

# Lawrence Berkeley National Laboratory

## Recent Work

### **Title**

MICROSTRUCTURE AND IONIC RESISTIVITY OF CALCIUM CONTAINING SODIUM BETA ALUMINA

### **Permalink**

<https://escholarship.org/uc/item/3vw1492f>

### **Author**

Buechele, A.

### **Publication Date**

1978-12-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA, BERKELEY, CA

## Materials & Molecular Research Division

Submitted to the American Ceramic Society Bulletin

MICROSTRUCTURE AND IONIC RESISTIVITY OF CALCIUM  
CONTAINING SODIUM BETA ALUMINA

A. Buechele and L. C. De Jonghe

December 1978

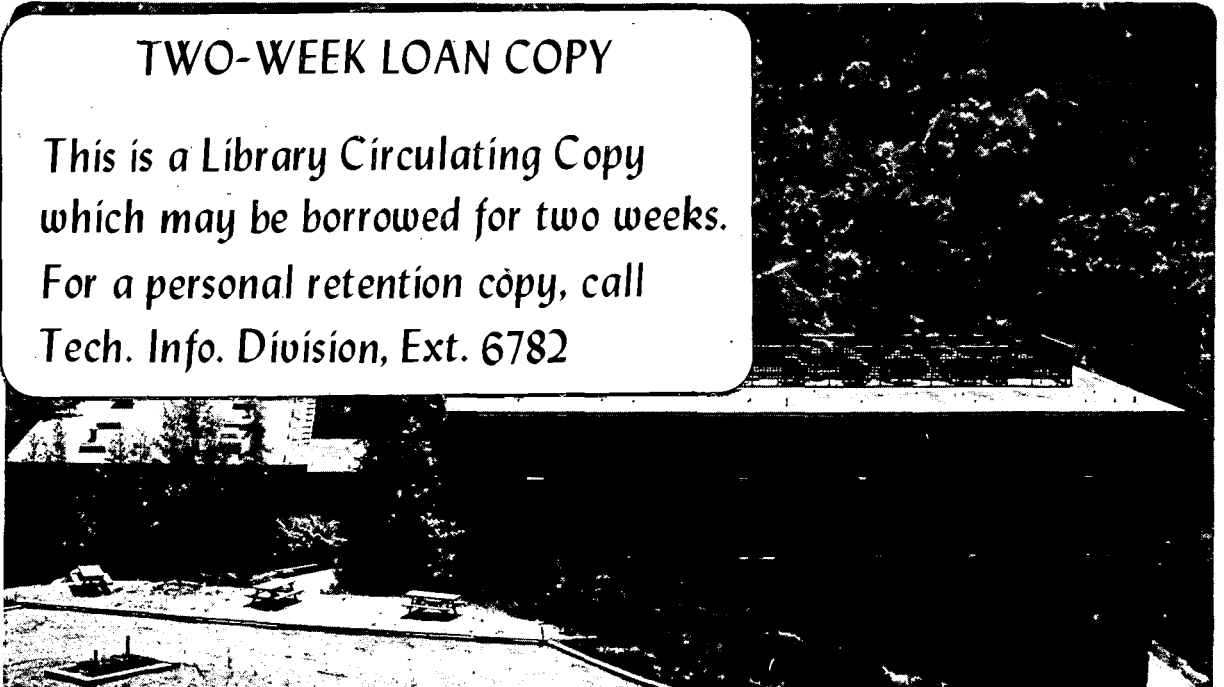
RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

JUL 23 1979

LIBRARY AND  
DOCUMENTS SECTION

### TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 6782*



Prepared for the U. S. Department of Energy under Contract W-7405-ENG-48,  
EPRI under Contract 252-2 and the National Science Foundation.

LBL-8461e.2

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Microstructure and Ionic Resistivity of Calcium Containing  
Sodium Beta Alumina

A. Buechele\* and L.C. De Jonghe\*

Materials and Molecular Research Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

ABSTRACT

Calcium containing sodium beta aluminas were prepared, and their microstructure and ionic resistivity was studied. The calcium significantly promotes abnormal grain growth at temperatures above 1700°C, and leads to the formation of highly blocking intergranular calcium aluminate phases. Evidence was also found for partial solution of calcia in  $\beta$ -alumina. The D.C. resistivity,  $\rho$ , at 300°C was found to increase exponentially with calcium content [C] leading to a relationship of the type:  $\log(\rho/\rho_0) = B \cdot [C]$ , where the proportionality factor B depends on the sintering conditions.

I. INTRODUCTION

Calcium is one of the impurities frequently found in trace quantities in ceramic powders. In commercial sodium beta aluminas it may be present at levels of up to several hundred ppm by weight as CaO. When such powders are used to fabricate solid electrolytes for sodium-sulphur batteries certain undesirable effects, such as shortened service lifetime or increased ionic resistivity, may be associated with the presence of calcia. Some work has been reported on the effects of calcium on the structure and

---

\* Member American Ceramic Society.

The majority of this work was performed at Cornell University in the Department of Materials Science and Engineering

properties of sodium beta alumina, though no detailed or systematic studies have been made. Torpov and Stukalova (1,2) observed the sodium exchange for calcium from molten calcium chloride, leading to the formation of  $\text{CaO} \cdot 6 \text{Al}_2\text{O}_3$ . Jones and Miles (3) reported conductivity and density measurements on electrolytes containing a number of additives including calcium. They noted that although calcia seemed to enhance densification it led to an undesirable increase in electrolyte ionic resistivity. Imai and Harata (4) similarly reported on the adverse effects of calcium on the conductivity. Nuclear magnetic resonance was used by Roth, Chung and Story (5) to study the effects of a number of additives, including calcium, on the sodium ion motion in  $\beta$ -aluminas. Their findings indicated that calcium dissolved in the conduction planes of the  $\beta$ -alumina. The calcium ions presumably were organized into  $\text{Ca Al O}_3$  units, replacing  $\text{NaO}$  thereby significantly reducing the sodium ion conductivity.

In this paper we report on the systematic effects of calcium on the conductive properties and the microstructure of sodium beta alumina polycrystalline electrolyte. The starting material was preconverted, commercial sodium beta alumina with a calcia content of about 200 ppm by weight. It was necessary to increase the calcia contents well above this level; while electrolytes with more than a few hundred ppm of calcia are of no interest as practical solid electrolytes, the higher calcia levels facilitated electron microscope observations of second phases, and permitted a more reliable establishing of microstructural and conductive trends.

