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Publication Date

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SOLUBILITY OF ALUMINUM IN LEAD ZIRCONATE TITANATE

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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 aluminate¹ 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 $1.20\text{\AA}$) in 12-fold coordination sites and Ti^{4+} ($0.68\text{\AA}$) and Zr^{4+} ($0.79\text{\AA}$) octahedrally coordinated. Trivalent aluminum ($0.51\text{\AA}$) 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 contaminants 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 $1200^\circ C$ 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 hysteresis 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 hysteresis 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 hysteresis 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 Jaffe³ 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 spontaneously 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 boundaries⁴ 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.

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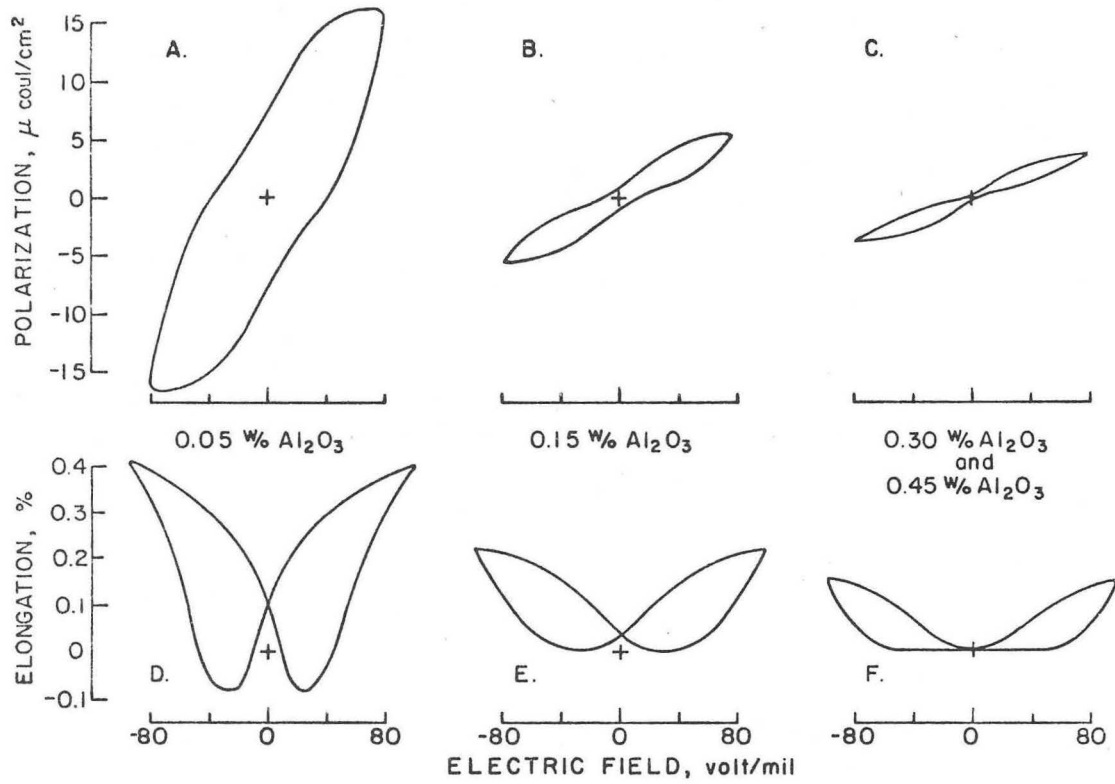
ACKNOWLEDGMENT

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. Hysteresis 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).

