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M.N. Rahaman, L.C. DeJonghe, S. Shinde, and P.H. Tewari

July 1987

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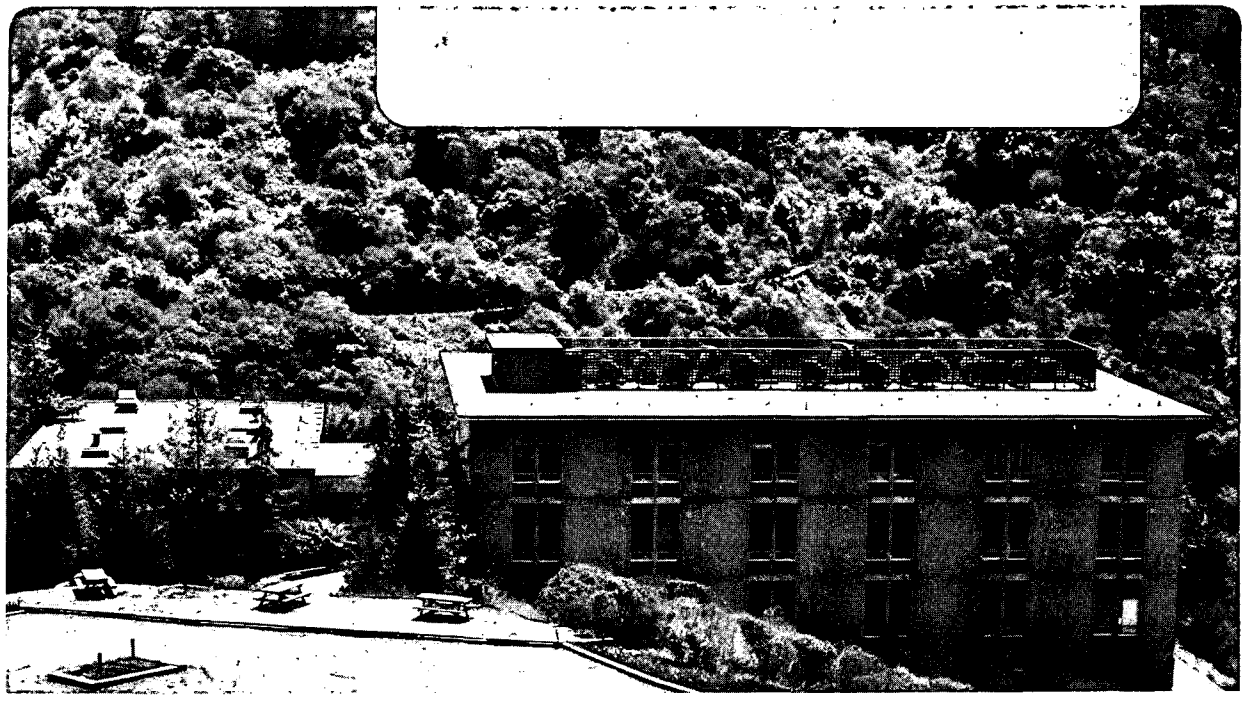

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SINTERING AND MICROSTRUCTURE OF MULLITE AEROGELS

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ABSTRACT

Mullite ($3Al_2O_3 \cdot 2SiO_2$) was prepared by a sol-gel route and dried by supercritical extraction with CO_2. The aerogel (<0.05 of theoretical density of mullite) experienced a shrinkage of up to 0.6 and reached a density of only ~0.5 after 1 hour at 1350°C. Mechanically compacted aerogels, however, sintered to nearly theoretical density below 1200°C. This density is somewhat higher than those of gels prepared by conventional drying (i.e. exposure to the atmosphere) and is considerably better than mullite prepared from mixed powders. Although the x-ray diffraction pattern of the sintered gels was almost identical to that of mullite, transmission electron microscopy and energy-dispersive microanalysis showed two types of grain structure. Elongated grains with an Al/Si atomic ratio corresponding to that of stoichiometric mullite were surrounded by equiaxed grains with a lower Al/Si ratio.

