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Modelling and characterization of piezoelectric and polarization gradients

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Abstract A gradient of the piezoelectric properties in monolithic ceramics can be useful to minimize mechanical stresses inside piezoelectric bending actuators or at interfaces between layers with different electromechanical properties, and increase the bandwidth of ultrasonic transducers. Piezoelectric gradients can be prepared by different techniques. We use a powder pressing technique to prepare a gradient of the chemical composition, which is transformed to the piezoelectric gradient by the poling process. Conventional mixed-oxide powders of $BaTiO_3$ with different amount of Sn from 7.5 up to 15 mol% and Mn-doped $BaTiO_3$ were used to produce lead-free ceramic samples. We describe the poling process using a equivalent circuit approach. The ferroelectric behavior of the different layers are described by the Preisach model. In the $Ba(Ti,Sn)O_3$ system the properties can be changed from ferroelectric to paraelectric depending on the Sn content. A gradient of polarization and piezoelectric properties can be observed in monolithic ceramics with a tin gradient. The profile of the polarization distribution was measured by the thermal wave method. A gradient of polarization where the sign of polarization changes can be induced in a system consisting of piezoelectric hard and soft materials. We describe a special poling process using our poling model. The principle is demonstrated in a two layer model system.

Keywords Functionally graded materials · Piezoelectric · Poling process · LIMM

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1 Introduction

Functional graded materials (FGM) are suitable in applications where materials with different properties should be mechanically connected. FGM can reduce the mechanical stresses at the interfaces. Piezoelectric FGM with a gradient of the electromechanical properties can be used in microelectromechanical systems (MEMS) or actuators to connect piezoelectric active parts with substrates or other inactive parts. In this way reliability and lifetime can be improved.

A special application are bending actuators. The bending effect strongly depends on the difference of the lateral strain at the top and the bottom surface of the actuator. Usually, two layers with different piezoelectric properties or with an electrode between them were bonded together.

It was shown that FGM can reduce the mechanical stresses at the interface [1]. Haertling used this principle in monolithic actuators, the well-known RAINBOW-actuator [2]. A good performance of the bending actuator depends on the quality of the piezoelectric gradient. In monolithic samples the gradient have to be induced by a poling process. The poling mechanism in a layered system of at least two ferroelectric components is a time-dependent process where the conductivity of the material should be taken into account [3, 4].

The characterization of the piezoelectric gradient in monolithic ceramics is difficult. However, the local piezoelectric coefficient is correlated with the polarization degree. For the characterization of the polarization profile a thermal wave method, for instance LIMM (laser intensity modulation method) is a helpful tool [5].

In the first part of this work, monolithic Ba(Ti,Sn)O_3 (BTS) ceramics with a gradient of the tin content along the thickness were investigated. They were prepared using up to four layers of powder with different chemical composition. The powder layers are pressed and sintered together. Due to diffusion during sintering a chemical gradient in the monolithic ceramics are observed. In a good approximation the graded BTS ceramics can be described by a multilayer model using the bulk material coefficients of the BTS ceramics corresponding to the used powders.

In the second part, a new material combination for monolithic bending actuators is discussed. Layers of piezoelectric hard and soft ceramics were poled in different directions. Consequently, the longitudinal strain will have different signs and the bending deflection should be improved. The special poling process for this system is modelled by a two-layer model. The theoretical results were confirmed by experimental data of a model system. This system consists of two ceramic layers, a pure $BaTiO_3$ and a Mn-doped $BaTiO_3$ layer, electrically connected by a wire. This model system can be considered as a preliminary stage of a FGM with a change of the direction of polarization .

2 Poling model

The poling process of a functional graded piezoelectric material can be described by a multilayer model. The gradient of the ferroelectric properties along the thickness has to be transformed to a step function. Each layer of the model structure consists of a homogeneous material with constant parameters. The layers are connected only electrically. Mechanical effects like clamping are neglected. The layers can be regarded as serial connected RC-elements [4]. The electric conductivity σ and the dielectric polarization P are taken into account for each layer. The conductivity is considered constant and independent of the electric field. Using the constitutive equations for each layer and basic electric laws, a system of ordinary differential equations (ODE) is resulting. For describing a graded material the number of layers has to tends to infinity. However, the principles of the poling process of electrically connected layers with different ferroelectric properties can be discussed in a first approximation using only two layers.

In this simplest case of a two layer system follows

$$\sigma_1 E_1 + \epsilon_0 \dot{E}_1 + P'_1 \dot{E}_1 = \sigma_2 E_2 + \epsilon_0 \dot{E}_2 + P'_2 \dot{E}_2 \tag{1}$$

$$\dot{E}_{\mathrm{appl}} = \frac{d_1}{d}\dot{E}_1 + \frac{d_2}{d}\dot{E}_2, \tag{2}$$

where E_1 and E_2 are the local electric field strength in the layers, and d_1 and d_2 the thickness of the layers. The applied electric field E_{appl} in Eq. 2 is the applied voltage per overall thickness d.

In order to solve the ODEs the knowledge of the ferroelectric behavior is necessary. That means the function $P(E)$ and, in particular the derivative P′(E) is needed. This quantity is estimated by means of the Preisach model. The advantage of this model relies on the feasibility to simulate incomplete hysteresis loops and partial depolarization or switching processes. The theoretical background of the poling model is described in detail in [6].

