



DEPARTMENT OF  
ENERGY, MINES AND RESOURCES  
MINES BRANCH  
OTTAWA

*LEAD ZIRCONATE-LEAD TITANATE  
PIEZOELECTRIC CERAMICS WITH  
IRON OXIDE ADDITIONS*

T. B. WESTON  
MINERAL PROCESSING DIVISION

A. H. WEBSTER  
MINERAL SCIENCES DIVISION

V. M. McNAMARA  
EXTRACTION METALLURGY DIVISION

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# Lead Zirconate-Lead Titanate Piezoelectric Ceramics with Iron Oxide Additions

T. B. WESTON, A. H. WEBSTER, and V. M. McNAMARA

Mines Branch, Department of Energy, Mines, and Resources, Ottawa, Ontario, Canada

An investigation of the effects of small additions of  $\text{Fe}_2\text{O}_3$  to lead zirconate-lead titanate ceramics with compositions between 45 and 60 mol% lead zirconate has shown that, with 2 moles of  $\text{PbO}$  to balance each mole of  $\text{Fe}_2\text{O}_3$ , the solubility of  $\text{Fe}_2\text{O}_3$  was about 0.8 wt% in compositions near the tetragonal-rhombohedral boundary. The dielectric constant and dissipation factor for both rhombohedral and tetragonal materials were decreased by addition of iron oxide, whereas the mechanical quality factor and frequency constant were increased. The dependence of the electro-mechanical properties on grain size was qualitatively similar for both undoped and iron oxide-doped materials; the presence of iron oxide inhibited grain growth and lowered the limiting grain size below which the electromechanical properties change rapidly with grain size.

## I. Introduction

THE piezoelectric properties of lead zirconate-lead titanate ceramics with compositions near the rhombohedral-tetragonal boundary can be usefully modified by adding small quantities of various oxides. The effects of such additives as  $\text{CaO}$ ,<sup>1</sup>  $\text{SrO}$ ,<sup>1</sup>  $\text{Nb}_2\text{O}_5$ ,<sup>2</sup>  $\text{La}_2\text{O}_3$ ,<sup>2</sup>  $\text{Nd}_2\text{O}_3$ ,<sup>3</sup> and many others have been reported. One of the more interesting additives is  $\text{Fe}_2\text{O}_3$ ,<sup>4</sup> which has been reported to decrease the dielectric loss and increase the mechanical quality factor of lead zirconate-lead titanate ceramics.<sup>5</sup> However, it has also been shown that  $\text{Fe}_2\text{O}_3$  decreases the electrical resistivity above  $150^\circ\text{C}$ <sup>6</sup> and the dielectric constant.<sup>3</sup> It appeared desirable to extend these studies in order to describe the effects of iron oxide additions more completely. In the present investigation, the changes in properties with variations in iron oxide level, in zirconate-titanate ratio, and in grain size were studied.

## II. Experimental Procedure

The powders used in fabricating the ceramics were prepared by coprecipitation from blended nitrate solutions of lead, zirconium, and titanium using ammonia as the precipitating agent.<sup>6</sup> The precipitates were washed, spray-dried, and calcined at  $700^\circ\text{C}$ . The required amount of ferric oxide (Fisher reagent grade with particle size less than  $1\ \mu\text{m}$ ) was mixed with the calcined powder (particle size about 5 to  $10\ \mu\text{m}$ ) in an agate mortar, and disks were prepared by cold-pressing. The pressed disks were then sintered in an oxygen atmosphere in the presence of lead zirconate disks. In this manner a partial pressure of  $\text{PbO}$  was maintained. The sintered disks were ground and lapped to a standard size, 18.5 mm in diameter by 1.5 mm thick, and gold electrodes were applied by sputtering.

