

Study of the pyroelectric behavior of $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ piezo-ceramics

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Abstract In this work, the thermal square wave method at single-frequency (TSWM) was applied to functionally graded $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ samples with a tin gradient of $0.075 \leq x \leq 0.15$. The samples were fabricated by sintering of bi-, tri- and tetramorph green bodies. The polarization at the back side with a higher tin content was in opposite direction to the polarization of the surface with a lower tin content. This was attributed to the appearance of a space charge layer. The determined depth profiles of the pyroelectric coefficient illustrate the appearance of a nearly constant polarization in the region of lower tin concentration of tri- and tetramorph samples. The pyroelectric coefficient profiles were in good agreement with the averaged over sample thickness pyroelectric coefficient obtained separately by the quasistatic method.

Keywords Ferroelectric ceramics · Thermal wave method · Pyroelectric coefficient profile

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1 Introduction

Research in the development of novel lead-free piezoceramics is very much in demand. $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ (BTS) ceramics are widely used as piezoelectric actuators and micro-sensors. Ceramics with continuously varying chemical composition show, after poling, an inhomogeneous distribution of dielectric and piezoelectric properties. Such functional gradient materials especially are suitable for bending actuators, e.g., in bimorph layered systems. Advantages are low internal stresses, low production costs and the possibility to design systems from materials which are lead-free.

However, there are still problems in reproducible fabrication of ceramic specimens. On the other hand, maximizing the piezoelectric coefficient is of considerable importance in reducing the driving voltage or increasing the speed or sensitivity of a piezoelectric device. The piezoelectric response of commercial samples could be further increased by the optimization of the poling procedure. Since low-field piezoelectric response correlates with the magnitude of the remanent polarization, pyroelectric coefficient measurement techniques are appropriate to judge the poling procedure and the profile of polarization distribution.

In dynamic pyroelectric response measurement techniques [1], a modulated light beam is absorbed by the top electrode and generates a thermal wave travelling into the sample. The temperature change caused by the advancing thermal wave leads to the appearance of a pyroelectric current which is registered by an external measuring device.

Modulation of a light beam is mostly performed in two ways: sinusoidal modulation (laser intensity modulation method—LIMM [2]) and rectangular modulation (dynamic method [1] and thermal square wave method at single frequency—TSWM [3]). In the LIMM method, polarization profile reconstruction is carried out using the pyroelectric

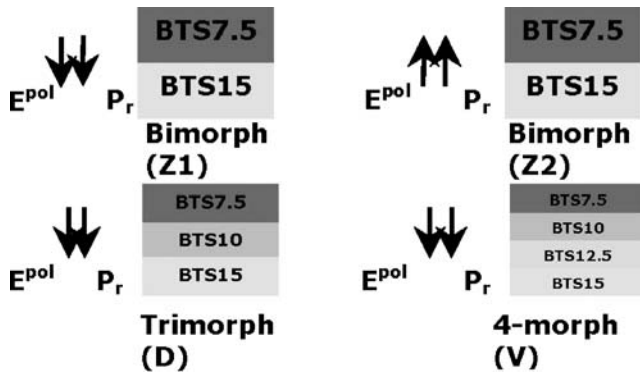


Fig. 1 Layer arrangement before sintering and polarization direction of BTS functional gradient samples

current spectrum including the phase shift between pyroelectric response and heat flux [2, 4–8]. Usually, this method is used for modulation frequencies between 1 kHz and 20 MHz. Thus, it allows to study only thin films and surface layers of the bulk samples, respectively. In TSWM, the depth dependence of the effective pyroelectric coefficient is determined by analyzing the time dependence of the pyroelectric response. TSWM allows to study the profile of polarization distribution in bulk material when using digital methods of signal processing. The measuring frequency is determined by the condition that the penetration depth of the thermal pulse should not exceed the sample thickness. Due to a linear relation between the pyroelectric response and the spontaneous polarization of ferroelectrics, thermal wave methods are often regarded as a technique for polarization profiling.

In this work, we describe the application of the TSWM to graded BTS samples fabricated by sintering of bi-, tri- and tetramorph green bodies.

