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Piezoelectric properties of sol–gel-derived samarium-dysprosium-modified lead titanate ceramics

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Samarium- and dysprosium-modified lead titanate ceramics have been prepared by a sol–gel route to utilize the finer control of the process on homogeneity and microstructure. By varying the sintering schedule (temperature and time) for samarium-modified $PbTiO_3$, ceramics with grain sizes ranging from submicrometre to $4\,\mu m$ have been prepared. The dielectric and piezoelectric properties of ceramics poled sequentially from 0 to $60\,kV\,cm^{-1}$ are reported. The dependence of the electromechanical properties on grain size and poling conditions is discussed. It is shown that dysprosium behaves very differently to samarium, and the successful insertion of dysprosium into the Pb^{2+} sites to produce true dysprosium-modified $PbTiO_3$ ceramics was not possible.

1. Introduction

Modified lead titanate ceramics are attractive materials for high-frequency (> 5 MHz) array transducers [1–5] as a result of their large anisotropy of the electromechanical coupling factors. These ceramics have large thickness coupling factors (k_t) of approximately 0.50, similar to lead zirconate : lead titanate (PZT) ceramics. However, some of these modified lead titanates show vanishingly small planar coupling factors (k_p), [1–6], while the PZT ceramics have k_p values in excess of 0.50. These properties allow the width-to-thickness ratio of a transducer element to be chosen as $w/t > 1$, which facilitates the fabrication of transducer arrays that operate at higher frequencies than allowed by PZT ceramics.

The electromechanical properties of $(Pb_{1-(3/2)x}Ln_x)(Ti_{1-y}Mn_y)O_3$ ceramics, where Ln in a rare-earth element, have been shown to be very dependent on the processing conditions employed. To the best of our knowledge, sol–gel technology has not been utilized in the formation of such modified $PbTiO_3$ ceramics. Sol–gel processing offers high purity, molecular homogeneity and lower processing temperatures in comparison to conventional processing methods. It then follows that sol–gel methodology grants a finer control of the microstructure, and consequently the dielectric and piezoelectric properties, of the resulting ceramic.

In the present work, samarium- and dysprosium-modified $PbTiO_3$ ceramics have been prepared through a sol–gel route. The physical and chemical properties of the sol–gel-derived ceramics are compared with those of ceramics prepared by the mixed-oxide process. The electromechanical properties and the temperature dependence thereof are reported, and again comparisons with mixed-oxide ceramics are drawn.

The overall objective of this work was to investigate the electromechanical properties of such modified $PbTiO_3$ ceramics, with the intent of advancing our understanding of the mechanisms responsible for this anisotropic behaviour. A more complete understanding of the mechanisms may promote the development of similar materials with other desirable properties. For example, in the case of transducer array applications, a larger dielectric permittivity is desired to reduce the electrical impedance of each element for improved matching with driving electronics.

2. Experimental procedure

2.1. Powder preparation

Ceramic powders with compositions $(Pb_{0.85}Ln_{0.10})(Ti_{0.98}Mn_{0.02})O_3$, where Ln = Sm or Dy (hereafter called PST and PDT, respectively), were prepared by a sol–gel process similar to that reported by Gurkovich and Blum [7, 8] for the preparation of $PbTiO_3$ monoliths. The reaction vessel employed was a simple distillation assembly, consisting of a three-neck round-bottom flask equipped with an N_2 gas purge (to prevent moisture from entering the system during cooling cycles) and a thermometer to monitor solution temperature, a Claisen stillhead adapter (for sequential addition of reagents), a thermometer for monitoring vapour temperature, and a condenser. The complex alkoxides, or sols, were prepared by reacting $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, $Sm(C_2H_3O_2)_3 \cdot 3H_2O$ or $Dy(C_2H_3O_2)_3 \cdot 4H_2O$, $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ and $Ti(OC_3H_7)_4$ according to Fig. 1*. The three-neck

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*Starting material sources and purities: $Pb(OAc)_2 \cdot 3H_2O$ (Aldrich, 99+%), $Sm(OAc)_3 \cdot 3H_2O$ (Alfa, 99.9%), $Dy(OAc)_3 \cdot 4H_2O$ (Alfa, 99.9%), $Mn(OAc)_2 \cdot 4H_2O$ (Aldrich, 99+%), $Ti(O\text{-}i\text{-}Pr)_4$ (Aldrich) and 2-methoxyethanol (Aldrich, 99%).

