SCISPACE
formerly Typeset

Open access • Journal Article • DOI:10.1111/J.1151-2916.1970.TB11999.X

Solubility of Aluminum in Lead Zirconate Titanate — Source link

Robert B. Atkin, Richard M. Fulrath

Published on: 01 Jan 1970 - Journal of the American Ceramic Society (Blackwell Publishing Ltd)

Topics: Lead zirconate titanate and Solubility

Related papers:

- Method for combined synthesis of lead zirconate titanate film
- Method for preparing lead zirconate titanate film
- Method of producing lead-lanthanum zirconate-titanate
- Lead zirconate-titanate containing manganese additive
- Single Crystals of Lead Zirconate-Titanate Solid Solutions

Share this paper:

View more about this paper here: https://typeset.io/papers/solubility-of-aluminum-in-lead-zirconate-titanate-52x9xh4afv

Lawrence Berkeley National Laboratory
Recent Work

Title
SOLUBILITY OF ALUMINUM IN LEAD ZIRCONATE TITANATE

Permalink
https://escholarship.org/uc/item/80w596n1

Authors
Atkin, Robert B.
Fulrath, Richard M.

Publication Date
1969-06-01

eScholarship.org Powered by the California Digital Library
University of California

Submitted as a Note to J. of Am. Ceramic Soc.

UCRL-19038
Preprint

c.2

RECEIVED
LAWRENCE
RADIATION LABORATORY

AUG 25 1969

LIBRARY AND
DOCUMENTS SECTION

SOLUBILITY OF ALUMINUM IN LEAD ZIRCONATE TITANATE

Robert B. Atkin and Richard M. Fulrath

June 1969

AEC Contract No. W-7405-eng-48

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. 5545

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-19038

c.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.

SOLUBILITY OF ALUMINUM IN LEAD ZIRCONATE TITANATE

Robert B. Atkin and Richard M. Fulrath

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
and Department of Materials Science and Engineering,
College of Engineering, University of California,
Berkeley, California

June 1969

Recent processing studies[1,2] have shown that aluminum contamination can drastically alter the sintering behavior, piezoelectric, and ferroelectric properties of lead zirconate titanate (PZT). The alteration of ferroelectric properties indicates that aluminum enters the crystal lattice while the change in sintering behavior is attributed to the formation of a second phase. This secondary phase has been identified with the electron microprobe as a lead aluminate[1] which would be liquid at sintering temperatures. This note describes an experimental measurement of the solid solubility of aluminum in PZT and reports the effect of aluminum on the ferroelectric and piezoelectric properties of that material.

Lead zirconate titanate has the perovskite crystal structure with Pb^{2+} (ionic radius 1.20Å) in 12-fold coordination sites and Ti^{4+} (0.68Å) and Zr^{4+} (0.79Å) octahedrally coordinated. Trivalent aluminum (0.51Å) is undoubtedly too large to enter interstitially and too small to replace lead so substitution in octahedral sites is most probable. However, the size and valence differences should tend to limit this substitution. Three possible modes of balancing the valence discrepancy are: (1) the formation of anion vacancies, (2) the solution of

interstitial cations, e.g., H^+, and (3) the simultaneous substitution of cations with excess valence, e.g., Nb^{5+} for Ti^{4+} or Bi^{3+} for Pb^{2+}. Thus the extent of aluminum solubility will depend upon the activity of the other components in the crystal and upon the concentration and identity of impurities.

The material studied had a Zr:Ti ratio of 53:47 and was prepared by mixing, calcining and grinding high purity oxides. The mixing and grinding operations were performed with acrylic plastic or low-ash rubber equipment so that processing contaminents could be removed by oxidation. Semi-quantitative spectrographic analysis indicated the final powder contained approximately 0.05 wt% Al_2O_3, 0.02 wt% SiO_2, 0.02 wt% CaO and 0.002 wt% MgO. The desired quantities of aluminum were introduced as an aqueous solution of aluminum nitrate. This compound decomposes to Al_2O_3 at a low temperature. Reaction and densification were achieved by heating pressed pellets for 30 hours at 1200°C in one atmosphere of oxygen. The pellets were buried under PZT powder of the same composition inside a double wall, tightly covered platinum crucible. This arrangement provided the equilibrium PbO vapor pressure above the specimens and thereby prevented evaporation of that component. Several specimens doped with niobium and with scandium were also prepared.

