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Traveling Reaction Zone Method for Preparation of Textured Ceramic Superconductor Thick Films

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Textured thick films of superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) have been prepared on ceramic substrates using a traveling reaction zone method. The technique utilizes the rapid reaction between $Y_2Cu_2O_5$ and $BaCuO_2$ to form YBCO as the film passes through a steep temperature gradient furnace. The films consist of a single, continuous superconducting phase with strong c-axis orientation normal to the translation direction of the film. [Key Words: superconductor, texture, processing, yttrium, barium.]

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Supported thick films of high temperature ceramic superconductors offer an attractive alternative to unsupported wires and tapes for high-current applications. They may also be useful in electronic and microwave devices. The high critical current densities required for these uses can best be achieved by inducement of texture (grain alignment). This not only reduces intergrain resistances but may also limit microcracking which occurs during processing. Development of texture in a randomly-oriented preform requires conditions in which considerable mass transport is possible. This has been achieved over short distances in melt-textured $YBa_2Cu_3O_{7-x}$ (YBCO).[1] The usefulness of this technique in processing continuous conductors is, however, limited by the decomposition which accompanies melting and the rather slow processing rate (about 1 mm/hr). A modified traveling solvent zone process has recently been developed which produces highly oriented YBCO thick films at rates as high as 1 mm/min.[2] Conditions of rapid mass transport can also be present during reaction sintering in a steep temperature gradient. Here we report a traveling reaction zone technique for rapid fabrication of textured YBCO thick films.

Yttrium cuprate and barium cuprate react rapidly near 950 °C to form $YBa_2Cu_3O_{7-x}$:

$$Y_2Cu_2O_5 + 4BaCuO_2 \Rightarrow 2YBa_2Cu_3O_{7-x} \qquad (1)$$

This reaction provides a convenient route to single-phase YBCO that avoids the long processing times and arduous regrinding required by the commonly-used oxide route.[3,4] In addition, since dense YBCO is formed at temperatures well below those required for densification of prereacted

YBCO powder, it is also an ideal reaction for production of textured thick films by steep temperature gradient (STG) reaction sintering.

$Y_2Cu_2O_5$ was prepared by heating an intimate mixture of Y_2O_3 and CuO in air at 980 °C for 20 h. $BaCuO_2$ was prepared by heating a mixture of BaO_2 and CuO in air, first to 450 °C, and then at 50 °C/h to 900 °C where it was held for 2 h and slowly cooled. Both cuprates were shown to be pure by x-ray diffraction. $Y_2Cu_2O_5$ and $BaCuO_2$ were mixed in a 1:4 mole ratio and ball milled in acetone or isopropanol until the average particle size was about 0.5 μm.

To determine the optimum reaction sintering temperature for rapid densification and high phase purity, the reaction was first carried out in the absence of a temperature gradient. Uniaxially pressed pellets of the precursor powder were introduced into an open tube furnace held at 940 °C or 960 °C and then quenched in air after 5, 10, or 20 minutes. The pellets were examined by x-ray diffraction and scanning electron microscopy. At 940 °C, the reaction is complete after 20 minutes (Fig. 1), giving high purity YBCO. Considerable densification and grain growth occur during the first ten minutes at 940 °C, after which grain growth proceeds with little further densification (Fig. 2). The reaction is much more rapid at 960 °C, where nearly complete conversion is observed after 5 minutes (Fig. 3). After 20 minutes at 960 °C, however, there is some $BaCuO_2$ present, perhaps due to partial decomposition of YBCO at this temperature.[5] The sintered density increases much more rapidly at 960 than at 940 °C, reaching 90% after 5 minutes and 95% after 20 minutes (Fig. 4).

The fine precursor powder was mixed with enough iso-amyl alcohol to form a paste. Films 25 to 250 μm thick were applied by the doctor blade method to 1 mm thick alumina plates. The supported films were dried at 100 °C and then passed through a resistively heated steep temperature gradient furnace (maximum gradient 50 °C/mm, maximum temperature 960 °C) to produce coherent textured films of YBCO. A scanning electron micrograph of the film surface (Fig. 5) shows clearly the characteristic morphology of YBCO. The x-ray diffraction pattern taken normal to the film surface (Fig. 6) shows the strong c-axis orientation, as evidenced by the enhanced intensities of reflections with large l-indices. The magnetic susceptibility of the films indicated a broad superconducting transition beginning at about 87K. Due to thermal mismatch between the substrate and the superconductor films, large cracks developed during cooling. These prevented the measurment of transport current densities.

Single crystals of YBCO grown slowly from melts and fluxes are plate-like, with smallest dimension in the c-direction, indicating most rapid growth in the a-b (Cu-O) plane.[6] When molten YBCO is cooled in a temperature gradient, growth occurs in one direction within the Cu-O plane, resulting in needle-like grains[1]. Rapid growth of needle-like grains of YBCO is also observed during the initial stages of reaction sintering, with or without a steep temperature gradient. Densification then takes place as the reaction is completed, with grain growth in both directions in the Cu-O plane. The surface morphology of a partially reacted film is shown in Fig. 7.