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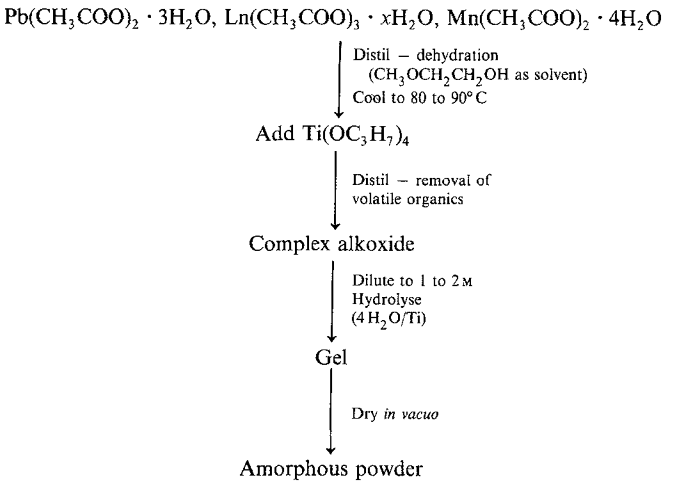

Figure 1 Flow diagram for the processing of rare-earth-modified lead titanates.

reaction flask was charged with the hydrated acetates of lead, the desired rare-earth element and manganese, as well as the solvent, 2-methoxyethanol ($C_3H_8O_2$). All solids dissolved at 70 to 80° C and the resulting solution was distilled to remove all water from the system (at which point the temperature of the vapours reaching the condenser was 124° C, the boiling point of 2-methoxyethanol). The solution was cooled under a nitrogen purge to 90 to 100° C and the stoichiometric amount of titanium isopropoxide was added. Distillation was resumed to allow for reaction of the various reagents to form the sol, and collection of the volatile organics produced as a result. These volatile organics consisted of isopropanol, isopropyl acetate and 2-methoxyethyl acetate, the proportions of which were dependent on the concentration of the sol at the time of $Ti(OC_3H_7)_4$ addition [9]. Again, the distillation was halted when the temperature of the vapours reaching the condenser levelled out at 124° C.

The concentration of the dark brown sol obtained was then adjusted to 1 to 2 M, and the reaction vessel immersed in a liquid-N_2–isopropanol bath (≈ -20° C). To this was added dropwise a 1 : 1 (by volume) solution of distilled H_2O and 2-methoxyethanol, such that 4 moles of H_2O per mole of titanium were added. Complete gelation occurred within 60 to 75 min to give a dark brown, transparent gel (for both samarium and dysprosium). The gels were then dried *in vacuo* to yield amorphous powders.

2.2. Property measurement

Sintered ceramic discs were poled sequentially to $60\,kV\,cm^{-1}$ at 100° C in silicone oil for 10 min. These poling conditions resulted in very near saturation of the values for both the thickness coupling coefficient (0.45 to 0.50) and the piezoelectric d_{33} coefficient (60 to $65\,pC\,N^{-1}$). The thickness coupling coefficient was calculated from the ratios of the overtone frequencies, f_2 and f_3, to the fundamental frequency f_1, of the thickness mode series resonance, f_2/f_1 and f_3/f_1, using the table provided by Onoe *et al.* [10]. The piezoelectric d_{33} coefficient was measured with a Berlincourt piezo d_{33} meter. The planar coupling coefficient was calculated from the measured frequencies of the series, f_s, and the parallel, f_p, resonances of a thin disc using the equation derived by Mason [11]. All capacitance and impedance measurements were performed using an HP 4192A LF impedance analyser interfaced with a HP 9121 computer.