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I. INTRODUCTION

Stoichiometric mullite,[1] ($3Al_2O_3 \cdot 2SiO_2$) is attracting increasing interest for both electronic applications (e.g. substrates) and high temperature structural applications (e.g. engine components, ceramic composites). This interest stems from a number of desirable properties, such as low thermal expansion,[2] low dielectric constant,[2] high creep resistance,[3] and high mechanical strength[4] even at elevated temperatures (>1200°C). Considerable efforts are therefore devoted to the processing and microstructural control of mullite, since these determine the final properties of fabricated material.

Early work on the processing of mullite has been documented briefly by Metcalfe and Sant.[5] The sol-gel route to mullite formation has been the subject of numerous studies since it is capable of providing good mixing of the starting materials and chemical homogeneity of the product (see, e.g. Yoldas,[6] and Zelinski and Uhlmann,[7] for general reviews). Recently Roy and co-workers[8] have described the preparation of both single phase and diphasic mullite gels. Single phase gels were prepared from $Al(NO)_3 \cdot 9H_2O$ and tetraethoxysilane, TEOS, precursors followed by gelling at 60°C. Diphasic gels were prepared in two ways: first using one sol (bohemite) and one solution (TEOS), and second, using two sols (bohemite and silica), followed by gelling at room temperature. The densities achieved by sintering the diphasic gels at 1200°C and 1300°C were higher than those for the single phase gels, and were also much higher than those reported by others[4,9] for mullite powder prepared by more conventional techniques.

Both the hydrolysis-condensation-gelation parameters and the drying conditions affect the gel structure and this, in turn, can affect the thermodynamic driving force for sintering. According to Scherer,[10] the sintering rate, $\dot{\varepsilon}_p$, of amorphous (or glassy) materials can be expressed by an equation of the form

$$\dot{\varepsilon}_p = A\gamma_{sv} n^{1/3}/\eta \qquad (1)$$

where A is a constant, γ_{sv} is the solid-vapor surface energy, n is the number of pores per unit volume, and η is the viscosity of the solid phase. Thus the gel structure affects $\dot{\varepsilon}_p$ through the parameters on the right hand side of Equation (1).

The widely used, conventional method of drying gels involves exposure to the atmosphere (or vacuum) at room temperature (or below ~100°C). Evaporation of liquid and liquid redistribution lead to large capillary stresses,[11] which in turn cause shrinkage (and cracking) and lead to an increase in the effective viscosity of the gel. A less widely used method involves supercritical extraction[12,13] of the liquid in the gel structure. This method eliminates the liquid-vapor interface and prevents the development of capillary stresses. Drying shrinkages are therefore small, and the gel has a relatively low effective viscosity. Thus, from Equation (1), it might be expected that supercritically dried gels would have different sintering characteristics compared with similar gels dried by the conventional method.

In the present study, the sinterability of supercritically dried mullite gels is investigated. The phase composition is studied by x-ray diffraction, and the microstructure of the sintered, dense samples is investigated by scanning electron microscopy, SEM, and transmission electron microscopy, TEM, and energy-dispersive x-ray analysis, EDX. The data are compared with published results for mullite materials prepared by more conventional techniques.

II. EXPERIMENTAL PROCEDURE

Gels of the stoichiometric mullite composition $3Al_2O_3 \cdot 2SiO$ were prepared by a hydrolysis and gelation of aluminum sec-butoxide* and tetraethyl-silicate* (TEOS). A solution of aluminum butoxide (H_2O:butoxide=50:1) was hydrolyzed by refluxing at 86°C for an hour and then peptized by HCl (Butoxide:Acid=1.0:0.1). As the mixture becomes transparent, the required amount of TEOS was added to the mixture. Gelation occurred within minutes. The gelled material was aged, washed and supercritically dried with liquid CO_2 as described previously.[13] The dried gels, in the form of disks (30 mm diameter by 10 mm), were heated at ~150°C for 24 hr. and then stored in a vacuum dessicator prior to sintering.

Sintering experiments were performed using the dried gel discs and pelletized gels formed by compacting the dried gels. The pelletized gels (6 mm diameter by 5 mm) were made by uniaxial pressing in a die at a pressure of 20 MPa to a green density of 44% of the theoretical density. The samples were sintered in air using a programmable furnace. The heating rates were 5°C/min below 800°C and 2.5°C/min above this temperature. The samples were heated for 1 hr at the final sintering temperature of 1350°C. The shrinkage of the dried discs was followed by photography at known temperature intervals, since they were not strong enough to withstand the force of a dilatometer push-rod. The sintering of the compacted gels was monitored using a dilatometer# that allowed continuous monitoring of the axial shrinkage of the samples. In another set of experiments, the heating

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schedule of the compacted gels was modified to include holding times of 1 hr at 1150°C and 1185°C with a final sintering temperature of 1200°C. The densities of the sintered samples were measured using Archimedes' principle.

