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A study of textured $YBa_2Cu_3O_{7-x}$ superconductor

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The effect of the starting powders, prepared by different heat treatment processes on the grain-oriented YBCO bulk materials, were studied by X-ray diffraction, scanning electron microscopy and a quantum design SQUID magnetometer. Results suggest that the specimens, which were calcined at 750 °C for 10 h, heated at 950 °C for 24 h, and then sintered at 930 °C for 20 h, were preferentially *c*-axis oriented. The grain-orientation was found to be due to the partial melting of the YBCO compound.

1. Introduction

The discovery of high temperature superconductors has generated the exciting possibility of practical applications of superconductivity at liquid nitrogen temperature [1]. However, the bulk $YBa_2Cu_3O_{7-x}$ (YBCO) superconductor has the characteristics of low critical transport current density (*Jc*) which limits its applications [2–5]. The *Jc* of YBCO bulk superconductor is usually less than that of the single crystal or the simple epitaxial film. Research on YBCO single crystals and epitaxial films showed that the upper and lower critical magnetic fields, *Hc*1 and *Hc*2, were lower with the magnetic field parallel to the *c*-axis rather than perpendicular to it [6, 7], and that the critical current density *Jc* was two orders of magnitude lower when the current flowed along the *c*-axis rather than in the *a–b* plane [8]. It was suggested that the *G–L* coherent length of YBCO along the *c*-axis is shorter than the distance between neighbouring conducting Cu–O layers, the interlayer coupling strength being so low that YBCO behaved electrically like series-connected Josephson tunnelling junctions along the *c*-axis, which limited the supercurrent in that direction [8]. To attain the high-*Jc* goal, one of the most important steps is, apparently, to manufacture grain-oriented YBCO materials in which supercurrents flow in the higher-*Jc a–b* planes.

Grain-oriented bulk polycrystals have been made by a press [9], a press-forging [10] and a melt method [11]. On the other hand, Zugang *et al.* [12] and Huang *et al.* [13] reported that the YBCO superconductor can have a textured structure by the conventional sintering technique. However, the authors did not describe details of the preparation of their samples or the mechanism of formation of the orientation. In this paper the texture structure of the YBCO bulk material was made by the technique below; and the mechanism of the formation of the orientation is also described.

2. Experimental Procedure

The starting YBCO powder was made by oxalate coprecipitation and calcined at 750 °C for 10 h, as previously reported [14]. The calcined powder was then heated at 950, 930 and 900 °C for 20 h and cooled slowly to room temperature in flowing oxygen for samples A, B, and C, respectively. The YBCO powders were pressed into pellets of 10 mm in diameter at 400 MPa. The pellets were sintered at 930 °C for 16 h and annealed at 450 °C for 4 h in oxygen, and then cooled to room temperature in a furnace.

The structures of the sintered YBCO samples were analysed by X-ray diffraction with CuK_α radiation. The melting behaviour of the calcined powder analysed by the conventional DTA curves were obtained in air at a heating rate of $10\,^\circ C\,min^{-1}$. The microstructure was also examined by optical microscopy and a scanning electron microscope (SEM). The magnetization versus applied field was measured in a quantum design SQUID magnetometer.

3. Results and discussion

Fig. 1 show the X-ray diffraction patterns of samples A, B, and C, respectively, which were sintered at 930 °C for 16 h and then annealed at 450 °C for 4 h in oxygen. The X-ray diffraction pattern shows that these samples were of a single orthorhombic structure. This was consistent with the earlier work of Sheen *et al.* [14], who indicated that the orthorhombic phase of the YBCO was formed when the calcination temperature was raised to 810 °C. On the other hand, Fig. 1a shows that sample A, which was heated at 950 °C for 20 h and then sintered at 930 °C for 16 h, was preferentially *c*-axis oriented. This means that many crystals in the pellet were oriented in such a way that their *c*-axis pointed vertically to the pressed surface of the pellet. However, the peak corresponding to (0 1 3), (1 1 0), (1 0 3) reflections of the samples A and B had a maximum intensity (Fig. 1b and c). This shows clearly that the starting YBCO powders which were prepared by different heat treatment processes strongly influenced the grains-oriented on the YBCO bulk materials.

