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VARIATIONS IN PROPERTIES WITH
COMPOSITION IN LEAD
ZIRCONATE-TITANATE CERAMICS

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Variations in Properties with Composition in Lead Zirconate-Titanate Ceramics

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Ottawa, Ontario.

ABSTRACT

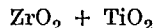
Lead zirconate-lead titanate ceramics, covering the compositional range 40 to 70 mole per cent lead zirconate, were prepared by cold pressing and sintering from co-precipitated powders. For these ceramics the maxima in the values of dielectric constant and electromechanical coupling factor that occur at the rhombohedral-tetragonal boundary were found to be higher and sharper than previously reported for unmodified lead zirconate-titanate. Dielectric and mechanical losses were lower in the tetragonal than in the rhombohedral phase. Determination of the variations in properties with temperature confirmed the previously reported shift in the phase boundary toward higher zirconate compositions with increasing temperature. It was found that changes in electro-mechanical properties resulting from loss of lead oxide could be explained on the basis of the formation of a more titanate-rich solid solution, accompanied by the precipitation of zirconia.

Introduction

The properties of lead zirconate-titanate piezoelectric ceramics are critically dependent upon their compositions, as expressed by the ratios of the major components. The relationships between the zirconate/titanate ratio and the electromechanical properties have been extensively studied (1, 2). The dielectric constant and electromechanical coupling factor pass through maxima near the boundary, situated at about 53 mole per cent zirconate (3), between the tetragonal (titanate-rich) and rhombohedral (zirconate-rich) solid solutions. Berlincourt et al (2) reported, however, that the maxima in the unpoled dielectric constant, K , and in the poled dielectric constant, K_{33}^T , did not occur at the same zirconate/titanate ratio, and suggested that a shift in the tetragonal-rhombohedral boundary may take place during poling. Furthermore, recent studies (4, 5) have yielded values for dielectric constants and planar electromechanical coupling factors, for unmodified lead zirconate-

titanate, that are higher than the maximum values reported by Berlincourt et al. It was of interest, therefore, to re-investigate systematically the compositions in the region of the observed maxima. A temperature dependence for the composition of the rhombohedral-tetragonal boundary has also been reported (6). The variations with temperature of some properties of the poled ceramics were experimentally determined to confirm this observation and to provide data that would be useful in selecting compositions for specific applications.

Generally, lead zirconate-titanate ceramics are prepared with the intention that they will be stoichiometric, that is, that they will have a



mole ratio of unity. Variations in this ratio, however, can take place during sintering due to volatilization of lead oxide, and such variations in the lead oxide content will affect the electromechanical properties of the ceramics (5). The nature and explanation of these changes in properties was not evident. Therefore an investigation of this problem was undertaken.

While the effects of changes in the ratios of the major constituents of the material were studied in the present work, it was known that other characteristics of the ceramic, principally density (7, 8), grain size (5, 8) and the presence of minor constituents (9, 10) could have considerable effects on the electromechanical properties. For this reason, care was taken to characterize the ceramics used in the present investigation with respect to those attributes known to affect the electrical properties.

Experimental procedures

The powders used to make the ceramics were produced by co-precipitation from blended nitrate solutions of Pb(II), Zr(IV), and Ti(IV), using ammonia as the precipitating agent (11). The precipitates were washed, spray-dried and calcined. Ceramic disks were fabricated from the calcined precipitates by cold-pressing, followed by sintering in the presence of lead zirconate. The disks were ground and lapped to a standard size, and gold electrodes applied by sputtering.

Electrical measurements for determining the properties of interest were carried out before poling and subsequently, 24 hours after poling at 100°C, usually at a field of 40 kV/cm. The methods used have been described previously (5), and are in accordance with the appropriate standards (12). For determination of the variations in properties with temperature, samples were held in a variable-temperature air chamber. In this case, capacitance measurements were obtained with the aid of a three-terminal, automatically-balancing bridge. The methods used for the chemical analyses (13, 14) and for the determination of average grain diameters (4) have been described previously. The hafnium content of the zirconia was determined by X-ray fluorescence. X-ray diffraction patterns were taken on a Guinier focussing camera, using CoK α radiation with CaF $_2$ as an internal standard.

