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Large electromechanical anisotropic modified lead titanate ceramics

Part 2 *Dielectric, piezoelectric and mechanical properties*

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Dielectric, piezoelectric and mechanical properties of $Pb_{0.88}Ln_{0.08}(Ti_{0.98}Mn_{0.02})O_3$ and $Pb_{0.76}Ca_{0.24}((Co_{0.5}W_{0.5})_{0.04}Ti_{0.96})O_3$ ceramics as a function of the tetragonality (c/a) have been investigated. The influence of the poling field on such properties was studied, and it was found that, generally, the electromechanical coupling factor thickness mode, K_t, increases as the poling field was increased reaching a limiting value of 0.47 in the case of samarium-modified lead titanate (PT) (the highest value in the Ln–PT series), and ~0.60 in the case of Ca–PT. The coupling factor planar mode, K_p, became zero at 40 kV cm^{-1} in Ca–PT, and almost zero in the case of Sm–PT at 60 kV cm^{-1}. In the other members of Ln–PT, K_p was lower than 10 to 15%. It was suggested that both the grain size and the 90° domain rotation, caused as a consequence of the strong poling field, could explain such a phenomenon.

1. Introduction

In view of their small dielectric constant and high Curie temperature, $PbTiO_3$-based ceramics are now known as very promising piezoelectric materials for high-temperature and high-frequency applications. Furthermore, the $PbTiO_3$ ceramics present a large anisotropy between the transverse and longitudinal piezoelectric factors K_p and K_t which render these very attractive as both ultrasonic transducers for non-destructive testing of metals and, because of its high hydrostatic g-constant, for hydrophone applications. However, one of the biggest problems present in the $PbTiO_3$ ceramics is the microcracking produced in the cubic–tetragonal phase transition on cooling which, on the other hand, is the main cause of its poor ageing behaviour. In Part 1 of this series of papers [1] it was established that a rigorous control of the microstructure is necessary in order to avoid c/a fluctuations which could provoke macro- or microcracking in the $PbTiO_3$-based ceramics. Most of the papers found in the literature [2–7] reported the use of a conventional method for sample preparation, and little attention was paid to producing $PbTiO_3$-based ceramics with controlled microstructures. Carl [8] reported that coarse-grained $PbTiO_3$ ceramics showed an extensive microcracking phenomenon during poling, and such a phenomenon was not present in fine-grained $PbTiO_3$ ceramics. Such microcracking in the samples was considered to be responsible for the degradation of their dielectric and piezoelectric properties. On the other hand, its potential application at high ultrasonic powers is closely related to its ability to support both high mechanical strengths and electrics fields without overheating. Therefore, control of the internal stresses present in $PbTiO_3$-based ceramics by controlling the different microstructural parameters is necessary.

In this way, the work reported in this paper was undertaken to evaluate the dielectric, piezoelectric and mechanical properties of modified lead titanates (PT) with a controlled microstructure prepared by using metal–organic precursors.

2. Experimental procedure

The samples were prepared as described elsewhere [1] and after characterizing crystallographically, the Curie temperature was obtained on sintered samples from the temperature dependence of the dielectric constant (ε_{33}^{T}) measured at 1 kHz by using an automatic impedance analyser HP 4192A.

Disc specimens, 10 to 17 mm diameter and 0.4 to 0.8 mm thick, were cut from the sintered samples, and silver paste was applied to both faces and platinum lead wires were attached to the electrodes. These specimens were then poled in silicone oil at 120° C under a field of 20 to 70 kV cm^{-1} for 20 min, and slowly cooled at room temperature with the poling field applied.

Electromechanical coupling factors, planar mode K_p, thickness mode K_t, longitudinal mode K_{33}, and frequency constants N_p and N_t were measured by the resonance antiresonance method according to IRE standard [9], taking into account the frequency at maximum admittance, the frequency at minimum admittance, and the admittances at each frequency.

