The effect of PbO content on a modified lead titanate ceramic

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Modified lead titanate ceramics were prepared from batches with compositions $Pb_xCa_{0.30}Ti_{0.94}(Co_{1/2}W_{1/2})_{0.06}O_{2.3+x}$ (x = 0.67, 0.68, 0.69, 0.70, 0.71 and 0.72) with 1 mol% MnO to determine the effect of PbO content on the dielectric and piezoelectric properties. An increase in PbO content increased the grain size and reduced the planar coupling factor k_p. The dielectric constant $\varepsilon_T^{33}/\varepsilon_0$ and the piezoelectric constant d_{33} reached a maximum for a ceramic made from a batch with stoichiometric PbO content (x = 0.70).

1. Introduction

Modified $PbTiO_3$ ceramics display a large electromechanical anisotropy, i.e. a large thickness coupling factor (k_t) compared to the planar coupling factor (k_p). Consequently these materials have been extensively investigated for high frequency and acoustic wave applications. Compositions similar to $Pb_{0.76}Ca_{0.24}Ti_{0.96}(Co_{1/2}W_{1/2})_{0.04}O_3$ have a particularly large electromechanical anisotropy [1, 2]. Ceramics of this family with various amounts of modifier content have been made (e.g. [1, 3, 4]) and it was found that an increase in the modifier ions calcium, cobalt and tungsten had the effect of reducing the tetragonality c/a and increasing the piezoelectric constant (d_{33}).

To optimize the properties of modified lead titanate ceramics it would also be necessary to control the PbO content. In this study the effect of PbO content on the dielectric and piezoelectric properties of the ceramic $Pb_{0.70}Ca_{0.30}$-$Ti_{0.94}(Co_{1/2}W_{1/2})_{0.06}O_3$ with 1 mol% MnO was examined.

2. Experimental procedure

The samples were prepared by the mixed oxide route. The starting raw materials were high purity PbO, $CaCO_3$, TiO_2, CoO, WO_3 and $MnCO_3$. Batches were accurately weighed according to the formula $PB_xCa_{0.30}Ti_{0.94}(Co_{1/2}W_{1/2})_{0.06}O_{2.3+x}$ (where x = 0.67, 0.68, 0.69, 0.70, 0.71 and 0.72) with 1 mol% MnO. These compositions are abbreviated to P67, P68, P69, P70, P71 and P72 respectively. The constituents were mixed by ball milling in water using zirconia balls. The mixtures were calcined in a covered alumina crucible for 2 h at 950° C. The calcined powders were ground in a mortar and pestle, mixed with binder and pressed into discs ± 12.5 mm in diameter and ± 1.5 mm thick. After the binder burnout the samples were placed on platinum foil in an alumina crucible which was covered to minimize the PbO loss and sintered at either 1120° C for 5 h, 1160° C for 10 h or 1200° C for 10 h. The discs were ground plane parallel and silver electrodes were fired on the two faces. Samples were poled in peanut oil by applying a d.c. field of $60\,kV\,cm^{-1}$ for 5 min at 110° C. Lattice parameters were measured by X-ray diffraction (XRD) using silicon as a standard. The mean grain size was measured from photomicrographs of polished and etched surfaces by the Fullman intercept method [5].

Measurements were made at 23 ± 2° C and, except for the ageing studies, at least 24 h after poling. Coupling factors were determined by the resonance method using frequency data from an impedance analyser (HP 4192A). The values of k_t were calculated from the ratio of the overtone frequency to the fundamental frequency of the thickness mode series resonance using Onoe's table [6]. The dielectric constant ($\varepsilon_{33}^T/\varepsilon_0$) and dielectric loss (tan δ) were determined at a frequency of 1 kHz. The d_{33} was measured at 100 Hz with a Berlincourt Piezo d_{33} meter.

3. Results and discussion

The weight losses during sintering and the observed densities of the samples are shown in Table I. The loss

TABLE I Physical properties and k_t/k_p ratio of ceramics

Composition	Sintering conditions (°C h $^{-1}$)	Weight loss during sintering (wt %)	Density (g cm $^{-3}$)	Mean grain size (μm)	k_t/k_p
P67	1120/5	0.32	6.77	2.1	5.9
P68	1120/5	0.46	6.81	2.2	6.2
P69	1120/5	0.38	6.83	2.4	6.4
P70	1120/5	0.63	6.84	2.5	6.9
P71	1120/5	0.80	6.84	4.6	12.9
P72	1120/5	1.22	6.90	12.6	112.6
P67	1160/10	0.02	6.67	7.7	7.9
P69	1160/10	1.78	6.65	8.4	9.4
P71	1160/10	2.25	6.70	9.0	15.7
P67	1200/10	2.47	6.49	8.7	11.0
P68	1200/10	3.72	6.49	9.8	12.3
P69	1200/10	5.20	6.55	10.8	13.0

