Title

SUB-EUTECTIC DENSIFICATION AND SECOND PHASE FORMATION IN Al2O3 - CaO

Authors

Wu, S.J.
Jonghe, L.C. De

Publication Date

1984-06-01

LBL-17954

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Presented at the 86th Annual Meeting of the
American Ceramic Society, Pittsburgh, PA,
May 2, 1984; and submitted to the Journal of
the American Ceramic Society

SUB-EUTECTIC DENSIFICATION AND SECOND PHASE FORMATION IN Al_2O_3 - CaO

S.J. Wu and L.C. De Jonghe

June 1984

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

SUB-EUTECTIC DENSIFICATION AND SECOND PHASE FORMATION IN Al_2O_3 - CaO

[+]Shun Jackson Wu and [*]Lutgard C. De Jonghe
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Materials Science and Mineral Engineering
University of California, Berkeley, CA 94720

ABSTRACT

The early and intermediate densification stages of calcia containing alumina were examined at sub-eutectic temperatures. Up to 0.15 wt% calcia causes a decrease in the densification rates; from 0.15 to 0.7 wt% calcia an increasing densification rate is observed; more than 0.75 wt% calcia leads to a monotonically decreasing densification rate. The data are interpreted as a competition between grainboundary defect chemistry, enhanced subeutectic densification, and formation of calcium-aluminate phases of lower calcia activity.

Presented in part at the 86th Annual Meeting, The American Ceramic Society, May 2, 1984.

Supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, Under Contract No. DE-AC03-76SF0098.

[*] Member, the American Ceramic Society.
[+] Now with Toshiba, Inc., Sunnyvale, California.

I. Introduction

When powder compacts containing a eutectic forming additive are sintered increased densification rates, compared to those of the pure powder, may be observed as the eutectic temperatures is approached.[1-4] These enhanced sub-eutectic densification rates might be understood in terms of surface energy changes, changes in the grainboundary structures, or increased transport rates caused by the additive.[4-7] If, for example, the additive concentrates sufficiently in grainboundaries, then local diffusion rates can be strongly increased since now their transport rates would scale as the melting point of the eutectic temperature rather than as the melting point of the pure components. If this hypothesis has validity enhanced sub-eutectic densification should be generally observed for powder compacts containing small amounts of eutectic-forming additives. A series of experiments, performed by Smothers and Reynolds[8] showed both enhanced and decreased densification rates of a number of such additives to alumina. Examination of the corresponding phase diagrams suggests a correlation showing that enhanced sub-eutectic densification occurs in those systems that are either simple eutectics or have intermediate phases with a melting point and composition close to that of the eutectic, but that the enhancement is suppressed if high melting point intermediate phases can form. To examine this postulate, the sub-eutectic densification in the system Al_2O_3 - CaO was examined more closely. This system[9] has a deep eutectic, at 1390° C, but forms a number of high melting point intermediate phases. A competition between enhanced sub-eutectic densification and densification retardation due to second phase formation should be expected.

The effect of calcia impurities on the densification of alumina has been considered by various authors in the context of separating it from the effect of magnesia on densification, as for example in the work of Johnson and Coble.[10] Such studies are usually carried out well above the highest melting peritectic in the calcia-alumina system, where even moderate segregation of calcia should lead to liquid phase activity. The present study is confined to temperatures below the lowest melting eutectic in this system and only considers early and intermediate sintering stages.

II. Experiments

A deagglomerated, fine grained alpha-alumina* was used as the matrix material. The general preparation procedure of the samples is shown in Fig. 1. Alumina powder was added to an appropriate solution of calcium nitrate** in anhydrous ethanol, to yield powders with up to 5 wt% CaO. The ethanol slurry was stir-dried, and hand ground in a mortar and pestle. The nitrate was decomposed to oxide by 400°C calcining for one hour in air. The calcined powder was reground in a

---

* Baikalox Cr-1; average particle size 0.5 micron; purity 99.99%; major impurities: Na: 30 ppm; Fe: 30 ppm; Si: 20 ppm; Ca: 10 ppm. Baikowski International Corp., Charlotte, North Carolina 28210.

** Malinkrodt, Inc., Paris, Kentucky 40361.

mortar and pestle and die pressed to 55% of the theorical density at about 350 MPa. Prior to the dilatometry the samples were dried again at 700°C for one hour in air. Undoped alumina samples were prepared by the same procedures as CaO doped amples. Also, some alumina powder was pressed directly to 55% theoretical density to examine if the mixing and calcining operations affected sintering. No difference was found between the behavior of the alumina samples fabricated by the two different routes.

The samples were sintered for various times at constant temperature in a quench furnace kept at 1330°C, 60°C below the lowest eutectic temperature of the alumina-calcia system.[9] The densities of the samples was determined from the change in dimensions measured with a micrometer. Constant heating rate sintering (CHR) was performed in Harrop* dilatometer at a heating rate of 5°C/min. The samples were separated from the alumina sample holders by a thin platinum foil to prevent interaction.

The phase composition of a number of partially sintered samples was examined with x-ray diffraction. Some sintered samples, containing 5 wt% CaO were studied in a high voltage and a high resolution transmission electron microscope to verify the phase distribution.

---

* Harrop Industries, Inc., Columbus, Ohio 43219.

The microstructure of the samples was examined in a scanning electron microscope, after grinding and vibro-polishing.