2 Theory

The TSWM is based on the analysis of the time dependence of the pyroelectric response. Taking into account the limited heating rate, the thermal wave passes to a depth of

$$x = 2\sqrt{\alpha f} \cdot t \tag{1}$$

within a time t [9], where α is thermal diffusivity and f the frequency of the thermal wave. Thus, the pyroelectric current becomes a function of the heating depth x . The pyroelectric coefficient p_{eff} of the heated layer may be determined from [10]

$$p_{\text{eff}}(x) = \frac{V(t)\omega_0\kappa}{8\pi\beta_0SW_0R_{0A}} \cdot \text{Re} \left\{ \left(\sum_{n=1}^{\infty} \frac{\sin^2(n\omega_0\tau/2)}{n\omega_0\tau/2} \cdot \frac{i}{\varphi_n^2 \sqrt{2\alpha\omega \cdot t}} \left(1 - \frac{\sinh[\varphi_n \cdot (d - \sqrt{2\alpha\omega_0 \cdot t})]}{\sinh[\varphi_n \cdot d]} \right) \right)^{-1} \right\}$$

$$\approx \frac{V(t)\omega_0\kappa}{8\pi\beta_0SW_0R_{0A}} \cdot \text{Re} \left\{ \left(\sum_{n=1}^{\infty} \frac{\sin^2(n\omega_0\tau/2)}{n\omega_0\tau/2} \cdot \frac{i}{\varphi_n^2 \sqrt{2\alpha\omega \cdot t}} \cdot [1 - \exp(-\varphi_n \cdot x)] \right)^{-1} \right\}$$

with

$$\varphi_n = (1 + i)\sqrt{n\omega_0/2\alpha} \tag{3}$$

where $\omega_0=2\pi/T$ is the fundamental frequency of the rectangular modulated pulse train, n the harmonic number, τ the pulse duration, d the sample thickness, S the electroded sample area, W_0 the heat flux power density, β_0 the heat absorption coefficient, κ the thermal conductivity, $V(t)$ the time dependence of the current-voltage converter output and R_{0A} its value of the feedback resistor. The approximation holds for $\omega > 2\alpha/d^2$.

In the quasistatic method, a very small constant heating rate is used in order to avoid nonuniform heating of the sample. Quasistatic measurements provide information on the averaged over sample thickness pyroelectric coefficient calculated according to:

$$p = \frac{V}{R_{0A} \cdot dT/dt \cdot S} \tag{4}$$

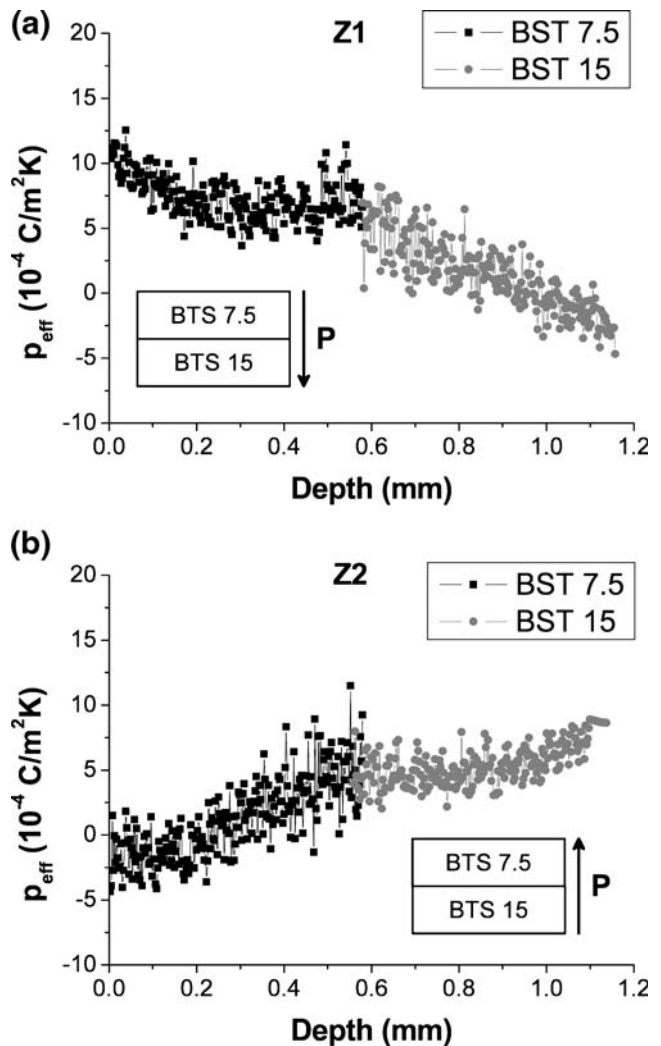


Fig. 2 Pyroelectric coefficient profile of BaTi_{1-x}Sn_xO₃ functional graded ceramics: (a) bimorph samples Z1, (b) bimorph samples Z2