The solubility limit was determined by monitoring several properties of specimens with increasing aluminum contents. Measurements were made of the X-ray diffraction patterns, microstructure, room temperature resistivity and hystersis loops (both polarization vs. electric field and dilation parallel to the field vs. electric field). All measurements

indicated saturation between 0.15 and 0.3 wt% Al_2O_3; for example, the hystersis loops (Fig. 1) did not change with aluminum content after 0.3 wt% was present.

Aluminum effects PZT in a manner similar to scandium, confirming the expected octahedral substitution. The ferroelectric hystersis loop of aluminum doped materials (Fig. 1c) resembled that of a specimen with 1 at.% scandium. The room temperature resistivity drops with aluminum substitutions as Gearson and Jaffe[3] have observed with scandium. They concluded that Sc^{3+} enters octahedral sites.

The substitutional aluminum and/or the associated vacancies alter the ferroelectric domain characteristics of PZT. When a polycrystalline specimen is cooled through the Curie temperature domains form to lower the strain and the electrostatic energy. The boundary between domains with their polarization vectors oriented anti-parallel are called 180° boundaries and they are, for tetragonal material, parallel to 100 directions. The 90° boundaries are formed by twinning on 110 planes. This second type of domain wall changes the shape of the grain and can thereby accommodate the anisotropic thermal expansion. Rhombohedral PZT spontaniously polarizes along the body diagonal of the unit cell so its 180° domain boundaries lie parallel to the 111 directions. Boundaries that separate domains oriented at 71° or 109° are planes and correspond to the 90° walls of tetragonal PZT. Domain boundaries may move under the influence of an electric field; this motion increases the polarization parallel to the field. Movement of 90° boundaries will, in addition, change the dimensions of the specimen. When the field is removed the domain boundaries may simply return to their

original (low energy) configuration or they may partially return, retaining some polarization in a metastable state. The latter behavior is observed with the higher purity PZT. When the material is saturated with aluminum domain wall motion is relatively difficult but the boundaries return to their original configuration when the field is removed.

The difference in domain boundaries is seen in the scanning electron micrographs of chemically etched specimens. The herringbone patterns seen in Figs. 2 and 3 are characteristic of 90° domain boundaries[4] while the curved boundaries observed in Fig. 3 and extensively in Fig. 4 are the 180° type. Aluminum additions clearly decrease the density of 180° domain walls and increase the density of 90° twins. When Nb^{5+} compensates for the trivalent aluminum virtually no 90° domains are present (Fig. 4). Apparently the material saturated with aluminum can accommodate the anisotropic thermal expansion only by extensive twinning. The configuration of these 90° domains appear quite rigid. The "pure" and niobium doped specimens are believed to have an additional mechanism of accommodating the mechanical constraints of neighboring grains. These materials minimize electrostatic energy with 180° domains. Those boundaries are relatively mobile and they retain their new configuration when the external field is removed.

The mechanism by which point defects determine domain boundary characteristics is under investigation.

REFERENCES

1. Gary Pryor, "Impurity Effects in Sintering Lead Zirconate Titanate," M.S. Thesis, University of California, Berkeley, UCRL-18191 (1968).

2. R. B. Atkin and R. M. Fulrath, "Practical Aspects of Sintering," to be published in the Proceedings of the International Conference on Interfaces, Melbourne, Australia, August 1969, Butterworth Ltd.

3. R. Gerson and Hans Jaffe, "Electrical Conductivity in Lead Zirconate Titanate Ceramics," J. Phys. Chem. Solids, Vol. 24 979-984 (1963).

4. Robert Gerson, "Variation in Ferroelectric Characteristics of Lead Zirconate Titanate Ceramics Due to Minor Chemical Modifications," J. Appl. Phys., 31 [1] 188-194 (1960).