The disks used to study the effects of variation in zirconate/titanate ratio were sintered from thirteen different 4-kg lots of precipitate ranging from 40 to 70 mole per cent lead zirconate. These materials were sintered at 1260°C and at 1240°C, with soaking times of two and four hours at each temperature. Electromechanical properties after poling were determined on two disks from each of the four sintering conditions.

The three groups of disks used to examine the effects of variation in lead oxide content were prepared from powder, initially slightly deficient in lead oxide, by sintering at 1260°C for two hours. The sintering was done in a series of cycles in which the amounts of PbO available to the furnace atmosphere were varied by changing the number and positions of the lead zirconate disks in the furnace. Each group of disks showed a range in the weight changes that occurred during sintering. The disks used in these experiments were poled at 36 kV/cm.

Experimental results and discussion

a. Characterization of the ceramics: The ceramics used for the determination of the variation of electrical properties as functions of the mole fraction of lead zirconate were characterized with respect to those attributes known to affect the electrical proper-

TABLE I

Chemical Analyses, Sintered Densities, and Grain Diameters of Lead Zirconate-Titanate Ceramics Used in the Study of the Variation of Electromechanical Properties with Mole Fraction Lead Zirconate

Molar Ratios (by Analysis) ⁽¹⁾					
ZrO ₂		PbO		Sintered Density ⁽³⁾ % Crystal Density	Average Grain Diameter ⁽⁴⁾ micron
ZrO ₂ + TiO ₂	Ceramic ⁽²⁾	Powder	Ceramic ⁽²⁾		
0.395	0.394	0.964	0.995	98.6	3.2
0.422	0.423	1.001	1.010	98.6	3.4
0.441	0.448	1.003	1.010	98.8	3.5
0.470	0.469	0.992	1.009	98.9	3.7
0.494	0.495	0.990	1.013	99.0	4.1
0.519	0.518	0.998	1.009	98.8	4.1
0.529	0.529	0.993	1.005	98.6	3.8
0.538	0.536	0.996	1.008	98.6	3.7
0.559	0.559	1.004	1.008	97.9	3.7
0.576	0.578	1.005	1.007	98.6	3.4
0.598	0.600	1.000	1.006	97.9	4.3
0.648	0.647	1.002	1.008	96.9	4.0
0.698	0.697	1.002	1.006	97.3	3.7

NOTES:

⁽¹⁾Hafnium considered equivalent to zirconium, except for difference in atomic weight. Molar ratio HfO₂/ZrO₂ = 0.0156.

⁽²⁾Ceramic sintered at 1260°C for 2 hours.

⁽³⁾Mean value for disks sintered at 1260°C.

⁽⁴⁾Determined on one disk sintered at 1260°C for 2 hours.

TABLE 2	
Maximum Limits of Impurities in Precipitates	
Element	Weight %
Si	0.01
Al	0.005
Fe	0.04
Mg	0.04
Ca	0.02
Mn	0.002
Cu	0.02
Sr	0.02

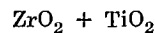
ties. The molar ratios of the major constituents, expressed as



and



are shown in Table 1, both for the precipitated powders and for the sintered ceramics. Hafnium was considered as being equivalent to zirconium on a mole basis. In agreement with previous work (5), no change in the



ratio occurred during sintering, but the ratio

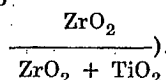


increased for all samples. The maximum deviation of this latter ratio from unity was 1.3% for the disks sintered at 1260°C for two hours. Weight changes during sintering indicated that the disks sintered at 1240°C generally had a slightly lower PbO content. Spectrographic analysis of the precipitated powders indicated the maximum limits of impurities shown in Table 2. Silicon and aluminum were determined quantitatively,

while the other elements were determined semi-quantitatively. The sintered densities listed in Table 1 indicated that the porosity in the ceramics sintered at 1260°C ranged from 1.0% to 3.1%, with the highest values occurring in the high-zirconate compositions. It is estimated that this variation could produce changes of, at most, 4% in values of the radial coupling factor. The average grain diameters in disks sintered at 1260°C for two hours (Table 1) were large enough that only small changes in properties would be expected with changes of grain diameter in the range reported. Examination of disks from one lot sintered at 1240°C indicated a smaller average grain diameter. Since the densities and average grain sizes of the disks sintered at 1240°C were lower than those of disks sintered at 1260°C, the results on 1260°C sintered disks are reported, except as noted otherwise.