The traveling reaction zone technique produces dense, phase-pure thick films of YBCO with c-axis grain alignment perpendicular to the direction of film travel through the steep temperature gradient furnace. Although the films described here were processed using resistive heating, the method is well-suited to the use of a focused lamp or laser beam to supply the steep temperature gradient. An advantage of the reaction processing technique is that the precursor powders, separate or mixed, are more stable in air than the superconductor compound, and can therefore be stored for longer times before use. In addition, they may be prepared with considerably less attention to oxygen partial pressures and heating schedules than for YBCO.

This work was supported by the Electric Power Research Institute and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U. S. Department of Energy under contract No. DE-AC03-76SF00098.

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FIGURE CAPTIONS

Fig. 1. Development of x-ray diffraction pattern of reaction mixture with time at 940 °C.

Fig. 2. Scanning electron micrographs showing reaction, grain growth, and sintering at 940 °C after: (a) 5 min, (b) 10 min, (c) 20 min.

Fig. 3. Development of x-ray diffraction pattern of reaction mixture with time at 960 °C. * indicates $BaCuO_2$.

Fig. 4. Scanning electron micrographs showing reaction, grain growth, and sintering at 960 °C after: (a) 5 min, (b) 20 min.

Fig. 5. Scanning electron micrograph of surface of textured thick film of YBCO.

Fig. 6. X-ray diffraction pattern of textured thick film of YBCO.

Fig. 7. Scanning electron micrograph of surface of incompletely processed thick film of YBCO showing needle-like morphology of initial grain growth.