ACKNOWLEDGMENT

The scanning electron microscope used was operated within the Electronics Research Laboratory, University of California. It was purchased under Grant No. GB-6428 from the National Science Foundation and is operated under Grant No. GM15536 from the National Institute of Health.

This work was done under the auspices of the United States Atomic Energy Commission.

FIGURE CAPTIONS

Figure 1. Hystersis loops showing polarization and dilation as a function of electric field. The polarization loops were recorded at 60hz and the dilation was measured at approximately 0.01 hz.

Figure 2. Scanning electron micrograph of PZT saturated with aluminum. The surface has been chemically etched to reveal the domain boundaries.

Figure 3. Scanning electron micrograph of "pure" PZT (etched).

Figure 4. Scanning electron micrograph of niobium doped PZT (etched).

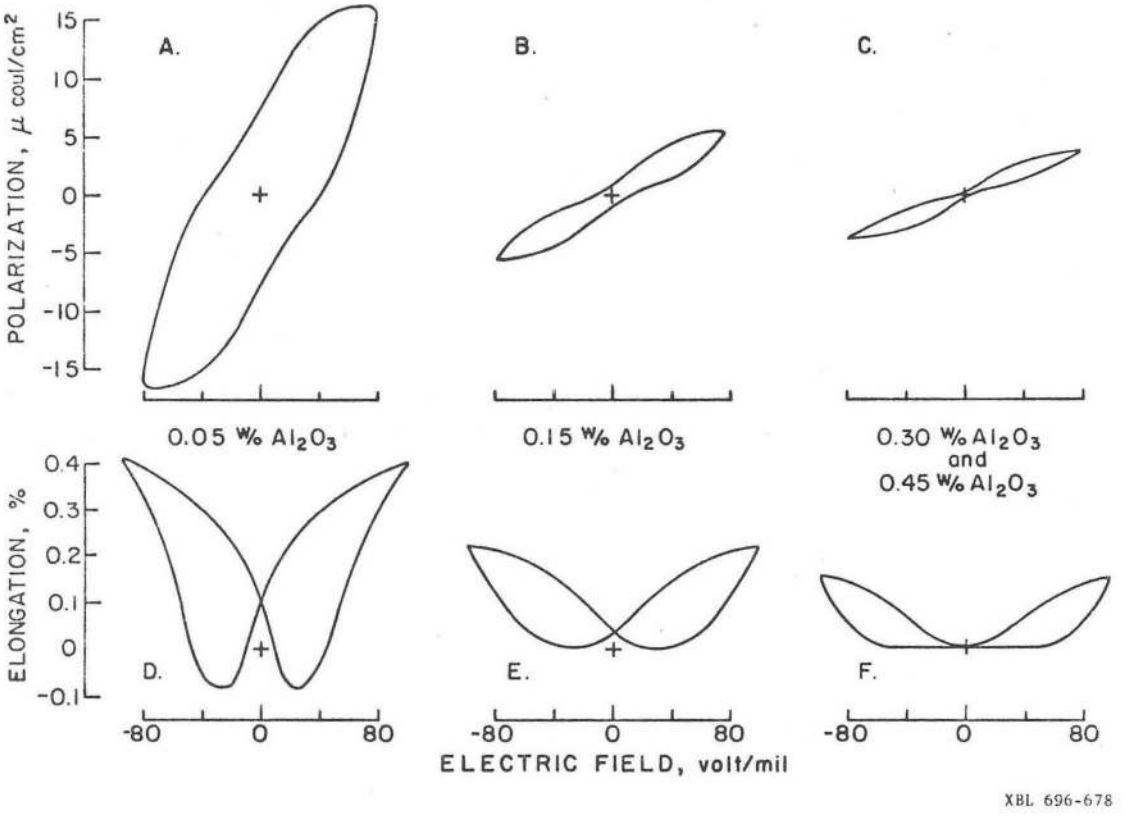

POLARIZATION, μ coul/cm²
15
10
5
0
-5
-10
-15
A.
B.
C.
0.05 W% Al2O3
0.15 W% Al2O3
0.30 W% Al2O3
and
0.45 W% Al2O3
ELONGATION, %
0.4
0.3
0.2
0.1
0
-0.1
D.
E.
F.
-80
0
80
ELECTRIC FIELD, volt/mil
XBL 696-678