The ceramics used in the study of lead oxide deficiencies all had densities between 98.5% and 99.6% of theoretical. Average grain diameters were found to decrease slightly with decreasing PbO content of the disks. The small changes in properties associated with these changes in grain size would not affect the conclusions drawn from these experiments.

b. Variation of properties with mole fraction of PbZrO₃ at room temperature: In Figure 1, the radial electro-mechanical coupling factor, dielectric constant before and after poling, low-field dielectric loss, and mechanical quality factor are plotted as functions of the mole fraction PbZrO₃ (i.e. the molar ratio



Maxima were found in the plots of coupling factor and dielectric constant as functions of composition. Berlincourt et al (2) reported that their peak for the poled dielectric constant (measured in the direction of poling) was displaced to a PbZrO₃ mole fraction 0.02 lower than the peak for the unpoled dielectric constant. The present results appear to indicate a much smaller shift of about 0.005 or less. In general, the peaks for coupling factor and dielectric constant, shown in Figure 1, are higher and more sharp than those reported by Berlincourt et al for ceramics not modified by the addition of minor constituents. The decrease in mechanical quality factor and the increase in dielectric loss on moving from the tetragonal to the rhombohedral phase, that were found in the present work, agree with the results of Berlincourt et al. However, the values of Q_m reported here are about one-half the values reported by Berlincourt; also, the dielectric losses found in the present work are higher than those reported by Berlincourt.

The dielectric loss under a rms field of 1 kV/cm, frequency constant (radial resonant frequency x diameter of disk) and specific resistivity are plotted in Figure 2 as functions of the PbZrO₃ mole fraction. An increase in the high-field dielectric loss on moving from the tetragonal to the rhombohedral phase, corresponding to the increase in the low-field loss, is observed. A further increase in high-field loss, near the 64 mole % zirconate composition, may be a reflection of the transition from the F_{R(HT)} to F_{R(LT)} ferroelectric phases reported by Dungan et al (15) and shown in more detail on the phase diagram presented by Jaffe and Berlincourt (6). The minimum in the plot of frequency constant corresponds to the minimum in the plot of

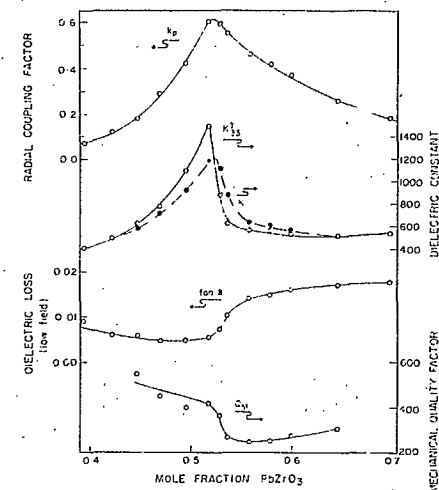
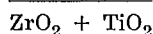


Fig. 1. Radial coupling factor (k_p), dielectric constant before poling (K), dielectric constant after poling (K_{33}), dielectric loss ($\tan \delta$) at 1 kHz (low field) as measured on poled disks, and mechanical quality factor, plotted as functions of the mole fraction PbZrO₃.

against composition shown by Berlin-court et al. The specific resistivity of the ceramics was higher for the rhombohedral phase than for the tetragonal phase.

Lattice parameters determined on unpoled disks sintered at 1260°C are also shown in Figure 2. The composition at 52.9 mole % zirconate showed a greater proportion of the tetragonal phase than the rhombohedral phase in a rather diffuse X-ray diffraction pattern.

The mole fractions of $PbZrO_3$ at which the extrema in electrical and mechanical properties occur average to a value of 0.522 ± 0.004 . The crystallographic results indicate that the change from tetragonal to rhombohedral symmetry occurs at a



ratio of 0.527 ± 0.008 .

Mean values of the properties under consideration are given for all thirteen compositions in Table 3.

c. Variation of electromechanical properties with temperature: Measured values of dielectric constant, radial coupling factor and frequency constant are plotted against temperature in Figures 3, 4 and 5, respectively, for most of the compositions prepared in this investigation. Although each curve displays the results of measurements on a single sample, other measurements on duplicate samples have confirmed that the curves are representative of the behaviour of ceramics of the indicated compositions.