3. Results and discussion

3.1. Ceramic preparation

Since sol–gel-derived materials usually require lower-temperature processing than their counterparts prepared through conventional mixed-oxide routes, our initial efforts were toward determining the optimum firing conditions which would yield the most dense sintered ceramic for PST. The calcination temperatures employed were 800, 850 and 900° C, all for 2 h periods. The particle sizes of the powders calcined at the above temperatures were determined by SEM to be 0.4 to 0.5 μm. The calcined powders were pressed into pellets (discs) after the addition of 2 wt % polyvinylalchohol (PVA). Pellets were sintered for 3 h in closed alumina containers at each of the following temperatures: 1130, 1160 and 1190° C. No appreciable weight losses were observed upon these sinterings.

For all of the three sintering temperatures, the most dense ceramics were achieved from the 850° C calcined powder (as opposed to the 800 and 900° C calcinations). Within this group, the 1130° C sintering yielded considerably less dense ceramics ($\varrho \approx 7.2\,g\,cm^{-3}$) than either the 1160 or 1190° C sinterings ($\varrho \approx 7.4$ to $7.5\,g\,cm^{-3}$). These latter densities are 97 to 98% of the theoretical value ($7.66\,g\,cm^{-3}$). The powder X-ray diffraction patterns of all the sintered ceramics showed the c/a ratios (relating the degree of tetragonality) to be 1.041 ± 0.002. These values are in the expected range, as the ionic radius of samarium is significantly smaller than that of lead, and the c/a ratio of pure $PbTiO_3$ is 1.065.

PDT behaves very differently to PST. When amorphous PDT powder was calcined at 850° C for 2 h, the X-ray diffraction pattern shows the c/a ratio to be 1.041. Upon sintering PDT at 1160° C for 3 h, the c/a ratio of the sintered ceramic was increased to 1.065, equal to that of pure $PbTiO_3$. This indicates that the Dy^{3+} atoms apparently are not entirely remaining in the Pb^{2+} sites within the sintered ceramic. SEM micrographs of the PDT ceramics show no apparent second phase, but do show the ceramic to be very porous. It may be that Dy^{3+} atoms are too small to be stable in the Pb^{2+} sites, and may be more stable occupying Ti^{4+} sites in the tetragonal structure. Thus, we conclude

TABLE I Comparison of the physical and chemical properties of sol–gel-derived and mixed-oxide-derived ceramics.

Property	Sol–gel-derived ceramic	Mixed-oxide-derived ceramic
Particle size (μm) (calcined powder)	0.4 to 0.5	–
Sintering temperature (° C)	1160	1230
Grain size (μm) (sintered ceramic)	1 to 4	4
c/a ratio	1.041	1.043
densities (g cm^{-3}) (sintered ceramics)	7.44 to 7.48 (97 to 98% theoretical)	7.10 to 7.40 (93 to 96% theoretical)

that the PDT ceramics prepared were not true modified lead titanates as the dysprosium atoms are not substituting for lead, and that this can probably be attributed to the relative sizes of the ions.

Hence, there seems to be a limit within the lanthanide series concerning which elements can be successfully substituted into the Pb^{2+} sites of the $PbTiO_3$ structure. This must be a size limitation, with the smaller lanthanides simply not being stable in the much larger lead sites. Gadolinium-modified lead titanates have been prepared by Takeuchi *et al.* [3], but to the best of our knowledge, the terbium-modified ceramics have not been investigated. Therefore either gadolinium or terbium would be the smallest lanthanide for which successful substitution into the $PbTiO_3$ structure could be made.

To determine the effect of grain size on the electromechanical properties, ceramics with various grain sizes were prepared by sintering at 1160° C for various periods of time. The sintering times chosen were 3, 10 and 20 h. The ceramic weight losses observed after sintering were always $\leqslant 1.0$ wt %. All these ceramics had similar c/a ratios of 1.041 to 1.042, and the same Curie temperature of 305° C. Therefore we conclude that the extended sintering times have not significantly altered the stoichiometry or chemical nature of the ceramics. SEM micrographs were used to determine the relative grain sizes. Ceramics sintered for 3 h had an average grain size of 1 μm, while those sintered for 10 h were 2.0 to 2.5 μm, and those sintered for 20 h were 3.0 to 3.5 μm. The densities of the ceramics were quite similar, regardless of sintering time, ranging only from 7.44 to 7.48 g cm^{-3}. In contrast, mixed-oxide-derived PST required sintering at 1230° C for 3 h and the densities varied between 7.10 and 7.40 g cm^{-3} (93 to 96% theoretical) (Table I). The dielectric constants for the 3, 10 and 20 h sintered ceramics were 195, 177 and 169, respectively. When sequentially poled from 0 to 60 kV cm^{-1}, the dielectric constant of the ceramics sintered 3 h decreased from 195 to 185, while those for the 10 and 20 h sintered ceramics both increased, from 177 to 180, and 169 to 176, respectively.

