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PYROELECTRICITY AND DIELECTRIC ANISOTROPY IN POLARIZED AND NIOBIUM MODIFIED BARIUM TITANATE CERAMICS

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ABSTRACT

The effect of time of soaking on bulk density and dielectric constant has been measured on pure and niobium-doped barium titanate pyroelectric specimens. The temperature dependence of the dielectric constant for both pure and niobium-doped barium titanate samples has been investigated before and after poling. The percentage dielectric anisotropy and ferroelectricity was also calculated for various pure and modified barium titanate pyroelectric materials. Our results can be explained in terms of the redistribution of the barium titanate lattice in a different crystallographic orientation, polarization, as well as the existence of lattice imperfection accompanying temperature, poling and niobium doping. The obtained results were in good conformity, and correlated with the increased proportion of the remnant 90° domains (the induced electrically charged vacancies as a result of Nb^{3+} substitution of Ti^{4+} in octahedral lattice sites). It was concluded that poling of Nb-doped barium titanate samples produces the best quality ceramic pyroelectrics.

INTRODUCTION

Pyroelectricity is the change in electric polarization caused by temperature variation. It is defined as the manifestation of the temperature dependence of the spontaneous polarization of a polar solid.

Mathematically, the definition can be expressed as $\gamma = \mathrm{d}P_s/\mathrm{d}T$ at zero electric field and constant stress, where γ is the pyroelectric coefficient in $\mathrm{cal}^{-1}\ \mathrm{cm}^{-1}\ \mathrm{K}^{-1}$; T is the absolute temperature in K; and P_s is the spontaneous polarization in $\mathrm{C\ cm}^{-2}$. The pyroelectric current is usually determined by measuring the generated current at the electrodes by a change in temperature using a sensitive microammeter [1,2].

The pyroelectric effect in ferroelectric materials has been extensively studied [3—10]. The pyroelectric coefficient was determined as a function of temperature, a peak value of the pyroelectric coefficient was always observed near the ferroelectric transition temperature.

Ferroelectrics form a subgroup of pyroelectrics [11,12]. One of the outstanding properties of ferroelectrics is the reversibility of the permanent polarization by an electric field. This reversibility is a consequence of the fact that the polar structure of a ferroelectric is a slightly distorted non-polar structure. The relation between the net microscopic polarization of a ferroelectric crystal and the externally applied electric field is given by a hysteresis loop. Thus, a ferroelectric crystal is known to consist of domains (regions of homogeneous polarization differing only in the direction of polarization). The domain formation may be called twinning. A polar structure of a domain may be obtained from a non-polar structure by a straight strain.

A ferroelectric material has a Curie temperature at which the dielectric constant exhibits a peak. Below this temperature, the material is ferroelectric while above it the crystal becomes paraelectric [13,14].

It is fortunate that ferroelectricity is a basic property of barium titanate ceramic and its related compounds as well as making piezoelectric ceramics possible. As is well known, barium titanate prepared by the ceramic methods contains individual crystallites which have essentially random orientations. The polarity is distributed statistically among the several permissible directions within each crystallite. Usually a strong electric field applied to $BaTiO_3$ ceramic, preferably at a temperature just below the Curie temperature ($\simeq 120°C$), changes the domain pattern and causes a preferential alignment of polarity in the direction subtending the smallest possible angles with the applied field.

After the poling process, it has an overall polarity and hence can be strongly piezoelectric. Thus, the piezoelectric constants, d_{31}, g_{31}, and their temperature dependence were previously studied. Alternatively, the orientation of domains remains there as the remnant polarization. Meanwhile, the $BaTiO_3$ single crystal is highly anisotropic in the tetragonal phase.

Therefore, if 90° rotation of domains remains after the poling process, the dielectrics of the polarized ceramics are expected to be very different from those of the unpolarized ones. The unpolarized ceramics are isotropic and have one dielectric constant [17]. The anisotropy is a few percent of about 12% of the factors affecting the behaviour.

The sintering and grain growth behaviour is quite sensitive to additions of certain trivalent ions [18]. Aluminium ions were found to affect the behaviour of this material [19,20].

It has previously been established [21—24] that lanthanum doping of the lead zirconate lattice increases its dielectric constant and decreases its resonance frequency (F_r) as well as the elastic properties (Young's modulus).

These foundations were attributed as evidence for increasing the ferroelectric sensitivity of the material under investigation [22—24].