III. Results and Discussions

(1). Constant Heating Rate Sintering

Constant heating rate sintering was used to follow the continuous dimensional changes of both pure and calcia doped alumina, and to verify if and when possible enhanced sub-eutectic densification occured. Three sample compositions were studied: pure alumina, alumina with 0.1 wt% calcia, and alumina with 1 wt% calcia. The dilatometry data are shown in Fig. 2. No shrinkage was detected below 900°C. For these sample compositions the addition of calcia reduced the shrinkage rate at all temperatures at the heating rate used here (5°C/min). Further, the addition of 0.1 wt% calcia decreased the densification rate more than the addition of 1 wt% calcia. It was also interesting to note that a sudden increase in the densification rate did not occur for the calcia containing samples when the eutectic temperature was exceeded in these constant heating rate experiments, suggesting that a liquid phase does not form. This was likely to be the result of the incorporation of most of the calcia in high melting point intermediate phases before the eutectic temperature has been reached. Slower heating rates produced essentially the same results. Heating rates in excess of 5°C/min could not be tolerated by the dilatometer without significant loss of accuracy. It was clear from these results that the effects of addition of calcia on the densification rates of alumina were complex. In such complex cases the constant heating rate method is not very suitable since it clouds interpretation, especially if transient phenomena such as second phase formation interfere with the densification process. The study therefore focused on constant temperature sintering.

(2). Constant Temperature Sintering.

The results of the densification measurements for the isothermal sintering are shown in Fig. 3. Each datumpoint represents a separate experiment in this figure. The densification rates show a non-linear dependence on the amount of calcia. Up to about 0.15 wt% calcia the densification rate decreases; between 0.15 and 0.7 wt% calcia the densificaiton rate increases, and at short sintering times the samples containing 0.5 to 0.7 wt% calcia actually densify somewhat faster than the undoped alumina powder; beyond 0.7 wt% calcia the densification rates decrease monotonically with increasing calcia content. Some densification data are shown in a log-(density)-vs-log (time) plot in Fig. 4. This figure shows that the slope of the densification curve for the 0.1 wt% calcia materials is very nearly the same as that for pure alumina, indicating that the densification mechanism is likely to be the same as for the undoped alumina. At the temperatures and submicron grainsize used in the present study the densification mechanism can be expected to be fully controlled by grainbounday transport with aluminum ions as the rate limiting species.[11] A lowering of the transport coefficient should then result from substitution of the aluminum ions by divalent calcium ions, depressing the aluminum vacancy concentration. Fig. 4 also shows that the increased densification trend for the 0.5 - 0.7 wt% calcia material is a transient one, being most prominent in the first hour or two of the sintering process.

Microstructural examination, Fig. 5, does not reveal any significant differences in the pore distribution between pure, 0.1 wt% and 0.5 wt% calcia samples after 20 hour at 1330°C. The grain sizes in this densification region are respectively 1.08 micron, 0.92 micron, and 0.81 micron, indicating that the grain size decreases monotonically while the densification rate shows the rate anomaly. Thus, the increase in sintering rate cannot be correlated with changes in grain growth rates.

The development of second phases could be deduced from the x-ray diffraction data, Fig. 6. In this figure the peak heights of characteristic reflections of various calcium alumunates are shown as a function of time for 5 wt% calcia containing samples. The first phase that forms is the CA phase (C=calcia; A=alumina). Not much of this phase could be detected, and it appeared to be present only in the first one or two hours of the densification, disappearing as the CA_2 phase forms. This time domain coincides with the increased densification rates observed for the 0.5 to 0.7 wt% calcia samples, as shown in Fig. 4. The CA_2 phase reached a maximum around four hours of heating, and started to disappear as the CA_6 phase formed. Such a reaction sequence is to be expected on the basis of the phase diagram, and is observed in $CaO - Al_2O_3$ interreaction.[12] The CA_6 phase formed both trans-and intergranularly, as shown in fig. 7. A high voltage transmission electron micrograph of such phases is shown in Fig. 8. The CA_6 develops by forming large plate bundels that are relics of the porous alumina grain structure. This peculiar second phase morphology is thought to be the result of highly anisotropic transport rates of calcium ions in the CA_6 phase.[12] A high resolution electron micrograph of an alumina-alumina grainboundary is shown in fig. 9. Within the limits of resolution no grainboundary phases were detected.

Initially one may expect the calcia to be concentrated on the surface of the powder, to be gradually incorporated into calcium aluminates of progressively lower calcia activity. At the same time the grainboundaries absorb calcia [13] roughly in proportion to the calcia activity established by the second phases. As the reactions proceed, it is thus to be expected that high grainboundary concentrations of calcia only occur as long as the CA phase is present. The anomalous dependence of the sub-eutectic densification rates on the amount of the calcia in alumina might then be explained plausibly by arguing that in the low calcia regimes, up to 0.15 wt% CaO, grainboundary diffusion coefficients are depressed by the presence of calcia in solid solution. Either insufficient calcia is present, or the CA phase is not sufficiently present to maintain a near-eutectic grainboundary composition. At higher calcia concentrations the Ca phase is present initially, permitting the eutectic composition to be approached in the grainboundaries, leading to enhanced a sub-eutectic densification which opposes the defect chemistry and the retarding effects of second phases. This enhanced sub-eutectic densification is, transient, since the phases of lower calcia activity, CA_2 and CA_6, deplete the grainboundaries of calcia, driving up their relative melting point. In this respect, the formation of the calcium-aluminate phases of lower calcia activity is akin to the absorption of the "activating" additive in the matrix solid solution, as discussed by

German.[5] At higher calcia contents, above 0.7 wt%, the retarding effects of the second phases would dominate the densification rates, leading to progressively slower sintering with increasing calcia contents. Whether or not enhanced sub-eutectic densification is observed will thus depend on the kinetics of formation of high melting point intermediate phases relative to the densification rates.

Acknowledgements: Dr. Ron Gronsky is thanked for providing the high resolution micrograph of the alumina grainboundary.