Densities of the lapped disks were determined from their weights and dimensions. Electrical measurements which determine the properties of interest were carried out before poling and 24 h after poling at  $100^\circ\text{C}$  under a field of 35 kV/cm for 5 min. Measurements of dielectric constant and dissipation factor ( $D = \tan \delta$ ) at low field (10 V/cm) were made on a GR 716 C bridge at a frequency of 1 kHz; corresponding measurements at a field of 2 kV/cm were made,

either with the same instrument or on a special high-voltage bridge that gave comparable results. The planar electro-mechanical coupling factor ( $k_p$ ) and the mechanical quality factor were determined from resonance-antiresonance measurements in accordance with the appropriate IRE Standards.<sup>7</sup>

Mean grain diameters were determined on etched polished sections by the intercept method and were taken as  $1.5\bar{l}$ , where  $\bar{l}$  is the average intercept per grain of a random straight line across a portion of the section.<sup>8</sup> X-ray diffraction patterns were taken using a Guinier focusing camera with  $\text{CoK}\alpha$  radiation, using sodium chloride as an internal standard. The methods used for the chemical analyses have been described previously.<sup>9</sup> In this paper, the compositions of the materials,  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ , to which iron oxide was added, will be expressed in terms of  $x$ , the zirconate/(zirconate+titanate) molar ratio, which is equivalent to the analytically determined  $\text{ZrO}_2/\text{ZrO}_2 + \text{TiO}_2$  molar ratio. The small hafnium content was considered as being equivalent to zirconium on a mole-for-mole basis.

## III. Experimental Results

### (1) Chemical and X-Ray Studies

In general, a small weight change is recorded when lead zirconate-titanate disks are sintered in an atmosphere containing a partial pressure of  $\text{PbO}$ . Part of this change is attributed to the loss of a small residue of volatile constituents. The remainder of the effect is due to the loss or gain of lead oxide from the furnace atmosphere, depending on whether the initial prepared composition had, respectively, an excess or a deficiency of lead oxide. When  $\text{Fe}_2\text{O}_3$  was added to the material, however, a weight increase greater than that observed for control samples without added iron invariably occurred. This weight increase, on the average, corresponded to 1.7, moles of  $\text{PbO}$  (std. dev. =  $\pm 0.56$ ) per mole of added  $\text{Fe}_2\text{O}_3$  for additions of 0.1 to 0.5 wt%  $\text{Fe}_2\text{O}_3$ . When, in one series of experiments, 2 moles of  $\text{PbO}$  were added to the material for each mole of  $\text{Fe}_2\text{O}_3$ , the weight increase on sintering corresponded to only 0.1, moles of  $\text{PbO}$  for each mole of  $\text{Fe}_2\text{O}_3$ . Therefore, it would appear that about 2 moles of  $\text{PbO}$  are required to balance each mole of  $\text{Fe}_2\text{O}_3$ . This is consistent with the substitution of iron ions into the 6-coordinated octahedral (zirconium, titanium) sites of the perovskite structure, together with the entry of one additional lead ion into a 12-coordinated site for each iron ion substituted.

In another experiment, lead zirconate-titanate powders, with and without iron oxide additions, were sintered in oxygen, in air, and in a 6% oxygen-94% argon mixture. As

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**Table I. Effects of Variation in Oxygen Partial Pressure During Sintering on the Properties of  $\text{Fe}_2\text{O}_3$ -Doped Lead Zirconate-Titanate Ceramics\***

$P_{\text{O}_2}$ (atm)	Sintered density (g/cm <sup>3</sup> )		$K_{33}^T$		$h_p$	
	Control	0.2 wt% added $\text{Fe}_2\text{O}_3$	Control	0.2 wt% added $\text{Fe}_2\text{O}_3$	Control	0.2 wt% added $\text{Fe}_2\text{O}_3$
1	7.96	7.90	893	624	0.56	0.55
0.21	7.80	7.76	866	590	.55	.54
0.06	7.78	7.80	826	591	.54	.53

\*Molar ratio  $x=0.529$ . Ceramics sintered at 1260°C for 3 h.

indicated in Table I, there was only a slight decrease in dielectric constant and in electromechanical coupling factor with decreasing oxygen partial pressure in the sintering atmosphere. This decrease was observed for both doped and undoped material and is probably due to the slight decrease in sintered density. Such an effect of oxygen-inert gas mixtures was observed previously<sup>10,11</sup> and is attributable to the entrapment of the inert gases in closed pores. It would appear from these results that the oxidation state of the iron incorporated in the lead zirconate-titanate solid solution did not vary with changes in the oxygen partial pressure.

