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# Piezoelectric and mechanical properties of ceria-doped lead zirconate titanate ceramics

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Phases, microstructures and properties of lead–zirconate–titanate (PZT) ceramics with the compositions $Pb(Zr_{0.535-\delta}Ce_{\delta}Ti_{0.465})O_3$ where $\delta = 0.0$, 0.001, 0.01, 0.02 and 0.05 were studied. Rhombohedral and tetragonal phases were present at $\delta = 0.0$. The amount of the rhombohedral phase increased with increasing $\delta$, and only the tetragonal phase was present for $\delta > 0.001$. The *c/a* ratio of the tetragonal phase also increases with increasing $\delta$. Particles of $CeO_2$ were found to be present in compositions with $\delta > 0.01$, indicating that the solubility of $CeO_2$ is less than 1 *a/o* on the metals basis. The piezoelectric and electromechanical constants achieved maximum values for $\delta = 0.001$. The hardness increased monotonically with increasing $\delta$. The modulus of rupture and the fracture toughness, however, went through a minimum and both stayed lower than their values for $\delta = 0$.

## 1. Introduction

A number of studies have been carried out on the effect of various dopants upon the properties of the lead–zirconate–titanate (PZT) family of ceramics [1]. PZT has an $ABO_3$-type perovskite structure. The A sites are occupied by $Pb^{2+}$ and the B sites by $Zr^{4+}$ or $Ti^{4+}$. A dopant can go either to the A or to the B site, its distribution on the two sites being a function of the valence and ionic radius of the dopant [2]. The dopant can act as an acceptor or a donor depending on whether its valence is lower or higher than that of the host site. The requirements of charge compensation also result in the creation of vacancies at the oxygen or lead sites. Because of these various possibilities, there has been much interest in studying the effect of the dopants with a valence of 3 or 5, while the study of the dopants with valence 4, the "isovalent dopants", has been neglected. It is known [3] that, in one case at least, the properties obtained by doping with an isovalent dopant ($Th^{4+}$) are comparable with or better than those obtained using $Nb^{5+}$ or $La^{3+}$, two of the most effective heterovalent dopants. It is therefore useful to study the influence of other isovalent dopants.

In the present work we have studied the effect of replacing part of $Zr^{4+}$ by $Ce^{4+}$ on the piezoelectric and mechanical properties and microstructure of a PZT composition near the morphotropic phase boundary.

## 2. Experimental procedure

Samples with a composition $Pb(Zr_{0.535-\delta}Ce_{\delta}Ti_{0.465})O_3$ with $\delta = 0.0$, 0.001, 0.01, 0.02 and 0.05 (0, 0.1, 1, 2 and 5 mol %, respectively, on metals basis) were prepared. The composition $\delta = 0.0$ corresponds to the morphotropic phase boundary (MPB) in PZT at which the piezoelectric constants are known to have their best values. Powders of PbO (yellow, > 99.0%); $ZrO_2$ (> 99.5%); $TiO_2$ (anatase, > 99%); and $CeO_2$ (99.5%) were ball milled in a plastic jar with alumina balls and isopropanol. The ball-milled material was dried and calcined at 960 °C for 4 h. The calcined powder was pressed into pellets (12 mm diameter) or disks (25 mm diameter) and sintered at 1200 °C for 4 h. A lead zirconate powder with small amounts of free $ZrO_2$ (as determined by X-ray diffraction; XRD) was used as the atmosphere powder during calcination as well as sintering. Such an atmosphere powder is known to produce a constant and reproducible amount (~ 0.8%) of PbO deficiency in the sintered material [4].

The density of samples was obtained from their weights when dry and suspended in water. Phases were determined using an X-ray diffractometer (Rich Seifert Iso Debyeflex 2002). The lattice parameters $a_T$ and $c_T$ of the tetragonal phase were obtained from the (2 0 0) and (0 0 2) reflections, respectively. Disk-shaped samples (12 mm diameter, 1 mm thick) were poled at 100 °C for 30 min by a 3.5 kV mm$^{-1}$ field. The $d_{33}$ coefficient was measured with a $d_{33}$ meter (model CADT, Channel Products). Other electromechanical coefficients were calculated [5] from the resonant and antiresonant frequencies measured using an impedance analyser (HP 4194A). Modulus of rupture (MOR) was measured on polished (0.3-μm) bar-shaped samples ($18 \times 4 \times 2$ mm$^3$) using a four-point bend method in a universal testing machine (Instron 1195). Mode I fracture toughness, $K_{IC}$, was measured on single-edge-notched samples. The notch was machined by a 0.3-mm-thick diamond-coated blade, and was 0.8–1.5 mm deep. Vicker's hardness was measured on 6-mm-high cylindrical samples, polished to a 0.3 μm finish.