The fracture toughness (K_{IC}) was measured by a microindentation technique using a micro Vicker's diamond indentor. The K_{IC} values were calculated with a constant indent load of 5 kg and a time of

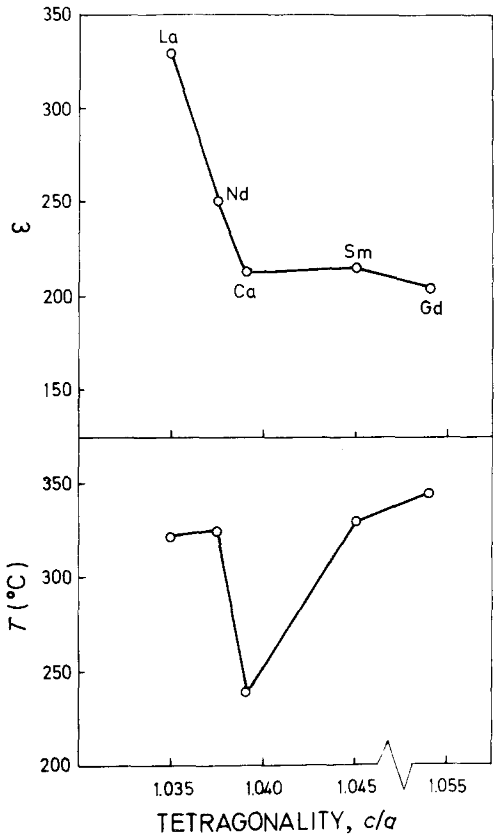

Figure 1 Crystal tetragonality dependence of Curie temperature and dielectric constant.

1 min. The Vicker's hardness measurements were carried out with the same indent load.

3. Results

First it must be mentioned that the grain size was less than 1 μm in the case of lanthanide-modified lead titanates and 8 μm for the calcium-modified lead titanate.

Figs 1a and b show the variation of the dielectric constant and T_c as a function of tetragonality (a/c). As can be seen, in close agreement with the thermal expansion measurements [1], the Curie temperature (T_c), in all cases smaller than that of pure $PbTiO_3$, increases monotonically with increasing lattice anisotropy provoked by the substitution of lanthanide elements for lead. The effect of the decrease in T_c was much more pronounced in the case of the calcium-modified lead titanates in spite of the fact that similar lattice anisotropy was produced. If we take into account that the grain size was greater in the case of calcium-modified lead titanates, then the cause for such a T_c decrease could be explained by the higher CaO content, compared to the rare earth concentration, leading to a less polarizable perovskite structure which implies a lower atomic displacement. Although these results are in agreement with those reported by Okazaki and Nagata [10] for PLZT ceramics, the reasons for such a behaviour are not clear from the literature [8, 11].

The dielectric constant, see Fig. 1a, decreases gradually with increasing tetragonality. In all cases the dielectric constants were much smaller than that of PZT, and very similar to that of the pure $PbTiO_3$ ($\varepsilon^T_{33} = 200$) in the case of samarium-, gadolinium- and calcium-modified lead titanates in which the dielectric constant values were below 210. This discovery seems to place samarium-, gadolinium- and calcium-modified lead titanates as very promising ceramic materials for high-frequency applications.

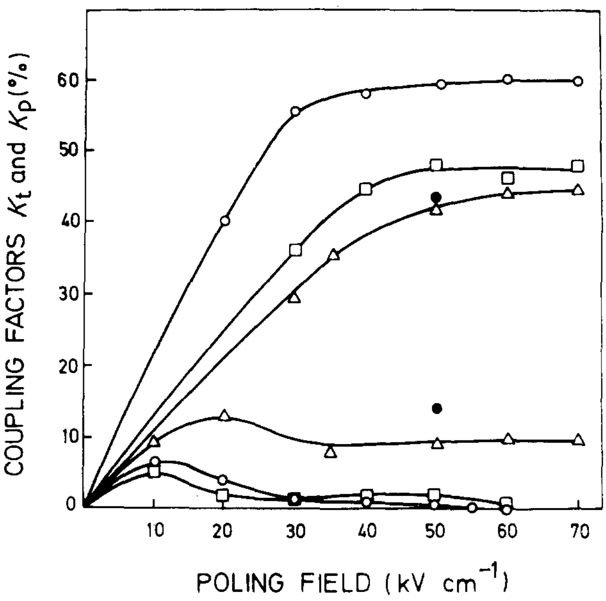

Figure 2 Electromechanical coupling factors K_t and K_p as a function of poling field in (○) Ca–PT, (●) La–PT, (□) Sm–PT, (△) Nd–PT.