References

[1] R. L. Coble and R. M. Cannon, "Current Paradigms in Powder Processing," Mater. Sci. Res., Vol.11, 151-70 (1977).

[2] L. C. De Jonghe and E. Goo, "Transient Eutectics in Sintering of Sodium-beta alumina", in Processing of Crystalline Ceramics, H. Palmour III, R. F. Davis, and T. M. Hare, Eds., Plenum Press, pp. 433-41, (1979).

[3] L. C. De Jonghe and H. Chandan, "Improving the Sintering Behaviour of Sodim-beta Alumina," Cer. Bull,, Vol. 55, 312-12 (1976).

[4] S. C. Hu and L. C. De Jonghe, "Pre-eutectic Densification in MgF_2-CaF_2," Ceram. Int., Vol. 9 [4] 123-26 (1983).

[5] R. M. German, "A Quantitative Theory of Diffusional Activated Sintering," Science of Sintering, Vol. 15 [1] 27-42 (1983).

[6] J. H. Brophy, L. A. Shepard, and J. Wulff, "The Nickel-activated Sintering of Tungsten," in Powder Metallurgy, W. Leszynski, Ed., AIME-MPI, Interscience, N. Y., 113-135 (1961).

[7] G. H. Gessinger, and H. F. Fishmeister, "A Modified Model for the Sintering of Tungsten with Nickel Additions," J. Less Common Met., Vol. 27, 130-40 (1972).

[8] W. J. Smothers and H. J. Reynolds, "Sintering and Grain Growth of Alumina," J. Amer. Ceram Soc., Vol. 37 [12] 588-95 (1954).

[9] A. K. Chatterjee and G. I. Zhmoidin, "The Phase Equilibrium Diagram of the system CaO-Al_2O_3-CaF_2," J. Mat. Sci., Vol. 7 [1] 93-97 (1972).

[10] W. C. Johnson and R. L. Coble, "A Test of the Second - Phase Impurity - Segregation Models for MgO - Enhanced Densification of Sintered Alumina," J. Amer. Ceram. Soc., Vol. 61 [3-4] 110-14 (1978).

[11] P. A. Lessing, and R. S. Gordon, "Creep of Polycrystalline Alumina, Pure and Doped with Transition Metal Impurities," J. Mat. Sci., Vol. 12, 2291-2303 (1977).

[12] L. C. De Jonghe, H. Schmid, and M. Chang, "Interreaction between Al_2O_3 and a CaO-Al_2O_3 Melt," J. Amer. Ceram. Soc. Vol. 67 [1] 27-30 (1984).

[13] J. J. Burton and E. S. Machlin, "Prediction of Segregation to Alloy surfaces from Bulk Phase Diagrams," Phys. Rev. Let., Vol. 37 [21] 1433-36 (1976).

Figure Captions

Fig. 1 Schematic sample preparation procedure.

Fig. 2 Linear shrinkage as a function of calcia content and temperature at a constant heating rate of 5°C/min.

Fig. 3 Density as a function of calcia content for isothermal and isochronal sintering.

Fig. 4 Density data as log (density) vs. log (time).

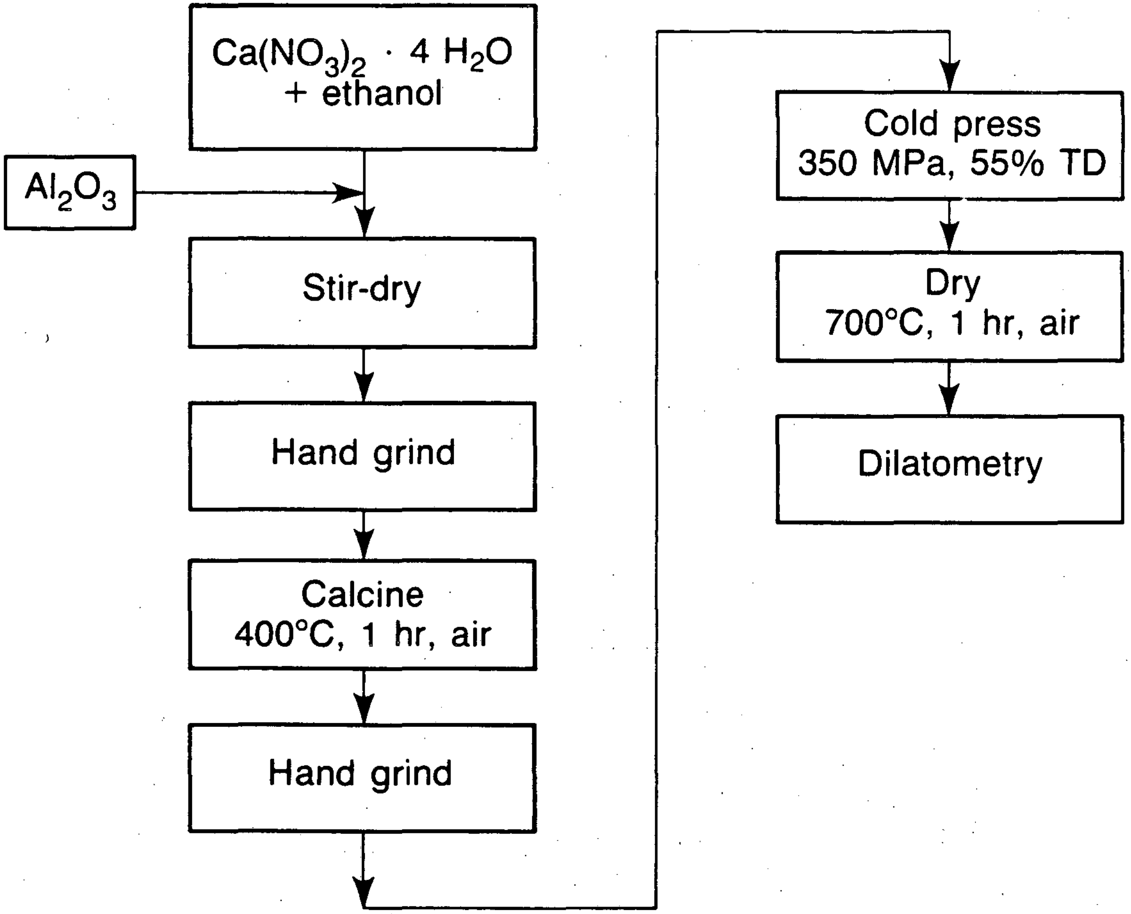
Fig. 5 Scanning electron micrographs of specimens heated for 20 hours at 1330°C. a) undoped alumina; b) 0.1 wt% CaO; c) 0.5 wt% CaO.