Fig. 1

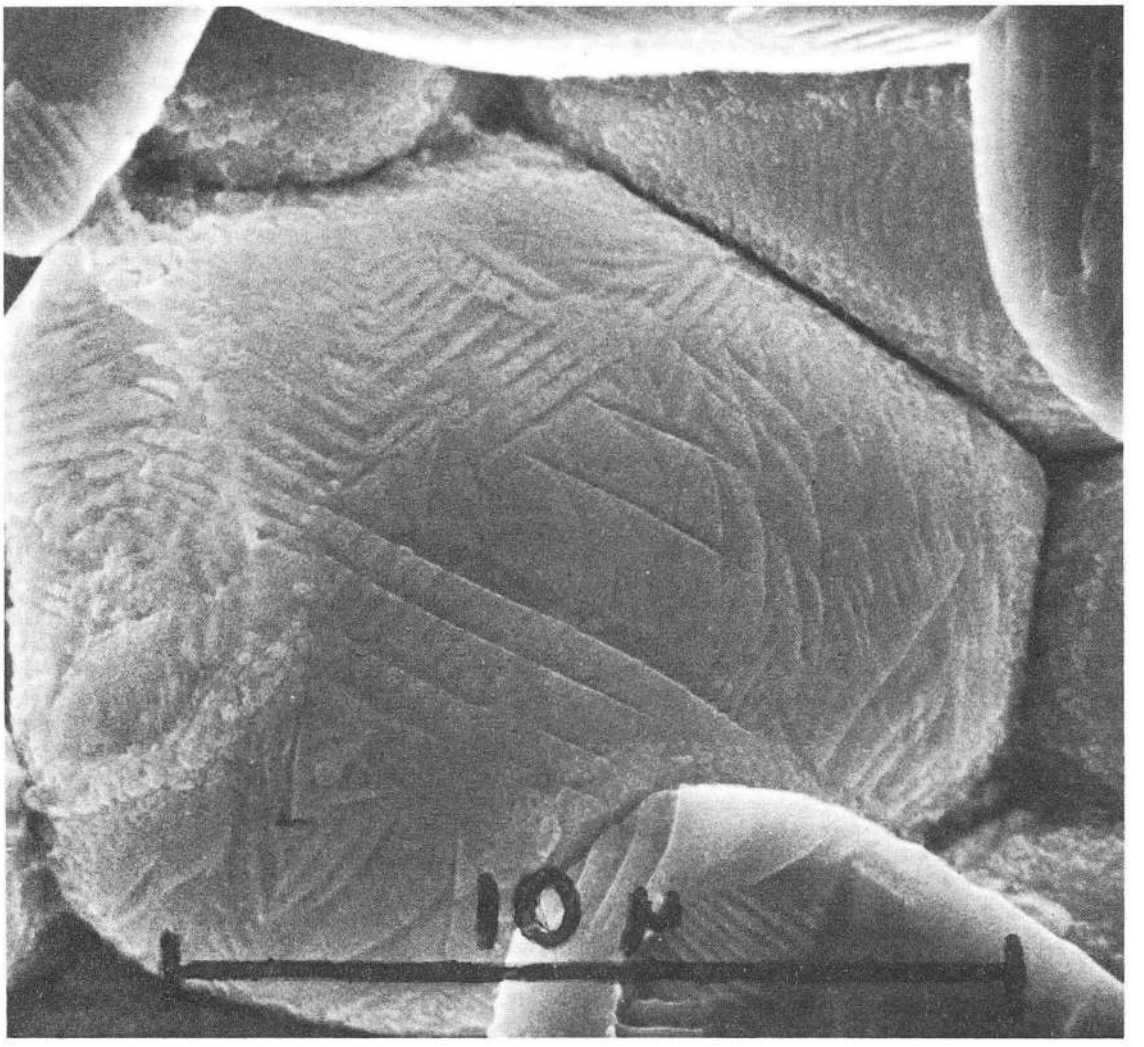
FIGURE CAPTIONS

Figure 1. Hystersis loops showing polarization and dilation as a function of electric field. The polarization loops were recorded at 60hz and the dilation was measured at approximately 0.01 hz.