Measurements were carried out on three or four samples at each composition in all the above cases. Further details are given in Reference 6.

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## 3. Results

Both tetragonal and rhombohedral phases are present in the undoped composition ($\delta = 0$) and in the composition with 0.1% $CeO_2$ ($\delta = 0.001$). In the higher $CeO_2$ compositions, only the tetragonal phase is present (Fig. 1). In addition, at the highest $CeO_2$ content ($\delta = 0.05$) free $CeO_2$ also appears (Fig. 2). The lattice parameters of the tetragonal phase and the $c/a$ ratio are given in Table I.

Fig. 3a–d shows the microstructures of fractured surfaces of the samples with different ceria contents. The average grain size increases gradually from about 3.5 µm for 0 mol % $CeO_2$ to about 7.5 µm for 5 mol % $CeO_2$. Small second-phase particles (0.1–0.5 µm) begin to appear at 1 mol % $CeO_2$, and are clearly present at the higher $CeO_2$ contents. The EDAX signal from these particles showed only the cerium lines. Cerium was also found to be present in the grains of the matrix phase, indicating that $CeO_2$ is dissolving in the lattice to a limited extent.

The density of the samples is shown in Fig. 4. It first decreases, and then increases with increasing amount of $CeO_2$.

Fig. 5a–e shows the values of the various piezoelectric and electromechanical coefficients at different $CeO_2$ contents. Fig. 6 shows the corresponding changes in hardness, modulus of rupture and fracture toughness.