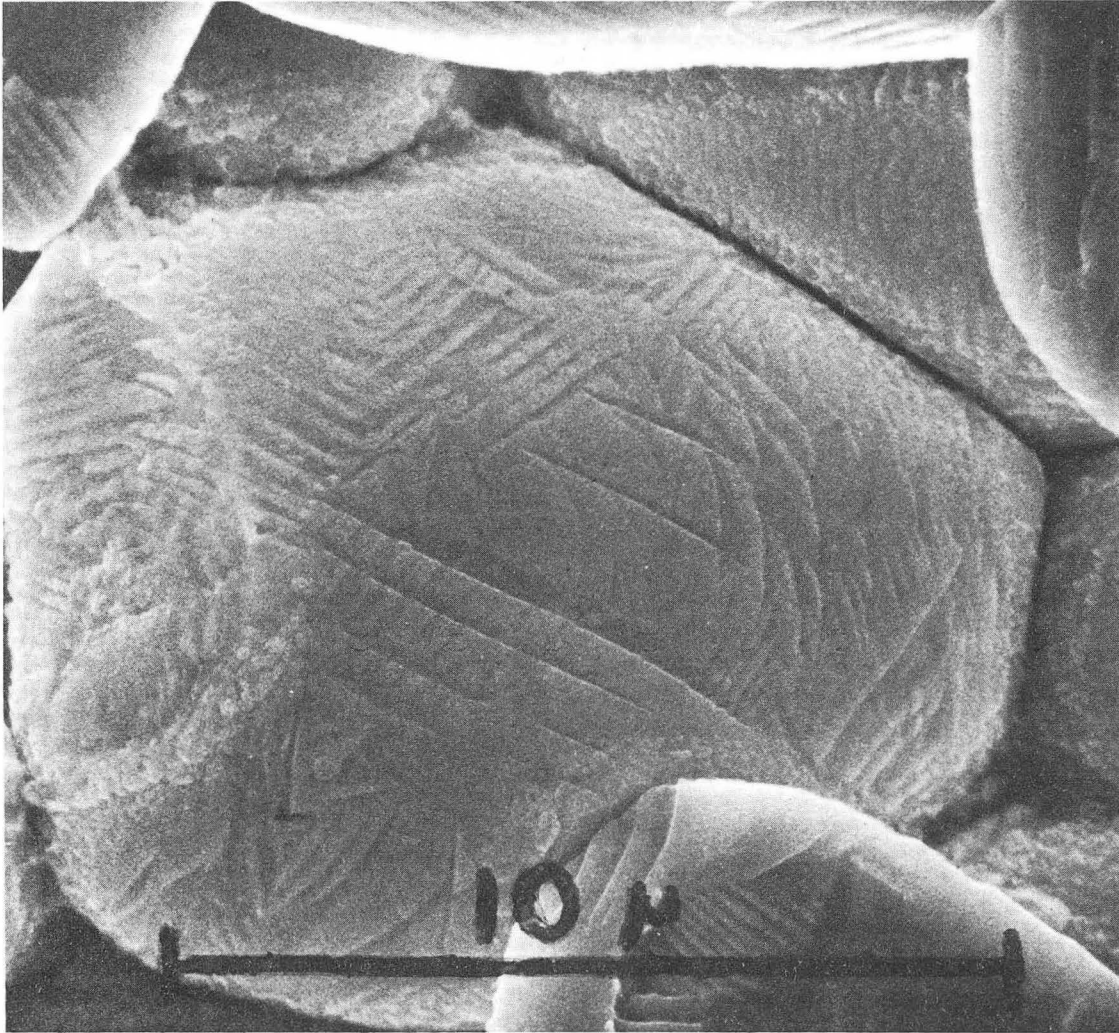


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Fig. 1

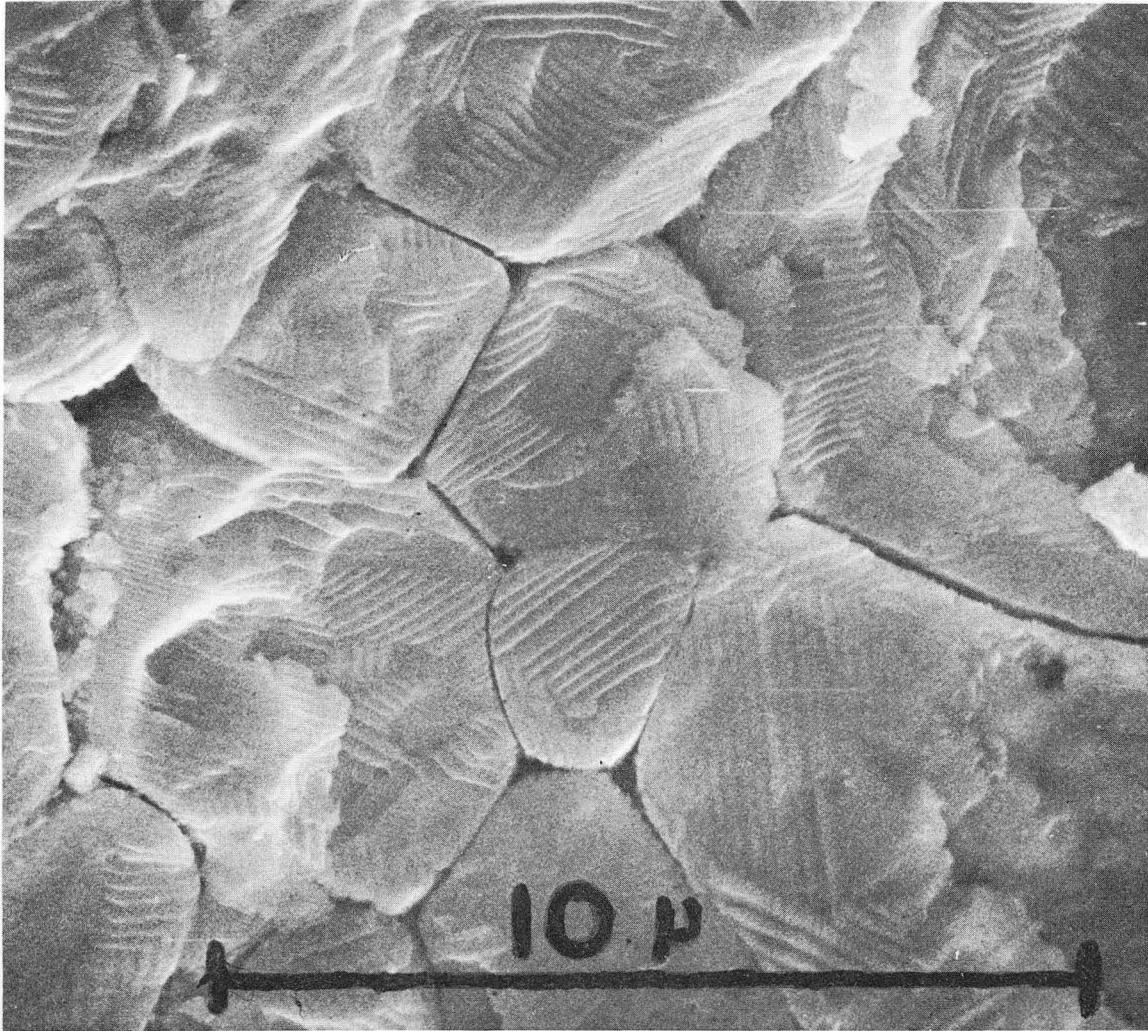