Fig. 6 Relative intensities of characteristic x-ray reflection of phases developing during the densification of alumina-5 wt% calcia. The CA $(21\bar{3})$ peak height has been multiplied by 10 relative to the CA_2 and CA_6 intensities.

Fig. 7 Scanning electron micrograph of CA_6 phase formed during densification of alumina-5 wt% calcia after 20 hours at 1330°C. The calcium aluminate phase (arrowed) can be readily recognized by its morphology.

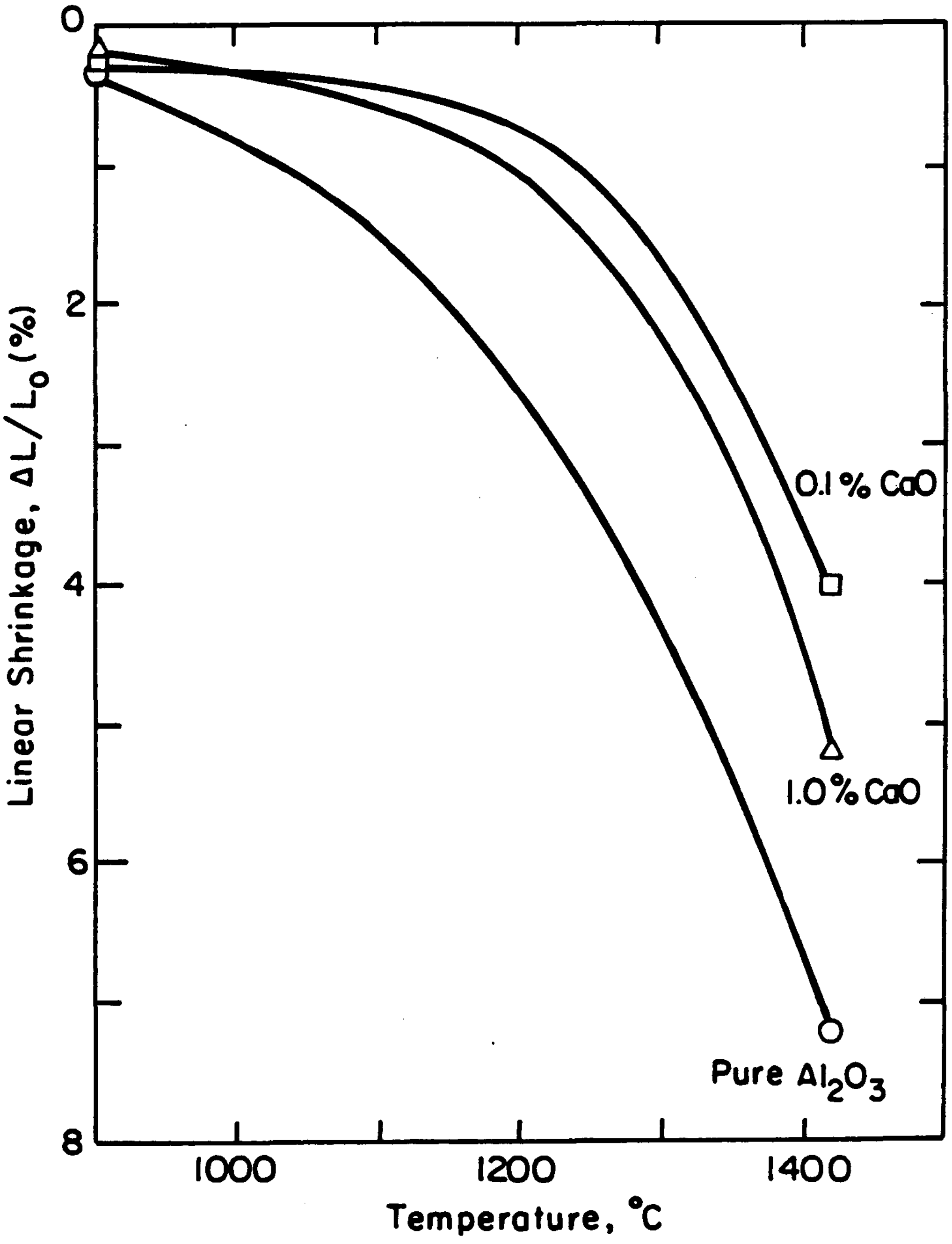
Fig. 8 High voltage transmission electron micrograph of CA_6 phase in alumina-5 wt% calcia after 30 hours at 1330°C. The phases were identified by selected area diffraction. A: Alumina; CA_6: calcium hexa-aluminate; P: pore.

Fig. 9 High resolution transmission electron micrograph of alumina-alumina grainboundary in alumina-5 wt% calcia after 20 hours at 1330°C. (courtesy Dr. Ronald Gronsky.)