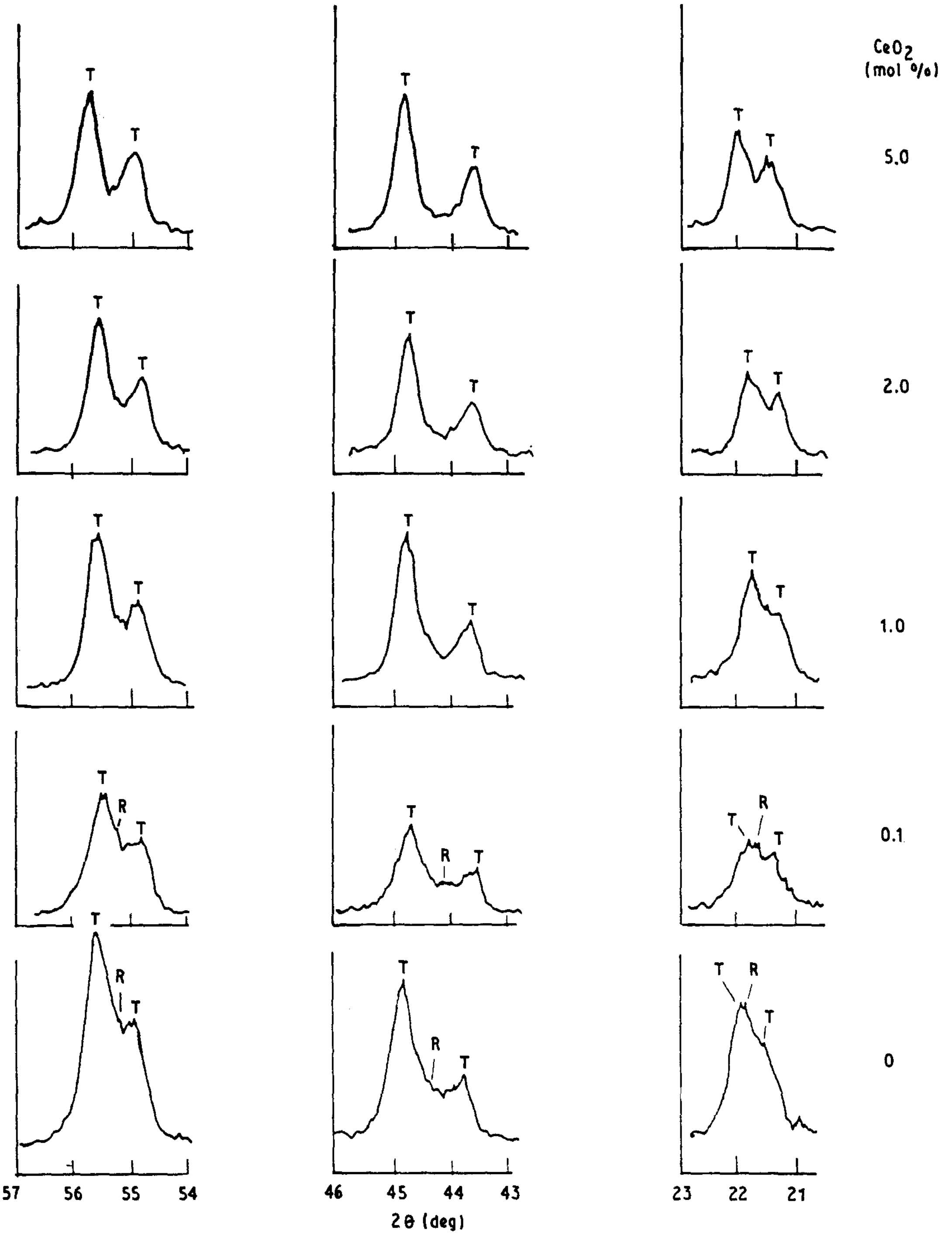


*Figure 1* X-ray scans in three different 2θ ranges, showing that the rhombohedral phase nearly disappears when 1 mol % $ZrO_2$ is replaced by $CeO_2$ ($\delta = 0.01$). T, tetrahedral; R, rhombohedral.

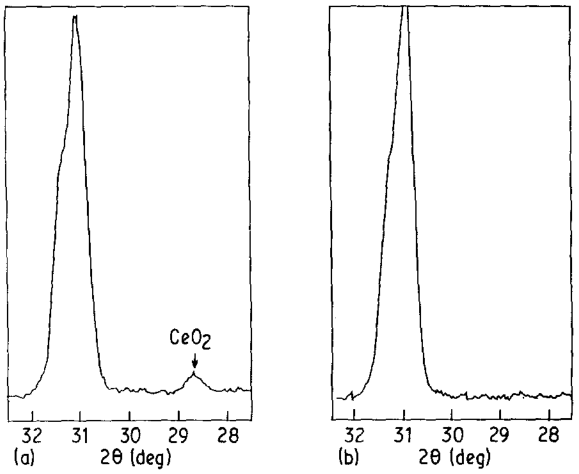


*Figure 2* X-ray scans showing the appearance of free $CeO_2$ in the composition with (a) 5 mol % and (b) 2 mol % $CeO_2$.

TABLE I Lattice parameters and the $c/a$ ratio for the tetragonal phase in $Pb(Zr_{0.535-\delta}Ce_{\delta}Ti_{0.465})O_3$

| Amount of $CeO_2$ | $c_T$ (nm) | $a_T$ (nm) | $c_T/a_T$ |
|---|---|---|---|
| 0 | 0.41276 | 0.40357 | 1.0227 |
| 0.001 | 0.41337 | 0.40408 | 1.0229 |
| 0.01 | 0.41373 | 0.40425 | 1.0234 |
| 0.02 | 0.41398 | 0.40374 | 1.0253 |
| 0.05 | 0.41355 | 0.40289 | 1.0264 |

# 4. Discussion

## 4.1. Phases and microstructure

$Pb(Zr_xTi_{1-x})O_3$ perovskite solid solution usually exists in one of the following three structures, depending on the composition: tetragonal for $0 < x < 0.535$; rhombohedral for $0.535 < x < 0.92$; and orthorhombic for $0.92 < x < 1.0$. The boundary between the tetragonal and rhombohedral phases at $x = 0.535$ is believed to be a morphotropic phase boundary. However, usually there is a range of compositions around $x = 0.535$ in which both tetragonal and rhombohedral phases coexist. The width of this region depends on the degree of composition homogeneity achieved by a particular processing route: it is very narrow for co-precipitated or sol–gel prepared material, and much wider for the mixed-oxide route used in the present work. The electromechanical coefficients are found to have their maximum value near the morphotropic phase boundary.

Both phases, tetragonal and rhombohedral, are found to be present in the undoped composition in the present case, as the composition chosen lies in the morphotropic phase-boundary region. In the undoped PZT compositions, it is known that as $x$ (the amount of zirconia) decreases, the amount of the rhombohedral phase also decreases and the $c/a$ ratio of the tetragonal phase increases. Both these effects are observed in the present experiments (Fig. 1 and