The phase composition of the dried and sintered gels were determined by x-ray diffraction. Microstructures of the sintered samples were studied by SEM of fracture and polished surfaces, and by TEM. Observations by TEM were accomplished by bright field (BF) techniques on samples prepared by wafering, grinding, and ion milling at an angle of 20°. In order to avoid charging effects during observations, the samples were coated with a thin layer of carbon. Energy dispersive x-ray microanalysis were performed in the TEM using a probe size of ≈40 nm. Relative peak intensities, I_{Al}/I_{Si}, of Al to Si were converted to atomic ratios, Al/Si, according to the Cliff-Lorimer expression.[14]

III. RESULTS AND DISCUSSION

Figure 1 shows the radial shrinkage, $\Delta R/R_o$, of the supercritically dried gel (in the form of a disc) vs. temperature, T (R_o = initial sample radius, $\Delta R = R_o - R$, where R = instantaneous sample radius). The data were obtained by photographing the sample at known temperature intervals; the error in $\Delta R/R_o$ was estimated at ±5%. The $\Delta R/R_o$ values cannot be converted accurately into density data because of appreciable weight loss (~20%) during sintering and the non-uniformity of the sample thickness. However, Fig. 1 shows clearly that almost all densification occurs below ~1250°C, and that the densification rate is highest between 1100 and 1200°C. The density of the dried gel was ~0.04 relative to the theoretical density of stoichiometric mullite (assumed as 3.16 Mgm^{-3}). The sintered gel was very porous; its final density as measured by Archimedes' principle was 0.51.

In Figure 2, the axial shrinkage, $\Delta L/L_o$, of the compacted, dried gel (in the form of a regular cylindrical pellet) is plotted vs. temperature, T (L_o = initial sample length, $\Delta L = L_o - L$, where L = instantaneous sample length). The data were obtained using a dilatometer, and the error in $\Delta L/L_o$ was less than ±2%. The initial density of the sample, calculated from the mass and dimensions was 0.44. The final density measured by Archimedes' principle was in excellent agreement with the value of 0.97 obtained from measurements of the mass and dimensions of the sintered sample. Again, appreciable weight losses (~20%) prevented an accurate determination of the sample density from the shrinkage data. The $\Delta L/L_o$ data, however, provide a good profile of the densification process. It is seen that all densification occurs below ~1200°C and that the densification rate is highest at ~1100-1150°C. The densification profile of the compacted gel appears to be in reasonable agreement with the data of Fig. 1 for the uncompacted gel.

The data of Fig. 2 indicates that with proper control of the heating schedule (and possibly the weight loss), nearly theoretical density might be obtained below 1200°C. This was indeed found to be so experimentally. The supercritically dried gel was further dried by heating for 4 hr at 800°C, compacted, and heated up to 1200°C for 1 hr, using the same heating rate as before but with holding times of 1 hr at 1150°C and at 1185°C. The $\Delta L/L_o$ values plotted as a function of T is shown in Fig. 3. The initial and final densities, obtained from the mass and dimensions of the samples, were 0.46 and 0.99, respectively; this final density was in excellent agreement with the value determined by Archimedes' principle. The weight loss during sintering was reduced to 13%. As a further test of the high final density, the fracture and polished surfaces of the sintered samples were examined in an SEM. The micrographs revealed no porosity (Fig. 4).