For most of the compositions studied, the dielectric constant (Figure 3) shows a steady increase with temperature; the curves steepen only at the upper end of the temperature

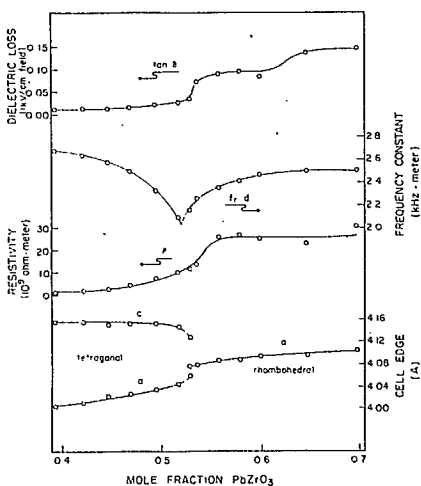


Fig. 2. Dielectric loss ($\tan \delta$) at 1 kHz (1 kV/cm rms field), frequency constant (f_r, d), resistivity (ρ) as measured on unpoled disks, and cell edge as determined by X-ray diffraction, plotted as functions of the mole fraction $PbZrO_3$.

TABLE 3

Mean Values of Properties for Lead Zirconate-Titanate Compositions Examined

ZrO ₂		tan $\delta^{(1)}$ (low field) 1 kHz after poling		tan $\delta^{(1)}$ (1 kV/cm) after poling	$\rho^{(6)}$ ohm-meter before poling	$f_r, d^{(1)}$ kHz-meter		
ZrO ₂ + TiO ₂ (mole ratio)	$k_p^{(1)}$	$K^{(2)}$	$K^{T(1)}_{33}$	$Q_m^{(3)}$				
0.394	0.07	410	416	0.0089	—	0.0133	1.0×10^9	2.68
0.423	0.12	488	496	0.0059	—	0.0132	1.8	2.64
0.448	0.18	589	620	0.0057	543	0.0131	2.2	2.58
0.469	0.29	709	780	0.0046	449	0.0170	4.2	2.50
0.495	0.42	914	1095	0.0046	398	0.0207	7.1	2.33
0.518	0.60	1188	1496	0.0053	417	0.0254	10.0	2.09
0.529	0.59	1119	881	0.0072	363	0.0356	11.8	2.16
0.536	0.55	874	623	0.0102	266	0.0741	13.7	2.26
0.559	0.46	632	569	0.0140	246	0.0886	26.0	2.35
0.578	0.42	601	562	0.0147	252	0.0968	27.0	2.42
0.600	0.37	550	534	0.0158	273	0.0828	25.4	2.47
0.647	0.26	512	514	0.0167	306	0.1387	23.3	2.50
0.697	0.18	545	535	0.0175	—	0.1466	30.8	2.52

NOTES:

(1) Mean of 4 disks sintered at 1260°C.

(2) Mean of 6 disks sintered at 1260°C.

(3) Mean of all disks on which values of Q_m could be determined, generally 7 or 8 disks.

(4) Mean of 2 disks sintered at 1240°C for 4 hours.

(6) Mean of 12 disks sintered at 1260°C and 1240°C.

range as the approach to the Curie point begins. However, compositions having zirconate mole fractions of 0.518, 0.529 and 0.536, which are close to the morphotropic phase boundary, show much larger variations in dielectric constant with temperature, and, in addition, each curve exhibits a discontinuity in slope which is presumed to indicate the change in structure from tetragonal to rhombohedral. Since the changes in slope occur at different temperatures for the three compositions, the position of the boundary would appear to move with respect to composition as the temperature rises.