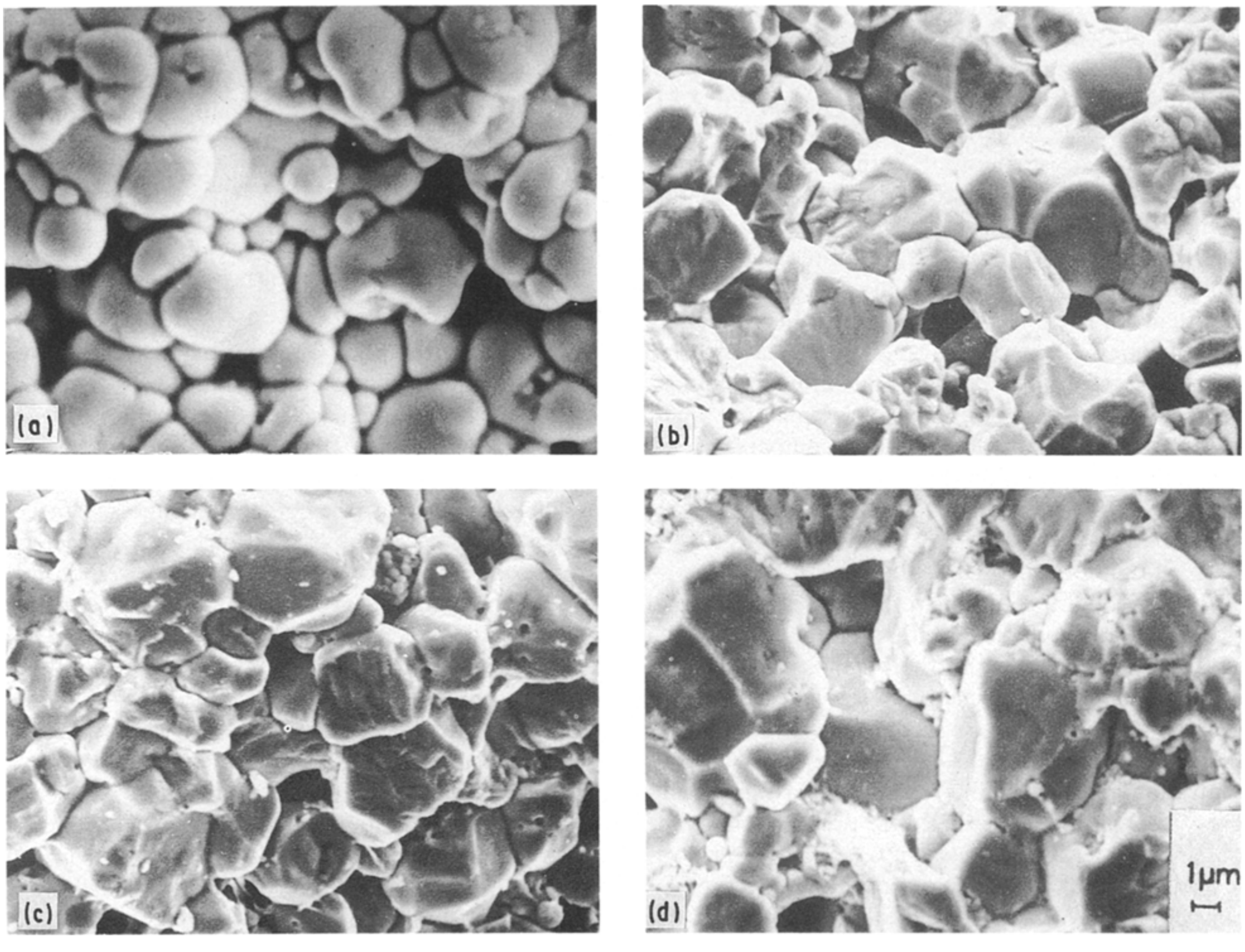


*Figure 3* SEM pictures of the fractured surfaces of samples with different amounts of $CeO_2$: (a) 0; (b) 1.0; (c) 2.0; (d) 5.0 mol %.

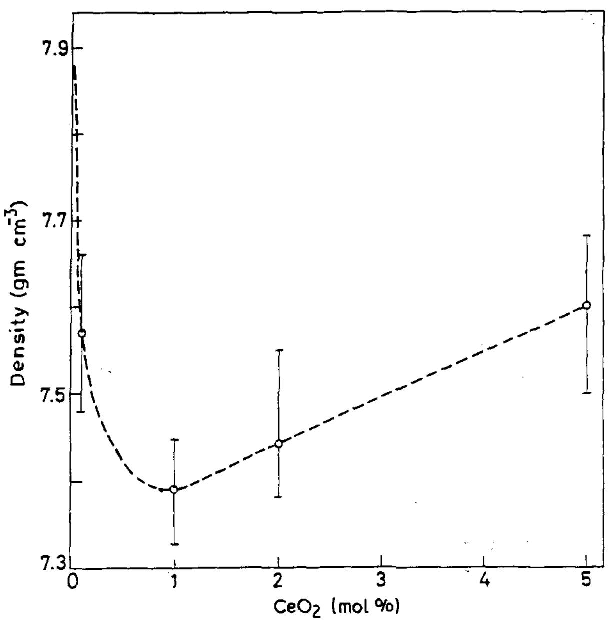


*Figure 4* Variation in sintered density with amount of $CeO_2$.