Figure 2. Scanning electron micrograph of PZT saturated with aluminum. The surface has been chemically etched to reveal the domain boundaries.

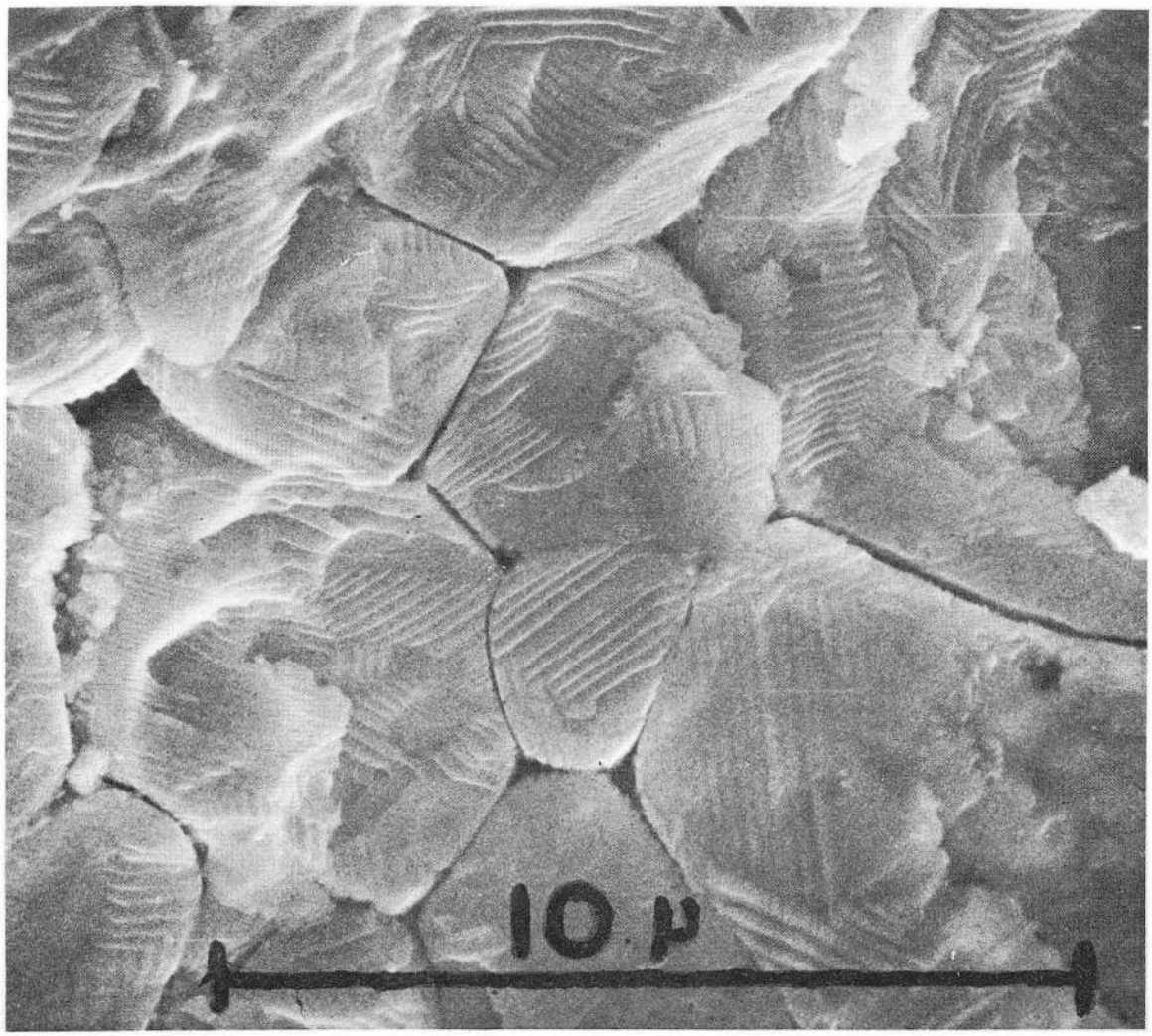
Figure 3. Scanning electron micrograph of "pure" PZT (etched).