3.2. Electromechanical properties

Figs 2 and 3 show the thickness and planar coupling factors, respectively, as a function of poling field, for the sol–gel-derived samarium-modified $PbTiO_3$ ceramics. From the figures it is apparent that k_t reaches near saturation at high poling fields, while k_p first increases and then decreases. These same trends were observed for the conventional mixed-oxide derived ceramics reported by Damjanovic *et al.* [12]. This results in k_t/k_p ratios of 18 for the ceramic sintered for 3 h, 29 for that sintered for 10 h and 63 for that sintered for 20 h all after poling at 60 kV cm^{-1} at room temperature.

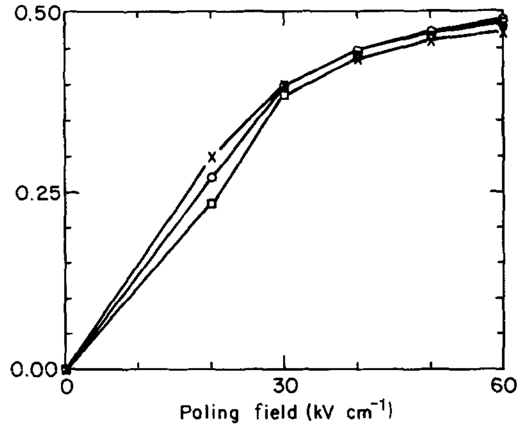

Figure 2 Thickness coupling coefficients (k_t) as a function of poling field for PST ceramics sintered various periods of time: (x) 3 h, (□) 10 h, (○) 20 h.

From Figs 2 and 3 it is apparent that the extended sintering time, and hence the increase in grain size, has no affect on the dependence of k_t upon poling field. The planar coupling factor behaviour, however, is markedly influenced by grain size. This dependence of k_p on grain size is seen only in the magnitude of k_p with poling and not in its overall poling field behaviour (ceramics with different grain sizes reach their maximum k_p value at the same poling field and k_p continually decreases thereafter).

The temperature dependence of k_t and k_p of the sol–gel-derived PST ceramics are shown in Figs 4 and 5. While k_t does not exhibit a significant change with temperature, k_p is strongly temperature-dependent, going to zero at a certain temperature (hereby referred to as the k_p zero point). Again these results for the sol–gel-derived ceramics are quite similar to those of the mixed-oxide derived ceramics. This k_p zero

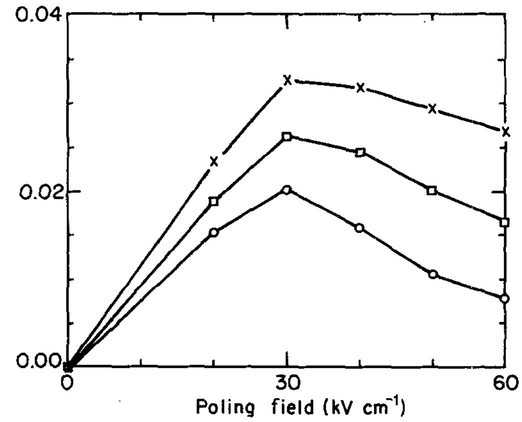

Figure 3 Planar coupling coefficients (k_p) as a function of poling field for PST ceramics sintered various periods of time: (x) 3 h, (□) 10 h, (○) 20 h.