## II. EXPERIMENTAL PROCEDURE

### 1. Sample preparations

Measured amounts of calcium nitrate were added to a methanol slurry

---

† Alcoa-XB-2 "superground"

of sodium beta alumina powder (Alcoa-XB-2 "superground"). The mixture was stir-dried and then hand ground with a mortar and pestle. The nitrates were decomposed in air at 800°C for one hour. After a brief hand regrinding, bar shaped samples were pressed at 16 Ksi. The green samples were packed in dried beta alumina powder and zone sintered at maximum temperatures between 1650°C and 1750°C. In this method samples are fed at a controlled rate through the hot zone of a furnace. The temperature profiles at 1700°C and 1750°C are shown in Figure 1. The heating schedule of a specimen is then determined by the rate at which it moves through the hot zone of the furnace. The zone sintering has been described in detail elsewhere (3,6).

## 2. *Microstructural Characterization*

Optical, scanning and transmission electron microscopy was used. Samples for transmission electron microscopy were ion milled from the sintered bars. Microscopy was carried out in a Siemens 102. The density of the samples was measured by the Archimedes method.

## 3. *Ionic Conductivity*

Two probe A.C. dispersive measurements between 10 Hz and 10 Mhz were carried out to determine the apparent transgranular and intergranular components of the D.C. resistivities. It should be noted, however, that this technique does not generally yield data that can be interpreted unambiguously. This problem has been discussed in some detail by De Jonghe (7).

## 4. *Chemical Characterization*

Samples were analyzed for sodium and calcium contents by atomic absorption spectroscopy. Analysis of sodium contents by the silver exchange method (8) proved unreliable in this case, since there was

evidence of formation of metallic silver in the pores of the electrolyte, and of partial calcium exchange.

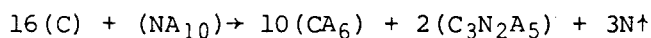
## II. RESULTS AND DISCUSSION

### 1. Phase Identification

The presence of second phases in the calcium containing sintered beta alumina was verified by means of X-ray analysis and transmission electron microscopy. The dominant second phase present after sintering was  $\text{CaO} \cdot 6 \text{Al}_2\text{O}_3$ . Fifteen lines in Debye-Scherrer patterns could be attributed to this phase.  $\text{CaO} \cdot 6 \text{Al}_2\text{O}_3 (\text{CA}_6)$  was also identified by transmission electron microscopy from diffraction patterns and dark field observations. Evidence for the presence of other phases was also found in the X-ray powder diffraction patterns. Four lines were attributable to  $3\text{CaO} \cdot 2\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3 (\text{C}_3\text{N}_2\text{A}_5)$ . The presence of calcium also caused a slight contraction of the  $c_0$  lattice parameters: from  $22.501\text{\AA}$  for undoped  $\beta$ -alumina to  $22.455\text{\AA}$  for  $\beta$  with  $\text{Ca}/\text{Al} = 0.055$ . This is consistent with a partial exchange of sodium with calcium in the conduction plane. EDAX analysis with the scanning electron microscope revealed the presence of Ca in the bulk of the beta alumina grains as well. Interestingly, it was found that the large grains and the small grains both contained approximately the same level of Ca. This is at variance with the findings of Yasui and Doremus (9) who reported a lower Ca concentration in large grain for  $\beta''$ -alumina. It is possible that the lower sintering temperature of the  $\beta''$ -alumina might account for the difference in Ca distribution. Evidence of partial calcium exchange in sodium beta alumina prepared under comparable conditions was also found by Roth et al. (5) by means of nuclear magnetic resonance.

Other transient phases are also likely to be present during the sintering while CaO is reacting with the beta alumina. Microscopic evidence of the presence of a liquid phase at sintering temperature was found when at high CaO content packing material caked to the sintering specimen. The actual reaction path between the  $\beta$ -alumina and the CaO could not be established from these sintering experiments, and therefore the chemical composition of the liquid phases preceding the formation of crystalline calcium aluminates is unknown.

The overall reaction based on the X-ray and TEM phase identification is therefore the type:



where C = CaO

NA<sub>10</sub> = sodium- $\beta$ -alumina, for the sake of simplicity

assumed to be Na<sub>2</sub>O · 10Al<sub>2</sub>O<sub>3</sub>

CA<sub>6</sub> = CaO · 6 Al<sub>2</sub>O<sub>3</sub>

C<sub>3</sub>N<sub>2</sub>A<sub>5</sub> = 3CaO · 2 Na<sub>2</sub>O · 5 Al<sub>2</sub>O<sub>3</sub>

N = Na<sub>2</sub>O; soda is expected to enter the gas phase.

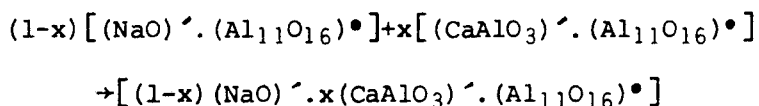
The extensive activity of the liquid phase in calcium containing beta alumina indicates, however, that the sample microstructure and phases must be significantly off equilibrium during the course of the rapid zone sintering, so that the above reaction is not likely to be completed. Further, substitution of Na by Ca is not included here. The substitution reaction is discussed in the next paragraph.

## 2. Microstructure

A pronounced exaggerated grain growth was observed in calcium containing samples sintered above 1700°C. The fraction of abnormally large



grains increases with increasing calcium content, as is shown in Figure 2 for samples sintered at 1750°C and at a rate of .5 cm min<sup>-1</sup>, at the same time the porosity increases. Figure 3 shows the dependence of the density on calcium content for two sets of samples sintered under two different conditions: (a) at 1700°C and 2.5 cm min<sup>-1</sup>, and (b) at 1750°C and 1 cm min<sup>-1</sup>. The corresponding microstructures at Ca/Al = 0.01 are shown in Figures 4a and 4b. The increased abnormal grain growth and trapped porosity at higher temperatures suggests anomalously high grain boundary mobilities, as may be caused by intergranular liquid phases. Further evidence of the presence of a liquid phase at sintering temperatures was found by transmission electron microscopy. An intergranular calcium aluminate phase, CaO · 6 Al<sub>2</sub>O<sub>3</sub>, was observed in a morphology (as shown in Figure 5) that strongly suggested that it crystallized from a precursor liquid phase. Details of wetting behaviour or wetting angle of the precursor liquid phase can, however, not be extracted from micrographs such as these. The system is chemically reacting with concurrent micro-morphological changes. The geometry of the distribution of the liquid precursor phase will therefore be influenced by factors such as viscosity, matrix grain growth rates, etc., besides interfacial energies. Once the calcium hexa-aluminate, CA<sub>6</sub>, has formed, continued reaction with β-alumina is still possible since calcium can enter the β<sub>1</sub>-alumina conduction planes. This reaction could be written as:



Here, we have adopted the notation of Roth et al. (9) and for simplicity have assumed the sodium beta alumina to be ideally stoichiometric.