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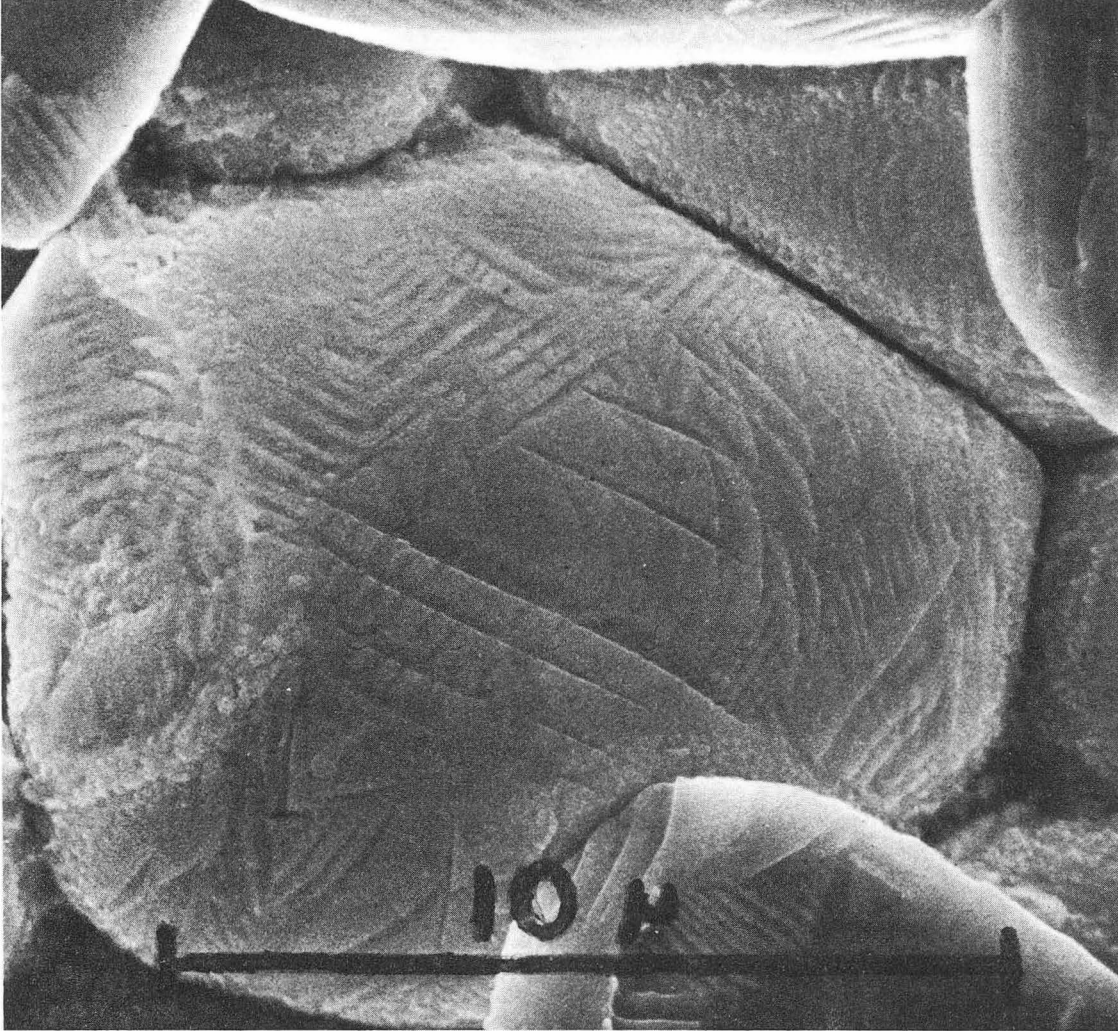
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Fig. 3