Thus, the present investigation deals with the variation of bulk density, dielectric constant and percentage anisotropy as a function of temperature before and after niobium doping of polarized and non-polarized $BaTiO_3$ samples. These observations were made in an attempt to attain the expected better pyroelectric behaviour of barium titanate by approaching a high anisotropic specimen containing Nb additive and fired at a relatively low sintering temperature. A low sintering temperature is economic for industry as it demands a low heating cost and fuel oil consumption. These experiments were also conducted in continuation with other related physical measurements [25,26], indicating that the piezoelectric response of $BaTiO_3$ containing 0.1 wt.% Al fired at 1200°C was higher than that of the same pure specimen fired at 1400°C.

Material preparation

The starting materials were analytically pure grades of $BaCO_3$, TiO_2 (BDH) type and pure powdered niobium metal (prolabo) type. In all cases, the purity of these materials exceeds 99.80%. A mixture composed of an equimolecular ratio (1 : 1) of $BaCO_3$ and TiO_2 was milled with distilled water by using a magnetic stirrer for 24 h. The obtained slurry was dried at 110°C overnight and compressed into cylindrical pellets at 1 ton cm^{-2} ($r = 2$ cm and thickness = 0.2 cm). Each pellet was then placed into a platinum crucible and fired at 1000°C for 20 h using an electric muffle furnace for the following calcination reaction to take place

$$BaCO_3 \xrightarrow{1000^\circ C} \underset{\text{Freshly prepared and very reactive}}{BaO} + CO_2$$

The calcined materials were then wet milled with 0.1 wt.% Nb powder for 24 h in distilled water. This percentage was chosen as it has previously been shown to be the optimum value for doping with aluminium [26]. The materials were then finely ground using an agate mortar for 3 h. The ground materials were compressed into disks under the same prementioned conditions, introduced into an electric muffle furnace and sintered at 1300°C for 10 h and then cooled quickly to room temperature to preserve the phase formed at high temperature.

Following the preparation careful X-ray diffraction studies were made to ensure complete reaction and the phase formed during the high temperature solid state reaction of

$$BaCO_3 \xrightarrow{1000^\circ C} BaO + CO_2 \qquad \text{(a)}$$

Freshly prepared more reactive

$$BaO + TiO_2 \xrightarrow{1200\text{–}1300^\circ C} BaTiO_3 \qquad \text{(b)}$$

Spectroscopic analysis was also performed indicating the highest purity of the prepared $BaTiO_3$ and the existence of minute traces of Pb, Fe, and Mn which may be ascribed as contaminants in the graphite electrode of the spectrometer.

Determination of Bulk Density

It was realized that changes in the bulk density of the prepared mixes fired under the present conditions would be so small that the accuracy of measuring was essential. After considering various possibilities, it was decided to make use of the mercury displacement measuring technique, but using the upthrust and not the volume of displacement. This was achieved by using the mercury balance as modified from that described by Clark and White [27]. The mathematical equation from which bulk density of the specimen (gm cm^{-3}) was calculated as follows

$$\text{Bulk density (BD)} = \frac{\text{Wt. of specimen in air}}{\text{Upthrust}} \times \text{Density of Hg at the temp. of the run}$$

The apparatus used can be balanced to ±0.002, meaning that this modified apparatus gives more accurate results than others in which volume differences are measured directly.

Dielectric Measurements

The dielectric constant was calculated from the measured capacitance of each sample at room and elevated temperatures. A bridge of type B-801 Cambridge with, an accuracy of ± 0.5 PF, with little modification [28] was used . The hysteresis loops were produced by the usual method of Sauer and Tower [28].

Determination of Percentage Anisotropy

This was determined by semiquantitative calculations at room temperature using the formula previously given by Marutake and Ikeda [29]

$$\text{Percentage anisotropy} = \frac{\epsilon'_{\text{polarized}} - \epsilon'_{\text{unpolarized}} \times 100}{\epsilon'_{\text{unpolarized}}}$$

RESULTS AND DISCUSSION

The variation of the obtained bulk density (gm cm^{-3}) as a function of soaking period for pure barium titanate and barium titanate doped with 0.1 wt.% Nb is clearly shown in Fig. 1, curves (a) and (b), respectively.

There is a considerable increase in bulk density with soaking time (at 1300°C) for the pure barium titanate sample and a pronounced increase in the case of the sample containing 0.1 wt.% Nb additive. This finding may be correlated with the propagation of sintering and the diffusion mechanism as the soaking period increases for the different samples. But for the modified sample containing 0.1 wt.% Nb, the high increase in values of bulk density is

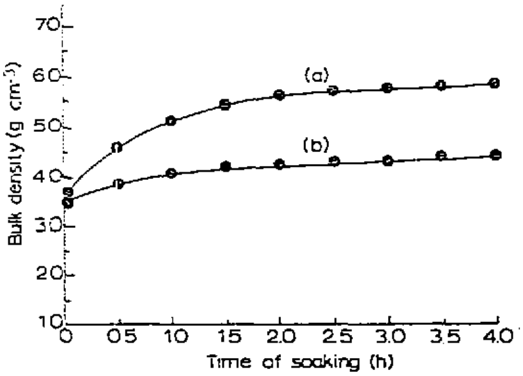


Fig. 1. Representation for the variation of bulk density (gm/cm^{-3}) with time of soaking (h) : (a) barium titanate + 0.1% Nb; (b) pure barium titanate.