Figure 6 shows part of an intragranular  $CA_6$  phase in detail. In the  $\beta$ -alumina grain A, a spinel ledge is indicated by an arrow. Growth of  $\beta$ -alumina in the  $[00.1]$  direction at elevated temperature is thought to proceed by the nucleation and propagation of such spinel ledges (10). The micrograph would then give a hint as to how the reaction between  $CA_6$  and  $\beta$ -alumina, Eq. (1), might proceed. It is interesting to note that these ledges seem to nucleate somewhere on the  $CA_6/\beta$  interface, and not at the  $\beta/\beta$  grain boundary edge.

The  $CA_6$  phase was most frequently found wedged between the 00.1 facets of  $\beta$ -alumina matrix grains, as shown in Figure 7. This can again be explained with the reaction mentioned in Eq. (1). Since this reaction involves the entrance of  $(CaAlO_3)'$  units into the  $\beta$ -alumina conduction planes it is reasonable to assume that the 00.1 facets are reaction sites with slow kinetics. The preponderance of  $CA_6$  in geometries such as shown in Figure 7 thus is of a kinetic origin, and has little to do with the relative liquid/solid interface energy anisotropy of the precursor liquid.

### 3. Ionic Conductivity

Both calcium content and sintering conditions affected the ionic resistivities of the samples. The 300°C extrapolated D.C. specific resistivity was found to follow in all cases an exponential dependence on calcium concentration. This dependence can be expressed as

$$\log (\rho/\rho_0) = B[C] \quad \text{Eq. (2)}$$

where

$\rho$  = D.C. specific ionic resistivity of a calcium  
containing sample at 300°C

$\rho_0$  = D.C. specific resistivity extrapolated to

$[C] = 0$ , at 300°C

[C] = calcium content, expressed here as the Ca/Al atom ratio

B = proportionality factor

The results are plotted in Figure 8 for Ca containing samples sintered under two different conditions: (a) at 1700°C and 1.2 cm min<sup>-1</sup>, and (b) at 1750°C and 0.6 cm min<sup>-1</sup>. This shows that the proportionality factor B in Eq. (2) is sensitive to the sintering conditions. Hsieh and De Jonghe (9) observed a similar dependence in sodium beta alumina containing significant amounts of silicates. In that case, low conductivity intergranular phases were formed as well. The constant B, however, is much larger in the case of the calcium containing material for samples sintered under comparable conditions. The values of B are compared in Table I. It should be noted that the observed behaviour as expressed in Eq. (2) cannot be attributed to a grain boundary solid solution atmosphere effect, although calcium is partly soluble in sodium beta alumina. A continued rise of the total specific ionic resistivity is inconsistent with a grain boundary impurity atmosphere effect once a second phase has formed. The significant differences between B for calcium containing samples versus silicate containing samples can then be rationalized by taking into account the ionic resistivity of sodium aluminosilicates and calcium aluminates. While no quantitative Na ion transport data are available for calcium beta aluminates it is expected that the calcium aluminate ionic resistivity will be many orders of magnitude higher than that of sodium aluminosilicates.

The observed relationship between ionic resistivity and calcium content as expressed in Eq. (2) is difficult to explain on a theoretical basis. A heuristic derivation of a similar relationship was first put

forth by Lichtenecker in 1909 (11). If it is assumed that the relationship can be used to extrapolate outside the region of the present measurements, a lower limit  $[C_{\min}]$  could be estimated to the Ca content below which no effect on the electrolyte ionic conductivity would be detected. If the detectability limit is practically taken at 1% of the resistivity value, then with  $[C_{\min}] = \frac{1}{B} \log (1.01)$ , and  $B \approx 100$  one gets  $\text{Ca/Al} = 4 \times 10^{-5}$  or about 40 ppm by weight.

### III. CONCLUSION

The presence of Ca in sodium beta alumina strongly promotes abnormal grain growth. X-ray and transmission electron microscope evidence was found for the presence of transient liquid precursor phases from which  $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$  formed as the dominant intergranular phase. Some evidence was also found for the presence of  $3\text{CaO} \cdot 2\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$ . Changes in lattice parameter of the matrix  $\beta$ -alumina are consistent with  $(\text{Ca AlO}_3)$  units entering the conduction planes. The total D.C. resistivity was found to be exponentially dependent on the calcium contents. The proportionality factor in this relationship depends on the sintering condition.

#### *Acknowledgements:*

This work was supported by the Electric Power Research Institute, Contract RP 252-2. Additional support was received from the National Science Foundation through the Cornell Materials Science Center, and from the Division of Materials Science, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. W7405-Eng-48.

#### *References:*

1. N.A. Torpov and M.M. Stukalova, "Interchange of Bases in Crystals of Beta-Alumina" C.R. (Doklady) Akad. Nauk U.R.S.S., 24, 459-461 (1939).

2. N.A. Toropov and M.M. Stukalova, "Replacement of Sodium in Crystals of Beta-Alumina with Calcium, Strontium, and Borium" C.R. (Doklady) Akad. Nauk U.R.S.S., 27, 974-977 (1940).
3. I. Wynn Jones and L.J. Miles, "Production of  $\beta$ -Al<sub>2</sub>O<sub>3</sub> Electrolyte", Proc. Brit. Ceram. Soc., 19, 161-178 (1971).
4. A. Imai and M. Harata, "Ionic Conduction in Impurity Doped  $\beta$ -Alumina Ceramics", Jap. J. Appl. Phys., 11, 180-185 (1972).
5. W.L. Roth, I. Chung and H.S. Story, "Characterization of Additive-Modified Beta Alumina Ceramics by Nuclear Magnetic Resonance", J. Amer. Ceram. Soc., 60, 311-315 (1977).
6. M.Y. Hsieh and L.C. De Jonghe, "Silicate-Containing Sodium Beta-Alumina Solid Electrolytes", J. Amer. Ceram. Soc., 61, 185-191 (1978).
7. L.C. De Jonghe, "Grain Boundaries and Ionic conductivity of Sodium Beta Alumina", J. Mat. Sci., (in press).
8. J.T. Kummer; pp. 141-175 " $\beta$ -Alumina Electrolytes" in Progress in Solid State Chemistry, No. 7, Edited by H. Reiss and J.O. McCaldin. Pergamon, Oxford, 1972.
9. I. Yasui and R.H. Doremus, "Effects of Calcium, Potassium, and Iron on Degradation of  $\beta$ -Alumina", J. Electrochem. Soc., 7, 1007-1010 (1978).
10. L.C. De Jonghe and E. Goo "Transient Eutectics in Sintering of Sodium Beta Alumina", pp. 433-441, in Processing in Crystalline Ceramics. Edited by H. Palmour and R. Davis. Plenum Publ. Cor., New York, 1978.
11. K. Lichtenecker, "Calculation of Resistance of Alloys Free From Solid Solutions", Physik. Z., 10, 1005-1008 (1909).

