superconductors.

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FIGURES

Fig. 1. Temperature vs. distance from one end of the gradient furnace. The sample was positioned with one end at x=0, i.e. at a temperature of $370^{o}C$, and the other end at x=20mm, i.e. $940^{o}C$.

Fig. 2. A sample sintered in the gradient furnace in air for 12h using a temperature profile described in Fig. 1.

Fig. 3. Scanning electron micrographs of polished surfaces taken from regions A,B,C, and D of the sintered sample (shown in Fig. 2).

Fig. 4. Normalized atomic percent of yttrium, barium and copper vs. distance from the hotter end of the sample.

Fig. 5. Atomic percentages of barium and copper relative to that of yttrium as a function of distance from the hot end of the sample.

Fig. 6. Compositional path after gradient sintering in BaO, Y_2O_3, CuO ternary diagrams. The letters correspond to the areas A, B, C and D of Fig. 3.

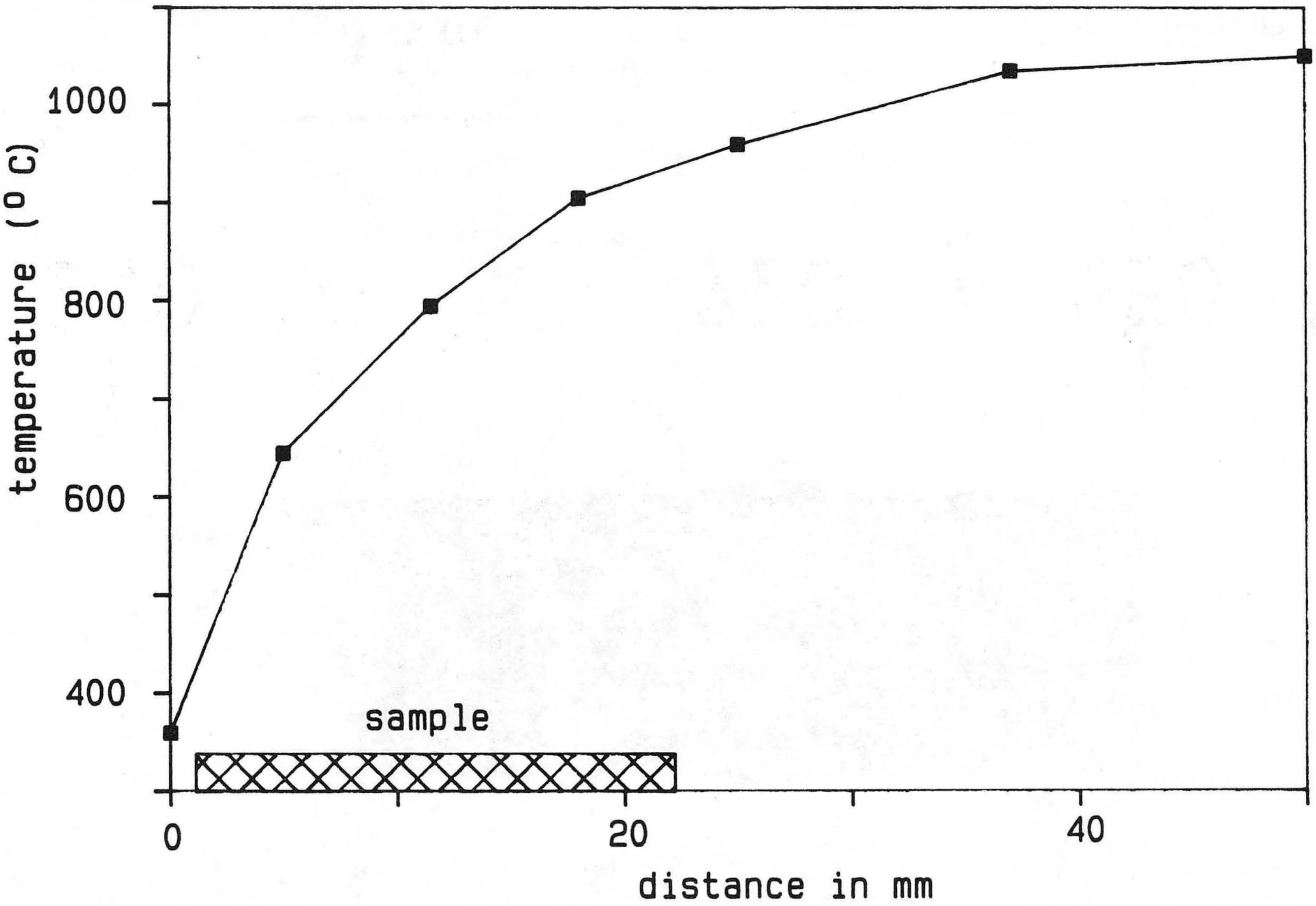

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Fig. 1

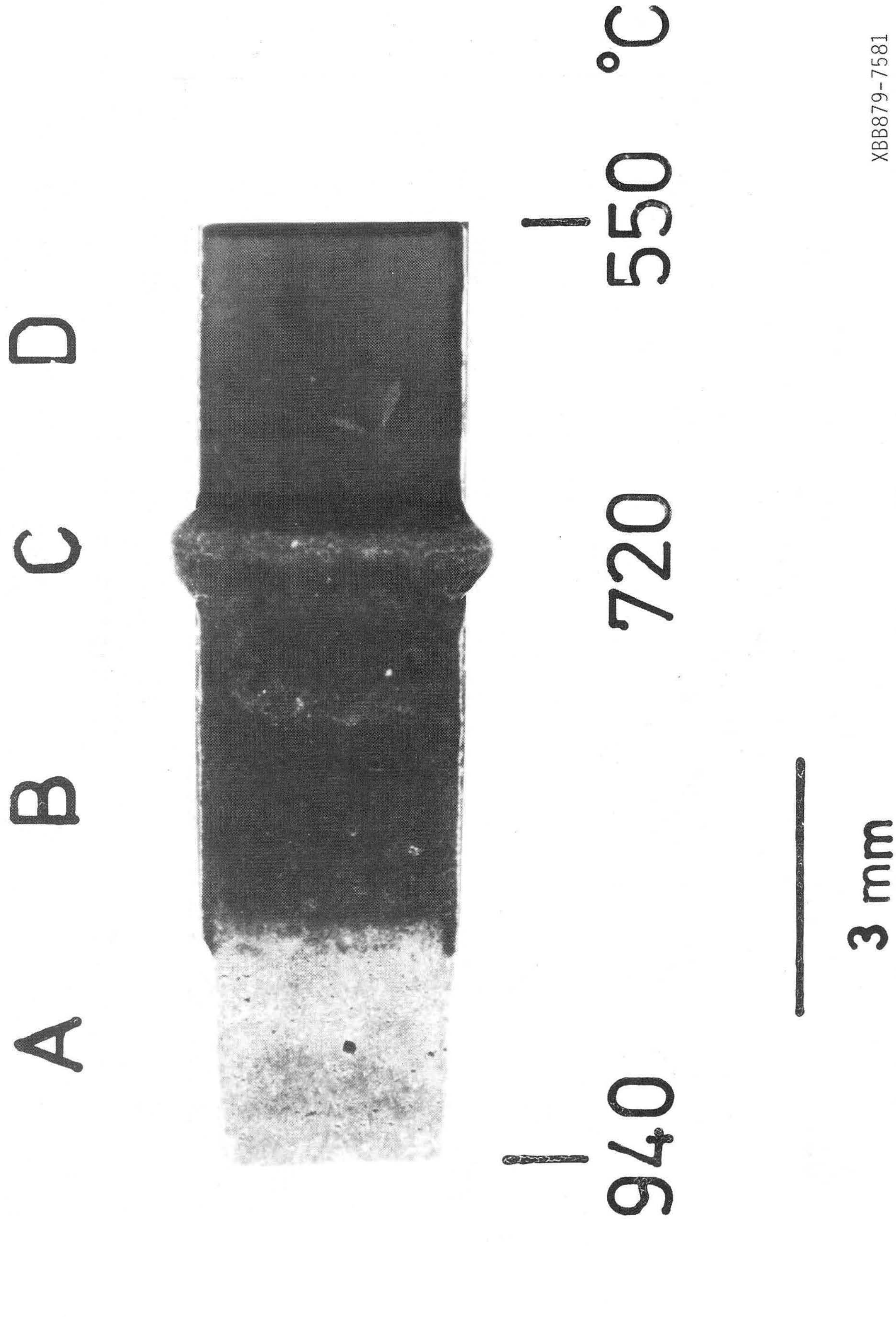

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Fig. 2

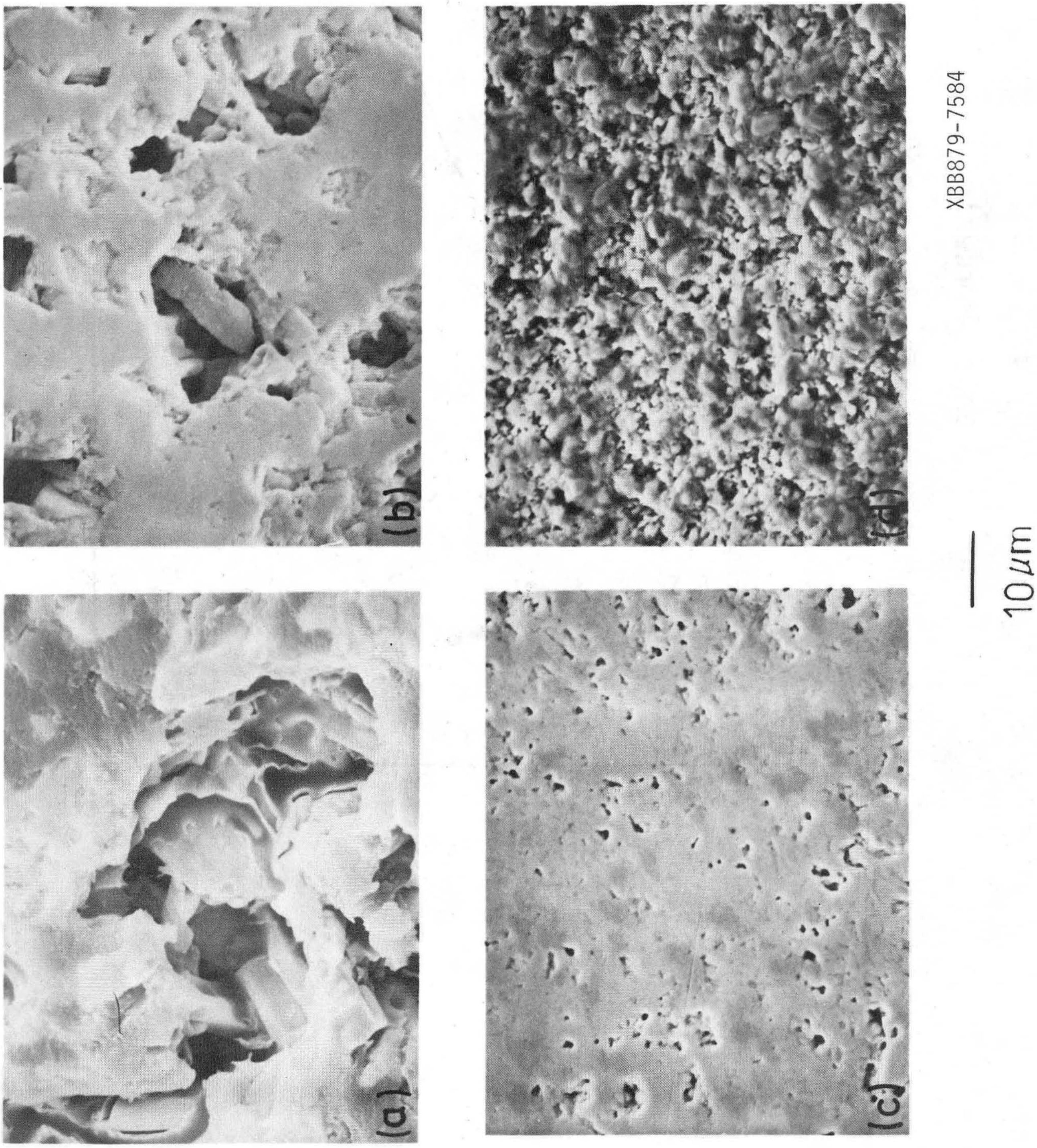