Figure 4. Scanning electron micrograph of niobium doped PZT (etched).



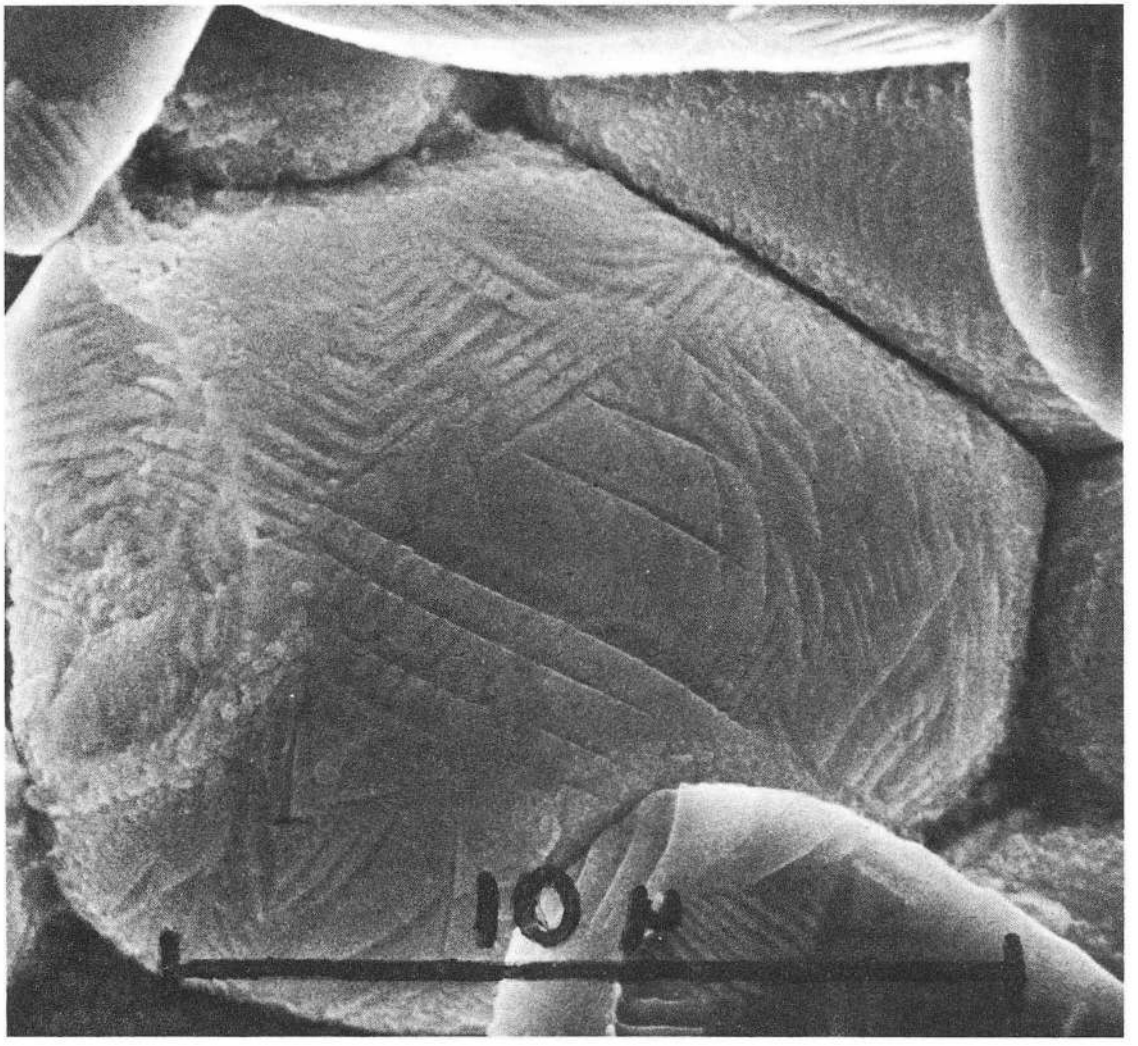
XBB 697-3971

Fig. 3