The low final density of the samples obtained by sintering the uncompacted gel discs may result from the deleterious effects of differential shrinkage produced by the very large shrinkage strains. These effects are greatly reduced in the compacted gels. The compacted gel density is much higher than the density of the aerogel. The compaction process can be thought of as being quasi-plastic, since the very low density of the aerogel powder permits considerable interparticle accommodation and pore collapse by microfracture in the fragile powder. The elimination of the interparticle pore spaces in the quasi-plastic compaction is likely to be the reason why the compacted aerogels show the considerably enhanced densification characteristics. For the compacted aerogels, the nearly theoretical density achieved using the controlled heating schedule below 1200°C is better than the densities of single-phase and diphasic gels reported by Komarneni et al[8] for similar compositions dried conventionally and sintered up to 1300°C. The final density is also much higher than those reported by others for mullite prepared by various, more conventional techniques.[4,9]

The x-ray diffraction patterns of two samples, denoted A and B, sintered for 1 hr at 1000°C and 1350°C, respectively, are shown in Fig. 5. The reference[16] peak positions for stoichiometric mullite are superimposed on the patterns. Sample A shows poor crystallinity, but there is evidence from the weak, broad peaks at ~45 and ~68 degrees 2θ of the formation of minor crystalline phases. These disappear, or become incorporated into the mullite crystal structure at higher temperatures; except for a small shift in 2θ values of <0.3°, the peak positions for sample B are almost identical to those of the reference. This small difference between the 2θ data and the reference is believed to be due to differences in instrument calibration and sample preparation.

Bright field TEM of a compacted aerogel sample sintered for 1 hr at 1350°C shows essentially two types of grain structure, Fig. 6(a). Large elongated grains are seen to be surrounded by small, nearly equiaxed grains. By TEM-EDX analysis it is possible to distinguish between the two types of grain composition, as is shown in Fig. 6(b). The large elongated grains are found to have a composition of $3Al_2O_3 \cdot 2SiO_2$; the small equiaxed grains are deficient in Al_2O_3 and have a composition of $Al_2O_3 \cdot 2SiO_2$. The bright field technique revealed no glassy phases in the grain boundaries or grain junctions. The two types of grain morphology (and grain composition) would indicate complex phase reactions and crystallization phenomena during sintering, as reported by Pask[17] for the $Al_2O_3 \cdot SiO_2$ system. At the present time, it is not known how these would affect the sintering characteristics of the mullite material used in this study.

IV. CONCLUSIONS

Stoichiometric mullite prepared by the sol-gel route, then dried by supercritical extraction of CO_2 and compacted into pellets can be sintered to nearly theoretical density below 1200°C. This density is higher than those reported for gels prepared by a similar route and dried conventionally (e.g. exposure to the atmosphere), and for mullite powder prepared by more conventional techniques. The microstructure of the sintered gels as observed by TEM-EDX analysis shows essentially two types of grain morphology: large, elongated, stoichiometric mullite grains surrounded by small, nearly equiaxed, Al_2O_3-deficient grains.

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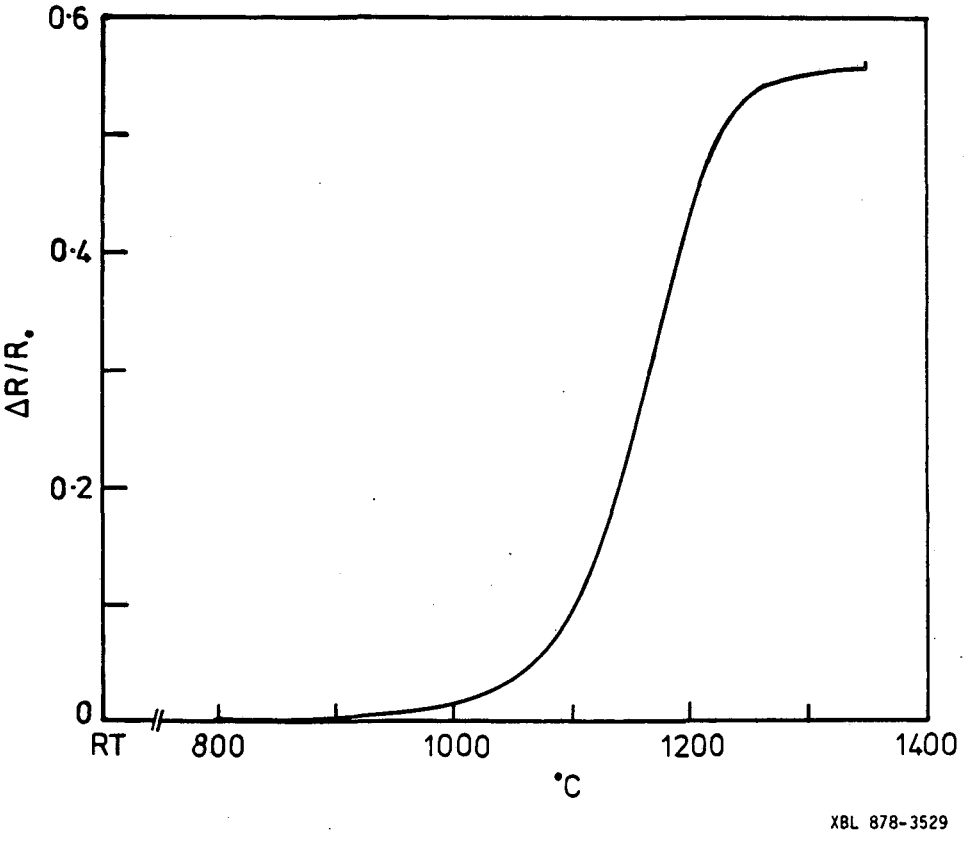