The radial coupling factor (Figure

4) shows much smaller variations with temperature than does the dielectric constant, yet broad maxima appear in the curves for compositions near the morphotropic phase boundary at temperatures approximately corresponding to those of the discontinuities in the dielectric constant curves. These maxima are matched by minima in the curves of frequency constant against temperature shown in Figure 5. For compositions bearing lead zirconate mole fractions of 0.600, 0.647, and 0.697, a "step" in the frequency constant curve was observed, which would appear to represent a transition between the low- and high-temperature forms of the rhom-

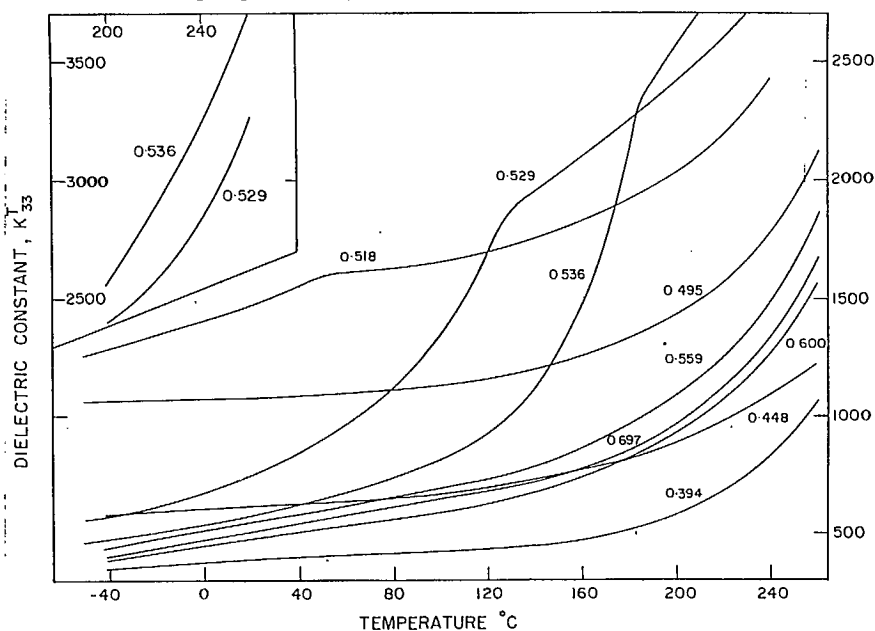


Fig. 3. Variation of dielectric constant with temperature. Mole fraction $PbZrO_3$ indicated for each curve. Insert shows continuation of the curves at the upper right hand corner of the diagram.

bohedral phase previously reported (6, 15).

If one of these properties is plotted against composition, with temperature as a parameter, as has been done for the dielectric constant in Figure 6, a set of curves is obtained which shows how the position of the tetragonal-rhombohedral boundary changes with temperature. It is clear from these curves that the boundary moves toward the high-zirconate end of the phase diagram as the temperature increases. Analogous curves have been plotted for all three of the properties discussed above and, from them, a mean position of the phase boundary for four different temperatures

has been derived. These positions are indicated in Figure 7. It is clear from this plot also, that the boundary moves toward higher zirconate/titanate ratios as the temperature increases, and that the slope of the boundary increases slightly at the higher temperatures. This result is in general agreement with previously reported results (6), within the limits of experimental error, which are estimated to be ± 0.003 in mole fraction zirconate.

The position of the boundary between the $F_{R(HT)}$ and $F_{R(LT)}$ rhombohedral phases cannot be derived with the same degree of precision, but a suggested position for this boundary, based on the frequency constant curves of Figure 5, is

also indicated in Figure 7. This position is in reasonable agreement with earlier results(6).

d. Effects of lead oxide deficiency on the properties of lead zirconate-titanate ceramics: The effects of lead oxide deficiency on the radial coupling factor, dielectric constant and low-field dielectric loss of these groups of lead zirconate-titanate ceramics are shown in Figure 8, in which these properties are plotted as functions of weight change during sintering. The weight change during sintering of these materials, initially slightly deficient in lead oxide, was assumed to indicate the relative lead oxide content of the disks, although it was realized that the disks, in most cases, would not be homogeneous with respect to lead oxide content. A small weight change, approximately constant for a given material, due to loss of residual volatile constituents (principally moisture and binder) is superimposed on the weight change due to change in lead oxide content. Exact compositions could not be calculated from the weight changes, since the outer portion of each disk had been removed by grinding. Some of the disks with the largest weight gains probably contained PbO slightly in excess of the stoichiometric requirement.