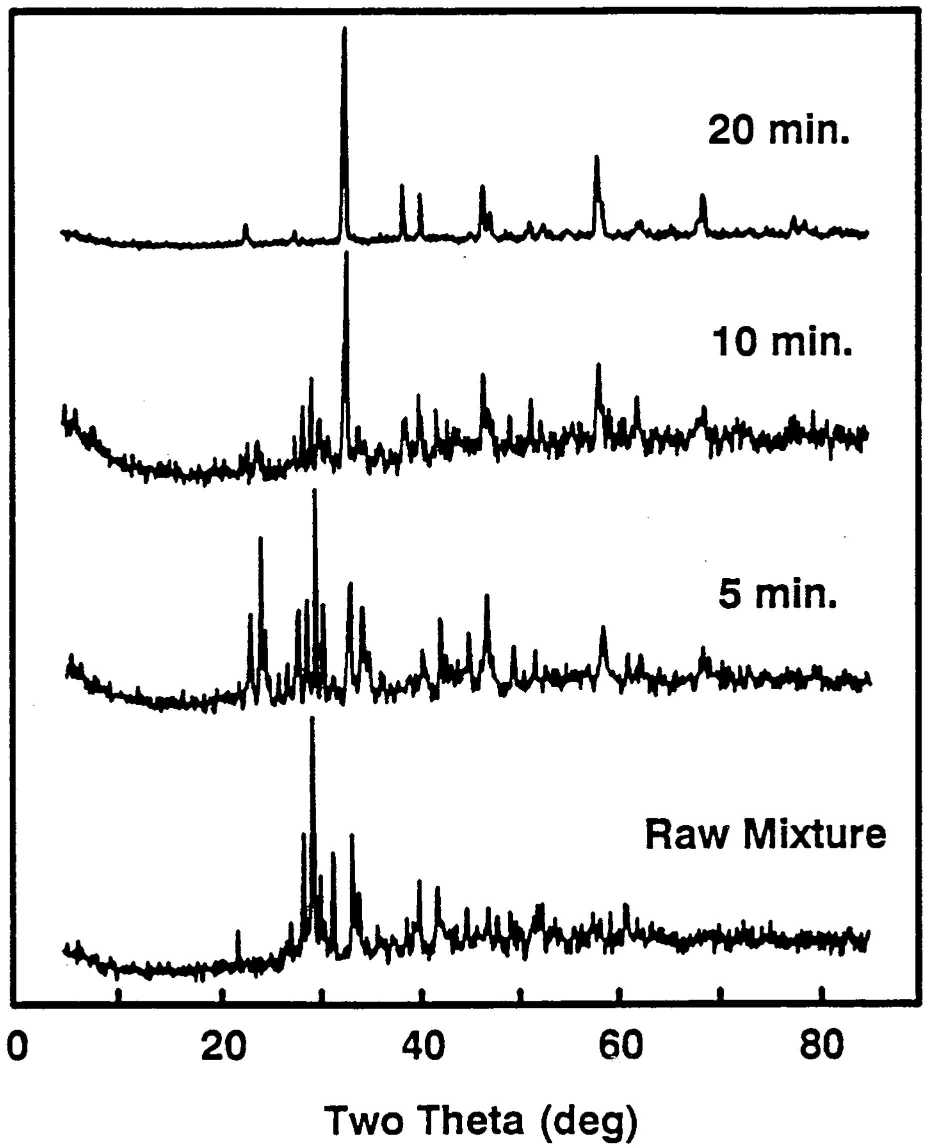

Figure 1

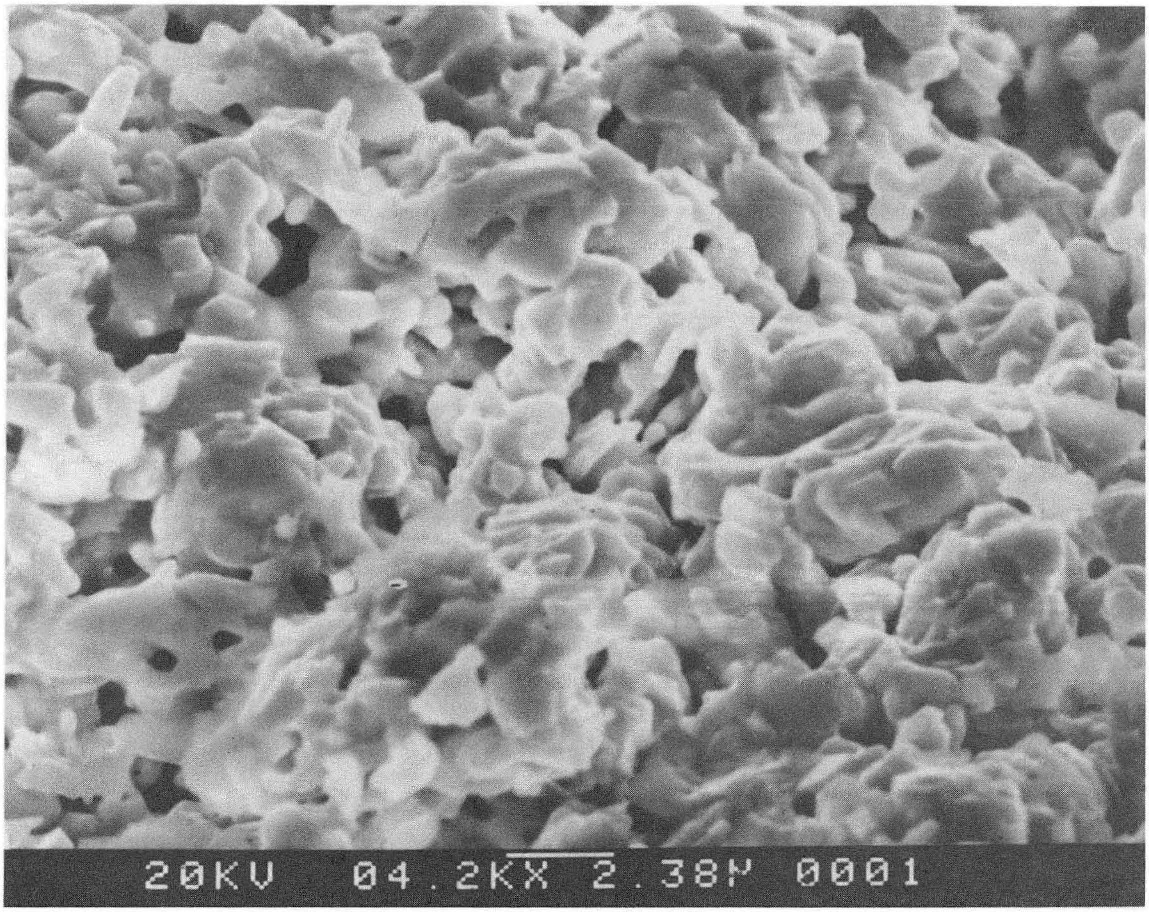

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Figure 2 (a)