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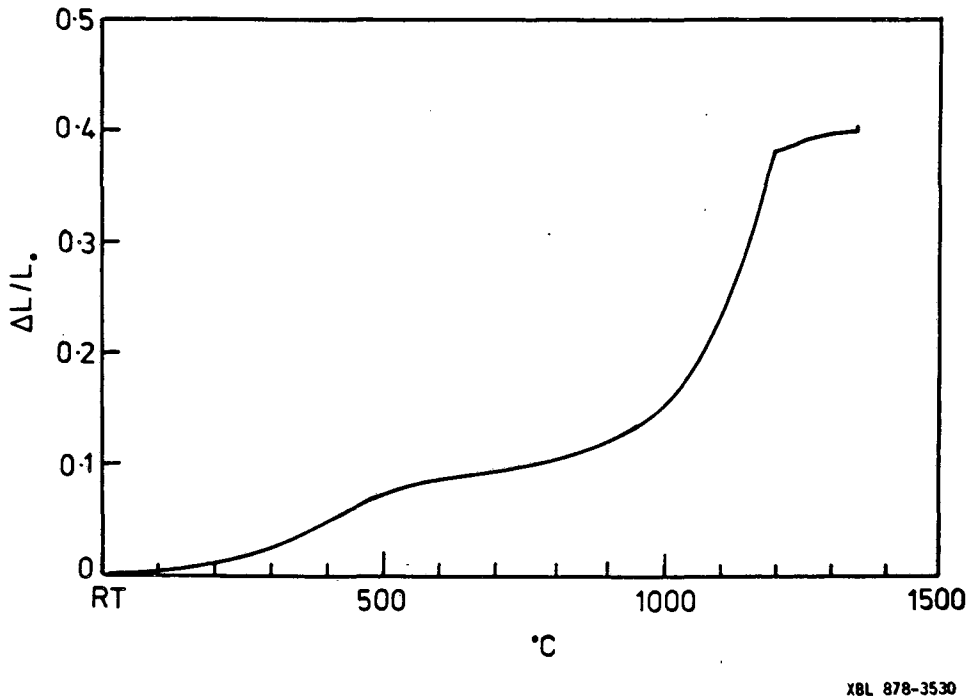