Magnetization as a function of field perpendicular and parallel to the pressed surface of the pellets was

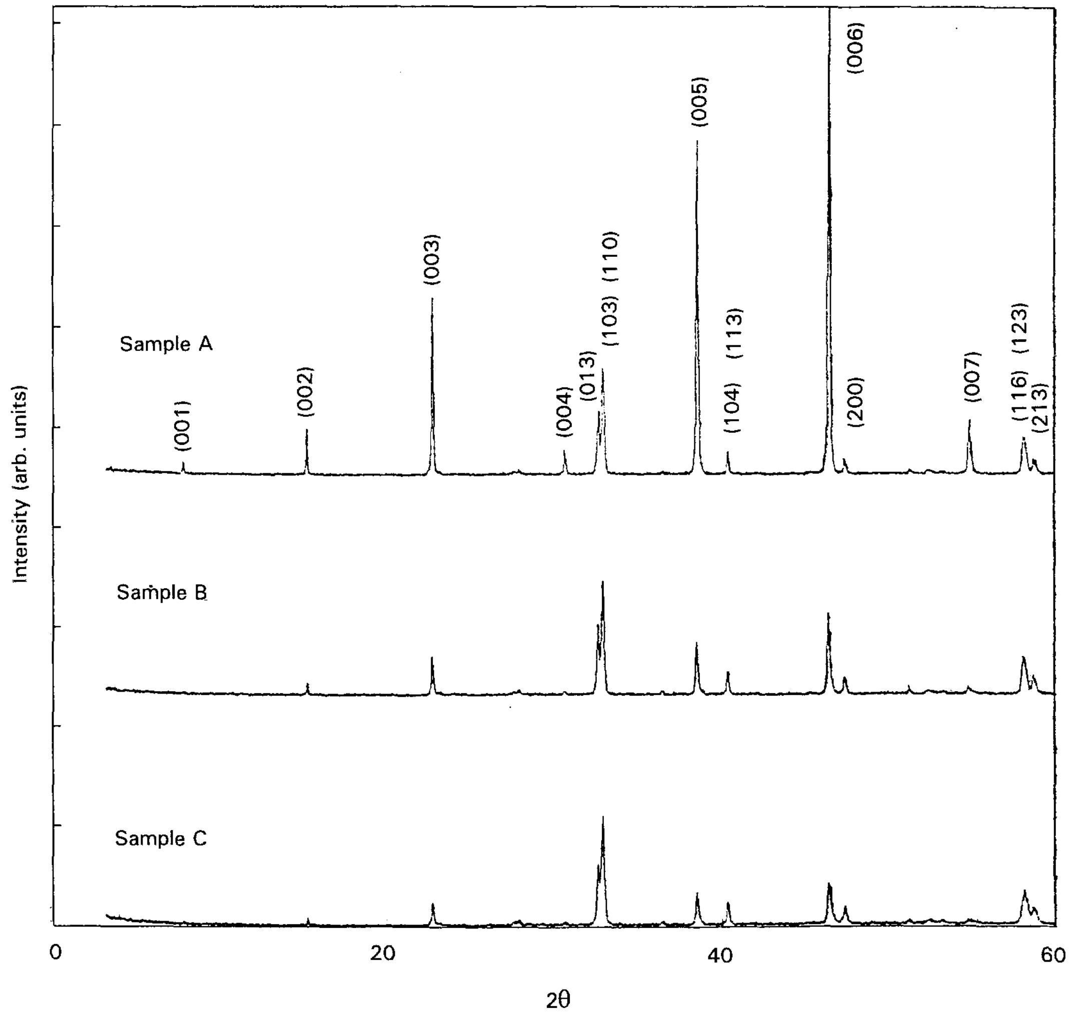

Figure 1 The X-ray diffraction patterns of samples A, B and C, which were sintered at 930 °C for 16 h and then annealed at 450 °C for 4 h in oxygen.

measured by using a quantum design SQUID magnetometer. The results are shown in Fig. 2a and b. The difference between the upper and lower magnetization branches (ΔM) with the field parallel to the pressed surface is smaller than that of the field perpendicular to the pressed surface. ΔM of sample A was larger than that of the samples B and C, supporting the conclusion drawn from the X-ray diffraction that there are more crystals with their *c*-axis vertical to the pressed surface in sample A.