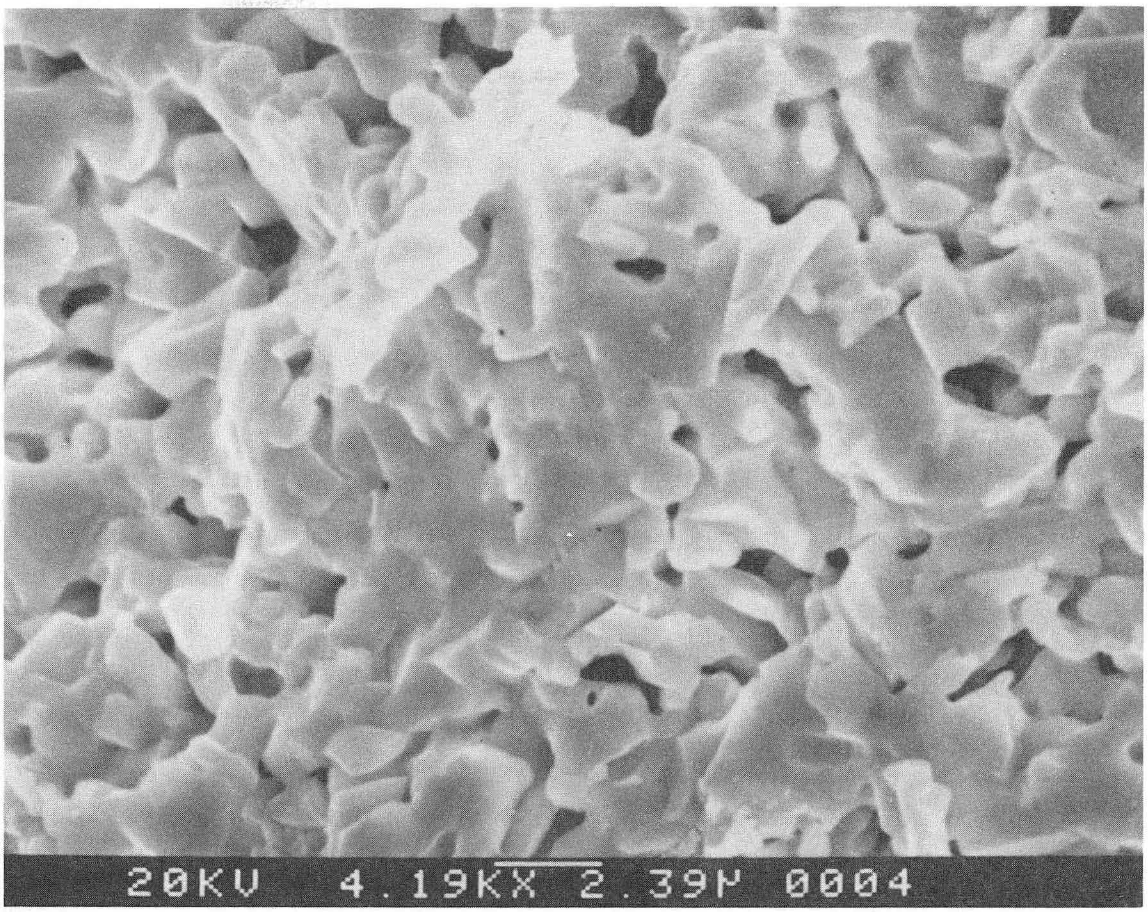

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Figure 2 (b)

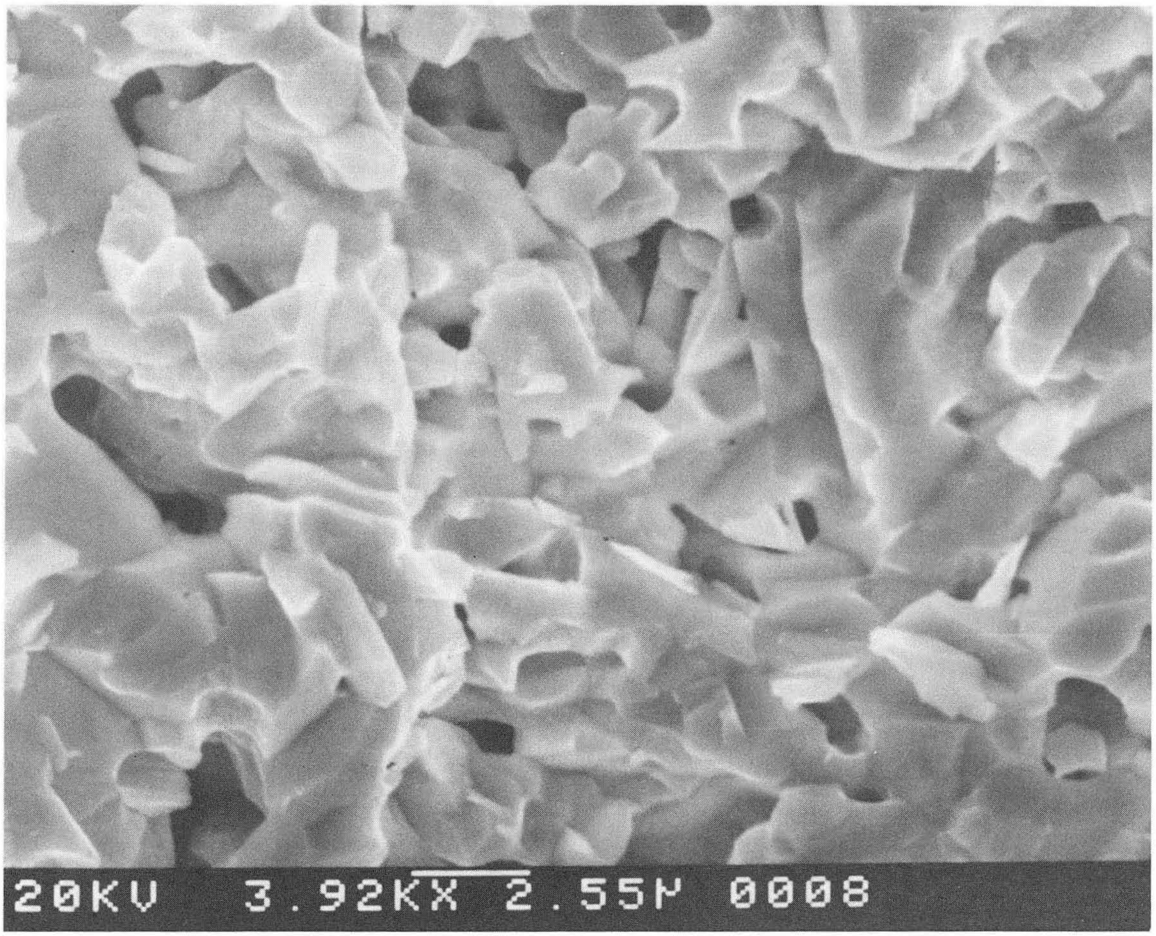

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Figure 2. (c)