The results shown in Figure 8 can be explained by consideration of the $PbO-ZrO_2-TiO_2$ phase diagram (3,16). For a material with a given

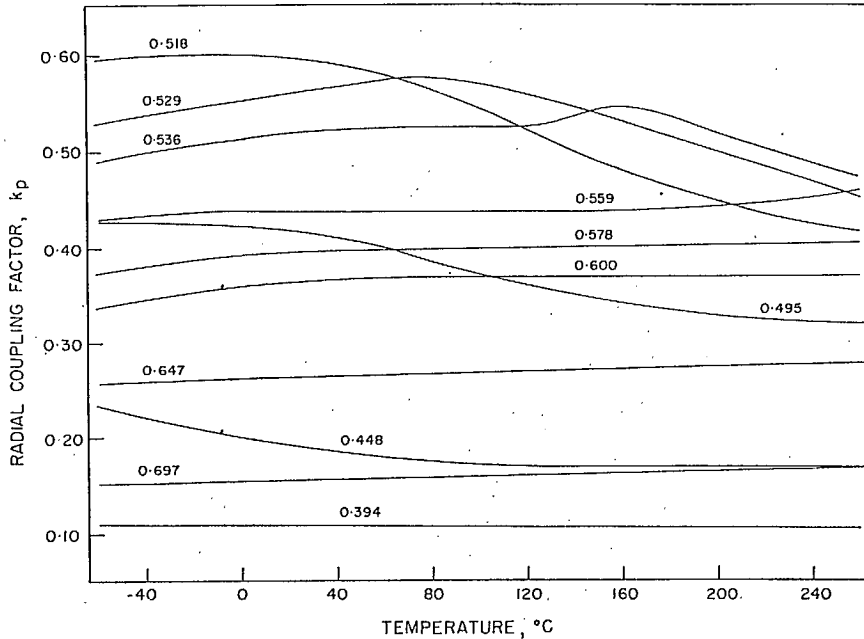


Fig. 4. Variation of radial coupling factor with temperature. Mole fraction $PbZrO_3$ indicated for each curve.

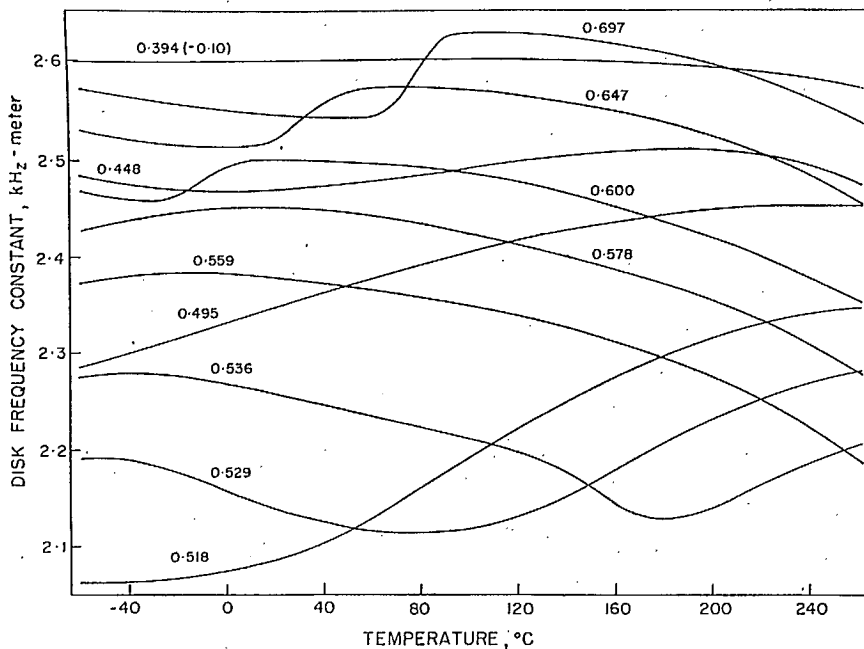


Fig. 5. Variation of frequency constant with temperature. Mole fraction $PbZrO_3$ indicated for each curve. Curve for 0.394 $PbZrO_3$ mole fraction has been displaced downward by 0.1 kHz-meter.