Fig. 3a to c show SEM micrographs of the surface of samples A, B, and C, respectively. Comparison of these micrographs clearly indicate the large plane microstructure on the surface produced by the above processes in sample A; which is not observed in samples B and C. This indicates that the large plane crystals have their *c*-axis vertical to the pressed surface, consistent with the X-ray diffraction pattern and the magnetization curves.

In order to better understand the formation of texture in sample A, the SEM micrograph of the fracture surface was observed, Fig. 4. It is interesting to note that in this pellet the grains were randomly distributed, indicating that the large plane crystals with their *c*-axis oriented existed only on the pressed surface of the pellet. Detailed X-ray studies show that the normalized relative intensity of the (0 0 L) peaks decreased with an increasing distance from the surface in sample A, Fig. 5. This indicates that there was a surface layer $\approx 20\ \mu$m deep with a high degree of orientation of the structure's Cu–O planes perpendicular to the pressing direction. These results are consistent with the observation of the SEM micrograph of the fracture surface (Fig. 4).

According to the results of X-ray, the magnetization curve and SEM, the starting YBCO powders prepared by different heat treatment processes strongly influenced the grain-oriented on the YBCO bulk materials. It is interesting to note that the grains have their *c*-axis vertical to the pressed surface in sample A. According to the work of Sheen *et al.* [14], the X-ray diffraction pattern indicated that the peaks for $BaCO_3$ existed when the calcination temperature was at 750 °C, corresponding to an endothermic peak in the DTA curve resulting from the gamma- to beta-phase transformation of $BaCO_3$ at 826 °C. From the DTA curve of this calcined powder the onset of the partial melting temperature was about 952 °C. It is believed that the calcined powder lowered the partial melting temperature, thus promoting extra liquid formation for sample A (calcined and then heated at 950 °C). It is proposed that the crystals grown from the partial melting YBCO compounds are generally plate-shaped with their *c*-axis perpendicular to the plate plane for much