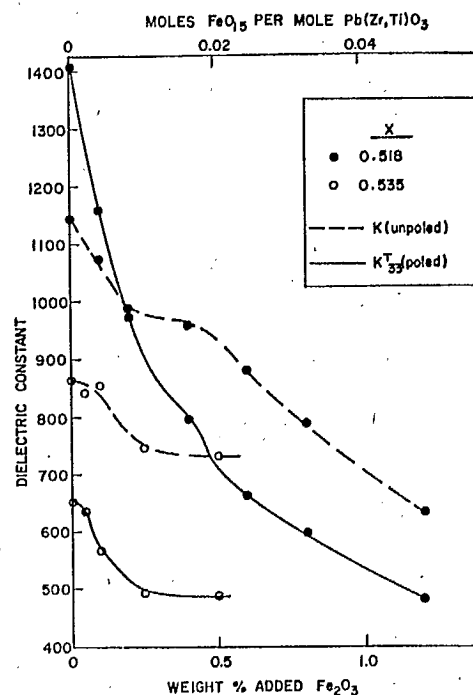
Microscopic examination of polished sections showed that a small proportion of an intergranular phase, which appeared to have been molten at the sintering temperature of 1260°C, began to be evident when about 0.8 wt%  $\text{Fe}_2\text{O}_3$  had been added to material with  $x=0.518$ . The amount of this phase increased with larger additions of  $\text{Fe}_2\text{O}_3$ . It would appear, therefore, that the solubility of  $\text{Fe}_2\text{O}_3$  in lead zirconate-titanate extends to about 0.8 wt% at 1260°C. Electron microprobe examinations, done by point-counting of the iron concentrations in different parts of the polished sections, indicated considerable inhomogeneity for the material with 1.2 wt%  $\text{Fe}_2\text{O}_3$ , whereas materials with less than 0.8 wt% iron oxide were relatively homogeneous. These results are consistent with the solubility limit indicated above.

X-ray diffraction examination of the same material, both with and without added  $\text{Fe}_2\text{O}_3$ , was made using crushed ceramic. The material was tetragonal when up to 0.4 wt%  $\text{Fe}_2\text{O}_3$  had been added, but, with 0.6 wt% or more, the material was rhombohedral. It would appear, therefore, that the tetragonal-rhombohedral boundary, which occurs at the zirconate/(zirconate+titanate) ratio of 0.527 in unmodified material,<sup>12</sup> is shifted to a zirconate/(zirconate+titanate) ratio of 0.518 by the addition of about 0.5 wt%  $\text{Fe}_2\text{O}_3$ .

## (2) Effect of the $\text{Fe}_2\text{O}_3$ Additions on the Properties of Lead Zirconate-Titanate Ceramics

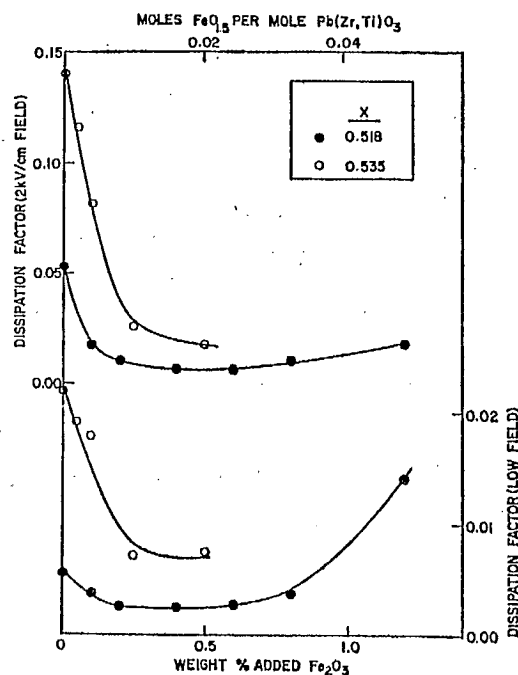
The effects of  $\text{Fe}_2\text{O}_3$  additions at several levels were examined on two lead zirconate-titanate compositions. Iron oxide, with two moles PbO added for each mole of  $\text{Fe}_2\text{O}_3$ , was added to calcined material with  $x=0.518$ . Disks were subsequently sintered at 1260°C for 5 h. Disks prepared from material with  $x=0.535$  were sintered at 1260°C for 2 h, after addition of  $\text{Fe}_2\text{O}_3$ , without a corresponding addition of PbO.