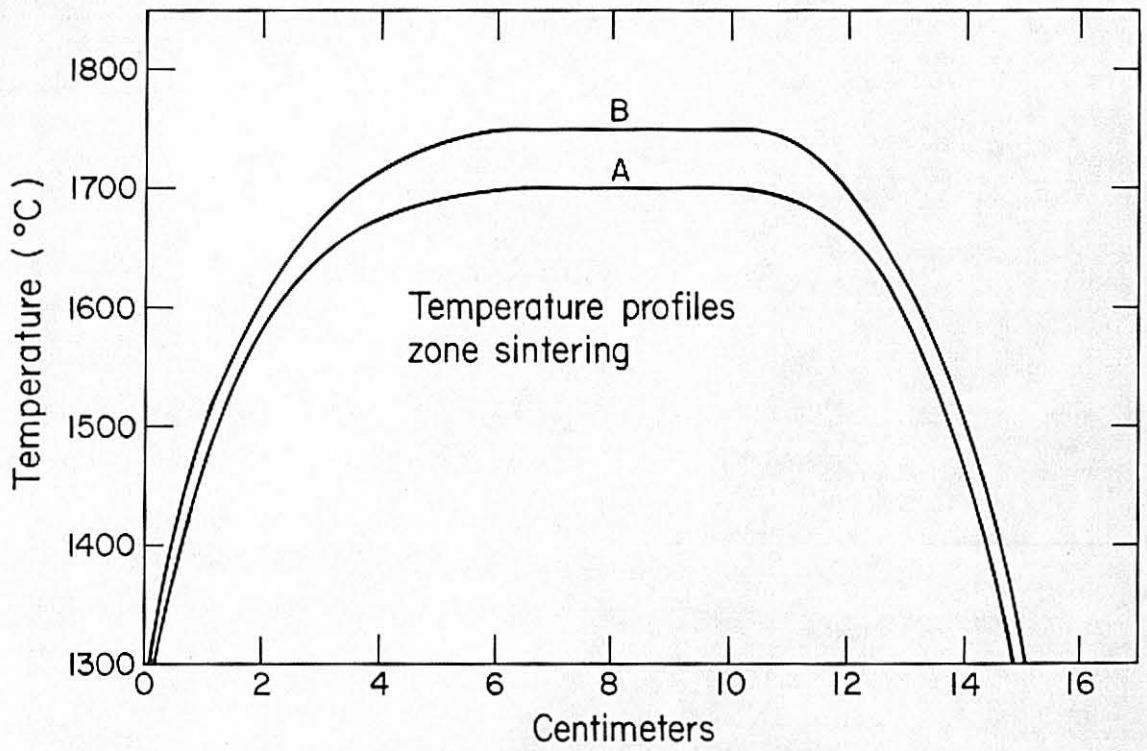
Tables

Table I. Values of B in  $\log_{10} (\rho/\rho_0) = B [C]$

Sintering Conditions	Ca containing $\beta$ -alumina	Si containing $\beta$ -alumina
1750°C 0.6 cm min <sup>-1</sup>	96	12
1700°C 2.5 cm min <sup>-1</sup>	187	--