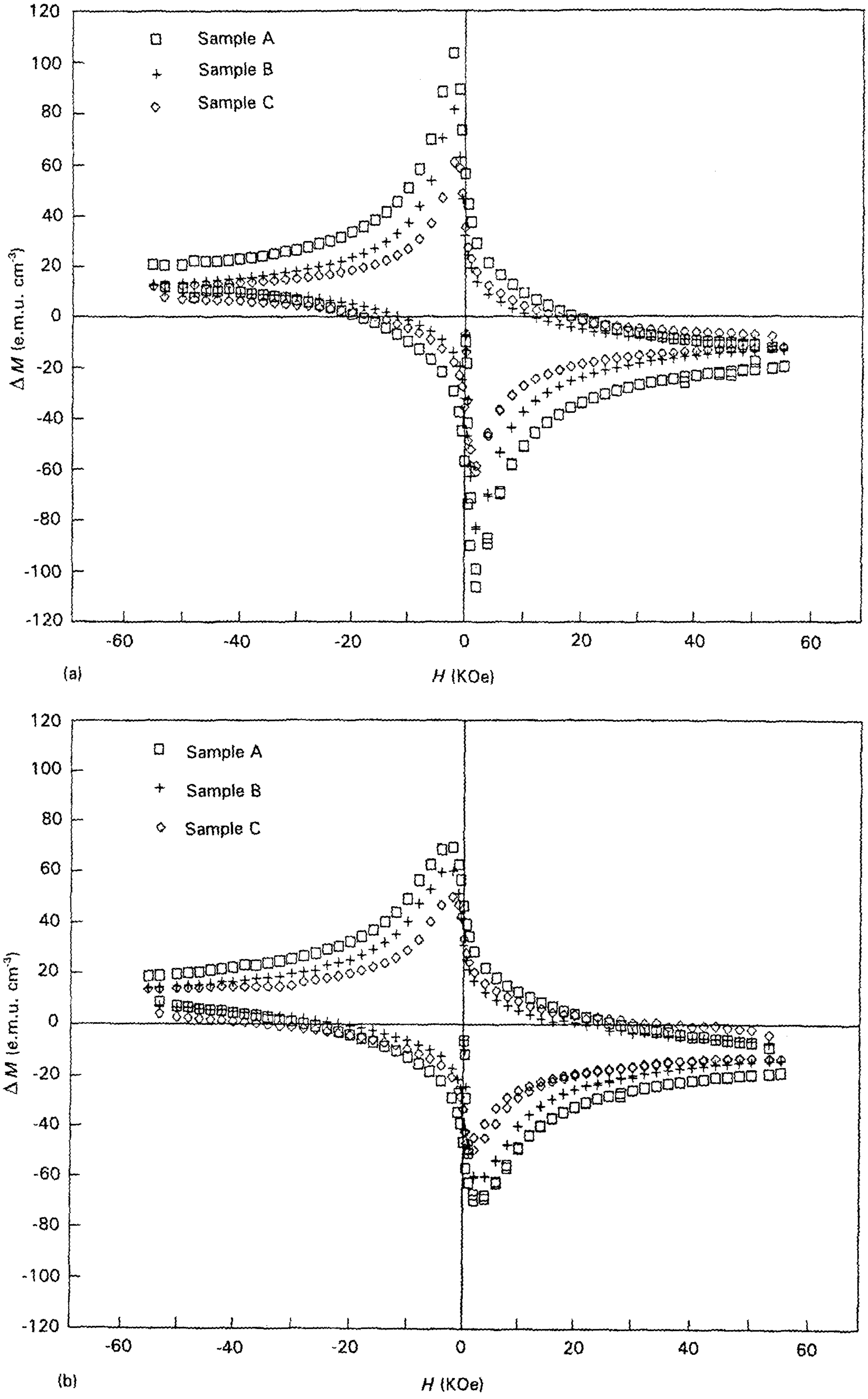

Figure 2 (a) Magnetization as a function of field perpendicular to the pressed surface of samples A, B and C. (b) Magnetization as a function of field parallel to the pressed surface of samples A, B and C.

higher growth rates in the *a* and *b* directions than along the *c*-axis. Upon pressing, the plate-shaped crystals tended to parallel themselves with the surface of punches, i.e. the pellet surface; therefore, the surface of sample A exhibited *c*-axis orientation. This picture can explain qualitatively why the starting YBCO powders which were prepared by different heat treatment processes strongly influenced the grains-oriented on the YBCO bulk materials, and why there is only $\approx 20\ \mu m$ surface layer for sample A exhibiting *c*-axis orientation.

Similar results were also obtained on the starting powder derived from the solid-state reaction technique in this investigation. Texture can be developed