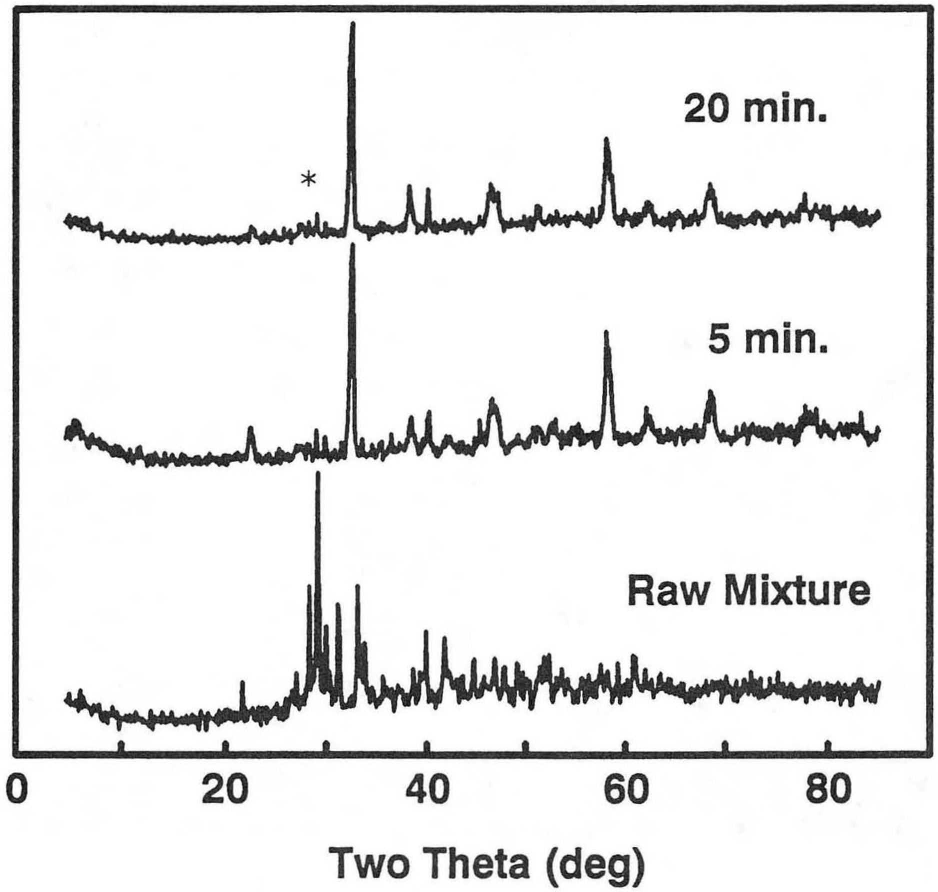

Figure 3

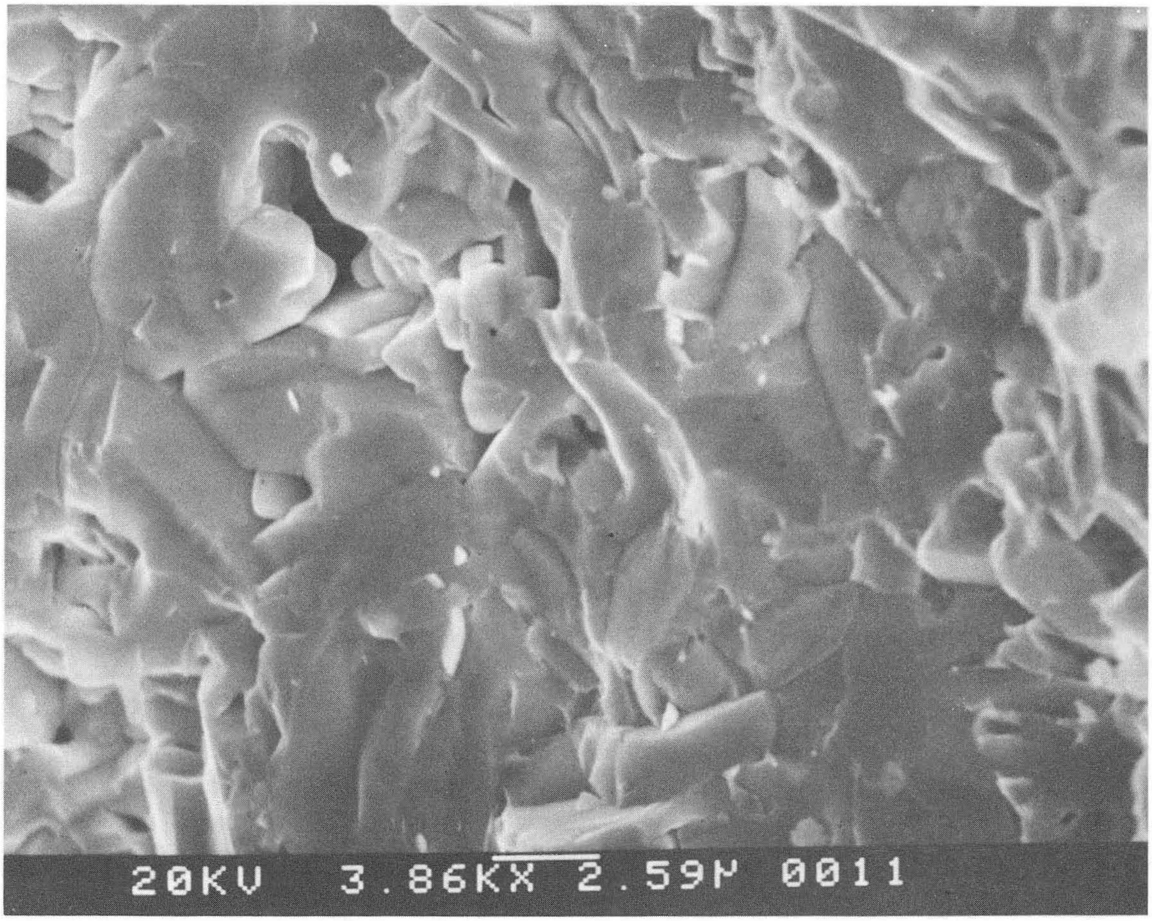

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Figure 