The dielectric constants both before and after poling for the two compositions are shown as functions of the amount of added  $\text{Fe}_2\text{O}_3$  in Fig. 1. The dielectric constant decreases rapidly with the addition of iron oxide in both cases. The material with the lower zirconate content was tetragonal in the unmodified condition, but, as noted previously, be-



**Fig. 1. Effect of  $\text{Fe}_2\text{O}_3$  addition on the dielectric constants of lead zirconate-lead titanate ceramics.**

came rhombohedral on the addition of about 0.5 wt%  $\text{Fe}_2\text{O}_3$ . The irregularity observed in the curve for this material at just under 0.3 wt%  $\text{Fe}_2\text{O}_3$  is due to the peak in dielectric constant that is observed on passing across the rhombohedral-tetragonal boundary, superimposed on the decrease in dielectric constant due to the  $\text{Fe}_2\text{O}_3$  addition. The curves for the poled and unpoled dielectric constants intersect at about 0.2 wt%  $\text{Fe}_2\text{O}_3$ . Hence, there is a small compositional range near the rhombohedral-tetragonal boundary in which



**Fig. 2. Effect of  $\text{Fe}_2\text{O}_3$  addition on the dissipation factor of poled lead zirconate-lead titanate ceramics.**

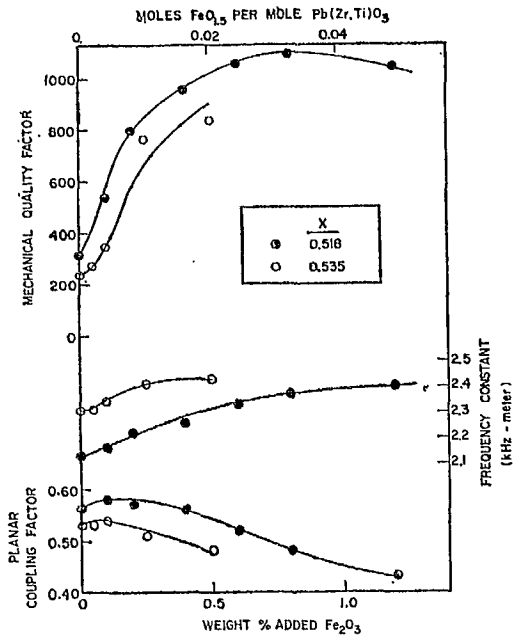


Fig. 3. Effect of Fe<sub>2</sub>O<sub>3</sub> addition on the mechanical quality factor, frequency constant, and planar electromechanical coupling factor of lead zirconate-lead titanate ceramics.

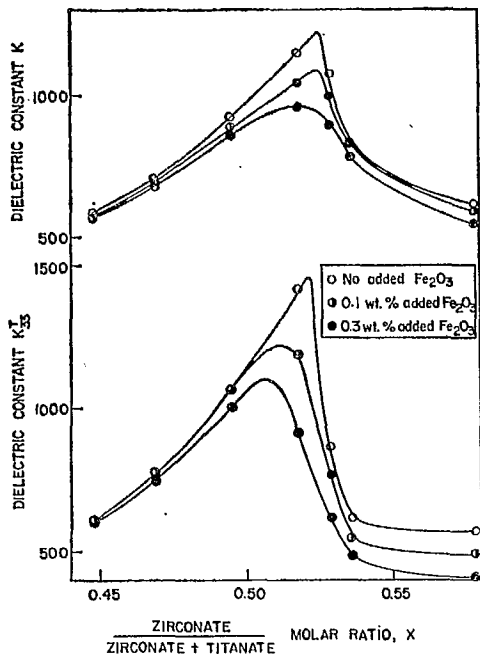


Fig. 4. Variation of dielectric constant with the molar ratio  $x$  for lead zirconate-lead titanate ceramics with added iron oxide. Ceramics were sintered at 1260°C for 3 h.

