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TEMPERATURE-DEPENDENCE OF ELECTROMECHANICAL COUPLING AND STRAIN IN BARIUM TITANATE HAFNATE TRANSDUCER

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The electromechanical coupling factor and ferroelectric hysteresis loops were investigated at different temperatures for $BaTi_{0.85}Hf_{0.15}O_3$ transducer. Maximum polarization and strain were obtained near the transition of the crystal structure. This correlated with increases in the ease and extent of ferroelectric domain boundary motion. The change in the crystal structure varied the unit cell volume, leading to higher strain.

$BaTiO_3$ and $Pb(Ti, Zr)O_3$ and their compositions containing different concentrations of doping ions have strong piezoelectric effects. The earliest investigations of the piezoelectric properties in these compositions [1–7] showed the coupling factor to be highest near the tetragonal-rhombohedral phase boundary. Compositions rich in $PbTiO_3$ were not successfully poled, but a significant piezoelectric effect existed throughout the rhombohedral range. It is believed that the proximity to such a phase boundary between ferroelectric phases favours strong piezoelectrics in a ceramic, because of the increased ease of reorientation during poling. Subsequent work has yielded samples with much stronger piezoelectric coupling [5]. This resulted from a better ceramic quality and an improved poling technique. Instead of a maximum planar coupling factor of 0.4, values over 0.6 at room temperature have been achieved, both in these unmodified solid solutions and in others with various degrees of additional compositional modification. These compositions, as a class, are more useful than $BaTiO_3$ compositions. In the present work, the electromechanical coupling factor and the ferroelectric hysteresis loops were investigated, with particular attention to tme behaviour of the system $BaTi_{0.85}Hf_{0.15}O_3$ near the rhombohedral-cubic phase boundary. Large values of the coupling k_p and spontaneous polarization p and strain have been reported near this phase boundary from cheap and unvolatile materials during the sintering process.

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Experimental procedure

1) Sample preparation

Samples for this investigation were prepared from 99.8% pure HfO_2 and reagent grade $BaCO_3$ and TiO_2. Batches were weighed, dry-mixed and calcined in a platinum crucible at 1000° for 2 hours. The calcined batch was then ground to pass a 100 mesh screen, mixed with 5% distilled water by weight and pressed at 5000 kg/cm^2 into disks 15 mm in diameter and 1 mm thick. The pressed samples were fired on platinum sheets at 1350° in an electric muffle furnace with a 2 hr soak. The prepared samples containing 15 mol % $BaHfO_3$ were polished and painted with silver paste on opposite surfaces.

2) Measurements

The electromechanical coupling factor K_p of the poled $BaTi_{0.85}Hf_{0.15}O_3$ material was determined from electrical measurements on the disks acting as piezoelectric resonators vibrating in radial modes. The radial mode coupling factor, K_0, is defined in terms of these quantities [8]:

$$K_p^2 = 2.5\,(F_a - F_r)/F_r$$

The experimental procedure followed the convential practice [9] of measuring the fundamental resonance, F_r [5], and the antiresonance, F_a.

High-field ferroelectric measurements were made to determine the ease and extent of domain reorientation. An alternating electric field of 1000 V/mm was applied and the resulting dielectric polarization was recorded. Hysteresis loops were run at 50 Hz.

Results and discussion

Effect of temperature on the coupling factor K_p for $BaTi_{1-x}Hf_xO_3$

Figure 1 presents the variation of K_p in the system $BaTi_{1-x}Hf_xO_3$ as a function of temperature.

It can be seen that K_p increases near the temperatures 120, 90 and 60° for $x = 0$, 10 and 15 mol % $BaHfO_3$, respectively. This could be explained in that the substitution of Hf^{4+} for Ti^{4+} in $BaTiO_3$ resulted in a shift of the tetragonal-cubic inversion temperature to the rhombohedral-cubic one at 60° [10] for $BaTi_{0.85}Hf_{0.15}O_3$. This is a case which results in an increase of the distance between the constituents of the dipoles. This may cause an early vibration of the ions. Thus,

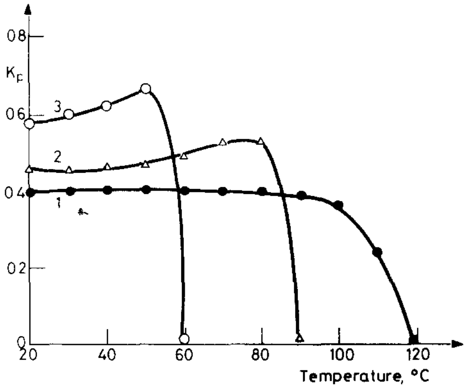


Fig. 1 Effect of temperature on the coupling factor K_p for: 1. ● $BaTiO_3$; 2 × $BaTi_{0.9}Hf_{0.1}O_3$; 3 ○ $BaTi_{0.85}Hf_{0.15}O_3$

the resonance frequency decreases and high values of K_p are obtained near the transition temperature. Since the presence of an abnormally high K_p is connected with the looseness of the crystal lattice of this substance, the sum of the atomic radii of titanium or hafnium and oxygen = 1.96 Å is less than the distance between these ions near the transition temperature.