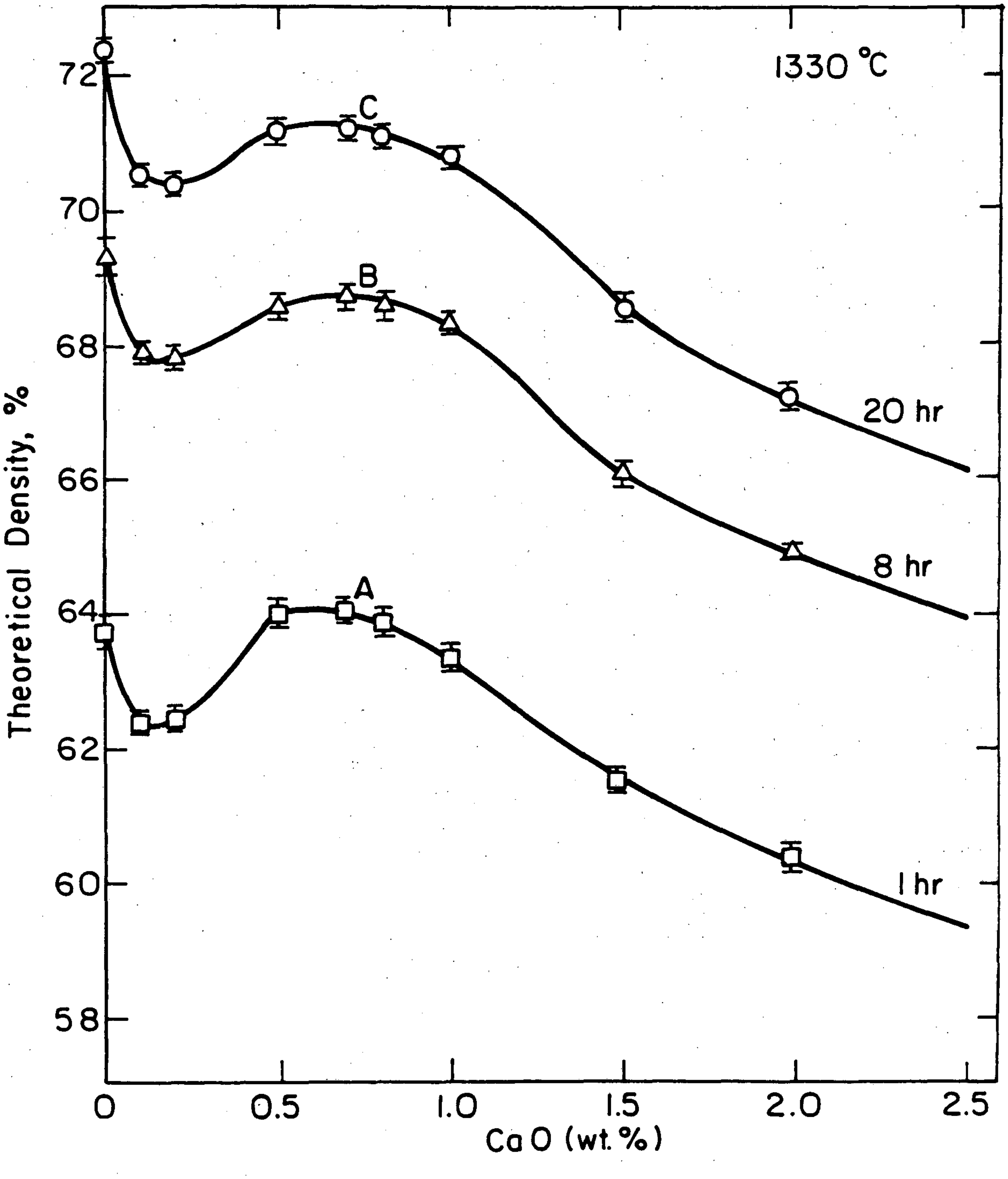
XBL 846-10675

Fig. 1



XBL 8312-6644

Fig. 2



XBL 8312-6647