4 (a)

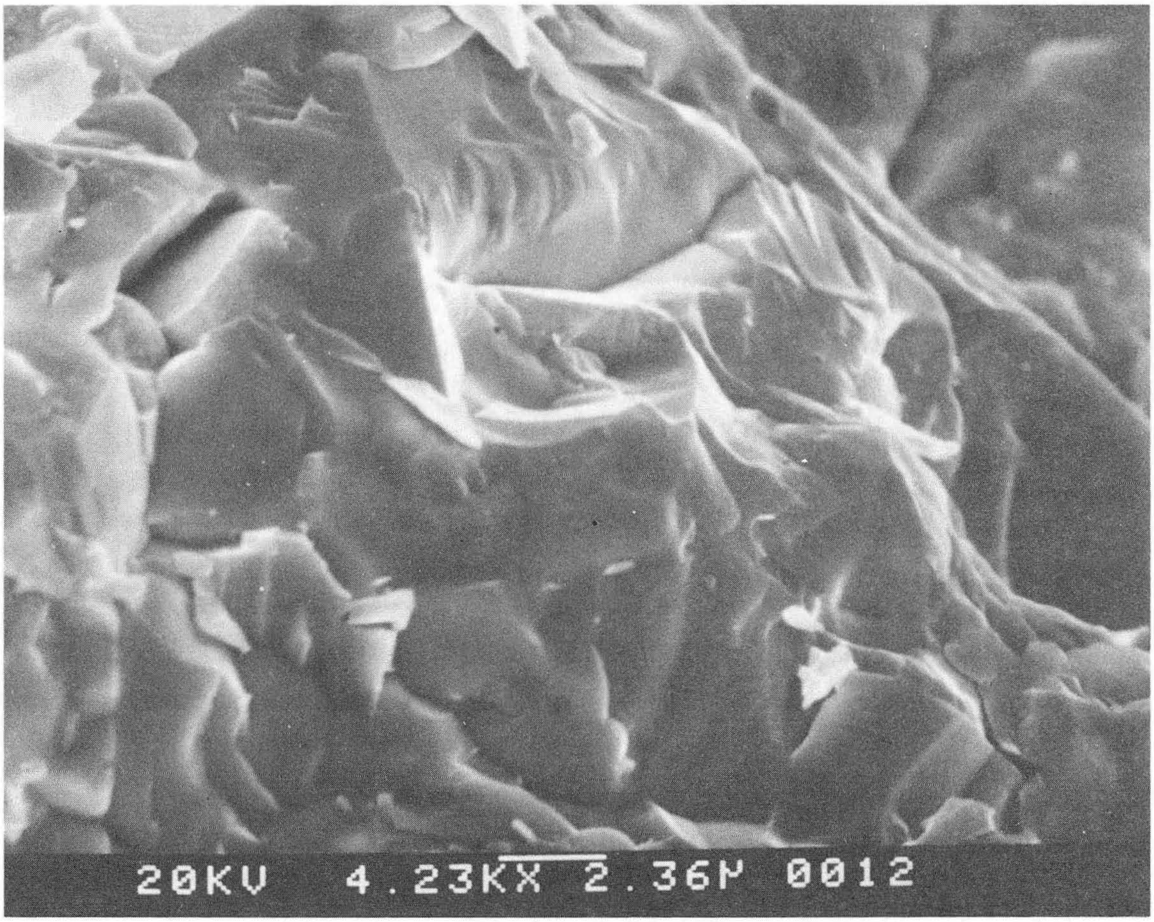

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Figure 4 (b)