the dielectric constant for a tetragonal material decreases on poling, in contrast to the increase in dielectric constant on poling generally observed for tetragonal lead zirconate-titanate ceramics.<sup>12</sup> A similar decrease in dielectric constant of a tetragonal material on poling was also reported for lead zirconate-titanate with BiFeO<sub>3</sub> additions.<sup>13</sup>

The marked decrease in dissipation factor produced by Fe<sub>2</sub>O<sub>3</sub> additions of up to 0.6 wt% is shown in Fig. 2. The effect on the dissipation factor measured under a high field

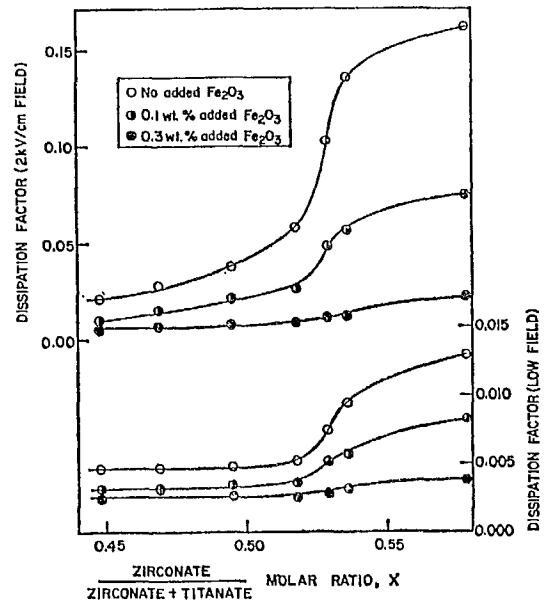


Fig. 5. Variation of dissipation factor with molar ratio  $x$  for poled lead zirconate-lead titanate ceramics with added iron oxide.

(2 kV/cm) is especially pronounced. For greater additions of iron oxide, however, the dissipation factor begins to increase. The mechanical quality factor increases considerably with Fe<sub>2</sub>O<sub>3</sub> additions up to 0.8 wt%, as indicated in Fig. 3. An increase in frequency constant with addition of Fe<sub>2</sub>O<sub>3</sub> is also indicated. The planar coupling factor appears to increase slightly to a maximum value on the addition of 0.1 to 0.2 wt% Fe<sub>2</sub>O<sub>3</sub>, and then decreases gradually with larger additions.

(3) Variations in Properties of Fe<sub>2</sub>O<sub>3</sub>-Modified Ceramics with Changes in Zirconate/Titanate Ratio

Additions of 0.1 and 0.3 wt% Fe<sub>2</sub>O<sub>3</sub> were made to lead zirconate-titanate compositions having molar ratios,  $x$ , ranging from 0.45 to 0.60. A decrease in the dielectric constant, both before and after poling, with addition of Fe<sub>2</sub>O<sub>3</sub>, is shown for all compositions in Fig. 4. Iron oxide also lowers the zirconate/(zirconate+titanate) ratio at which the maximum dielectric constant occurs. This trend is consistent with the results of the X-ray diffraction studies, which indicated that the presence of Fe<sub>2</sub>O<sub>3</sub> favored the rhombohedral structure. This shift of the dielectric constant after poling is, however, somewhat greater than would have been expected on the basis of the X-ray results.

The dissipation factor, plotted in Fig. 5, decreased with the addition of Fe<sub>2</sub>O<sub>3</sub> for all compositions. The relative decrements were greater for the rhombohedral compositions, which, in the unmodified state, have higher dissipation factors than the tetragonal materials.<sup>12</sup> The addition of Fe<sub>2</sub>O<sub>3</sub> produced an increase in mechanical quality factor for all compositions, as shown in Fig. 6. The increase was relatively greater for the rhombohedral materials. The changes in frequency constant and in planar coupling factor resulting from Fe<sub>2</sub>O<sub>3</sub> modification are also shown in Fig. 6. These changes are smaller than for the other properties discussed, and the compositions at which extreme values occur did not shift appreciably on the addition of iron oxide.