Because electromechanical properties strongly depend on poling conditions, both the best poling field and best poling time were evaluated. Fig. 2 shows the poling-field dependences of planar coupling factor K_p, and thickness dilatational, K_t, for the samarium-, neodymium- and calcium-modified lead titanates. As can be seen, the electromechanical properties are nearly saturated after poling above 35 kV cm^{-1} at 120° C for 20 min; therefore these poling conditions were used for the different samples under experimentation. The samarium-modified lead titanate reached saturation for $K_t = 47\%$, while the calcium-modified lead titanate saturated at $K_t = 60\%$. The planar coupling factor, K_p, became almost zero in these poling conditions. In the case of Nd–PT the saturation was reached at $K_t = 40\%$, and the K_p never was lower than 8 to 10% even under the best poling conditions. As shown in Fig. 3, the dielectric constant, ε^T_{33}, decreases gradually with increasing poling field reaching a limiting value of 205 above 60 kV cm^{-1} in the case of Sm–PT, 190 for Ca–PT and 250 in the case of Nd–PT.

Fig. 4 shows piezoelectric frequency response for planar mode under the best poling conditions. It can be observed as the piezoelectric planar mode signal decreases from Nd–PT to Ca–PT in which no signal was detected above 45 to 50 kV cm^{-1}.

The remanent polarization, P_r, decreases from La–PT in which the P_r value is 35 μC cm^{-2}, to 32 μC cm^{-2} in Sm–PT. Calcium-modified lead titanate showed an extremely high P_r value of 36 μC cm^{-2}.

The frequency constants N_p and N_t decrease almost linear with tetragonality increasing in the La–PT series, showing a relatively low value for N_t in the case

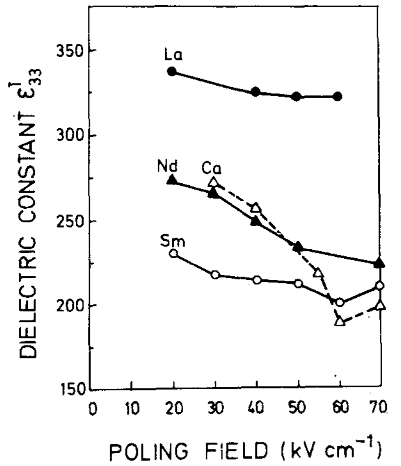

Figure 3 Dielectric constant change as a function of poling field in several modified lead titanates.

of Ca–PT. Fig. 5 shows the variations of electromechanical properties as a function of tetragonality.

Piezoelectric constants d_{33} and g_{33} increased as the tetragonality increased, showing an abrupt increase in the case of Ca–PT. The figure of merit for the hydrostatic constant $d_h g_h$ increased monotonically with increasing tetragonality, and an extremely high value was found in the Ca–PT ceramics in spite of their lower tetragonality compared to Sm–PT ceramics. The mechanical quality factor (Q_m) was in all cases lower than 200 and decreased with the increasing grain size from La–PT to Ca–PT ceramics. Fig. 6