ZrO_2
 $ZrO_2 + TiO_2$

ratio near the tetragonal-rhombohedral boundary, a deficiency of PbO should result in the precipitation of a small amount of zirconia (with, perhaps, some titania in solid solution), and the formation of a $Pb(Zr, Ti)O_3$ solid solution with a $PbZrO_3$ mole fraction lower than that indicated by the bulk composition of the sample. Hence, as the PbO deficiency increases, the properties of the ceramics should become those characteristic of

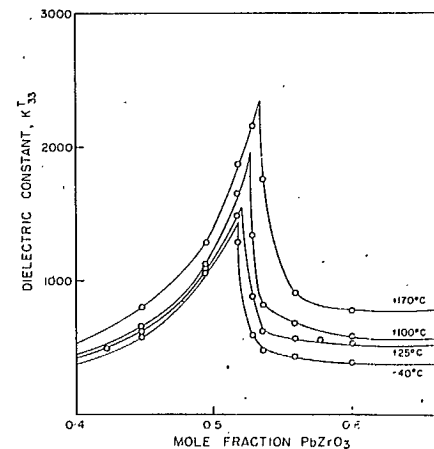


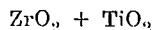
Fig. 6. Dielectric constant as a function of the mole fraction $PbZrO_3$ for four different temperatures.

material with a lower lead zirconate content.

In Figure 8(a), the results for a tetragonal material are shown. As the lead oxide content decreases, the composition of the $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ solid solution moves away from the rhombohedral-tetragonal boundary and, as expected, the coupling factor and dielectric constant decrease. The low-field dielectric loss does not change appreciably. These observations are all consistent with the results shown in Figure 1.

The results for a rhombohedral material are shown in Figure 8(c). As the lead oxide content decreases, the composition of the $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ solid solution moves toward the rhombohedral-tetragonal boundary and the coupling factor and dielectric constant increase. The low-field dielectric loss decreases with the decrease in lead oxide content, again in agreement with the results shown in Figure 1.

For material with a



ratio of 0.528, X-ray diffraction indicated the presence of the rhombohedral phase (with a trace of tetragonal) for a weight change of +1.4%, and of the tetragonal phase for a weight change of -1.8%. This shows directly the change in the $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ solid solution with lead oxide content of the material. The curves for K_{33}^T and K intersect show maxima, and a behaviour consistent with changing zirconate content in the solid solution across the rhombohedral-tetragonal boundary. The dielectric loss decreases, as expected, in passing from the rhombohedral to the tetragonal phase.

The results of the experiments shown in Figure 8 indicate a relative displacement of the peaks for coupling factor and for dielectric constant. This effect may be due to inhomogeneity, since the changes in lead oxide content of the ceramics take place by diffusion of PbO into or out of the disks. The effect of this inhomogeneity will probably be to give properties that are averaged over the effective mole per cent zirconate range produced by the variation in PbO content within the disk. This averaging effect will lower and broaden the peaks for coupling factor and for dielectric constant. For an asymmetric peak, it will also shift the maximum toward the side that has the more gradual slope. Examination of Figure 1 indicates that the expected effect of inhomogeneity would be a shift in the position of the dielectric constant maximum relative to the coupling factor maximum.

The proposed explanation was supported also by examination of etched polished sections of disks with lead oxide deficiency. A small amount of a second phase, presumably zirconia, was found in these disks, but not in those disks which showed large weight gains.