Ferroelectric hysteresis loops of $BaTi_{0.85}Hf_{0.15}O_3$ *as a function of temperature*

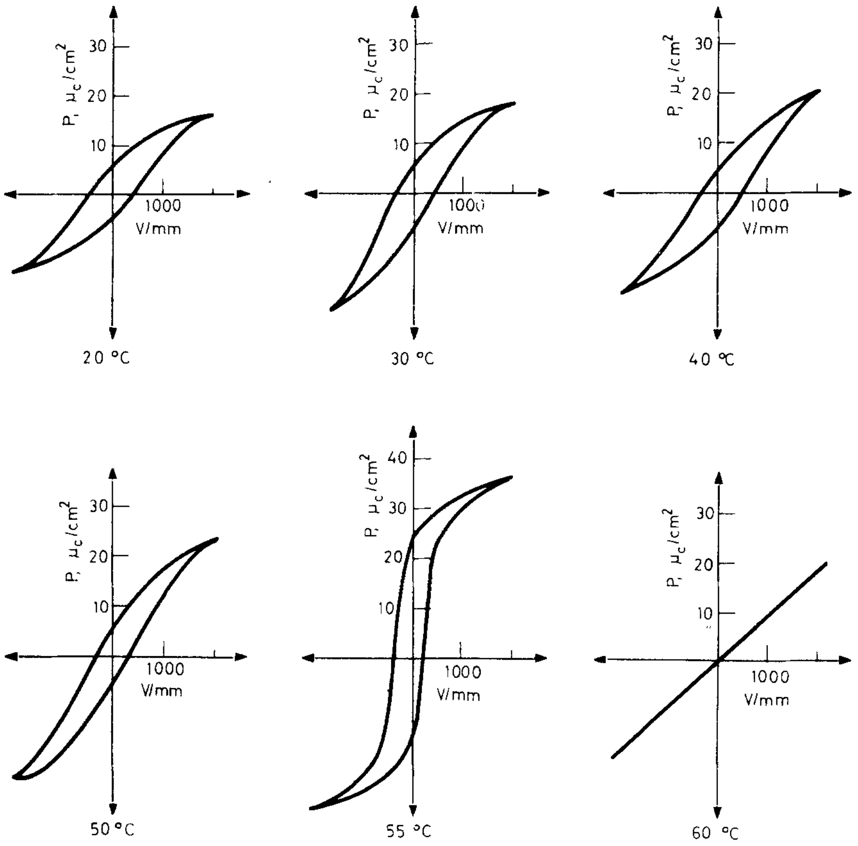
The ferroelectric hysteresis loops (Figs 2 and 3) confirm that maximum polarization was obtained near the transition temperature. This correleted with increases in the ease and extent of ferroelectric domain boundary motion due to the change of the lattice structure, which helped the increased looseness of the dipole constituents. This resulted in an increased spontaneous polarization under the action of a high a.c. field. Above 60°, the material assumed a paraelectric cubic structure, leading to the disappearance of the hysteresis loop (Fig. 2).

Temperature-dependence of strain in $BaTi_{0.85}Hf_{0.15}O_3$

The effect of temperature on the strain in a sample of $BaTi_{0.85}Hf_{0.15}O_3$ is illustrated in Fig. 4. A pronounced increase of the strain was observed near the transition point (60°). This could be explained on the basis of the observed increase in spontaneous polarization near the transition of the crystal structure. The change in the crystal structure alters the unit cell volume, leading to higher strain.

The strain in ferroelectric crystals is given by the following equations:

The relations between strain X_h, stress X_h, electric field E_h, and electric



20 °C

30 °C

40 °C

50 °C

55 °C

60 °C

Fig. 2 Temperature-dependence of hysteresis loops

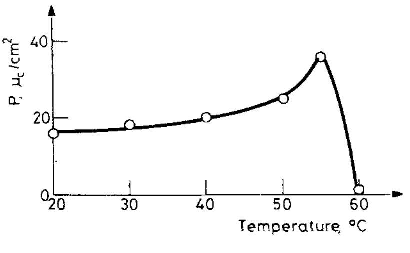


Fig. 3 Temperature-dependence of spontaneous polarization for $BaTi_{0.85}Hf_{0.15}O_3$ sample