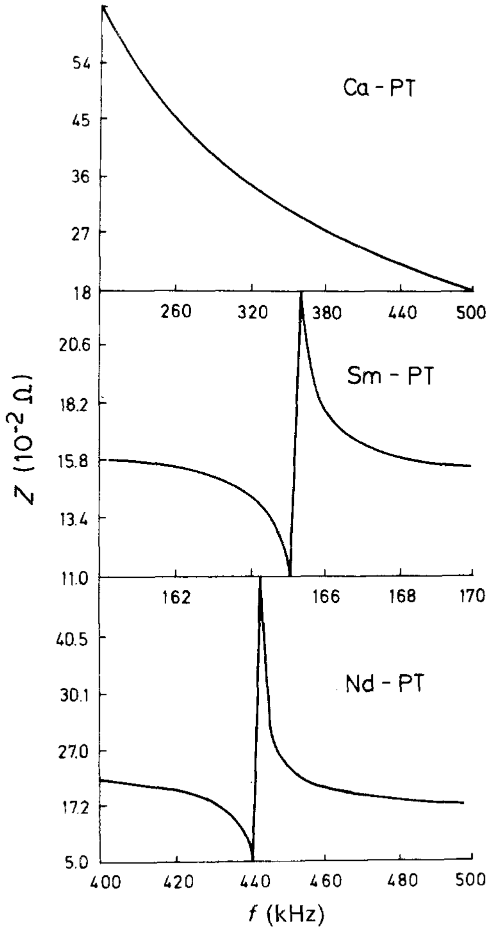

Figure 4 Piezoelectric frequency response for planar mode K_p at the best poling conditions in Ca–PT, Sm–PT and Nd–PT.

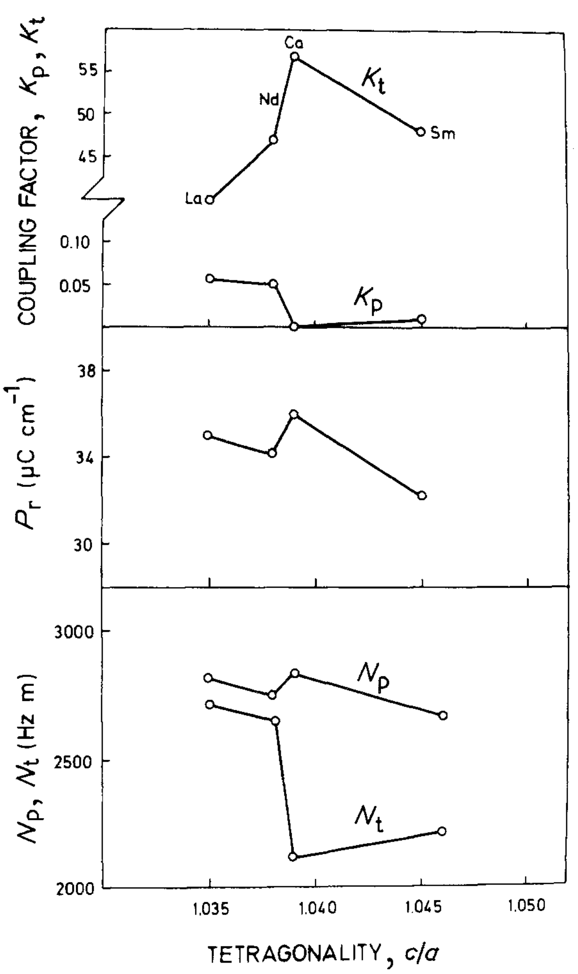

Figure 5 Crystal tetragonality dependence of coupling factors, K_t and K_p, remanent polarization, P_r, and frequency constants, N_p and N_t.