Table I). As the ($CeO_2$ + $ZrO_2$) is held constant, an increased amount of $CeO_2$ implies a decreased $ZrO_2$ content. Although some amount of $Ce^{4+}$ is dissolving into the lattice, as determined by chemical analysis of the matrix grains, this amount is believed to be less than 1 mol %, as at 1 mol % and above the particles of ceria can already be seen (Fig. 3b). The observed disappearance of the rhombohedral phase and the increase in the $c/a$ ratio of the tetragonal phase can therefore be attributed primarily to a decrease in the amount of $ZrO_2$.

The second phase particles observed in the SEM pictures are those of pure $CeO_2$. Generally the XRD technique is able to detect a phase in a mixture if its amount is ~ 5% or more. For this reason, the pure $CeO_2$ peak appears only at the highest $CeO_2$ content (5 mol %) (Fig. 2), even though the particles of $CeO_2$ begin to appear at 1 mol % $CeO_2$ in the micrograph. This also shows that the solubility of $CeO_2$ in PZT is less than 1 mol %. At higher concentrations, some of the original $CeO_2$ particles (especially the larger ones) do not dissolve fully. Partial dissolution results in a much finer size distribution of the remaining $CeO_2$ particles in the sintered samples, as compared to the original size distribution (Fig. 7).

### 4.2. Piezoelectric properties

The most significant result from the measurement of the piezoelectric properties is that the coupling coefficients $k_p$, $k_{33}$ and $k_{31}$ and the strain coefficients $d_{33}$ and $d_{31}$ increase appreciably on the first addition of $CeO_2$ to 0.1 mol %. There is a decrease in the values of these coefficients on a further increase in $CeO_2$ concentration. The possibility exists that a further improvement in these piezoelectric properties may be obtained if the region between 0.1 and 1% $CeO_2$ is investigated. To get a perspective on the effect on piezoelectric properties of $CeO_2$ addition, the properties at $CeO_2$ contents corresponding to 0 and 0.001 are compared with the data of Jaffe *et al.* [7] in Table II. The data give the changes in properties of a base PZT composition upon addition of $Sr^{2+}$ and $Nb^{5+}$, two of the most effective additives for PZT ceramics. The percentage changes on addition of $CeO_2$ to our composition, and on addition of $Sr^{2+}$ and $Nb^{5+}$ to Jaffe *et al.*'s composition [7] are also presented. It can be seen that $CeO_2$ at 0.001 is almost as effective as SrO at 0.06 in influencing most of the tabulated properties. Addition of $Nb^{5+}$ is, however, the most effective of the three, especially with regard to $k_{33}$, $d_{31}$ and $d_{33}$. The properties obtained by Kulcsar [3] for a thoria-doped composition are also given in Table II. Kulcsar has not provided the data for the corresponding undoped composition, which makes any comparison difficult. However, taking the values from the undoped composition from Jaffe's data, it is seen that doping by thoria results in a much higher increase in dielectric constant, while the increase in $k_p$, the planar coupling coefficient, is comparable to that obtained by doping with ceria.