Fig. 3

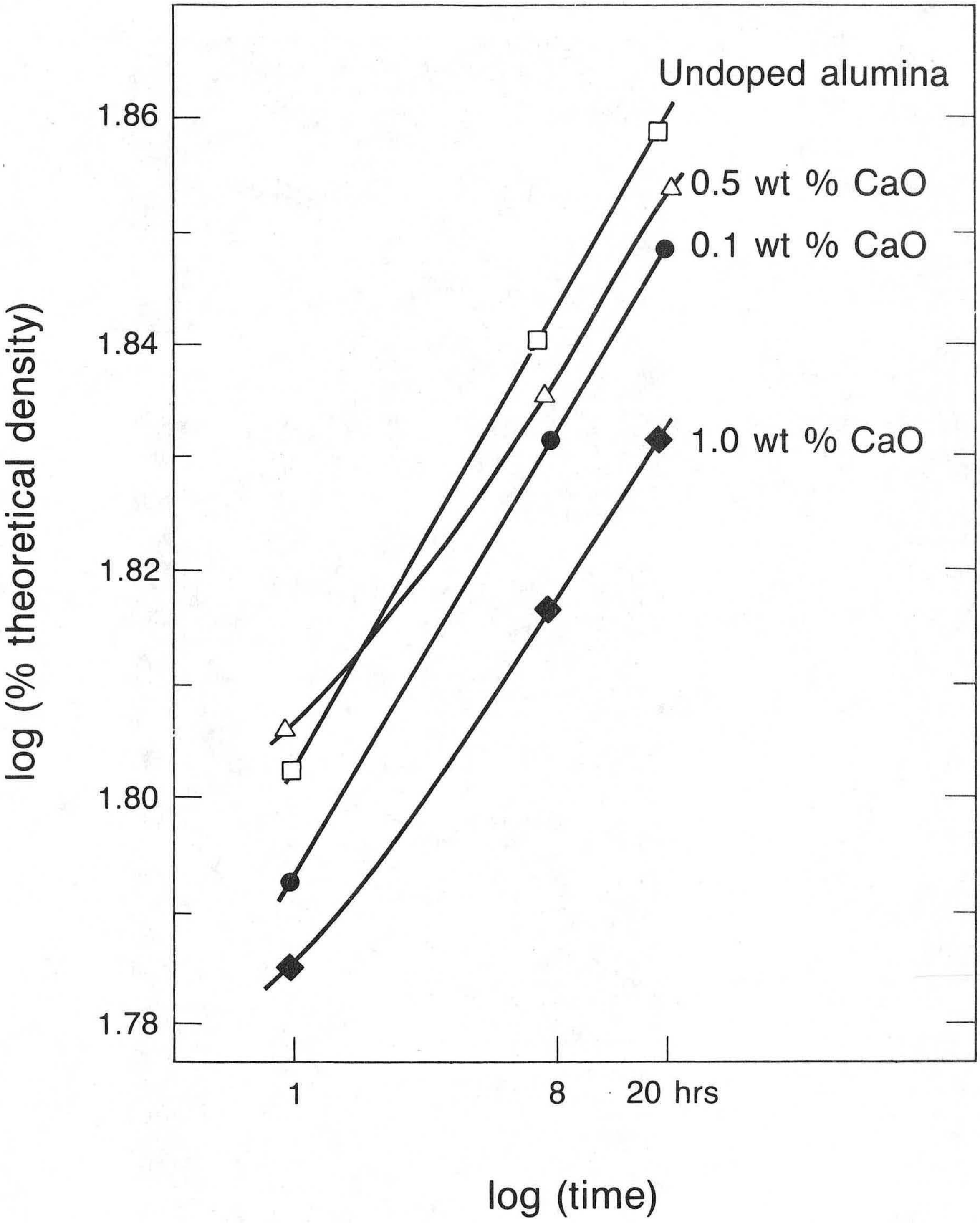
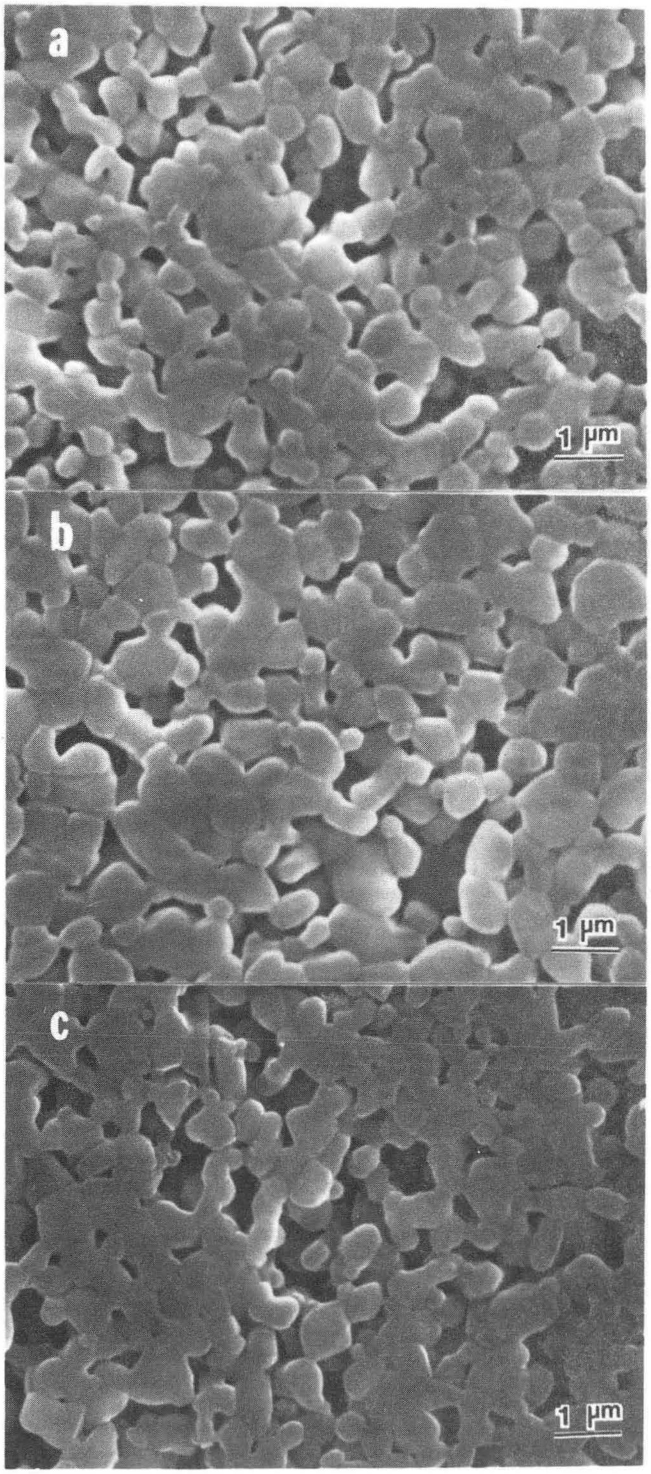