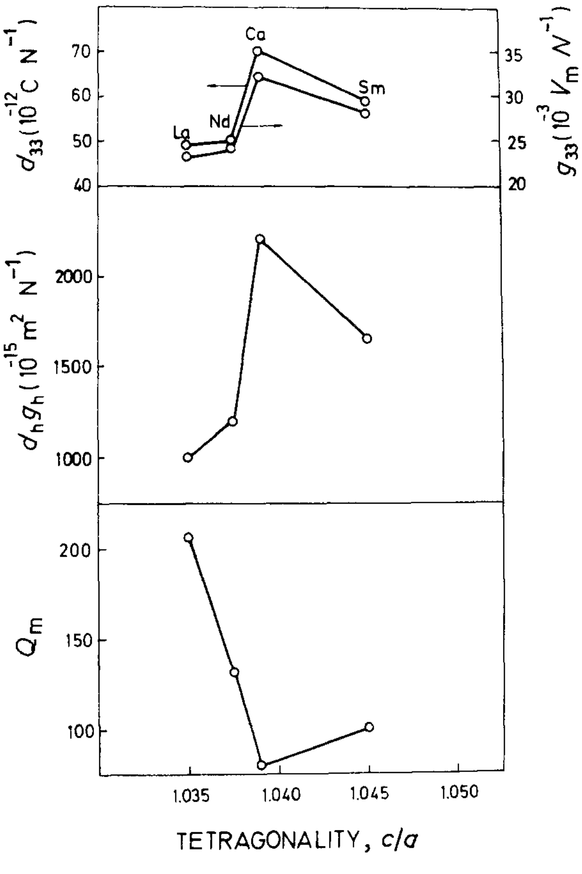

Figure 6 Crystal tetragonality dependence of d_{33}, $g_h d_h$ and Q_m.