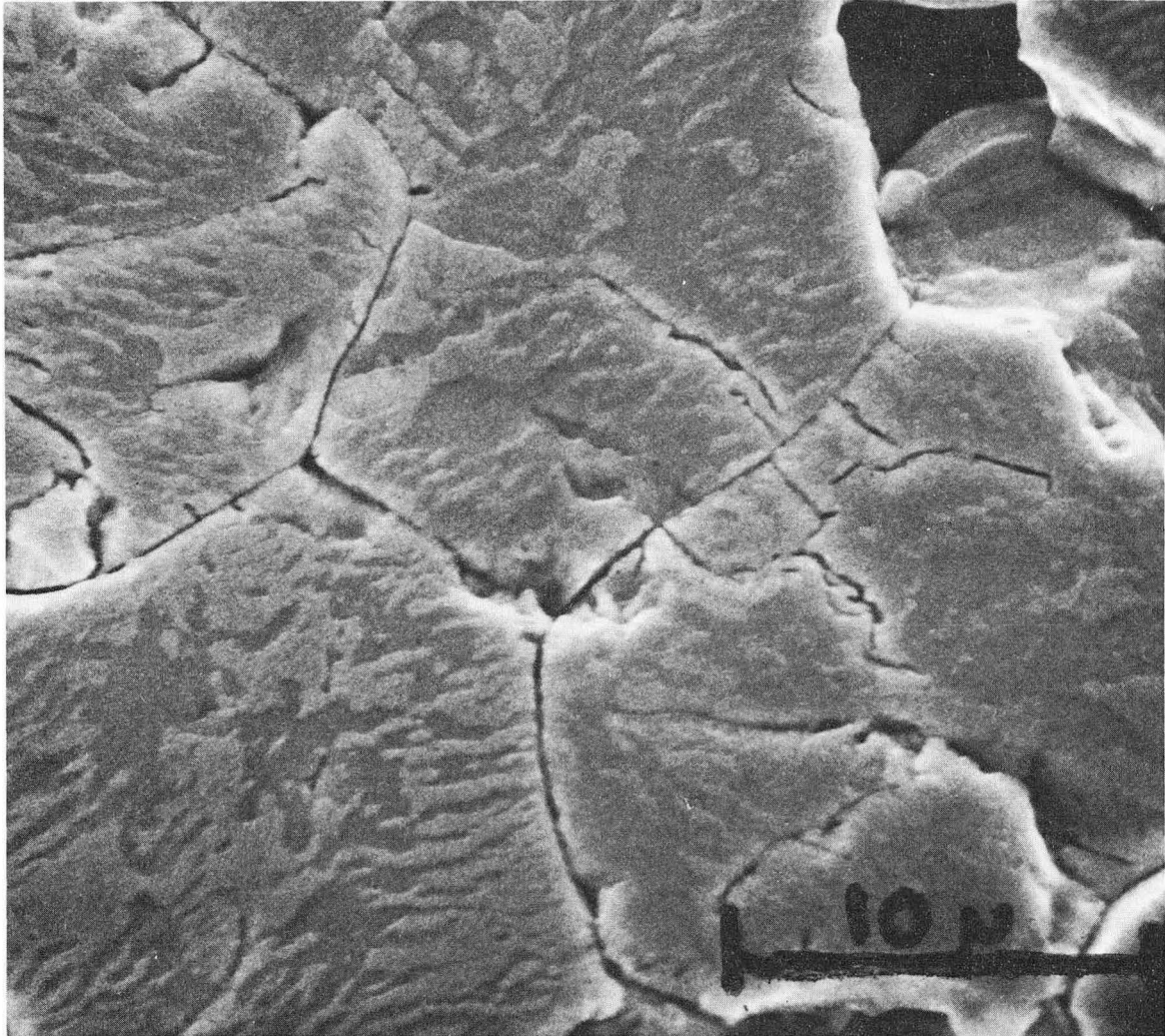
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Fig. 2



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Fig. 3



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Fig. 4

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