*Figure Captions*

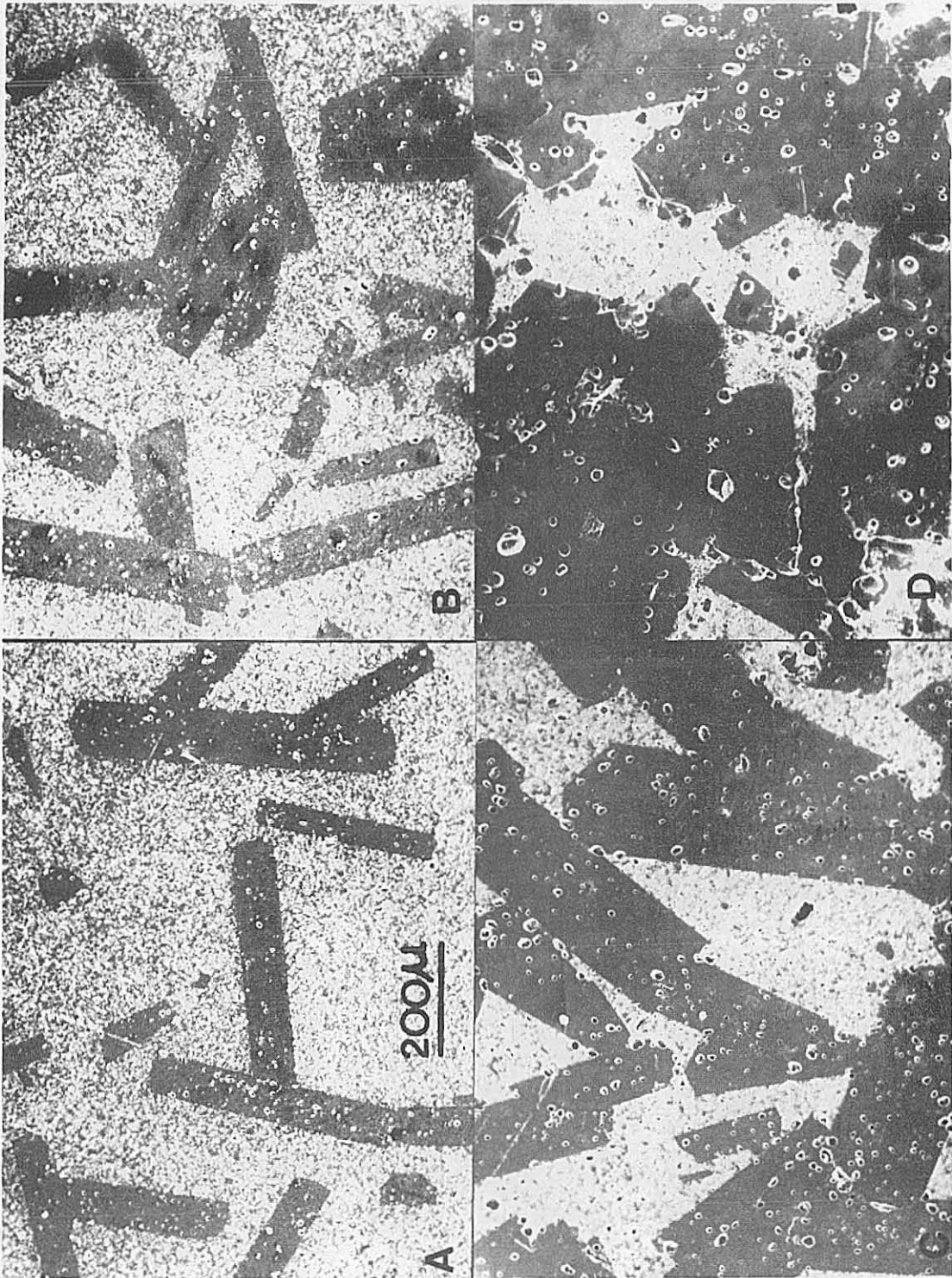
- Figure 1. Temperature profiles for zone sintering at 1700°C (A) and 1750°C (B). The samples are moved through these hot zones at a specified rate, thus determining the sintering heat treatment. XBL 7812-13346
- Figure 2. Abnormal grain growth increases with increased calcium contents: a) Ca/Al=.0002 b) Ca/Al=.001 c) Ca/Al=.005 d) Ca/Al=.01 Samples sintered at 1750°C at a rate of 0.5 cm min<sup>-1</sup>. XBB 791-708
- Figure 3. Densities of calcium containing samples for two different sintering conditions: (A) 1700°C and 2.5 cm min<sup>-1</sup>, (B) 1750°C and .6 cm min<sup>-1</sup>. XBL 7812-13347
- Figure 4. Microstructures of samples corresponding to Figure 3 at Ca/Al=0.01. The abnormal grain growth is most significant for samples sintered above 1700°C. XBB 791-706
- Figure 5. Examples of T.E.M. observations of intergranular CaO·6Al<sub>2</sub>O<sub>3</sub> (CA<sub>6</sub>). The geometry of the intergranular phase suggests that it formed from a precursor liquid. Sintering conditions: (A) 1700°C and 2.5 cm min<sup>-1</sup>; (B) 1700°C and 2.5 cm min<sup>-1</sup>; (C) 1750°C and 1.2 cm min<sup>-1</sup> Ca/Al=0.03. XBB 791-707
- Figure 6. Detail of an intergranular region containing CaO·6Al<sub>2</sub>O<sub>3</sub> (CA<sub>6</sub>). In the β-alumina grain marked A, a spinel ledge on a 00.1 faceted interface is indicated by an arrow. Ca/Al=0.03 sample sintered at 1700°C and 2.5 cm min<sup>-1</sup>. XBB 791-704
- Figure 7. CaO·6Al<sub>2</sub>O<sub>3</sub> (CA<sub>6</sub>) phase between 00.1 faceted grains of β-alumina. This geometry is found frequently suggesting it has kinetic rather than energetic origins. 00.1 facets should be slowly reacting interfaces for calcium uptake in the conduction planes. Ca/Al=0.03; sample sintered at 1700°C and 2.5 cm min<sup>-1</sup>. XBB 791-705
- Figure 8. D.C. specific ionic resistivities at 300°C for samples sintered under different conditions: (A) 1700°C and 2.5 cm min<sup>-1</sup>; (B) 1750°C and 0.6 cm min<sup>-1</sup>. The results illustrate Eq. (2) and document the dependence of B on sintering conditions. XBL 7812-13345