### 4.3. Mechanical properties

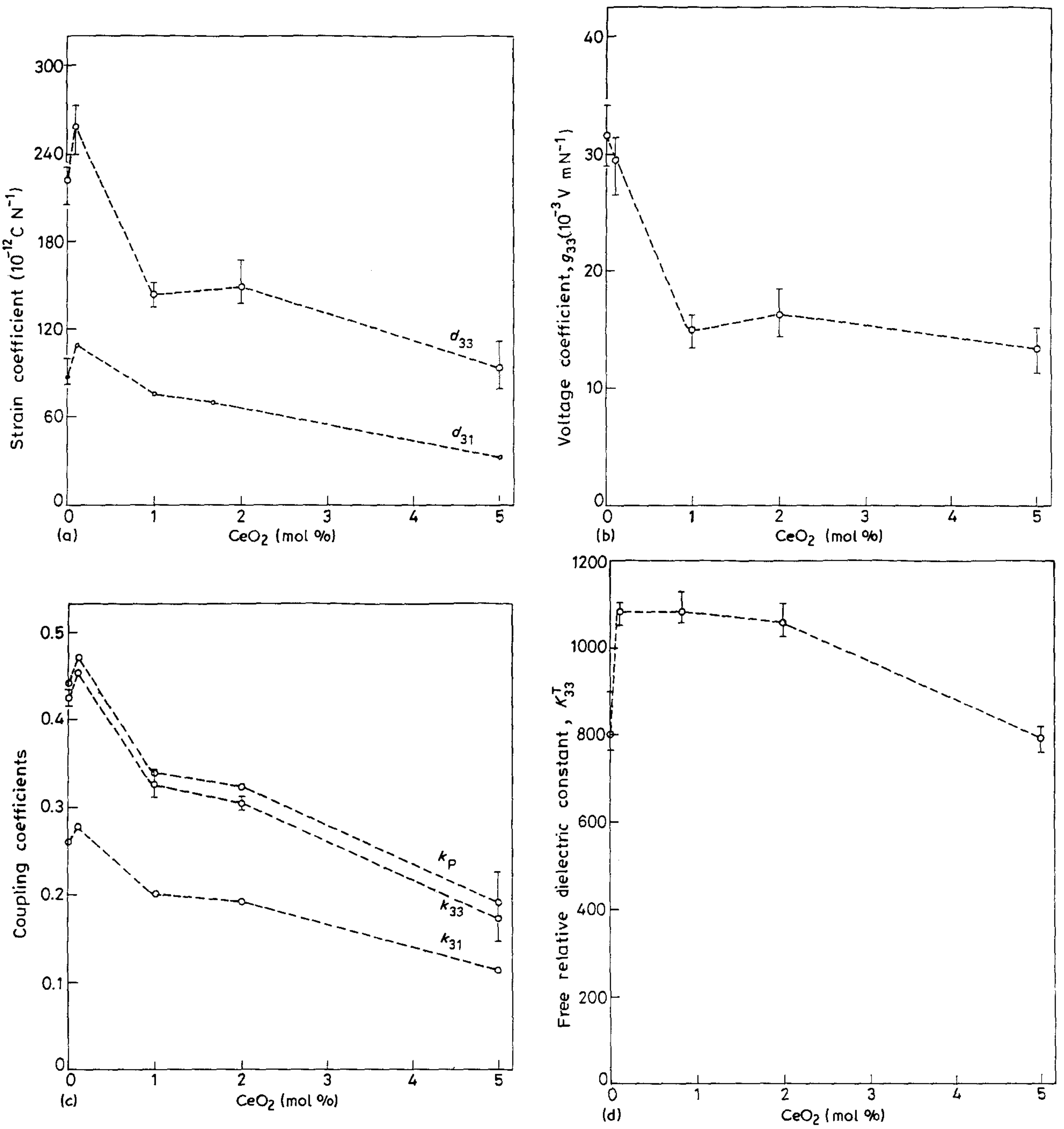
The mechanical properties of piezoelectric ceramics are of importance in understanding and preventing the failure of components due to electrically or thermally induced stresses. In the present study, it is found that the fracture toughness and modulus of rupture go through a minimum and both stay lower in the $CeO_2$-doped samples than in the pure composition. The fracture toughness, $K_{IC}$, is a material property and represents the resistance to unstable crack propagation in a material. It depends on the microstructure, the crystal structure and the chemistry of the material, amongst other properties. In the present experiments, the following microstructural changes are observed with increasing ceria contents.

(i) The average grain size increases from ~ 3.5 to ~ 7.5 μm as the $CeO_2$ content increases from 0 to 5 mol %.

(ii) Particles of $CeO_2$ are observed when the $CeO_2$ content is 1 mol % or more.

The dependence of $K_{IC}$ on grain size is not well understood; conflicting results have been reported [8]. In our results, there is a good correlation between the rise in the $K_{IC}$ after the minimum and the increase in number of $CeO_2$ particles. Second-phase particles are known to increase the fracture toughness by mechanisms such as crack deflection and microcrack formation. Thus the ceria particles may be responsible for the observed enhancement in the fracture toughness in samples with more than 1 mol % ceria. The initial decrease in the modulus of rupture and $K_{IC}$ appears to be linked to the change from a two-phase (rhombohedral + tetragonal) to a single phase (tetragonal) microstructure.