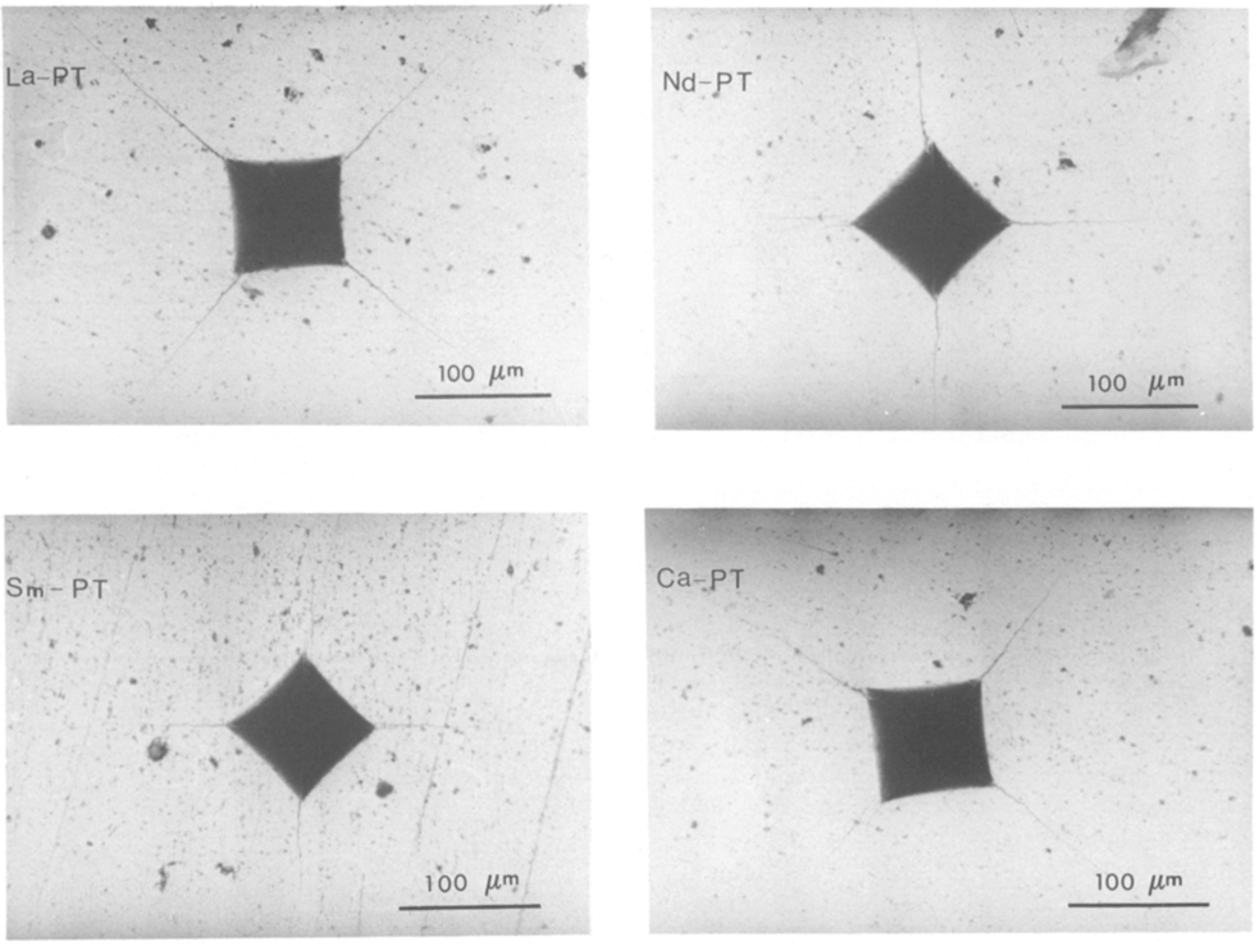

Figure 7 Typical indentation micrographs of the different modified lead titanates.

shows the influence of the tetragonality on these properties.

Because the cubic–tetragonal phase transition could induce internal stress in the samples, the microhardness, H, and the fracture toughness, K_{IC}, can serve as measures of its extent. The microhardness decreases with increasing tetragonality. Typical indentation micrographs are shown in Fig. 7. From the diagonal length of the indentation, $2a$, the crack lengths, $2c$, and taking into account the known Evans and Charles expression [12], the fracture toughness, K_{IC}, could be measured. As seen in Fig. 7, the indentation cracks are very clear and a strong symmetry was present in all cases, probably due to a very uniform microstructure. Fig. 8 shows the H and K_{IC} dependence of the tetragonality for the different modified lead titanates. The fracture toughness increases as the tetragonality increases, but the curve was depressed in the case of Ca-PT and Gd-PT. A similar trend was obtained on samples after polishing although the K_{IC} values were lower.

4. Discussion

Although the properties of ferroelectric ceramics are very complicated it could be assumed, in principle, that poling in lead titanate ceramics is induced by 180° reversal and by the rotation of 90° domains and, in addition to this, that only the rotation of 90° domains contributes to the dimensional changes in these ferroelectric materials. If this is so then, when poling the modified lead titanate ceramics, the dimensional changes and the variations found in the dielectric constant, ε_{33}^{T}, will be a consequence of the percentage of rotated 90° domains. As shown in Fig. 3, the dielectric constant, ε_{33}^{T}, gradually decreased with increasing poling field, and this was more pronounced in the case of modified Ca-PT. For La-PT and Nd-PT no saturation was obtained under these poling conditions, while Sm-PT and Ca-PT showed a maximum ε_{33}^{T}, decreasing at 60 kV cm^{-1}. Such a decrease coincides with the poling field value at which the planar

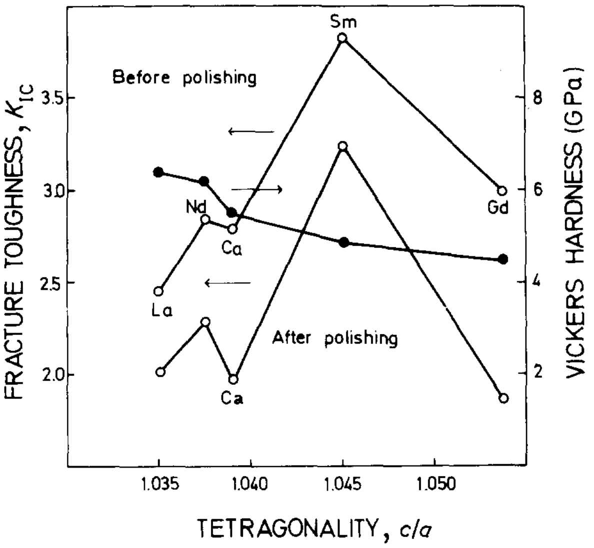

Figure 8 Fracture toughness, K_{IC}, and Vicker's hardness, H, as a function of tetragonality.

mode, K_p, disappears. If, as before, the large electromechanical anisotropy is considered to be due to the rotation of 90° domains, caused as a consequence of the strong applied poling field, then both the decreasing ε_{33}^T and the zero planar mode phenomena could be closely related. The presence of large grain size in the Ca–PT microstructure and a lower c/a ratio probably favoured this phenomenon compared to that occurring in Sm–PT.