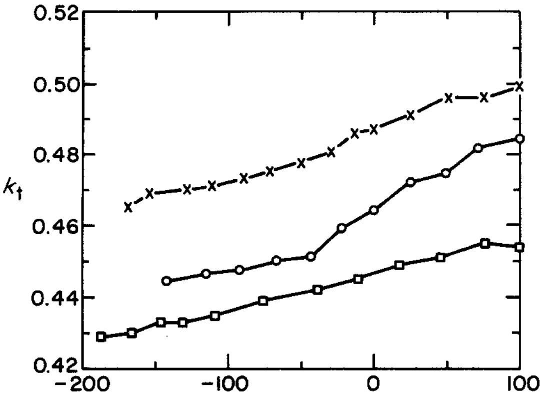

Figure 4 Thickness coupling coefficients (k_t) as a function of temperature for PST ceramics sintered various periods of time: (x) 3 h, (□) 10 h, (○) 20 h.

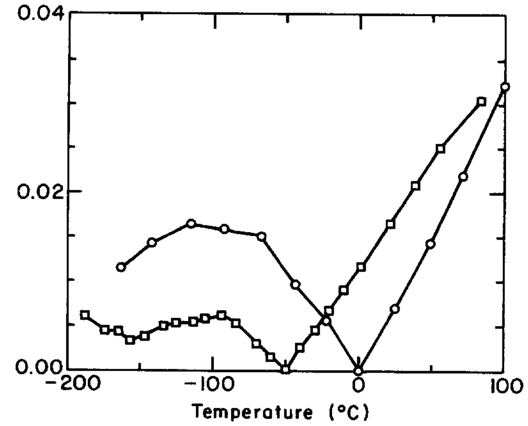

Figure 6 Planar coupling coefficients (k_p) as a function of temperature for PST ceramics sintered 20 h, but poled to different degrees: (□) 30, (○) 60 kV cm^{-1}.

point seems to be dependent on the sintering time. The zero points are 0° C for ceramics sintered for 20 h, −40° C for those sintered for 10 h and −100° C for those sintered for 3 h (all poled at 60 kV cm^{-1}). These results suggest that the temperature at which k_p goes to zero is dependent on the grain size of the ceramic. Since the degree of poling within a ceramic is proportional to the grain size, this k_p zero point must then also be dependent on the degree of poling (when comparing similarly poled ceramics). To verify this, ceramics sintered 20 h were poled only to 30 kV cm^{-1} and the resulting k_p zero point of −40° C is consistent with our conclusions (Fig. 6).

A detailed discussion of a possible explanation for the disappearance of k_p can be found in the work of Damjanovic *et al.* [12–14], and a brief interpretation of this follows. From the definition of the planar coupling coefficient (Equation 1 below) it is seen that k_p could disappear at a certain temperature due to the zero value of the piezoelectric coefficient d_{31}:

$$k_p = k_{31}\left(\frac{2}{1-\sigma^E}\right)^{1/2} = \frac{|d_{31}|}{[(s_{11}^E)(\varepsilon_{33}^t)]^{1/2}}\left(\frac{2}{1-\sigma^E}\right)^{1/2} \qquad (1)$$

where $|d_{31}|$ is the magnitude of the piezoelectric coefficient, s_{11}^E is the elastic constant measured at constant E field, ε_{33}^t is the dielectric constant measured at constant stress, and σ^E is Poisson's cross-contraction ratio. Such a possibility could be realized by a change of the sign of d_{31} or by d_{31} going through zero at its extremum point. Damjanovic *et al.* [13] measured the complex material coefficients d_{31}, s_{11} and ε_{33} as a function of temperature to describe the temperature dependence of k_p for the mixed-oxide derived PST ceramics. Fig. 7 is plot of their results for the real part of d_{31} (d'_{31}) as a function of temperature. This shows that d'_{31} passes through zero by changing its sign. Similar d'_{31} behaviour was observed for the sol–gel-derived PST ceramics (Fig. 8). Fig. 7 also shows that the temperature corresponding to the zero value of d'_{31} depends very much on the poling field. Thus, the temperature at which the k_p zero point occurs must also be dependent on the poling field, which substantiates our conclusion concerning the relationship of k_p and the degree of poling within the ceramic.