In contrast with the other mechanical properties, the hardness continuously increases with increasing ceria content. The hardness rises sharply up to 0.1 mol % $CeO_2$ and then rises monotonically, but with a lower slope. This correlates rather well with the observations that (i) the amount of the rhombohedral phase is greatly reduced by the very first addition of



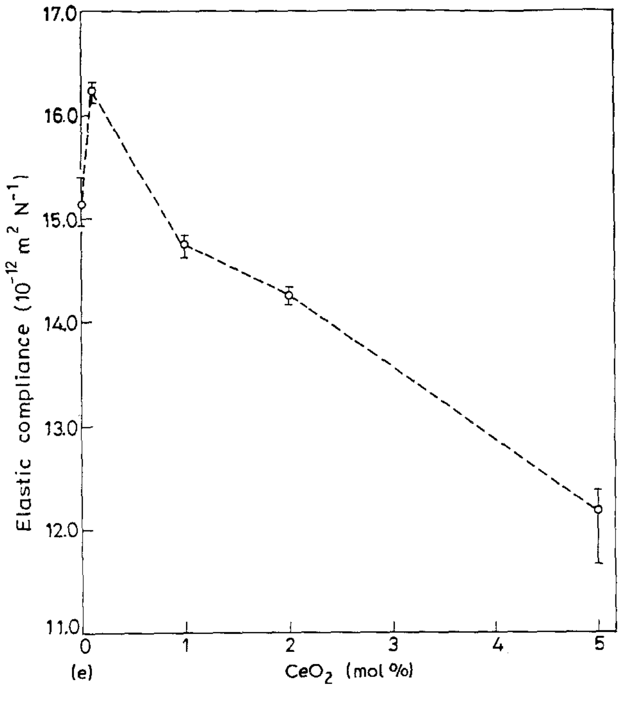


*Figure 5* Changes in piezoelectric and other coefficients with increasing CeO$_2$: (a) strain coefficients $d_{33}$ and $d_{31}$; (b) voltage coefficient $g_{33}$; (c) coupling coefficients $k_p$, $k_{33}$ and $k_{31}$; (d) free relative dielectric coefficient $K$; (e) elastic compliance (dashed lines are a guide only).

CeO$_2$ and only the tetragonal phase is present beyond 0.1 mol % CeO$_2$; and (ii) the $c/a$ ratio of the tetragonal phase increases with increasing CeO$_2$. It thus appears that the tetragonal phase is much harder than the rhombohedral phase, and its hardness increases with increasing tetragonality.

## 5. Conclusions

1. Significant improvement in piezoelectric properties results upon substitution of 0.1 a/o ZrO$_2$ by CeO$_2$ in a PZT composition near the morphotropic phase boundary. Further improvement may possibly be obtained by investigating the region $0.0 < \text{CeO}_2 < 1$ a/o.

TABLE II A comparison of the effects of $Ce^{4+}$ with those of $Nb^{5+}$, $Sr^{2+}$ and $Th^{4+}$ on the properties of PZT

| Composition | $k_{33}$ | $k_p$ | $k_{31}$ | $k_{33}$ | $d_{31}$ ($10^{-12}$ CN$^{-1}$) | $d_{33}$ ($10^{-12}$ CN$^{-1}$) | $g_{33}$ ($10^{-3}$ VmN$^{-1}$) | $S^F_{11}$ ($10^{-12}$ m$^2$N$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| This work | | | | | | | | |
| $Pb(Zr_{0.535}Ti_{0.465})O_3$ | 804 | 0.43 | 0.26 | 0.43 | − 86.01 | 222.7 | 31.6 | 15.1 |
| $Pb(Zr_{0.534}Ce_{0.001}Ti_{0.465}O_3)$ | 1083 | 0.46 | 0.28 | 0.46 | − 109.7 | 278.8 | 29.4 | 16.2 |
| Percentage change | 34.7 | 7.0 | 7.7 | 7.0 | − 23.7 | 25.0 | − 7.0 | 7.3 |
| Jaffe *et al.* [7] | | | | | | | | |
| $Pb(Zr_{0.52}Ti_{0.48})O_3$ | 730 | 0.52 | 0.31 | 0.67 | − 93.5 | 223 | 34.5 | 13.8 |
| $Pb_{0.94}Sr_{0.06}(Ti_{0.47}Zr_{0.53})O_3$ | 1300 | 0.58 | 0.33 | 0.70 | − 123.0 | 289 | 26.1 | 12.3 |
| Percentage change | 78 | 11.5 | 6.1 | 4.5 | − 31.5 | 22.8 | 24.3 | 10.9 |
| $Pb_{0.988}(Ti_{0.48}Zr_{0.52})_{0.976}Nb_{0.024}O_3$ | 1700 | 0.6 | 0.34 | 0.70 | − 171.0 | 374.0 | 24.8 | 16.4 |
| Percentage change | 133 | 15.3 | 9.7 | 4.5 | 82.9 | 67.7 | 28.1 | 15.8 |
| Kucslar [3] | | | | | | | | |
| $Pb_{0.988}Th_{0.006}(Zr_{0.52}Ti_{0.48})O_3$ | 1500 | 0.56 | | | | | | |
| Percentage change | 105.4 | 8.1 | | | | | | |