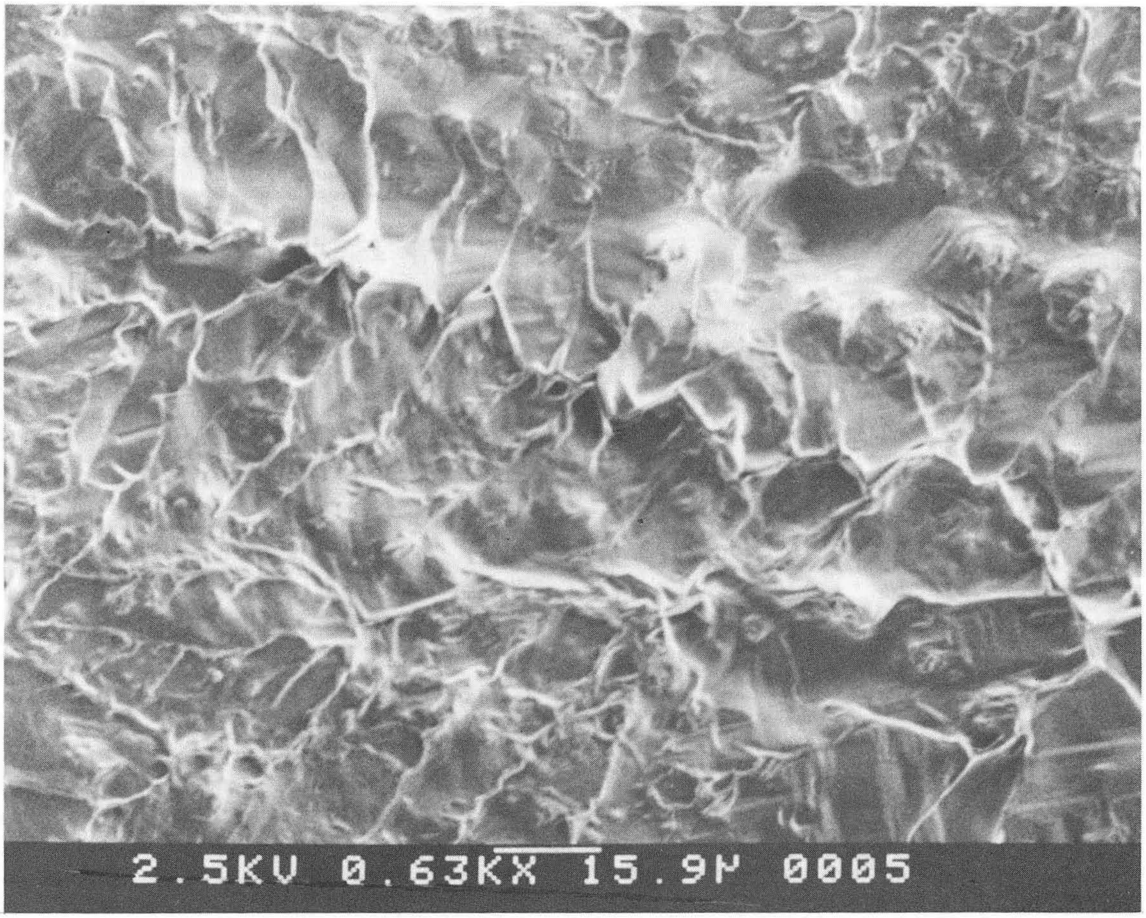

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Figure 5

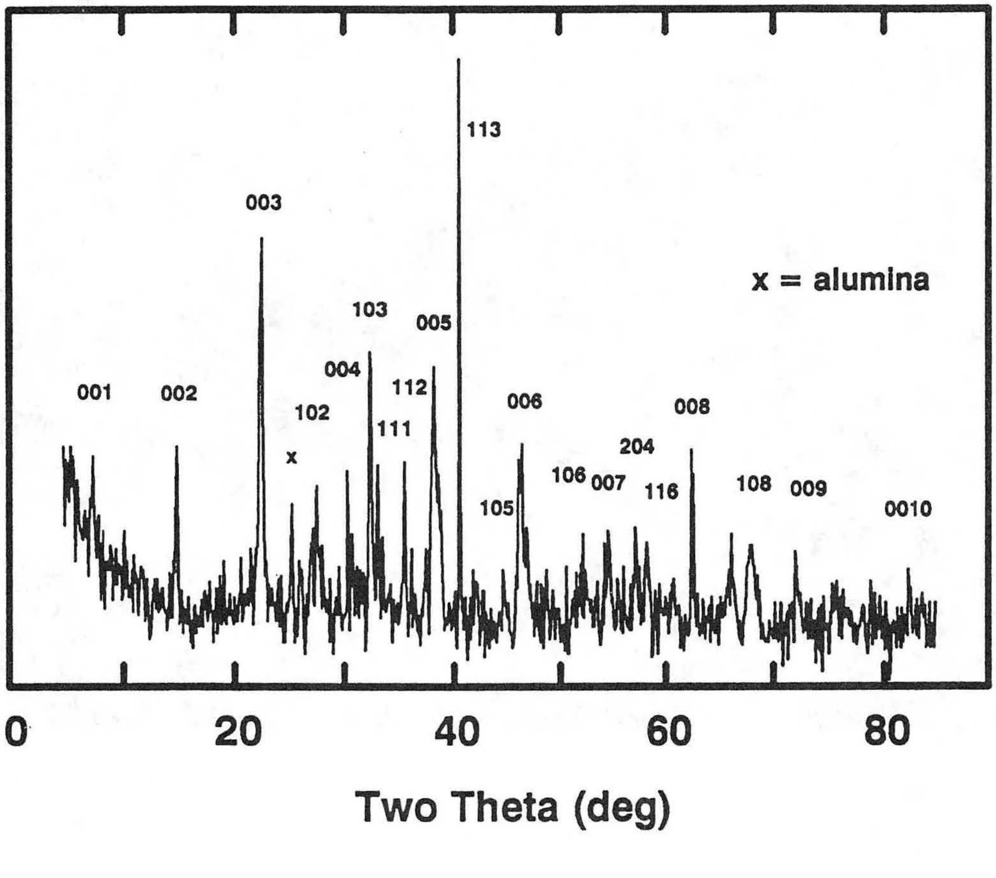
113
003
x = alumina
103
005
004
112
001
002
102