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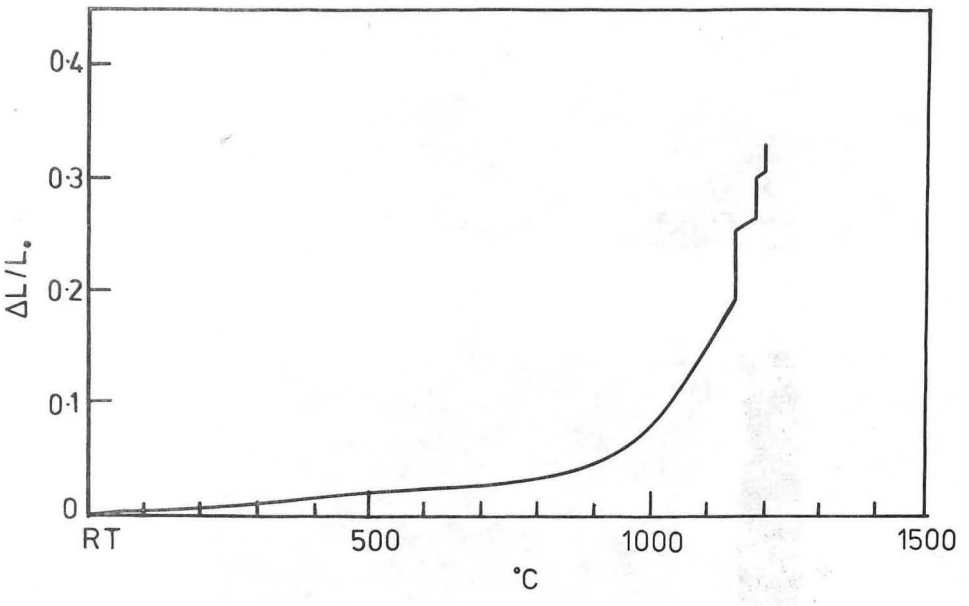