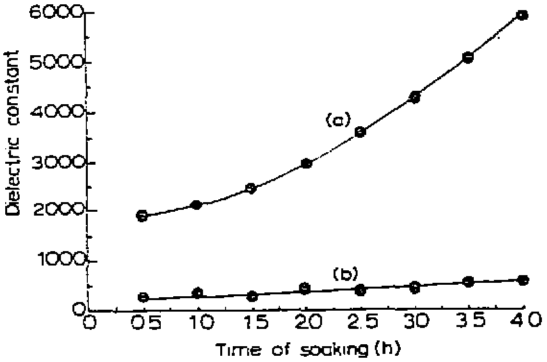


Fig. 2. Diagram representing the variation of the the obtained dielectric constant of: (a) barium titanate + 0.1% Nb; (b) pure barium titanate.

in conformity with that previously reported [30,31] for lead zirconate titanate doped with Fe^{3+}, considered as being due to the action of doping on grain growth inhibition and hence the resultant more sintered and compact bodies. In this case, the charged vacancies are created within the barium titanate lattice when Nb^{3+} replaces Ti^{4+}. These vacancies are mostly believed to associate with the impurity ions and cause them to be absorbed at grain boundaries and substantially reduce their mobility. This reduction of grain boundary mobility retards or inhibits the grain growth and thereby expedites more densification (see Fig. 1, curve b).

Behaviour similar to that of the dependence of bulk density on the time of soaking is also observed for the measured values of the dielectric constant (see Fig. 2). Curves (a) and (b) of Fig. 2 represent the variation of dielectric constant (ϵ') with sintering time (at 1300°C) for pure barium titanate and niobium-doped barium titanate samples, repectively.

This observed increase of dielectric constant with soaking period is probably caused by the increased values of bulk density (BD) in the same direction, particularly for pure barium titanate (Fig. 2, curve a). But for Nb-doped barium titanate (Fig. 2, curve b), another factor will contribute towards the rise in value of the dielectric constant with time of soaking.

This is most probably caused by the influence of the propagated charged vacancies which are introduced as a result of the doping mechanism when Nb^{3+}ions replace Ti^{4+} ions in the barium titanate lattice during the course of the high temperature solid state reaction mechanism. This may in turn cause lattice imperfection and induced lattice polarization, resulting in an increase of the obtained values of dielectric constant.

Further progress of this behaviour may take place at longer sintering times, enhancing the greater densification by the diffusion mechanism at this high sintering temperature, giving rise to more lattice imperfection and polarization of the lattice. Consequently, the increase of the dielectric constant of niobium-doped barium titanate compared with that of the pure sample was thought to be correlated with the induced internal strains retaining some of the 90° domains after the poling process and/or to lattice imperfection and more polarization caused by the disintegration of niobium powder and its subsequent oxidation to Nb_2O_3 at the sintering temperature which is the basic component in the ceramic industry.

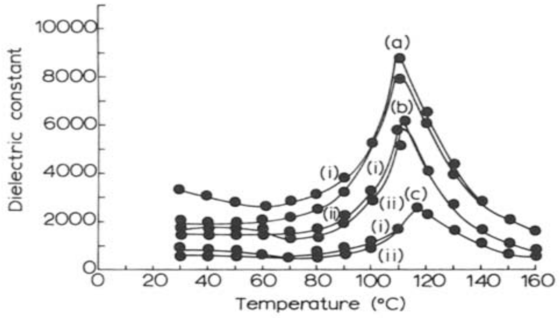
Figure 3 includes the variation of the obtained dielectric constant (ϵ') with temperature. The dielectric constant increased suddenly at 120°C having a value of $\simeq$ 8000 for the specimen of 0.1 wt.% Nb-doped barium titanate. This pronounced increase is attributed to phase transition in which the crystal structure passes from a tetragonal ferroelectric phase to a cubic paraelectric one. The latter modification may have a very high dielectric constant compared with that of the tetragonal modification.

It is of interest to note that values of the dielectric constant of polarized specimens are higher than those of the unpolarized ones at room temperature. At temperatures above 60°C, the dielectric constant is smaller for the polarized specimen. This was thought to be due to the reversal of 90° domains to their original positions at these relatively higher temperatures, diminishing the present polarization.