006
008
111
204
x
106
007
116
108
009
105
0010
0
20
40
60
80
Two Theta (deg)

Figure 6

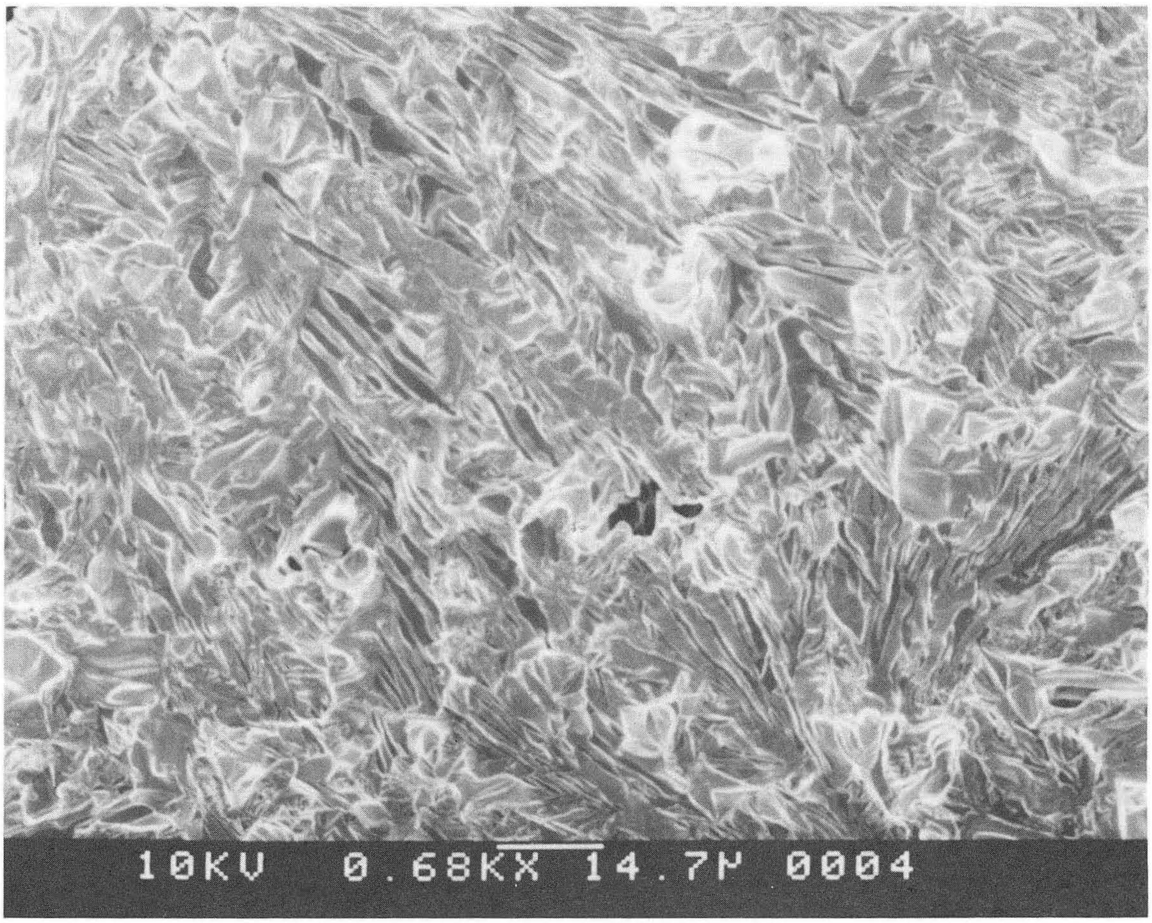

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Figure 7