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Fig. 3

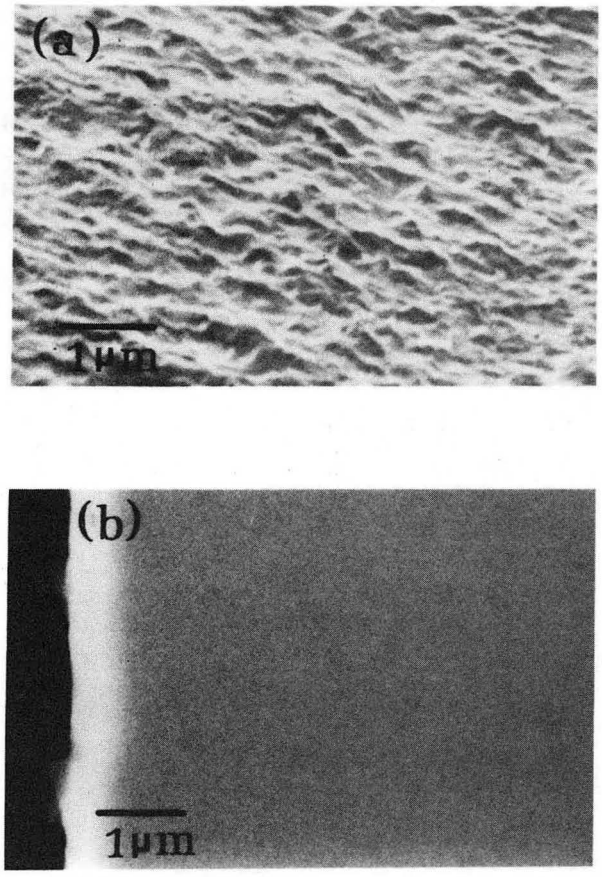

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Fig. 4

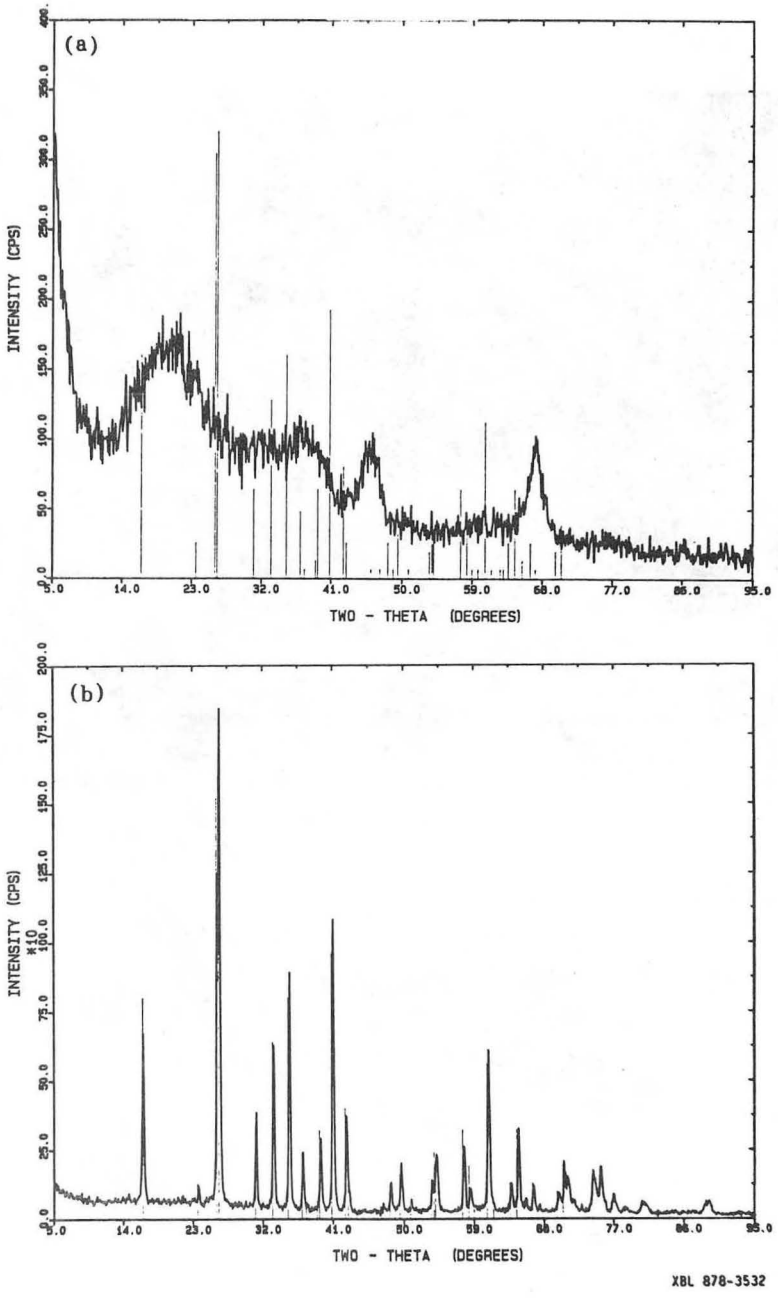
(a)
INTENSITY (CPS)
TWO - THETA (DEGREES)
(b)
INTENSITY (CPS)
TWO - THETA (DEGREES)
XBL 878-3532