(4) Grain-Size Effects

The two materials on which the effects of various levels of Fe<sub>2</sub>O<sub>3</sub> additions were studied (see Section III (2))

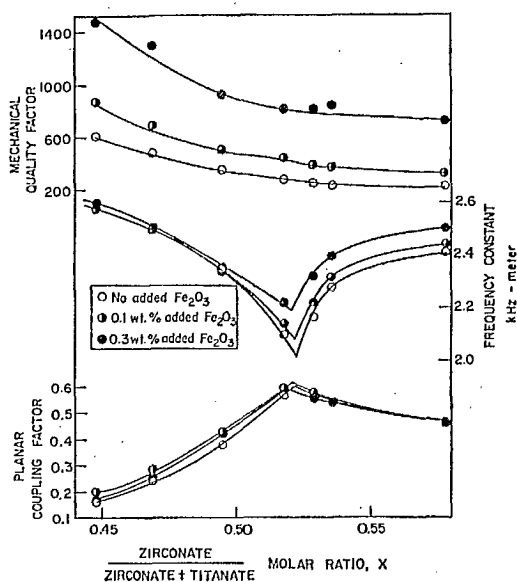


Fig. 6. Variation of mechanical quality factor, frequency constant, and planar electromechanical coupling factor with molar ratio  $x$  for lead zirconate-lead titanate ceramics with added iron oxide.

exhibited a decrease in grain size with increasing iron oxide content, as shown in Fig. 7. This decrease was very rapid for additions up to 0.2 wt% Fe<sub>2</sub>O<sub>3</sub>, but larger additions had little further effect on the grain size.

To investigate the effect of varying the mean grain diameter, disks were prepared from the material with  $x = 0.518$ , both unmodified and with 0.1 wt% Fe<sub>2</sub>O<sub>3</sub>. The disks were sintered at 1190°, 1240°, and 1290°C for 1 and 5 h. The planar electromechanical coupling factor and the dissipation factor, plotted in Fig. 8, showed qualitatively the same type of dependence on grain size both with and without added Fe<sub>2</sub>O<sub>3</sub>. However, the mean grain diameter below which the grain-size dependence of the two properties is large decreased with the addition of iron oxide.

#### (5) Addition of Iron Oxide by Coprecipitation

To determine whether there were any differences in properties of the ceramics when the iron was introduced by coprecipitation rather than added to the calcined lead zirconate-titanate powder, two powders were prepared by the coprecipitation method.<sup>9</sup> The appropriate concentration of ferric nitrate was added to the nitrate solution of lead, zirconium, and titanium before precipitation with ammonia. Some properties of ceramics fabricated from these materials are shown in Table II and are compared with the estimated values of the properties for materials to which iron oxide was added after calcination. There is fairly good agreement between the two sets of values, although the poled dielectric constants,  $K_{33}^T$ , are lower for the material with coprecipitated iron oxide by about 15 and 20%. The reason for this discrepancy is not clear, but it may be a consequence of the rapid change in properties with small changes in the molar ratio  $x$  near these compositions. It would appear that essentially equivalent results can be obtained by the two methods of iron addition.

## IV. Discussion

The substitution of Fe into the lead zirconate-lead titanate solid solution apparently takes place in the 6-coordinated site in the perovskite structure. This model is quite consistent with the fairly small differences between the ionic radius of Fe<sup>3+</sup> (0.60 Å) and those of Ti<sup>4+</sup> (0.68 Å)

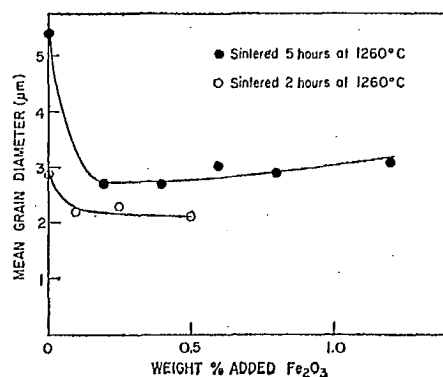


Fig. 7. Effect of iron oxide addition on the grain size of lead zirconate-lead titanate ceramics.