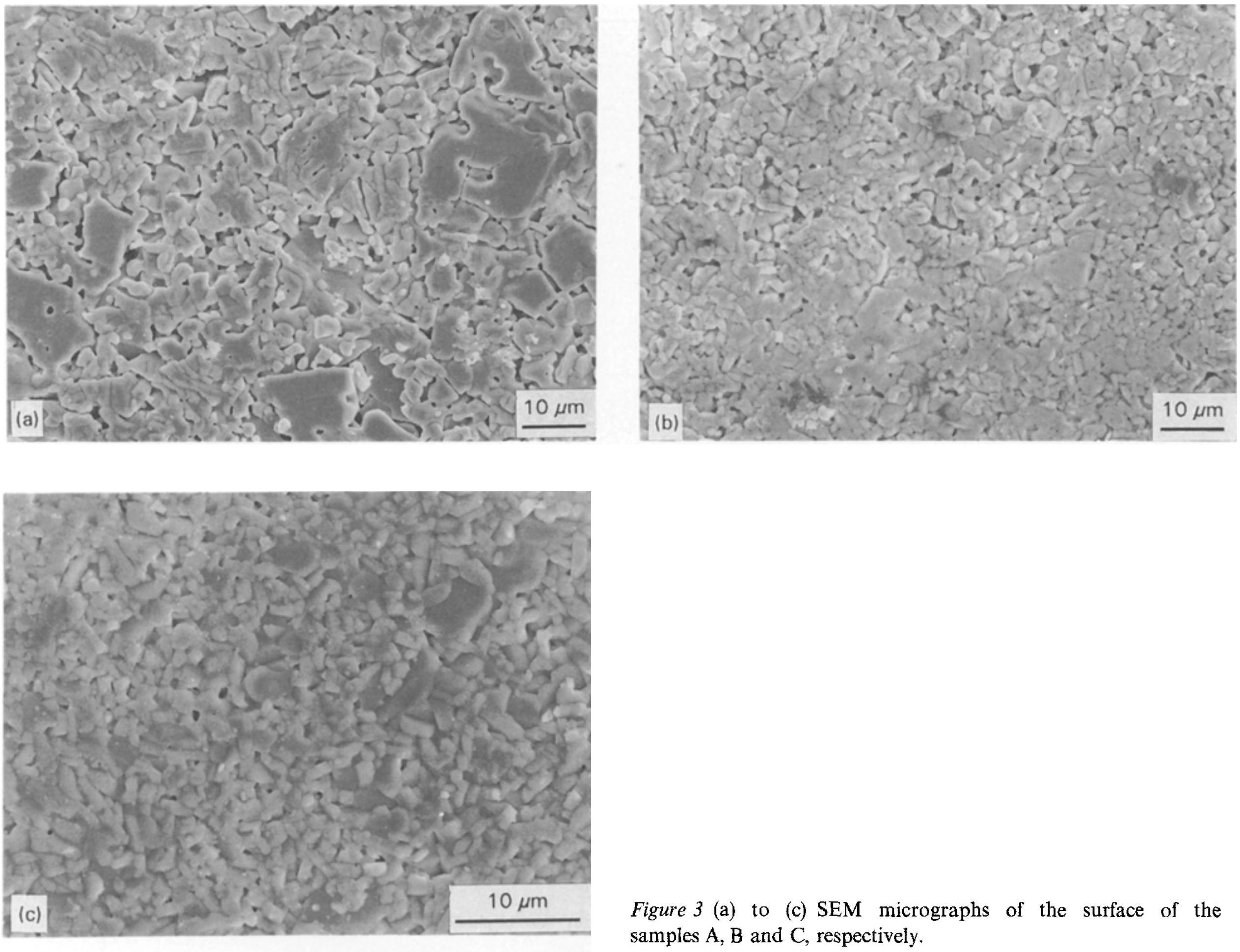

Figure 3 (a) to (c) SEM micrographs of the surface of the samples A, B and C, respectively.

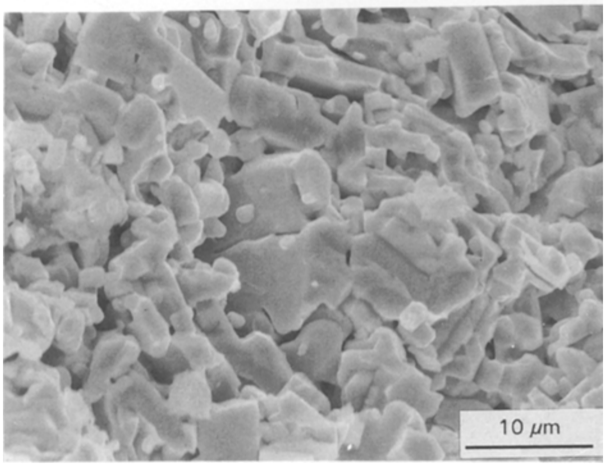

Figure 4 SEM micrograph of fracture section of sample A.

in a pressed YBCO pellet made from solid state powder if the heating temperature is about the partial-melting temperature, which is sufficient to allow the material's inherent growth anisotropy to develop plate-shaped crystals. This confirms our suggestion that the crystals grown from the partial melting YBCO compound are generally plate-shaped with their c-axis perpendicular to the plate plane for much higher growth rates in the a and b directions than along the c-axis.