XBL 7812-13346

Figure 1





XBB791 708

Figure 2

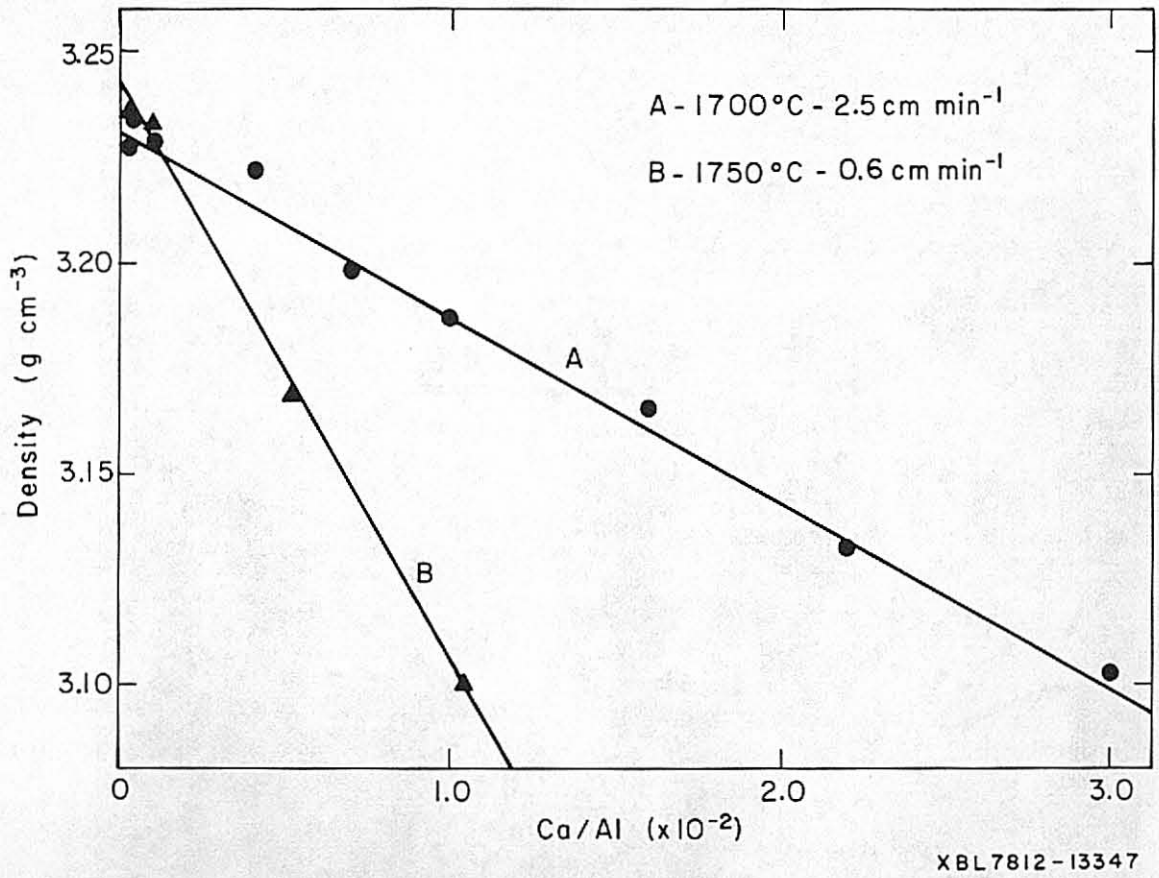
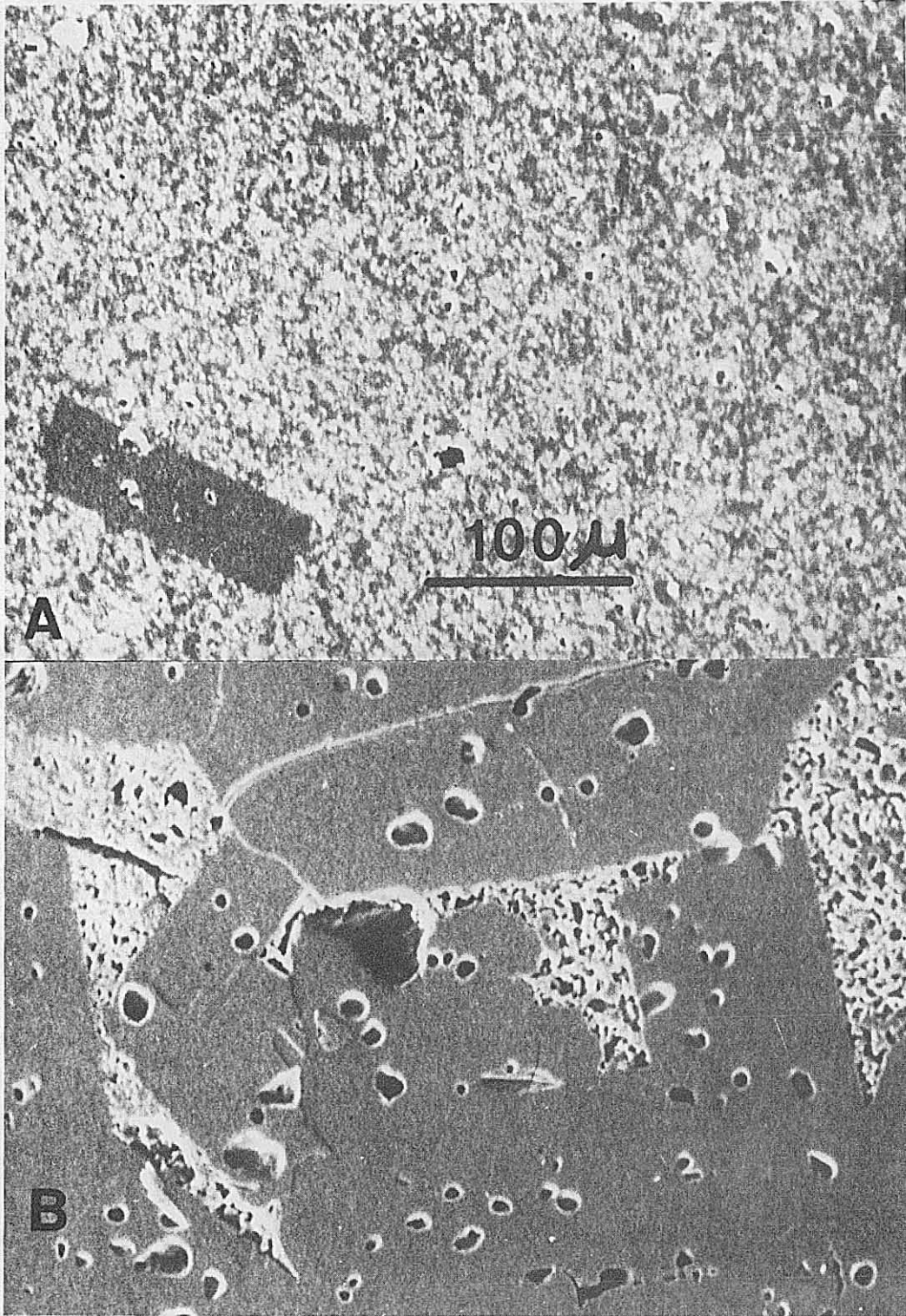