Fig. 4

XBL 846-10674



XBB 830-10026

Fig. 5

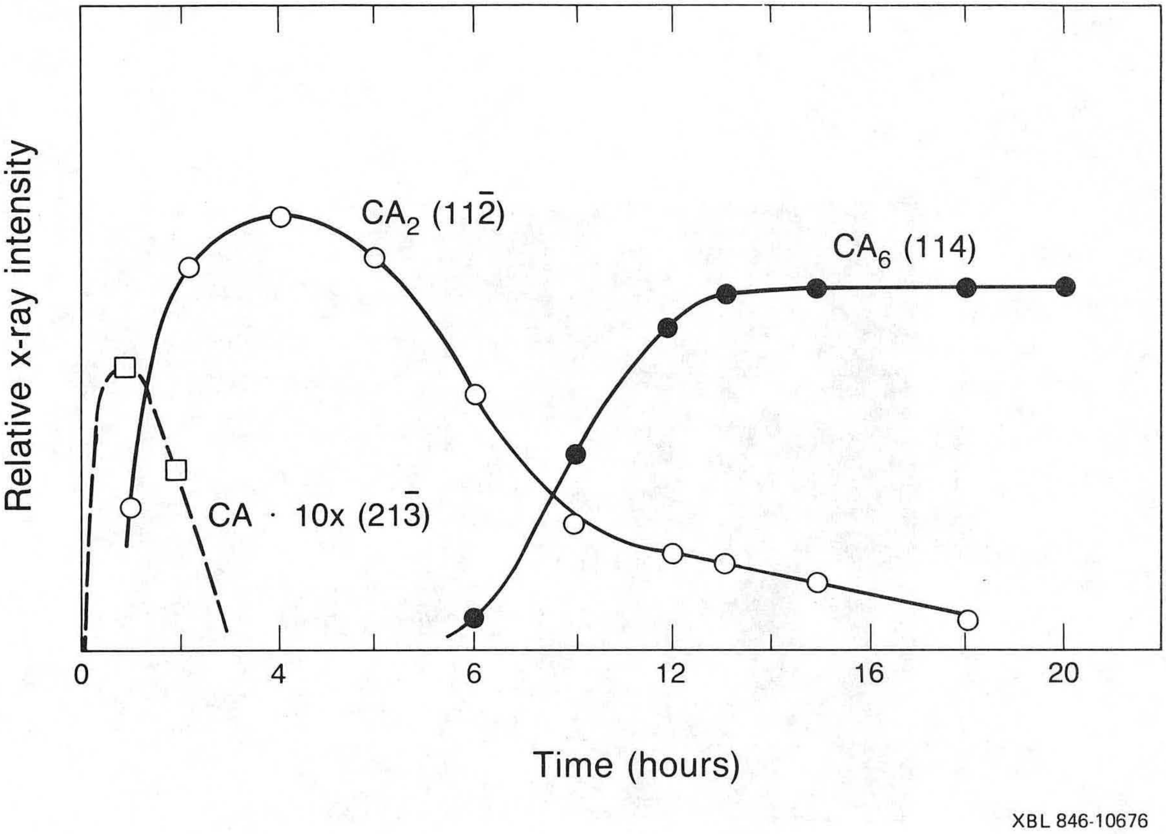
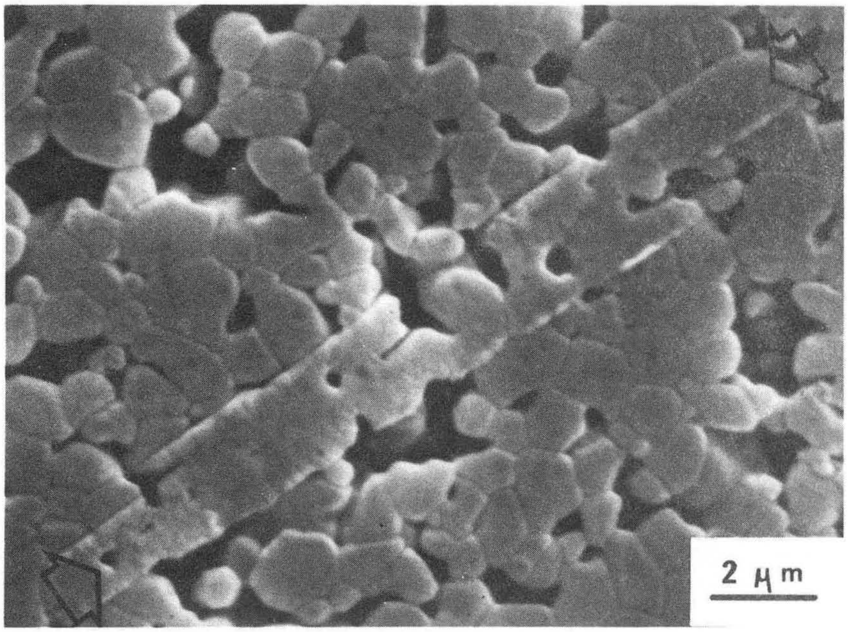
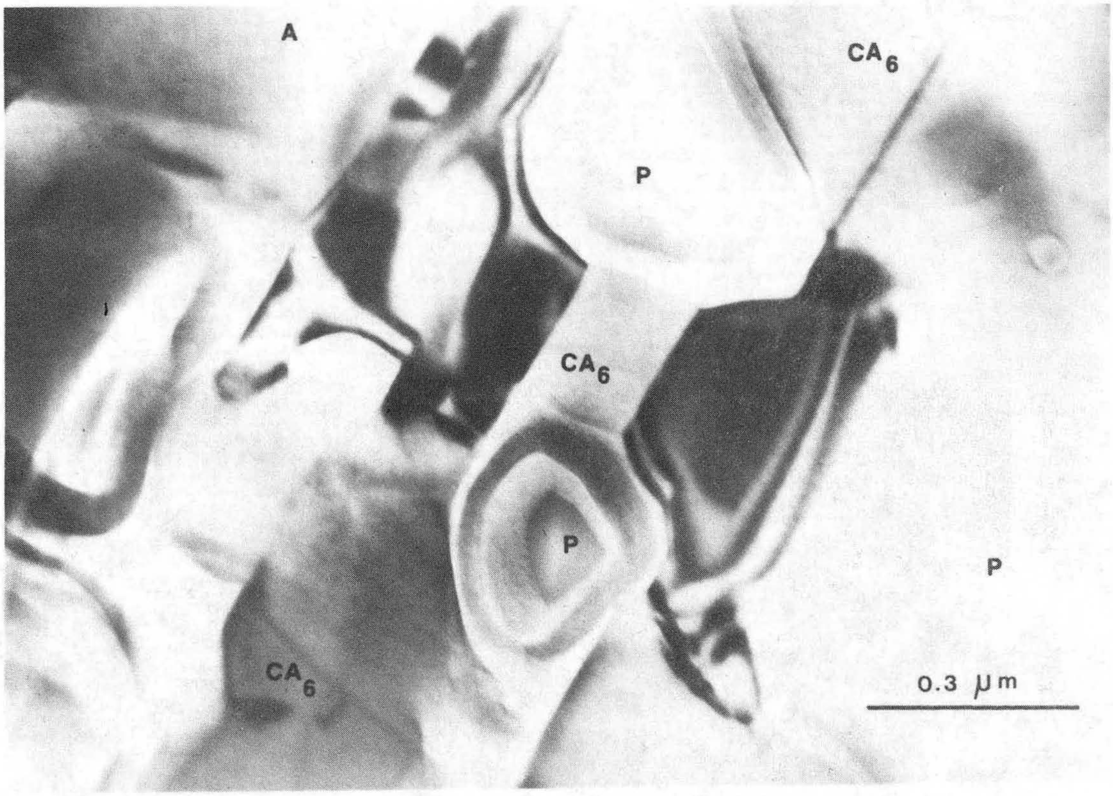