Although the number of 90° domains was not calculated, the high remanent polarization ($P_r > 33\,\mu\text{C cm}^{-2}$) measured in all the cases indicated that at least 45% domain alignment exists and that the 180° domain alignment could be almost perfect. Such a P_r value agrees very well with that reported by Remeika and Glass [13] on $PbTiO_3$ single crystal ($P_r = 75\,\mu\text{C cm}^{-2}$), if it is taken into account that in an ideally poled ferroelectric ceramic of tetragonal structure, one-third of the total polarization is due to 180° domain alignment and two-thirds to 90° domain alignment [14]. This result could explain the extremely high K_t found in the case of modified Ca–PT although it conflicts with the small planar mode $K_p \simeq 0$. This apparent controversy could be justified by the relatively low coercive field ($E_c \simeq 25\,\text{kV cm}^{-1}$) which, on the other hand, will favour the rotation of 90° domains under the actual poling conditions. Such a low coercive field in Ca–PT is compatible with the grain size present in the microstructure. In the case of the modified La–PT, the coercive field was always higher than $35\,\text{kV cm}^{-1}$. Furthermore, the small grain size present in their microstructures ($< 1\,\mu$m), could give rise to the presence of a certain clamping effect on the polarization reversal process. In this way a smaller electromechanical anisotropy was found in the modified La–PT ceramic series. Thus while a K_t/K_p ratio of infinity was found in the case of modified calcium–lead titanate ceramics, in the modified lanthanide–lead titanate ceramics such a ratio was never higher than 5, except in the case of modified Sm–PT in which a K_t/K_p ratio higher than 20 was found. Therefore both calcium- and samarium-modified lead titanate ceramics are very promising piezoelectric materials for use in high-temperature and high-frequency applications. A similar behaviour was found by Yamashita *et al.* [15] in a modified Ca–PT containing 24 mol % CaO and 2 mol % MnO in which the MnO additive facilitated the poling process by increasing electrical resistivity. However, this additive must be carefully used because above a determined MnO amount the conductivity of the ceramics is increased.

In view of the large anisotropy between the planar and longitudinal piezoelectric coupling factors, the constants d_{31} and g_{31} are negligible and, therefore, it can be considered that $d_{33} \simeq d_h$ and $g_{33} \simeq g_h$. From those values, a figure of merit for hydrostatic constant $d_h g_h$, as a guide to their applicability for hydrophones, was estimated. As seen in Fig. 6, such a figure of merit is considerably higher in the case of modified calcium–lead titanate ceramics which is a consequence of its very high d_h hydrostatic constant and very low relative permittivity, ε_{33}^T. Its value is comparable to that of $PbNb_2O_6$ ceramics. The low mechanical quality factor, Q_m, found for all specimens could be attributable to the presence of certain microcracking.

As shown in Fig. 8 the microhardness, H, increases with decreasing tetragonality. These experimental results are a consequence of the internal stresses induced in the sample on cubic-tetragonal phase transition. It seems clear that before polishing, the samples were anisotropically stressed and that the anisotropic stressing will depend on the c/a ratio. As the c/a ratio increases the stressing level will be raised, and the crack propagation in the modified lead titanate matrix will be arrested. Therefore, the fracture toughness, K_{IC}, will increase. This is so in the La–PT series in which the grain size is very similar. However in the case of Ca–PT, having a higher grain size, a considerable microcracking is present which facilitates crack propagation leading to a decreasing K_{IC}. After polishing, most of the internal stress was relaxed and the fracture toughness fell strongly. The mechanical behaviour of Gd–PT ceramics is a consequence of the large macrocracking present in the samples in view of its large c/a ratio. A similar behaviour was found by Yamamoto *et al.* [16] in calcium-modified lead titanate ceramics.