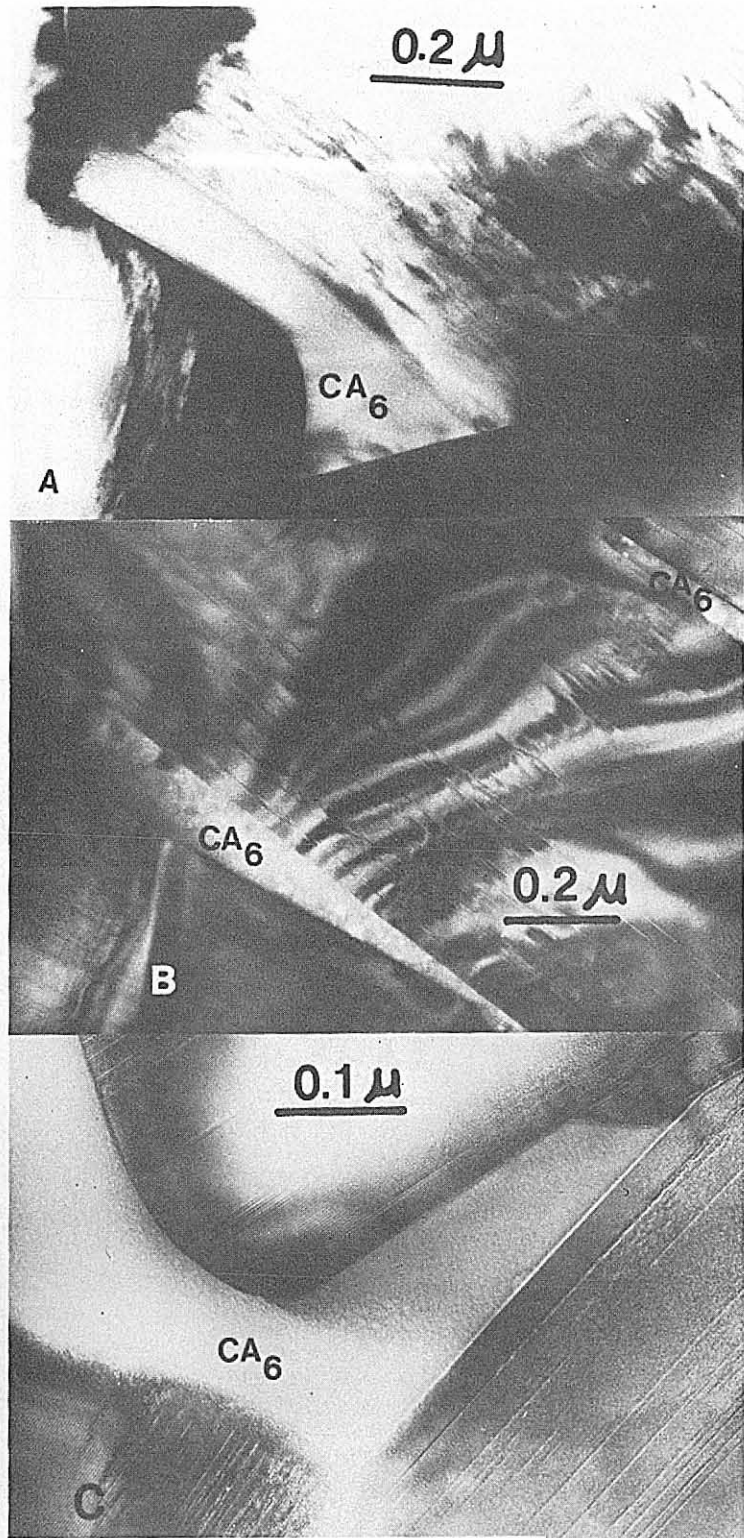
Figure 3





XBB 791-706

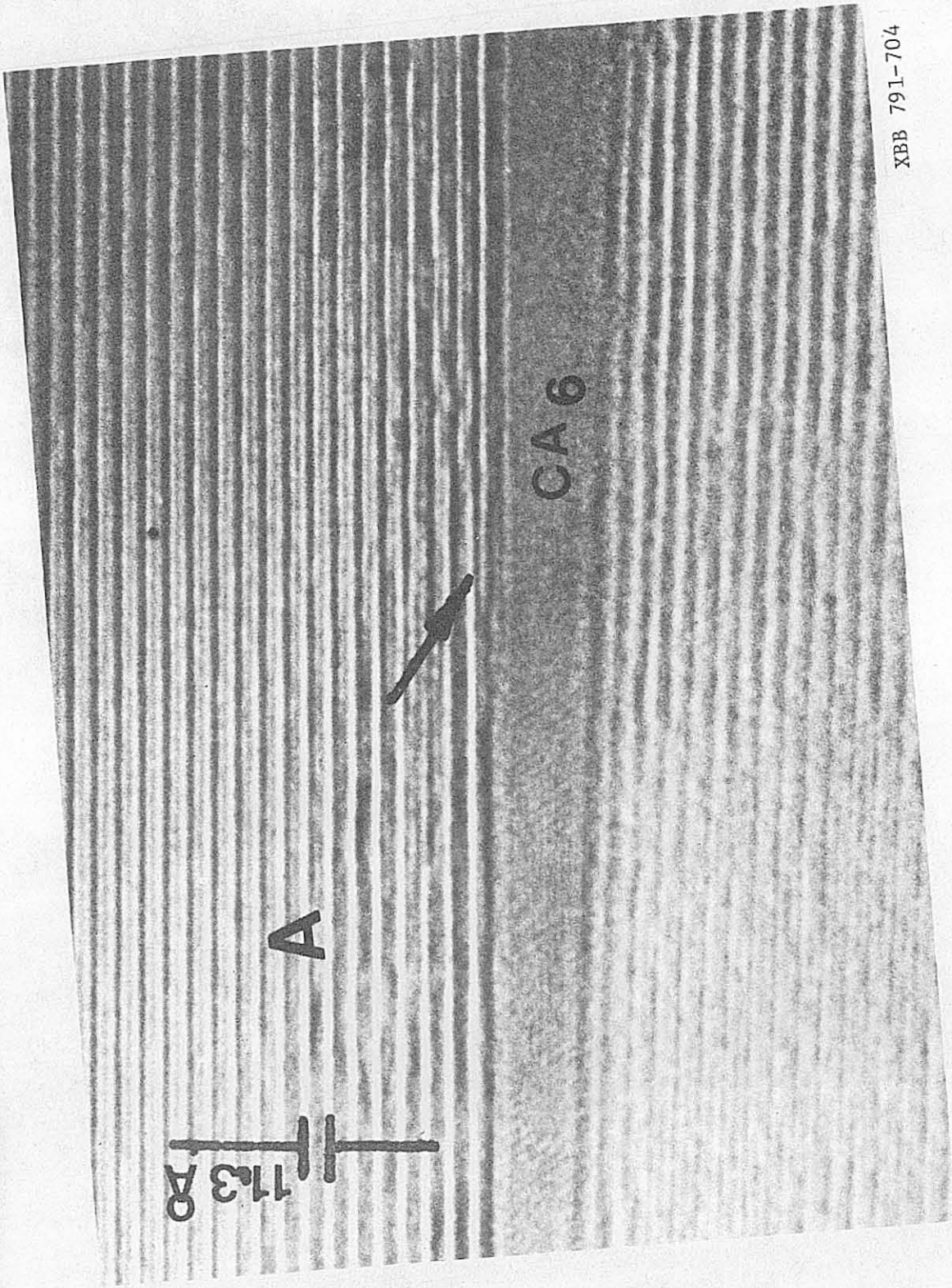
Figure 4



XBB 791-707

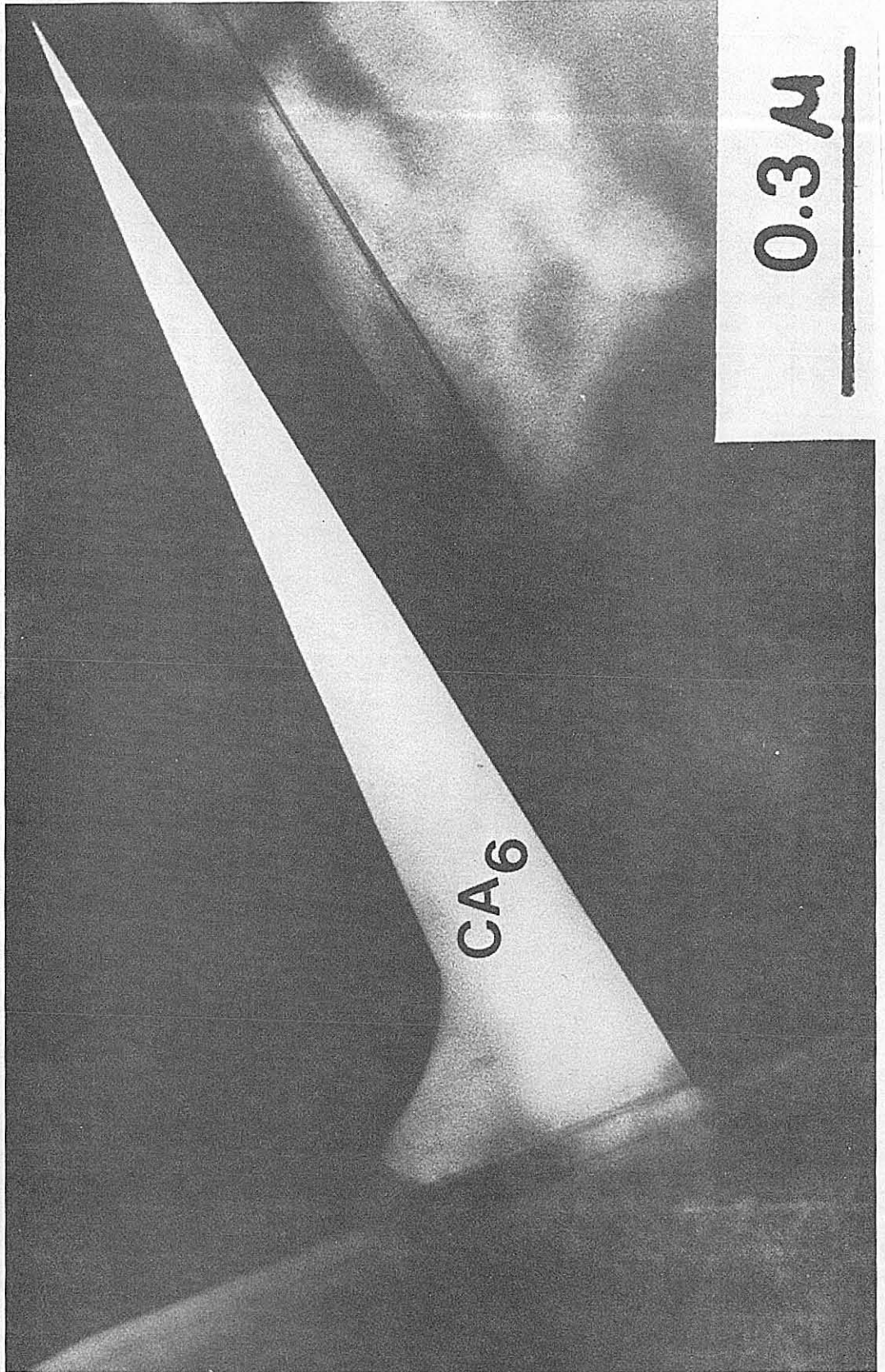
Figure 5





XBB 791-704