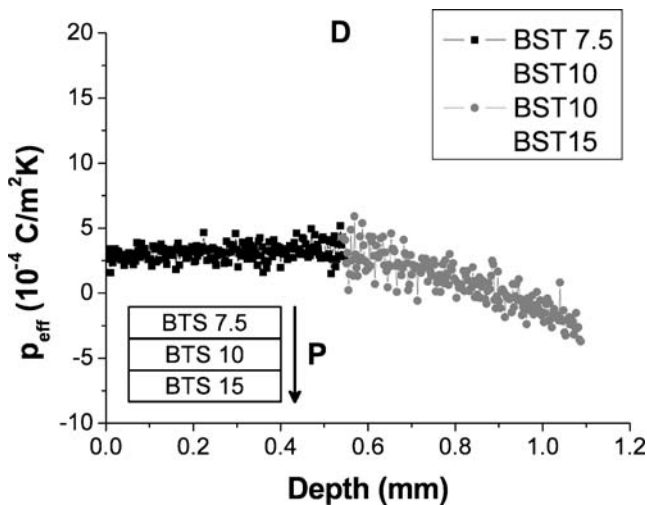


Fig. 3 Pyroelectric coefficient profile of trimorph $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ functional graded ceramics (sample D)

where V is the output voltage of the operational amplifier used as a current voltage converter and S the area of the sample electrode.

3 Experimental

$\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ functional ceramics with a tin gradient of $0.075 \leq x \leq 0.15$ were synthesized by successive pressing of granulated powder with different Sn content and a subsequent sintering for one hour at 1400°C under an uniaxial pressure of about 1 kPa. In this work, samples prepared with two, three and four different powders were investigated (Fig. 1). The top and the bottom layers of all samples have a tin content of 7.5 and 15 mol.%, respectively. For the so-called trimorph (sample D), an additional layer with

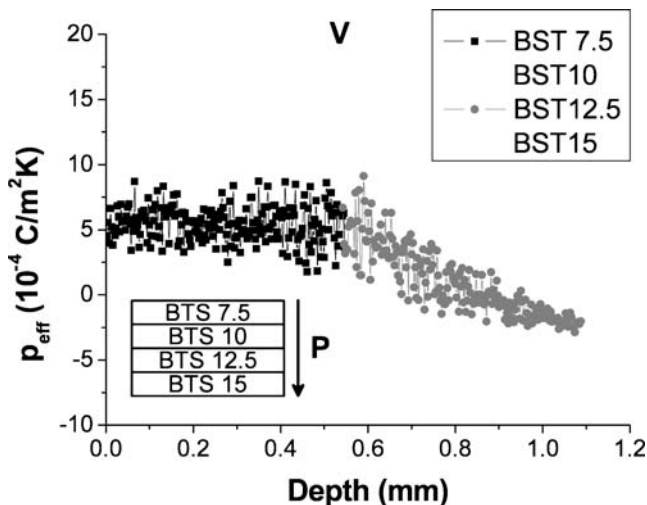


Fig. 4 Pyroelectric coefficient profile of tetramorph $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ functional graded ceramics (sample V)

10 mol.% Sn was used. The tetramorph (sample V) were prepared by adding $\text{Ba}(\text{Ti},\text{Sn})\text{O}_3$ with 12.5 mol.% Sn as the fourth layer [11]. Al electrodes were evaporated onto both sample sides. Poling is performed at 20 kV/cm by applying a positive DC voltage to either of the electrodes. The direction of the applied electric field is shown in Fig. 1.

The pyroelectric properties of BTS ceramics were studied by both quasistatic and dynamic methods in the short-circuit regime.

For quasistatic measurement, the samples were heated with a constant rate of about 0.35 K/min in a thermostat.

In TSWM measurement, the on-off cycle of an IR-phodiode ($\lambda=930\text{--}960\text{ nm}$) was controlled by a wave function generator G6-28 connected in series with a power amplifier. The pyroelectric current was converted to voltage by an operational amplifier OP297 with conversion coefficients of $250\text{ V}/\mu\text{A}$, $2,500\text{ V}/\mu\text{A}$, and at bandwidths of 1,000 Hz, 100 Hz, respectively. Signal sampling was performed by a 12-bit analog-digital converter LA-70M4 at a sampling frequency of 13 kHz. The pyroelectric coefficient was measured on both sample sides. The direction of the polarization vector was determined by comparing the phase of the main signal with the phase of the reference signal. By this way, we have a mean to determine the polarization direction ($-P_s$ and $+P_s$).