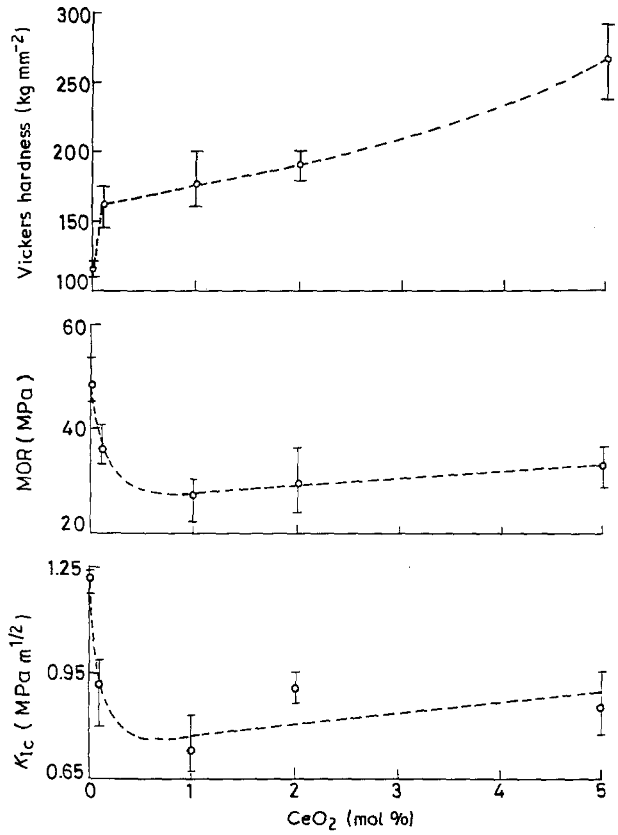


*Figure 6* Changes in Vicker's hardness, modulus of rupture and fracture toughness with $CeO_2$ content.

2. Solubility of $CeO_2$ in PZT is less than 1 a/o.

3. Addition of $CeO_2$ reduces the amount of the rhombohedral phase; only the tetragonal phase is present for $CeO_2$ contents > 1 a/o.

4. The hardness increases monotonically with increasing $CeO_2$ content, but the modulus of rupture and the fracture toughness are lowered.

## Acknowledgement

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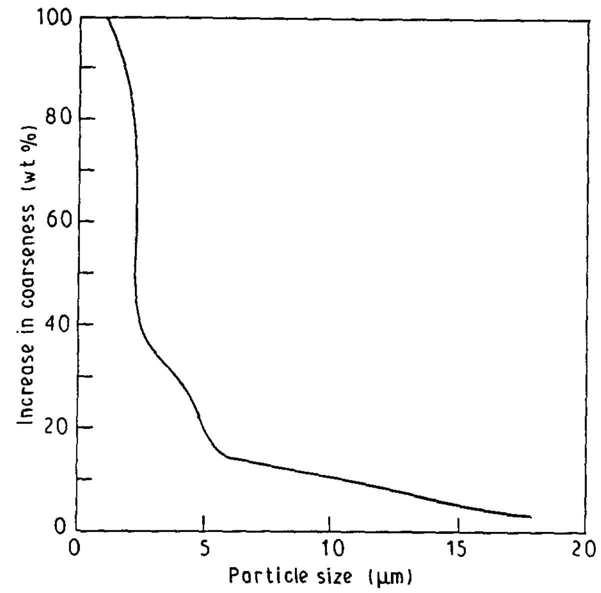

*Figure 7* Particle-size distribution of the $CeO_2$ powder used for preparing the samples.

## References

1. K. OKAZAKI, *Ferroelectrics* **41** (1982) 77.
2. P. GONNARD and M. TROCCAZ, *J. Solid State Chem.* **23** (1978) 321.
3. F. KULCSAR, *J. Amer. Ceram. Soc.* **48** (1965) 54.
4. A. I. KINGON and J. B. CLARK, *ibid.* **66** (1983) 253.
5. IRE Standards of Piezoelectric Crystals: "Measurements of Piezoelectric Ceramics", *Proc. IRE* **49** (1961) 1161.
6. S. K. NAG, M.Tech. thesis, I.I.T. Kanpur, India, July 1990.
7. B. JAFFE, W. COOK, Jr and H. JAFFE, "Piezoelectric Ceramics" (Academic Press, Orlando, 1971) p. 146.
8. NILS CLAUSSEN, BERNHARD MUSSLER and MICHAEL V. SWAIN, *J. Amer. Ceram. Soc.* **65** (1982) C-14.

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