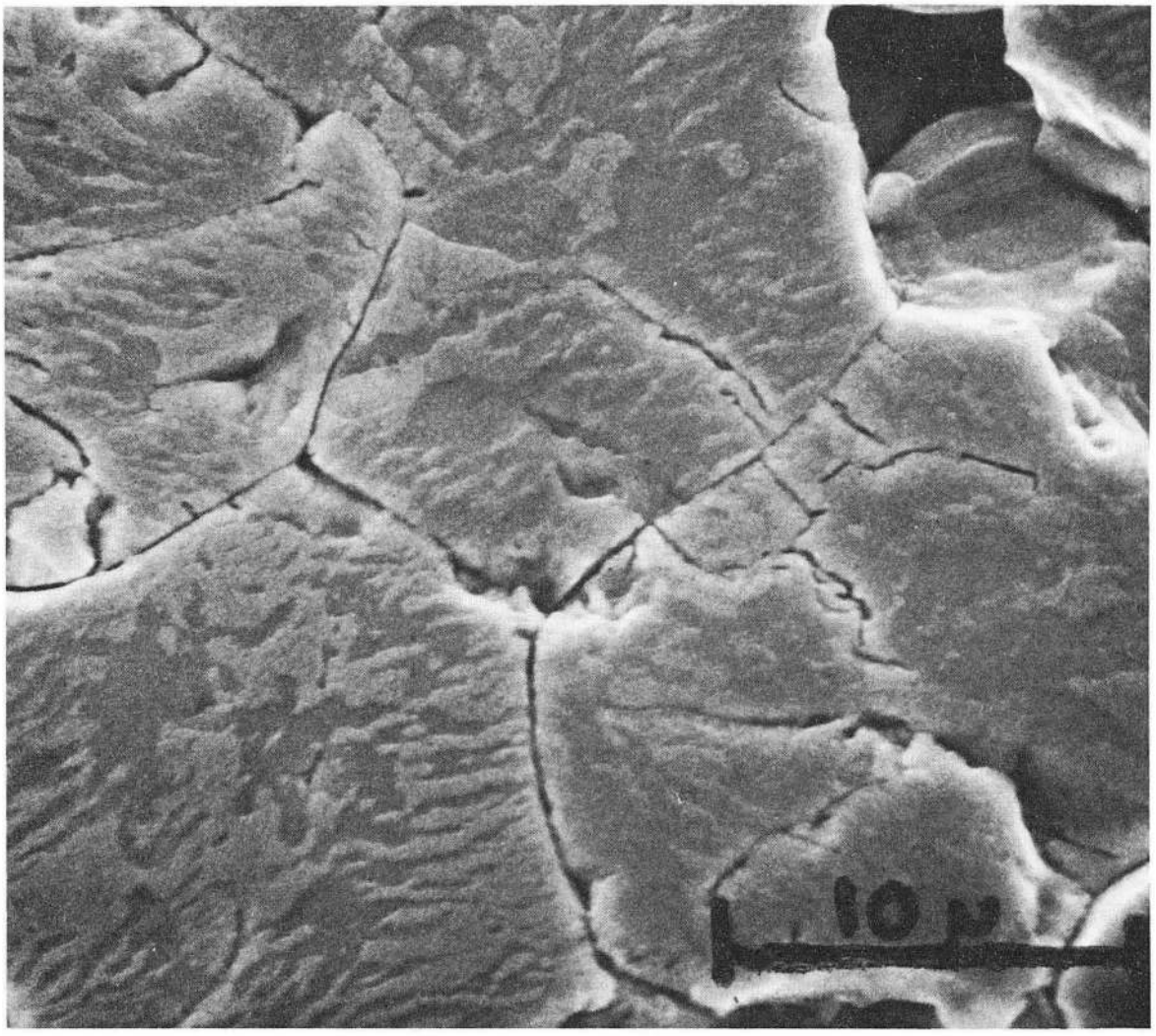
XBB 697-3972

Fig. 2



XBB 697-3971

Fig. 3



XBB 697-3970

Fig. 4

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720