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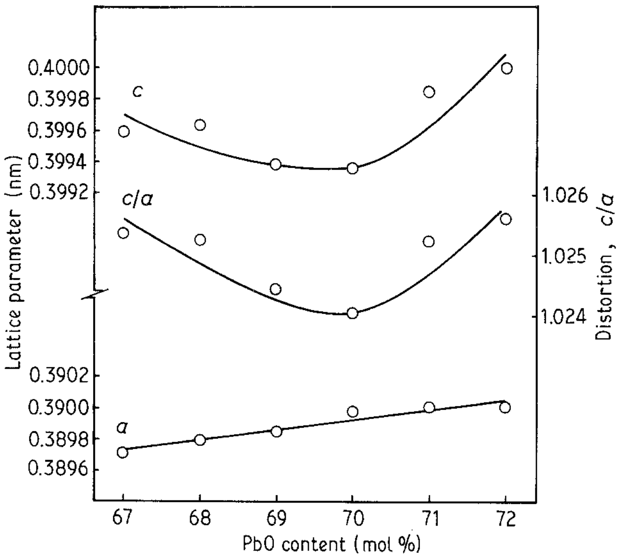

Figure 1 Lattice parameters and distortion plotted against PbO content in the batch.

is mainly due to PbO evaporation. The amount of PbO evaporation depends upon sample composition as well as other factors such as sample and crucible configuration, and furnace conditions. The samples sintered at 1120° C all had final densities of over 96% of the theoretical density and the densities decreased at higher sintering temperatures. Under the sintering conditions (5 h at 1120° C) the addition of excess PbO is therefore not necessary as a sintering aid. The decrease in the observed densities for the same compositions sintered at higher temperatures appeared to correspond more closely to an increase in porosity rather than the amount of PbO loss during sintering.

Figs 1 to5 refer to compositions sintered at 1120° C. Fig. 1 shows the increase in the lattice parameter *a* with PbO content. The lattice parameter *c* and the *c*/*a* ratio reached a minimum for composition P70. XRD revealed the presence of small amounts of second phases in the compositions P69, P68 and P67 with the concentrations of these phases increasing with increasing PbO deficiency. XRD peaks corresponding to $CaWO_4$ having tetragonal symmetry were found while the concentration(s) of the other phase(s) present was too low to be identified.

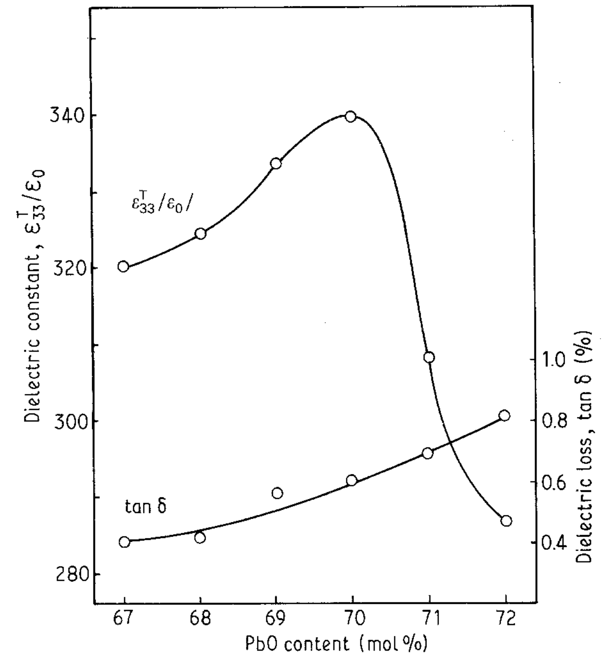

Figure 2 Dielectric constant and dielectric loss plotted against PbO content in the batch.

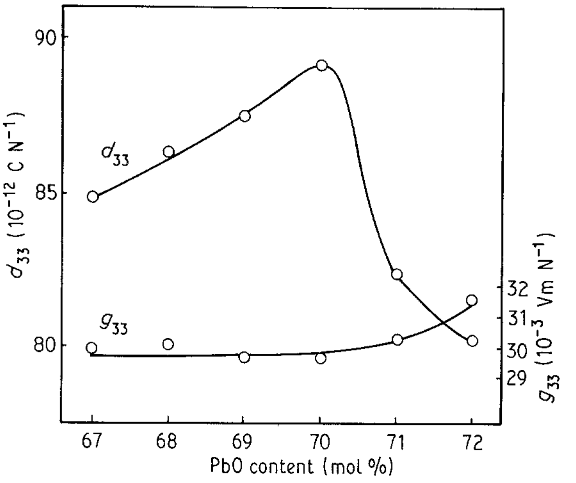

Figure 3 Piezoelectric constants d_{33} and g_{33} plotted against PbO content in the batch.

The dielectric constant and d_{33} (Figs 2 and 3) reached a maximum for composition P70. It is well known that for modified lead titanate ceramics a reduction in grain size increases the dielectric constant (e.g. [3, 4]). Clearly for the ceramics in this investigation the dielectric constant is influenced by the PbO content as well as the grain size. The dielectric losses increased with an increase in the PbO content (Fig. 2). This may be due to easier domain wall motion in larger grained ceramics and hence higher dielectric losses in these ceramics.