4 Results and discussion

Pyroelectric coefficient distributions were measured for the synthesized BTS ceramics at room temperature and a frequency of 1 Hz. As shown in Figs. 2, 3 and 4, the polarization distribution depends on the layer number in the green body [Figs. 2(a), 3 and 4] and the poling direction [Fig. 2(a) and (b)]. The different sign of the pyroelectric coefficient near opposite surfaces give evidence of an

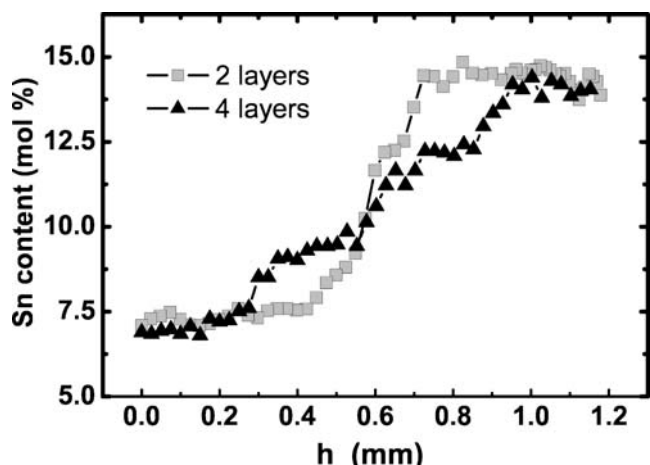


Fig. 5 Tin concentration profile of bimorph and tetramorph $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ functional graded ceramics

opposite polarization direction. For Z1, D and V samples, the polarization for both sample sides is directed from the surface to the bulk. For the Z2 sample, it is directed from the bulk to the surface. Such a polarization behavior accounts for a system of either anti-parallel domains or induced space charge. The physical properties of the BTS system support the latter assumption. It is well known, that at room temperature the spontaneous polarization in BTS bulk ceramics decreases in the range between 7.5 and 15 mol.% Sn with increasing tin content [12]. BTS7.5 (7.5 mol.% Sn) ceramics are at the phase boundary between orthorhombic and rhombohedral phase and exhibit maximum remanent polarization. On the other hand, the BTS15 ceramics are in the paraelectric phase and have a vanishing remanent polarization after the poling process.

The electric field strength distribution in monolithic graded ceramics is very inhomogeneous due to the gradient of the ferroelectric properties caused by the chemical gradient. The theoretical background is described in detail by Pientschke et al. [13]. Additionally, the gradient in local polarization should be compensated partially by space charges. The accumulation of space charges depends on the conductivity of the ceramics. This two aspects, different spontaneous polarization and conductivity, are responsible for the value of the local remanent polarization. Nevertheless, a maximum of the polarization is expected at the top (BTS7.5) and a vanishing polarization at the bottom (BTS15) of the FGM. This behavior is confirmed qualitatively in the graded samples by the measurement results. Additional investigations are needed to evaluate the appearing space charge more in detail. The trimorph (D) and tetramorph (V) samples provide a nearly constant polarization in the region of lower tin concentration (Figs. 3 and 4). This is a consequence of a lower concentration gradient in the sample as proved by the tin concentration profile. Furthermore, modeling predicts a slightly lower local electric field strength in the BTS7.5 region during the poling process. Therefore, it is possible that the ceramic is not completely poled. Longer poling times could be necessary to solve this problem. In all samples, the gradient of the polarization correlates with the chemical gradient determined by Electron probe micro analysis (Fig. 5). The averaged pyroelectric coefficients of all BTS

samples were nearly constant. They amount to about $420 \mu\text{C}/\text{m}^2\text{K}$ in good agreement with the results presented in Figs. 2, 3 and 4.

5 Conclusions

The pyroelectric coefficient profile of functionally graded BTS ceramics was determined by the thermal square wave method at single frequency (TSWM). Because of the polarization dependence of the piezoelectric coefficient, this techniques enables evaluation of the impact of ceramic fabrication on the expected piezoelectric response.

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