Fig. 5

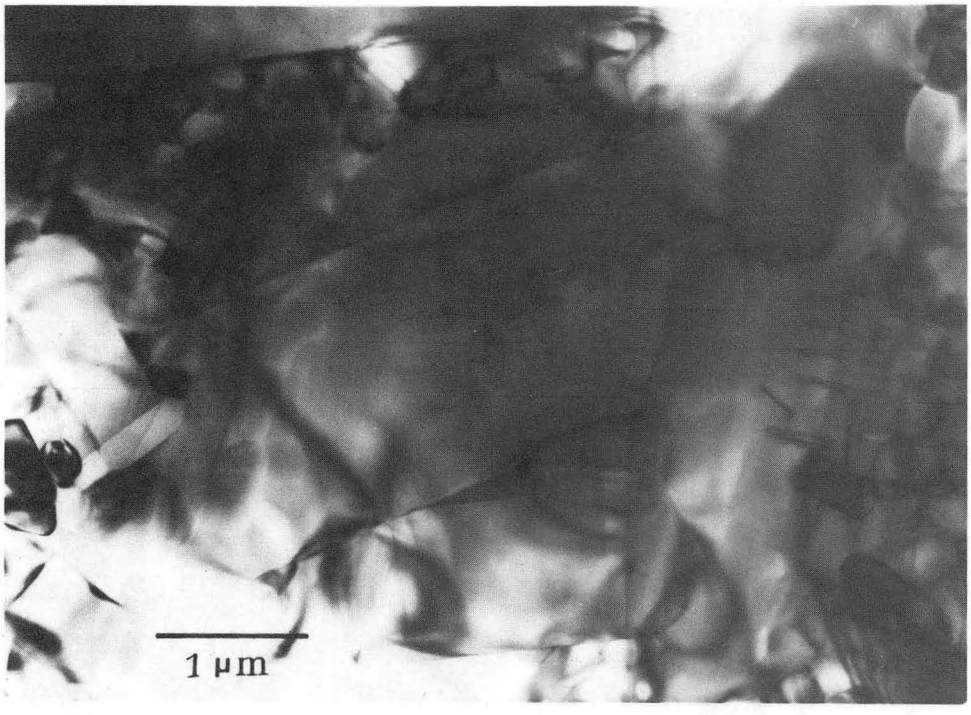

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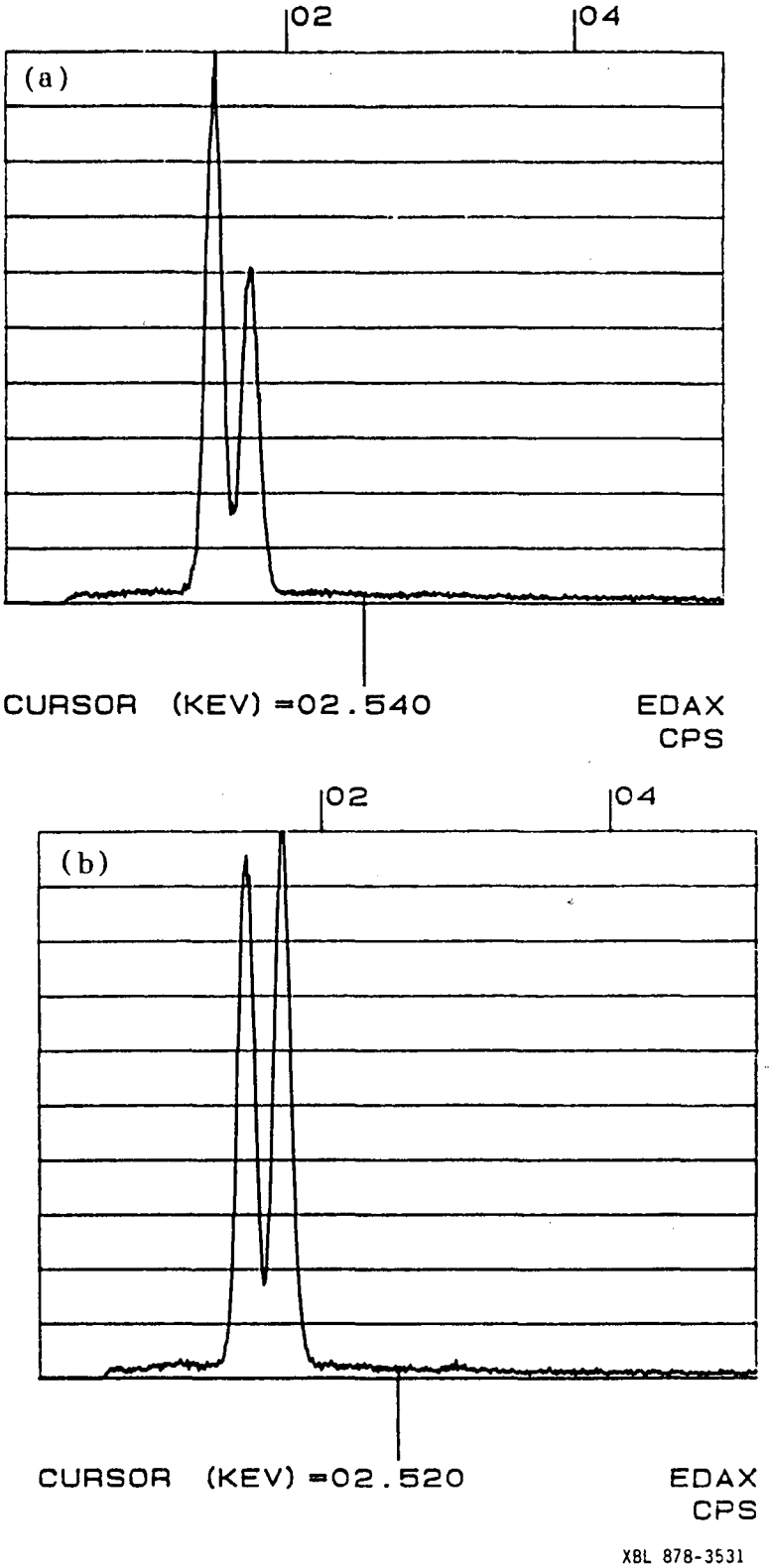
Fig. 6(a)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04
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EDAX
CPS
02
04
(b)
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EDAX
CPS
XBL 878-3531

Fig. 6(b)

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