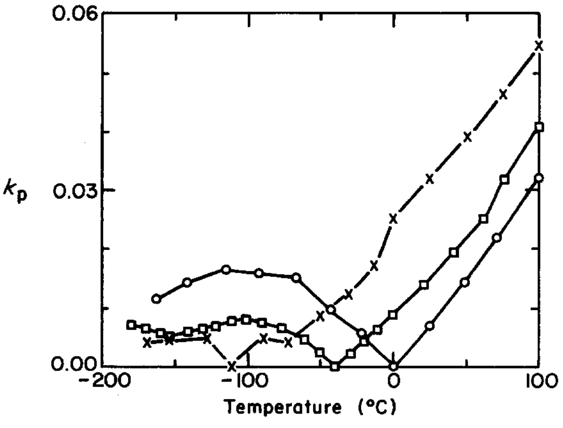

Figure 5 Planar coupling coefficients (k_p) as a function of temperature for PST ceramics sintered various periods of time: (x) 3 h, (□) 10 h, (○) 20 h.

The electromechanical properties of the PDT ceramics made were investigated even though they were not true modified lead titanates. Upon poling sequentially from 0 to 70 kV cm^{-1}, k_p remained zero and k_t increased to approximately 0.20 to 0.25. These

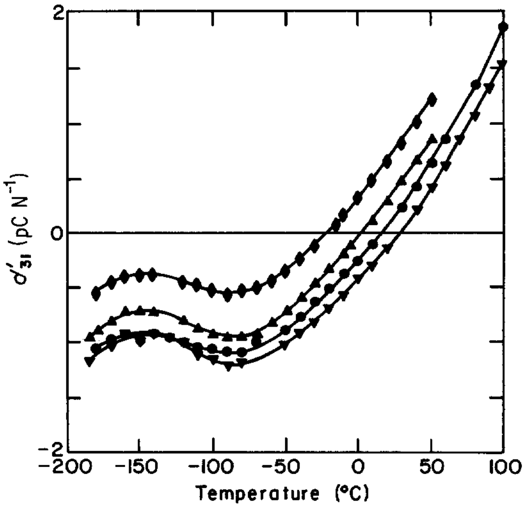

Figure 7 Real part of the piezoelectric coefficient, d'_{31} at different poling fields as a function of temperature for mixed-oxide-derived PST ceramics: (◆) 30, (▲) 50, (●) 70, (▼) 90 kV cm^{-1}.

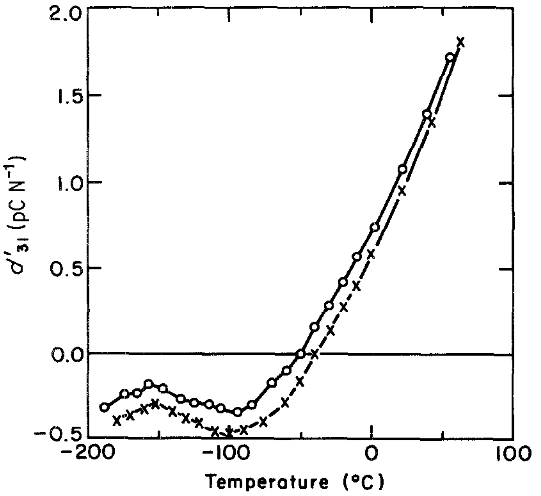

Figure 8 Real part of the piezoelectric coefficient, d'_{31}, as a function of temperature for various sol–gel-derived PST ceramics (sintering time and poling field specified): (x) 10 h, 60 kV cm^{-1}; (o) 20 h, 30 kV cm^{-1}.

ceramics presented problems during this analysis, as the thickness-mode series resonances (and thus the range in k_t values) were not clearly defined. This problem as well as the low k_t values discouraged us from attempting any temperature-dependence studies.