It can be seen from Fig. 3 that the Curie point (120° C) is considerably shifted towards lower temperature (104° C) by niobium doping. On the other hand, polarization of the various specimens has no consistent effect on the value of the Curie temperature.

The percentage anisotropy was evaluated in each case. However, results obtained indicated that the percentage anisotropy for pure barium titanate and barium titanate containing 0.1 wt.% Nb and sintered at 1200° C are 10% and 26%, respectively, while it is 12.5% for pure barium titanate sintered at 1400° C. Thus, Nb doping of the barium titanate lattice may increase its anisotropy. The increase of anisotropy, caused by the change of domain structure in the greater part, is due to the reversal of 180° domains to their original positions which remain entire after polarization. On the other hand, the increase of the proportion of 90° domain rotations may also remain in the polarized ceramic bodies. This proportion in turn is smaller than that of the pure unmodified barium titanate samples.

High field ferroelectric measurements (Fig. 4) were made to evaluate the ease and extent of domain reorientation. In this part, hysteresis loops were taken at 50° C s^{-1}. The magnitude of the maximum polarization is proportional to the extent of domain boundary motion which is sensitive to lattice vacancies. The ferroelectric hysteresis loops reflect this expectation (see Fig. 4), confirming the compensatory nature of Nb^{3+} doping. Alternatively, one can conclude that Nb doping increases the ease and extent of ferroelectric domain boundary motion. This explains the greater dielectric polarization of the specimens containing 0.1 wt.% Nb. The dielectric polarization depends to a large extent on the existence of lattice vacancies and lattice imperfections, as was also deduced from Fig. 4a, b, whereas the obtained ferroelectric loops confirm the neutralization effect of Nb^{3+} that persists there.



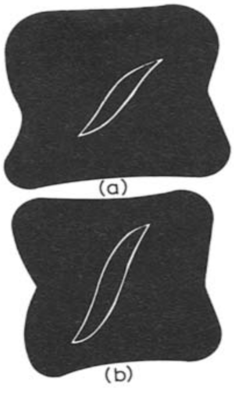


Fig. 3. A schematic illustration of the temperature dependence of the dielectric constant before and after polarization: (ai) polarized barium titanate + 0.1% Nb sintered at 1400°C; (aii) unpolarized barium titanate + 0.1% Nb sintered at 1400°C; (bi) polarized pure barium titanate sintered at 1400°C; (bii) unpolarized pure barium titanate sintered at 1400°C; (ci) polarized pure barium titanate; (cii) unpolarized pure barium titanate.

Fig. 4. The hysteresis loops for samples of: (a) unmodified barium titanate; (b) modified barium titanate containing 0.1% Nb.

This could be illustrated on the basis that during sintering of barium titanate at high temperature (>1000° C) the diffusion mechanism may take place through dislocation along certain preferred sliding planes. Therefore, niobium dopant may oxidize there at the sintering temperature giving rise to Nb_2O_3. The formed oxide may act as impurity centres enhancing dislocation along the sliding planes; that is to say, it provides an easier way for grain wall motion along the sliding planes. The net result of niobium doping would be an increase in the ease and extent of ferroelectric domain boundary movement.

Accordingly, the obtained best quality modified barium titanate ceramic pyroelectrics were ascribed as being due to the induced internal lattice strain caused by the residual 90° domains after poling. Under this condition, niobium substitution in octahedral lattice sites is most probable and increases the proportion of the remnant 90° domains after poling of the investigated samples.

CONCLUSIONS

The pyroelectric results indicate that:

(a) the pronounced increase of the bulk density of niobium-doped barium titanate with time of soaking is attributed to the influence of doping on the inhibition of grain growth giving rise to a more compact and dense ceramic body;

(b) the relatively high increased values of the dielectric constant with sintering time for the modified Nb-doped specimen is due to the greater polarization of the sample as caused by the propagated charged vacancies when Nb^{3+} ions replace Ti^{4+} in barium titanate lattice sites;

(c) the high percentage of dielectric anisotropy obtained for the polarized and doped sample as ascribed to the change of domain structure in the greater part, is caused by the reversal of 180° domains to their original situations which remain entire after poling and the increase of the proportion of 90° domains rotations.

Thus, niobium doping provides an easier way for grain wall motion along certain preferred sliding planes, resulting in an increase in the ease and extent of ferroelectric domain wall motions.

Consequently, the best quality industrial ceramic pyroelectrics were obtained in the case of poling of the Nb-doped barium titanate as sintered tablets including niobium substitution in octahedral lattice sites.

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