4. Conclusions

The starting YBCO powders which were prepared by different heat treatment processes strongly influenced the grains-oriented on the YBCO bulk materials. It is believed that in this investigation, the calcined powder lowered the partial melting temperature, thus promoting extra liquid formation for sample A, which was calcined and then heated at 950 °C. The crystals grown from the partial melting YBCO compound were generally plate-shaped with their c-axis perpendicular to the plate plane. Upon pressing, the plate-shaped crystals tended to parallel themselves with the surface of punches, i.e. pellet surfaces; therefore, the surface of sample A exhibited c-axis orientation. In addition, texture can therefore be developed in pressed YBCO pellets made from either the oxalate coprecipitation or the solid state powders, provided that the heating temperature is sufficient to allow the

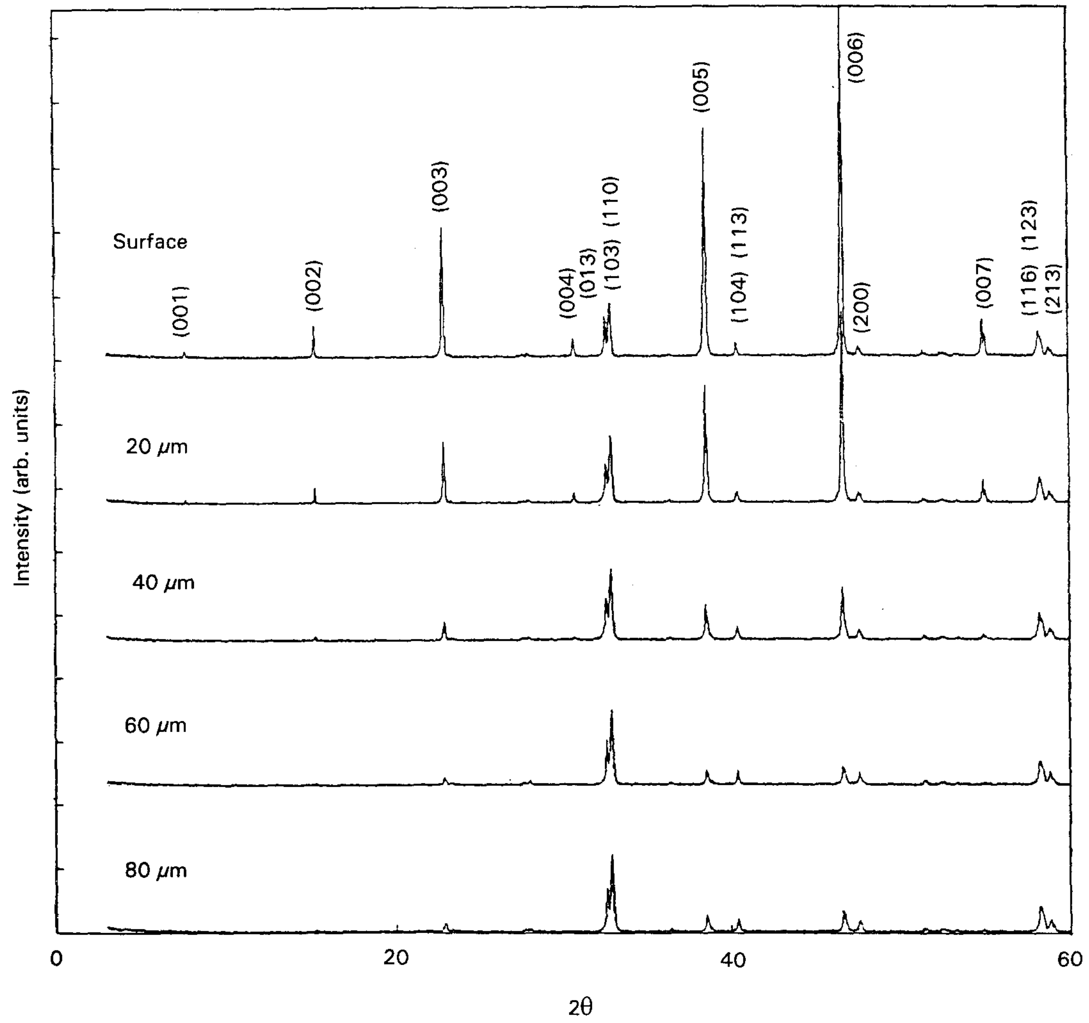

Figure 5 The X-ray diffraction patterns of different distances from the surface of sample A.

material's inherent growth anisotropy to develop the plate-shaped crystals.

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