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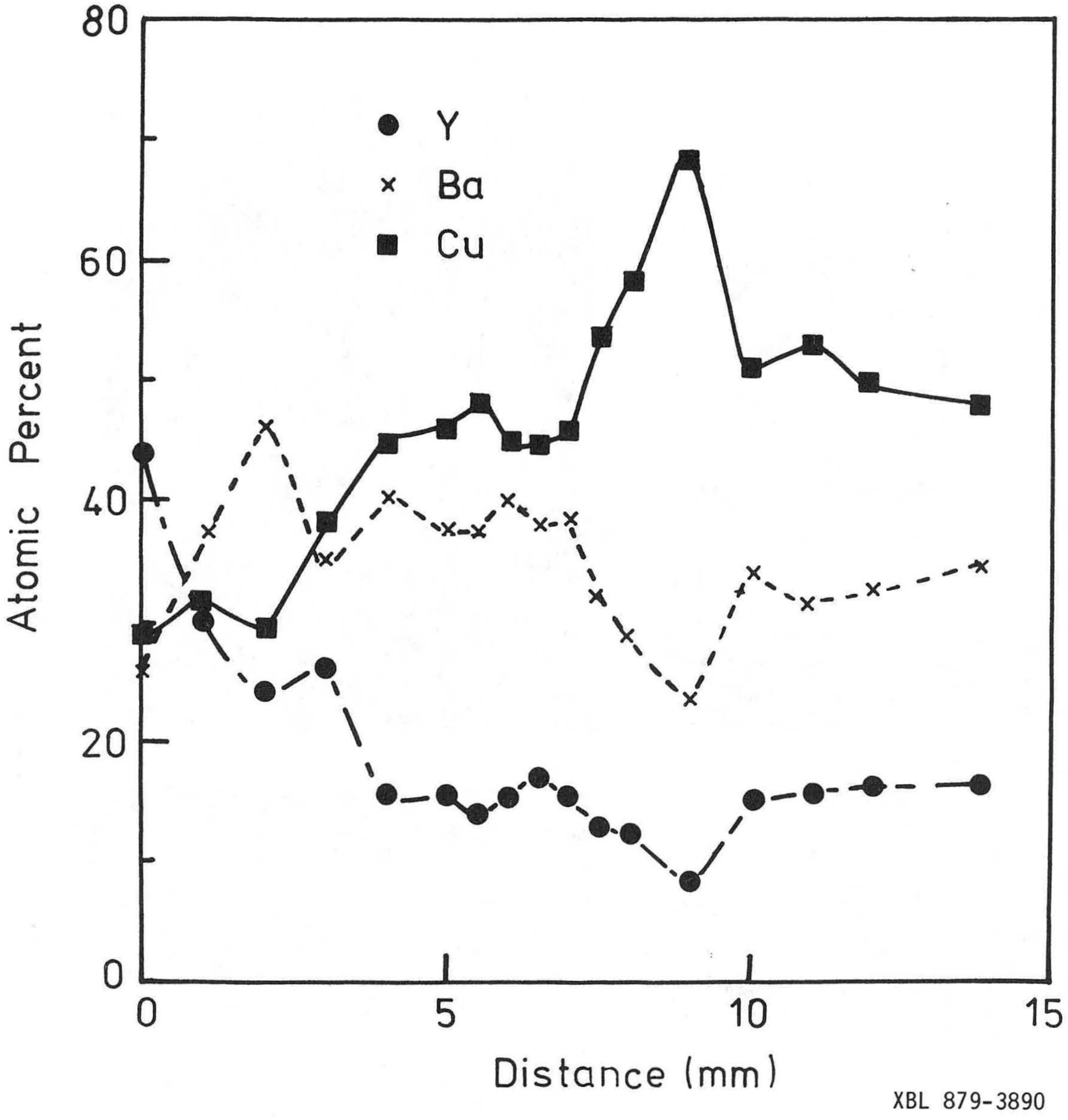
Fig. 3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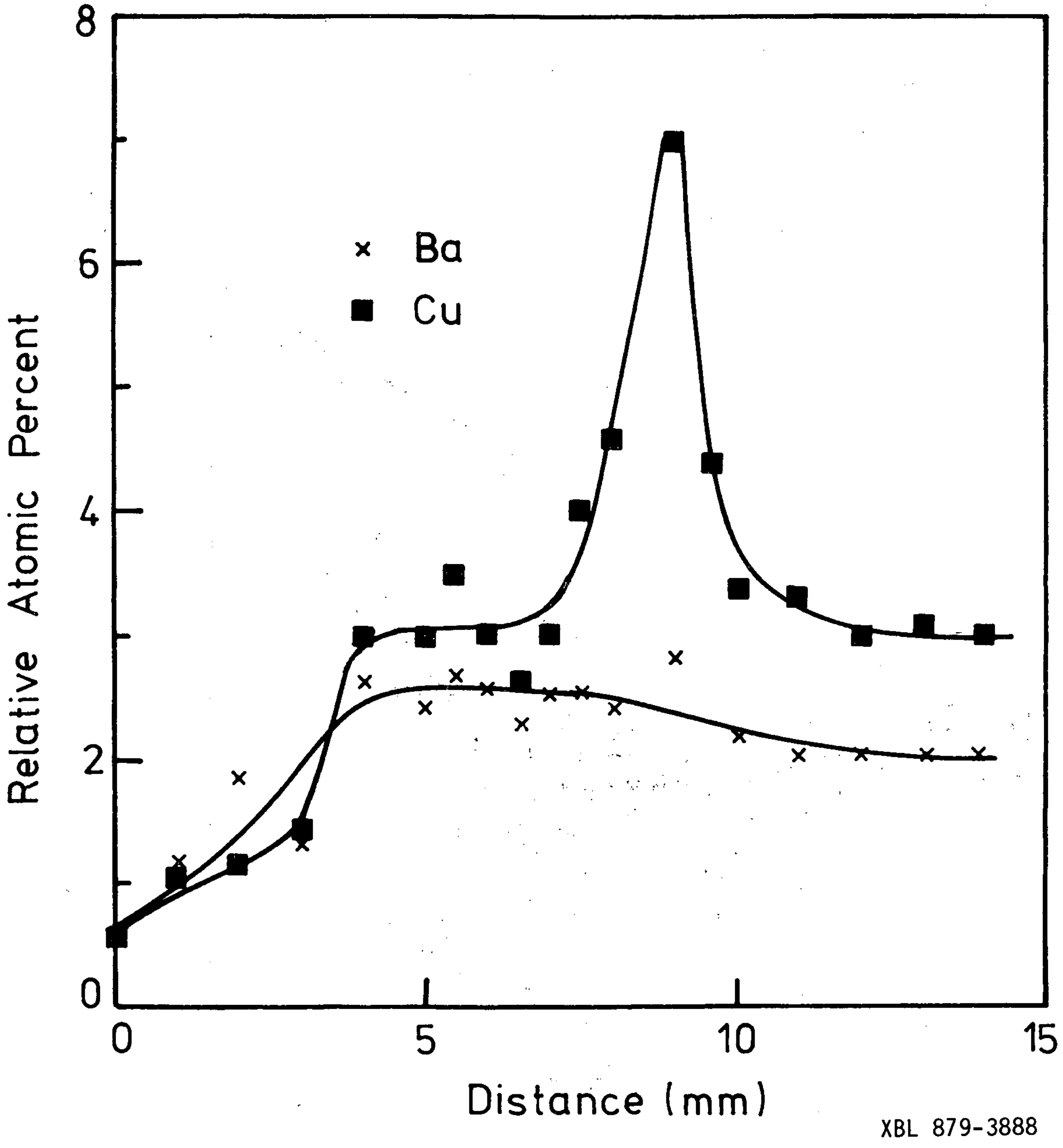
40
20
0
Atomic Percent
0
5
10
15
Distance (mm)
● Y
× Ba
■ Cu
XBL 879-3890