4. Summary

Sol–gel-derived samarium-modified lead titanate ceramics behave very similarly to those prepared by the conventional mixed-oxide process. The finer control of the ceramic microstructure that results from the sol–gel processing has afforded us further understanding of the anisotropic electromechanicl properties of such ceramics. It is apparent that the grain size of the ceamic has no influence on the thickness coupling factor, but greatly influences the planar coupling factor. This effect on k_p is seen in its magnitude during poling (Fig. 3) and the temperature of its zero point (Fig. 5). Fig. 3 shows that while grain size influences the overall magnitude of k_p, it has no effect on the poling behaviour (graphs have maximum k_p at same poling field and the same shape). With regard to the k_p zero point (Fig. 5), the grain size must also be influencing the temperature behaviour of the real part of the piezoelectric d_{31} coefficient.

Thus, in PST ceramics, the temperature behaviour of k_p is found to be dependent on the processing parameters, such as starting materials, sintering schedule and poling condition. However, all the samples prepared, either from the mixed-oxide process or the sol–gel route, have exhibited vanishingly small k_p. This behaviour suggests that there are at least two mechanisms responsible for the temperature dependence of k_p in PST ceramics, as indicated graphically in Fig. 9. The first mechanism is related to the anisotropy in electrostrictive coefficients, which is an intrinsic property of the ceramic. This, coupled with a large degree of tetragonality and the low anisotropy in dielectric permittivity, leads to the small values of k_p. It has been shown by the averaging of single-crystal values for $PbTiO_3$ that lack of anisotropy in the dielectric permittivity leads to a large anisotropy in piezoelectric properties [15]. The second mechansim responsible for the temperature dependence of k_p may arise from the extrinsic contributions to d_{31}, the origin of which is not clear. It is evident from Damjanovic *et al.* [16] and our work that this contribution is dependent on the extent of 90° domain reorientation and the electronic and ionic defects present in the ceramic. It has been postulated that at certain temperatures such a contribution to d_{31} may be different in sign and larger than the intrinsic d_{31} contribution, giving rise to the k_p zero point and an apparent positive d_{31} [16].

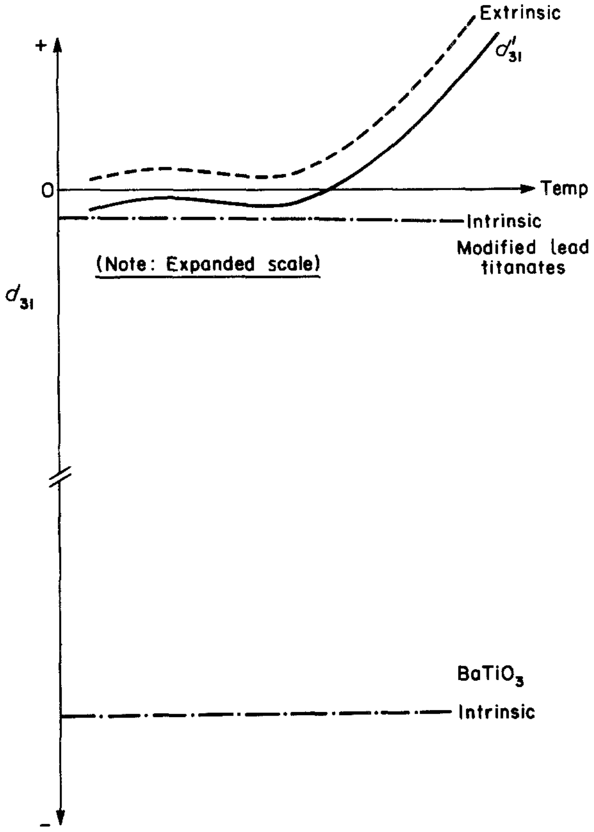

Figure 9 A hypothetical plot of d_{31} against temperature, showing the intrinsic and extrinsic contributions.

As indicated in Fig. 9 for $BaTiO_3$, since the intrinsic contributions to d_{31} are very large, the relatively small extrinsic contributions have no appreciable influence on the temperature dependence of d_{31} and k_p. However, in modified lead titanates the extrinsic contributions are now similar in magnitude to the intrinsic contributions, and thus significantly influence the temperature behaviour of d_{31} and k_p. Clearly more experiments are required before the different contributions to d_{31} can be fully identified and separated.

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