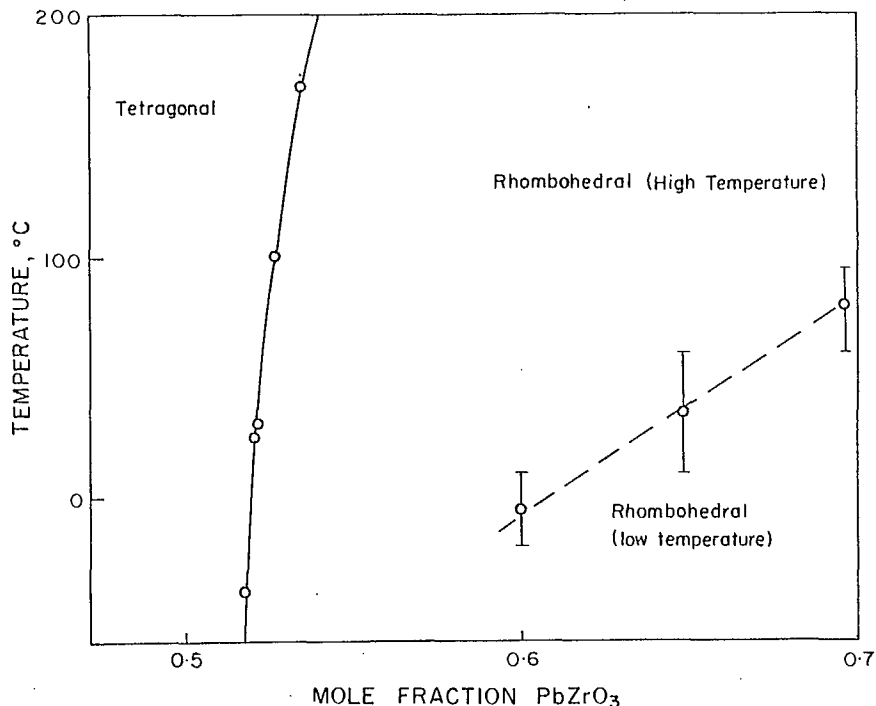


Fig. 7. Phase boundaries in the portion of the PbTiO_3 - PbZrO_3 system investigated in the present study.

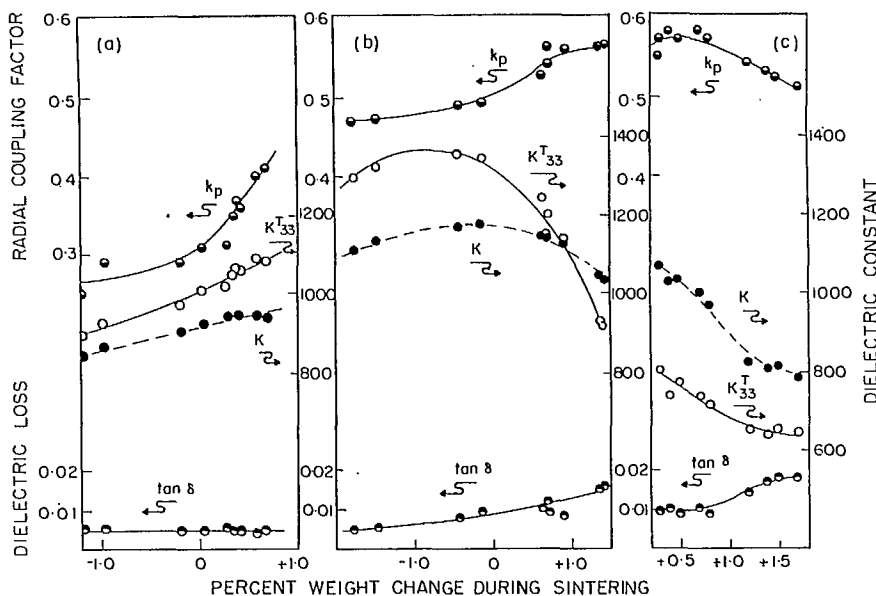


Fig. 8. Radial coupling factor (k_p), dielectric constant before poling (K), dielectric constant after poling (K_{33}^T), and dielectric loss ($\tan \delta$) at 1 kHz (low field) as measured on poled disks, shown as functions of percent weight change during sintering for materials with three different $\frac{\text{ZrO}_2}{\text{ZrO}_2 + \text{TiO}_2}$ molar ratios: (a) 0.495, (b) 0.528, (c) 0.537. Lead oxide content of the disks decreases from right to left.

Summary

Lead zirconate-titanate piezoelectric compositions of high purity and controlled stoichiometry, have been prepared and examined. The agreement between the compositions showing maxima in poled dielectric constant and electromechanical coupling factor indicates that the materials prepared by co-precipitation are effectively homogeneous with respect to the distribution of titanium and zirconium. The observation of two phases

in the composition with 0.529 mole fraction lead zirconate may indicate a small degree of chemical inhomogeneity or, alternatively, may be the result of inhomogeneous internal stress. The positions of the boundaries between the rhombohedral and tetragonal phases and between the high- and low-temperature rhombohedral phases are in agreement with the results of Jaffe and Berlincourt (6). The effect of lead oxide deficiency has been considered in terms of the

precipitation zirconia and the corresponding increase in the lead titanate content of the lead zirconate-lead titanate solid solution. The kinetics and mechanism of the loss of lead oxide from lead zirconate-titanate materials have been investigated by Northrop (17).

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