Relative x-ray intensity
Time (hours)
CA_2 (11$\bar{2}$)
CA_6 (114)
CA · 10x (21$\bar{3}$)
0
4
6
12
16
20
XBL 846-10676

Fig. 6



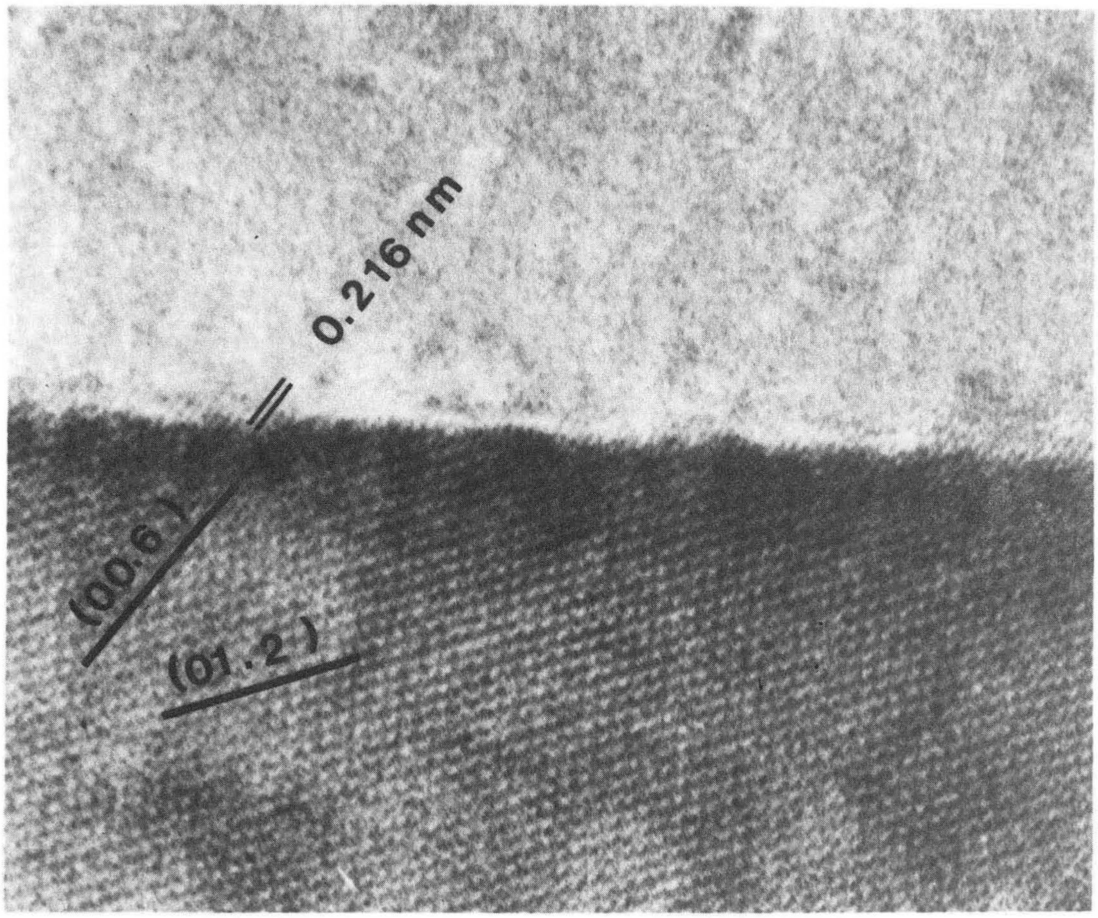
XBB 846-4718

Fig. 7



XBB 834-3343

Fig. 8



XBB 830-8848

Fig. 9

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720