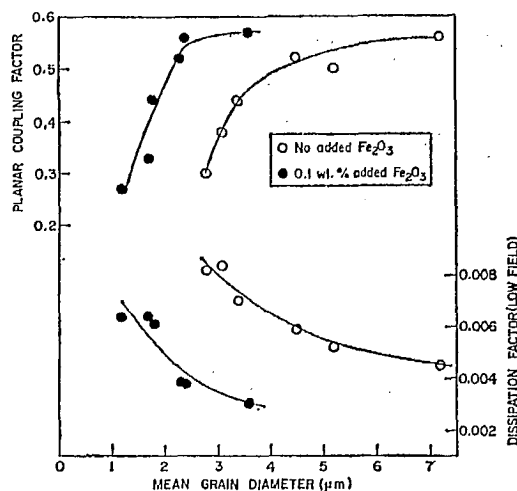
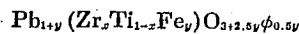


Fig. 8. Effect of grain size on the planar electromechanical coupling factor and dissipation factor of lead zirconate-lead titanate ceramics with and without added iron oxide.

and Zr<sup>4+</sup> (0.80 Å). The additional lead ion required for each iron ion added indicates that, under the conditions used in the present investigation, both 6- and 12-coordinated cation sites are essentially fully occupied. There remains, then, an oxygen deficiency if the iron is trivalent, giving a solid solution which can be designated as



where  $\phi$  represents an oxygen vacancy. If the iron were

Table II. Properties of Ceramics Made from Powders to Which Iron Oxide Had Been Added by Coprecipitation and by Mechanical Mixing

Composition	Method of Fe <sub>2</sub> O <sub>3</sub> addition	K	K <sub>33</sub> <sup>T</sup>	k <sub>p</sub>	D <sub>p</sub> (2 kV/cm)
x=0.527 0.12 wt% Fe <sub>2</sub> O <sub>3</sub>	Coprecipitation*	1038	710	0.58	0.038
	Addition to calcine†	1030	820	.59	.036
x=0.526 0.21 wt% Fe <sub>2</sub> O <sub>3</sub>	Coprecipitation*	973	643	.56	.019
	Addition to calcine†	990	760	.59	.020

\*Ceramics sintered at 1250°C for 3 h.

†Values estimated by interpolation of data in Figs. 4, 5, and 6.

quadrivalent, these vacancies would be filled. Both the existence of oxygen vacancies<sup>14</sup> and the presence of quadrivalent iron<sup>15</sup> have been demonstrated for certain perovskite-type solid solutions. Quadrivalent iron, however, was not found in the system  $\text{Sr}(\text{Ti}_{1-y}\text{Fe}_y)\text{O}_{3-z}$  for compositions with  $y < 0.2$ , even for material fired in 1 atm  $\text{O}_2$  pressure.<sup>15</sup> Since the properties of the solid solutions considered here are not changed by decreasing the oxygen partial pressure to  $P_{\text{O}_2}=0.06$  atm, it is probable that the iron is trivalent. The maximum value of  $y$  in the above formula would be about 0.03, based on the measured solubility of iron oxide in the lead zirconate-lead titanate solid solution.

Iron oxide and some other transition metal oxides have been described as "hardeners" in their effects on the properties of lead zirconate-lead titanate.<sup>3</sup> The results of the present investigation are in agreement with this description. The mechanical stiffness, as indicated by the frequency constant, and the dielectric stiffness, as indicated by the reciprocal of the dielectric constant, are both increased by iron oxide additions. Both mechanical losses, as indicated by the reciprocal of the mechanical quality factor, and dielectric losses, as indicated by the dissipation factor, are decreased by the addition of iron oxide. These effects are relatively greater for the rhombohedral (high zirconate) materials than for the tetragonal materials.

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