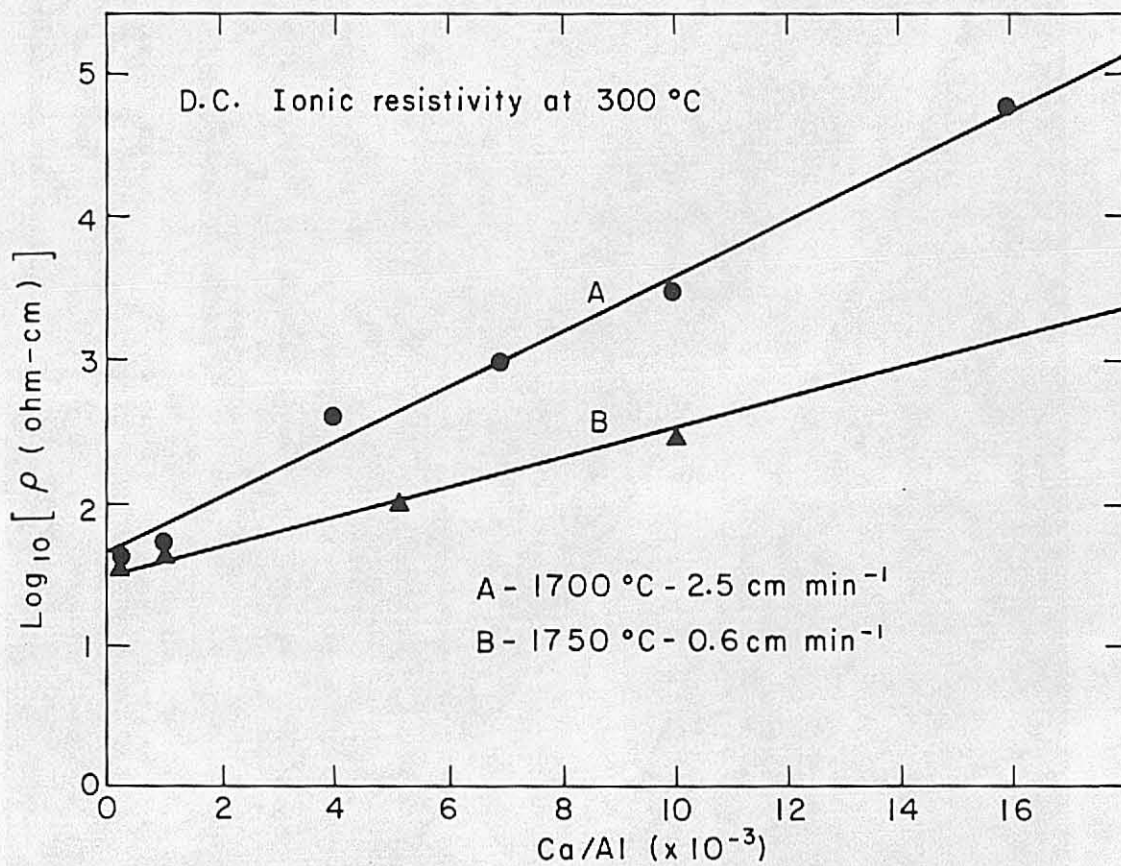
Figure 6



XBB 791-705

Figure 7





XBL7812-13345

Figure 8

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.



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