Fig. 4


8
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× Ba
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XBL 879-3888

Fig. 5

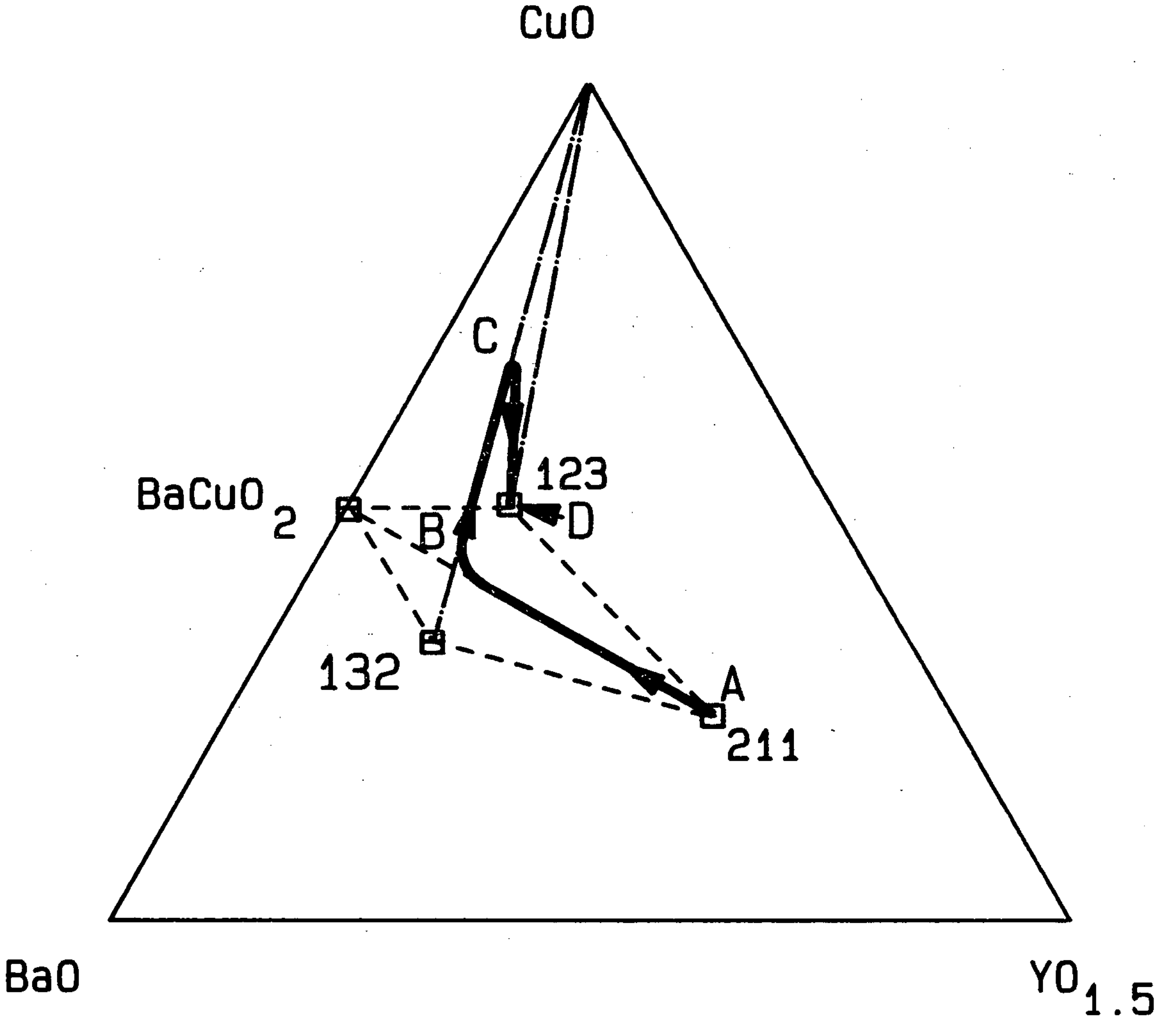

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Fig. 6

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