Fig. 4 shows that from composition P67 to P70 there is a gradual decrease in k_p and a steeper decrease from composition P70 to P72. k_t remained almost constant over the PbO range tested. It can be seen from Table I than at increase in the electromechanical anisotropy (k_t/k_p) corresponded to an increase in the grain size. This can be explained by assuming that the ceramics with a larger grain size have a lower coercive field which facilitates 90° domain rotation and reduces k_p [2]. Ceramics made from the batches with a PbO excess (P71 and P72) tended to have a larger electro-

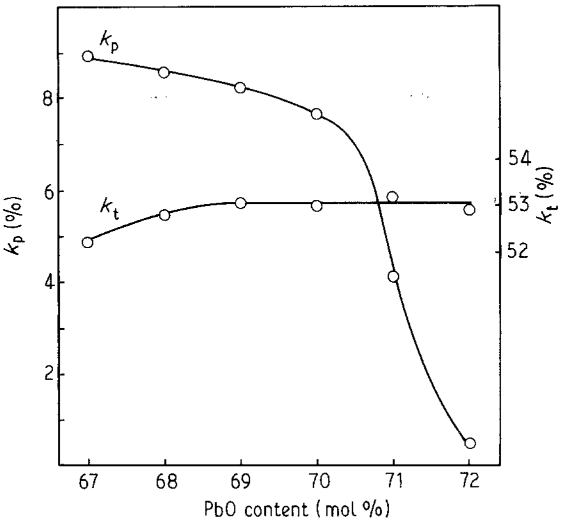

Figure 4 Planar coupling factor k_p and thickness coupling k_t plotted against PbO content in the batch.

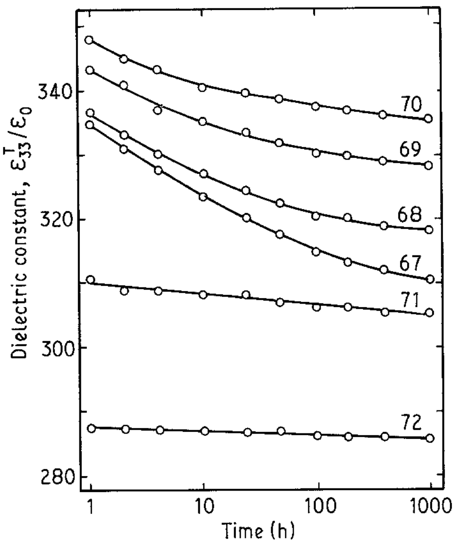

Figure 5 Dielectric constant plotted against time after poling for ceramics from batches with a PbO content of 67 to 72 mol %.

mechanical anisotropy than those made from batches with a PbO deficiency even though the former may have a smaller grain size. For example composition P71 sintered at 1120° C had a larger k_t/k_p than composition P67 or P69 sintered at 1160° C (Table I) although its grain size is smaller. The reason for this phenomenon is not clear. It should be noted that temperature has a significant effect upon the k_p of a calcium modified lead titanate ceramic and this aspect has been studied by Damjanovic *et al.* [7].

Scanning electron micrographs of unpoled samples sintered at 1120° C revealed that composition P72 contained many intragranular microcracks while the other compositions only had occasional intragranular microcracks. Normally a part of the crack terminated at a grain boundary. All the samples remained mechanically stable after poling showing no signs of disintegration due to microcracking. Composition P71 sintered at 1120° C was previously studied by transmission electron microscopy [4]. It was found that a glassy phase penetrates along grain boundaries, wetting the grain surfaces with a grain boundary film about 1 nm thick. Calculations indicated that the grain boundary film had a lower lead content than the bulk grain.

The time dependency of the dielectric constant is shown in Fig. 5. For all the compositions the absolute value of the slope of the curve decreased with time showing that the logarithmic time law is only partly obeyed. Mean values calculated for the ageing of the dielectric constant and tan δ are shown in Table II.

TABLE II Average decrease of $\varepsilon_{33}^{T}/\varepsilon_0$ and tan δ per time decade between 1 and 1000 h after poling

Composition	Decrease/time decade (%)	
	$\varepsilon_{33}^{T}/\varepsilon_0$	tan δ
P67	2.5	15.2
P68	1.9	11.8
P69	1.5	9.4
P70	1.2	6.3
P71	0.6	< 5.0
P72	0.2	< 5.0

The ageing of the dielectric constant and tan δ is lowered by an increase in PbO content. It is thought that the larger grained ceramics have a lower internal stress which reduces their ageing rates [8].

4. Conclusions

An increase in PbO content resulted in ceramics with a larger electromechanical anisotropy principally as a consequence of an increase in the grain size. The tetragonality c/a was the lowest for the material made from the batch with a PbO content of the stoichiometric composition, this material also had the highest dielectric constant and d_{33}. The ageing of the dielectric constant and tan δ was reduced by an increase in the PbO content. It may be concluded that the PbO content has a significant effect upon the properties of these modified lead titanates and should be taken into consideration for this type of material.

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