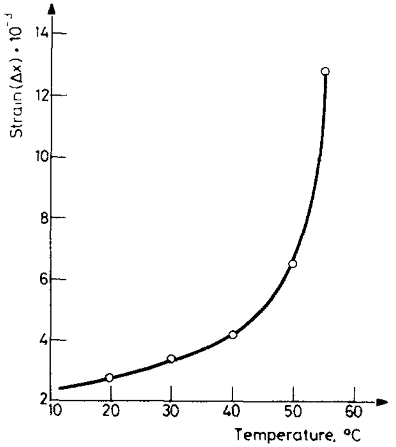


Fig. 4 Effect of temperature on the strain in $BaTi_{0.85}Hf_{0.15}O_3$

polarization P_h for nonferroelectric, piezoelectric crystals are

$$X_h(E, X) = \sum_{i=1}^{3} d_{ih}E + \sum_{i=1}^{3} g_{ih}E_i^2 - \sum_{i=1}^{6} S_{ih}X_i + \ldots (h = 1, 2, 3) \quad (1)$$

$$P_h(E, X) = \sum_{i=1}^{3} X_{ih}E_i - \sum_{i=1}^{6} d_{hi}X_i + \ldots \qquad (h = 1, 2, 3) \quad (2)$$

Here, X_{ih} are the components of the electric susceptibility, S_{ih} is the elastic compliance coefficient, and d_{ih} and g_{ih} are the first and second-order piezoelectric coefficients, respectively. For a crystal in the ferroelectric region, Eq. (1) reduces to

$$X_x = d_{31}E_z, \text{ ext.} + g_{31}E_z^2, \text{ ext.} \quad (3)$$

$$Z_z = d_{33}E_z, \text{ ext.} + g_{33}E_z^2, \text{ ext.} \quad (4)$$

where X_x and Z_z are the strain components along the x and z directions, respectively. These equations also hold for $BaTiO_3$ above the Curie point; however, in this cubic range the coefficients d_{ih} are zero, since the crystal structure has a centre of symmetry. These is now a spontaneous polarization, the magnitude of which depends on the temperature and the applied external field; thus, the piezoelectric coefficients are dependent on these parameters.

Secondly, a domain structure exists in these crystals, which changes with the applied field and thereby causes additional changes in the strain components.

The effect of the spontaneous polarization can be taken into account in the following way: if P_0 is the spontaneous polarization directed along the z axis of the crystal and $(Z_x)_0$ and $(X_x)_0$ are the spontaneous strain components along the z and

x directions, respectively, taken relative to the dimensions of the crystal at the Curie point, it has been demonstrated that the following relations hold:

$$(X_x)_0 = \mu P_0^2 \tag{5}$$

$$(Z_z)_0 = \varrho P_0^2 \tag{6}$$

where μ and ϱ are constants. Here, $(X_x)_0$ corresponds to a contraction and $(Z_z)_0$ to an elongation. The values for μ and ϱ [11] are

$$\mu = -10.5 \times 10^6 \text{ cm}^4/\text{Coul}^2$$

$$\varrho = +24 \times 10^6 \text{ cm}^4/\text{Coul}^2$$

When an external field is applied along the z axis, resulting in an additional external polarization P_z, ext., we obtain further changes ΔX_x and ΔZ_z in the respective strain components. Then, Eqs (5) and (6) become

$$X_x = (X_x)_0 + \Delta(X_x) = \mu(P_0 + P_z, \text{ext.})^2 \tag{7}$$

$$Z_z = (Z_z)_0 + \Delta(Z_z) = \varrho(P_0 + P_z, \text{ext.})^2 \tag{8}$$

From Eq. (7) and Fig. 2, the strain in barium titanate hafnate could be calculated as in Fig. 4.

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Zusammenfassung — Der elektromechanische Kopplungsfaktor und die ferroelektrische Hysteresisschleife wurde für $BaTi_{0.85}Hf_{0.15}O_3$-Transducer bei verschiedenen Temperaturen untersucht. Polarisation und Deformation nehmen in der Nähe des Umwandlungspunktes der Kristallstruktur maximale Werte an. Dies korreliert mit Leichtigkeit und Außmaß der Grenzbewegung im ferromagnetischen Bereich. Die mit der Umwandlung der Kristallstruktur zusammenhängende Veränderung des Elementarzellenvolumens führt zu größerer Verformung.

Резюме — Для преобразователей $BaTi_{0.85}Hf_{0.15}O_3$ при различных температурах были измерены коэффициент электромеханической связи и сегнетоэлектрические гистерезисные петли. Максимум поляризации и деформации были найдены около структурного фазового перехода. Установленный факт коррелируется с увеличением легкости и степени смещения границ сегнетоэлектрических доменов. Изменение кристаллической структуры сопровождается изменением объема элементарной кристаллической ячейки, что вызывает большуэ деформацию.