5. Conclusions

The ferroelectric properties of lead titanate ceramics modified by rare earths (La, Nd, Sm, Gd) + MnO and CaO + (Co + W), leading to the compositions $Pb_{0.88}La_{0.08}(Ti_{0.98}Mn_{0.02})O_3$ and $Pb_{0.76}Ca_{0.24}((Co_{0.5}W_{0.5})_{0.04}Ti_{0.096})O_3$, respectively, have been investigated. The experimental results described above lead to the following conclusions.

1. The substitution of lead by rare earths or CaO strongly influences the crystallographic, dielectric and piezoelectric properties of lead titanate ceramic. Thus the addition of 8 mol % lanthanide oxide diminishes the tetragonality of the $PbTiO_3$ perovskite structure changing monotonically from gadolinium to lanthanum. Such diminishing tetragonality allows the normal sintering of $PbTiO_3$ ceramics. In the case of the CaO additive, addition of at least 24 mol % was necessary to avoid macrocracking in the sintered samples.

2. The addition of 8 mol % La_2O_3 or 24 mol % CaO strongly diminishes the Curie temperature (T_c) and the dielectric constant ε_{33}^T of $PbTiO_3$, such a decrease being more pronounced in the case of the CaO addition.

3. The combined addition of La_2O_3 + MnO or CaO + (Co + W) facilitates the poling process of the modified lead titanates. In this way the calcium-modified lead titanate was sufficiently poled at $35\,\text{kV cm}^{-1}$, Sm–PT at 40 to $50\,\text{kV cm}^{-1}$ and higher than $60\,\text{kV cm}^{-1}$ for the other members of the lanthanide series.

4. The electromechanical coupling factors and the frequency constants are also influenced by these two kinds of additive changing gradually with increasing tetragonality (c/a). In all cases the longitudinal coupling factor, K_t, increases with increasing poling field and, on the other hand, the planar coupling factor, K_p, decreases. In the case of the calcium-

modified lead titanate, K_p was negligible at approximately $50\,\mathrm{kV\,cm^{-1}}$, and K_t was as high as 60%. Therefore, the K_t/K_p ratio is probably the largest value reported to date. In the lanthanide oxide series only Sm–PT showed a reasonably high K_t/K_p ratio, of approximately 20, and in the other cases such a ratio was never higher than 5.

5. The large electromechanical anisotropy present in these piezoelectric ceramics makes d_{31} and g_{31} almost negligible and, therefore, the hydrostatic constant, d_h, can be considered equal to d_{33}. In this way the figure of merit $d_h g_h$ was as high as 2200 in the case of calcium-modified lead titanate, which is comparable to that of $PbNb_2O_6$. In the La–PT ceramics $d_h g_h$ was always smaller than 1500.

6. The high remanent polarization, P_r, measured, $32\,\mu\mathrm{C\,cm^{-2}}$ in the titanate and, on the other hand, the relatively higher coercive field, E_c, found in the La–PT series leads one to think that the microstructure (grain size 1 μm) could have a clamping effect on the polarization reversal process. The higher grain size present in the Ca–PT microstructure contributes to both a larger total domain alignment and 90° domain rotation.

7. Both tetragonality and grain size are responsible for the appearance of macro–microcracking in the modified lead titanate ceramics and, therefore, for its mechanical behaviour. In that sense the fracture toughness, K_{IC}, increases with increasing tetragonality as a consequence of more compressively stressed microstructure. The hardness, H, decreases with the increasing tetragonality probably as a consequence of a higher microcracking present in the ceramic materials. In both cases a higher grain size produced a decrease in these two mechanical parameters.

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