In the system Ba(Ti,Sn)O_3 described in this work the ferroelectric behavior changes from hysteretic (7.5 mol% Sn) to non-hysteretic (15 mol% Sn) polarization loops. In the following a two-layer system will be discussed again. The virgin polarization loops of BTS ceramics with 7.5 and 15 mol% Sn, respectively, are used for the modelling. The virgin loop of BTS7.5 has a maximum polarization of 31 $\mu C/cm^2$ and a remnant polarization of nearly 17 $\mu C/cm^2$. The non hysteretic virgin loop of BTS15 has a maximum polarization of 13.7 $\mu C/cm^2$.

A DC electric field of 2.5 kV/mm is applied to the system for 50 s to polarize it. The voltage is switched on and off by a ramp of 10 s, respectively (Fig. 1). The local electric field strength in the layer with the lower

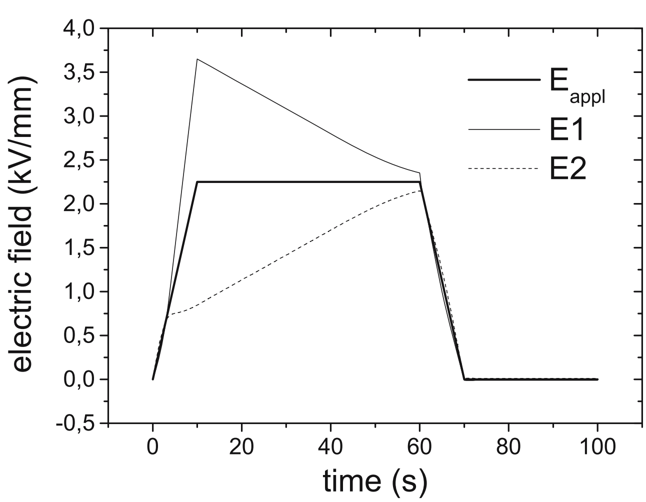

Fig. 1 Time dependence of the poling field and the local electric field strength in a two-layer system of ferroelectric and paraelectric materials

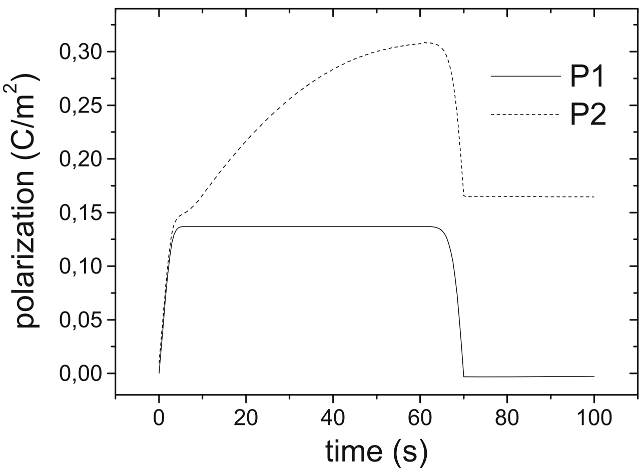

Fig. 2 Time dependence of the local polarization

maximum polarization rises very fast to a maximum value and then decreases slowly. In the other layer the local electric field increases slowly to a saturation value. When saturation is reached the electric field strength in each layer does not depend on time. From Eq. 1 it follows that

$$\frac{E_1}{E_2} = \frac{\sigma_2}{\sigma_1}. \tag{3}$$

The ratio of the saturated values of the electric field in both layers depends on the electric conductivity of the materials. Here, the conductivity was chosen as equal in each layer.

A relaxation of the local fields and the polarization was observed after switching off the poling field. The polarization of the paraelectric material tends to zero. In the ferroelectric layer a remnant polarization remains (Fig. 2). In this way, the polarization in a chemical graded material should be changed from the remnant polarization of the ferroelectric material to the nearly zero polarization of the paraelectric part.

The idea of a gradient of polarization with changing sign can be realized by ferroelectric soft and hard materials. Typical hysteresis loops used in the modelling are shown in Fig. 3. The soft material is characterized by low coercive field strength and high spontaneous polarization. The hard material exhibits an higher coercive field and lower polarization.

The poling regime for such a system is more complicated (Fig. 4). In a first step, a positive voltage is applied to the bilayer system. We used a ramp in the calculation to avoid numerical problems. In the experiment a DC voltage for a short time can be more useful. The poling time and maximum value of the poling field should be high enough to polarize the hard material completely. The poling degree of the soft material is not so important. In contrast, the lower the polarization of the soft material the better the polarization can be switched.

Then the applied voltage is reduced. The speed of this reduction depends on the conductivity of the materials. The higher the conductivity the faster the voltage can be reduced. If the conductivity is lower, more time is required to collect space charges at the interface compensating the difference in the local polarization.

The electrical field strength is then reduced to a negative value. This value should be higher than the coercive field strength of the soft material to shift its polarization. But it must be lower than the coercive field strength of the hard material to protect the positive polarization in this layer. The negative DC voltage is applied for a longer time to permit the switching of polarization. The length of time depends primarily on

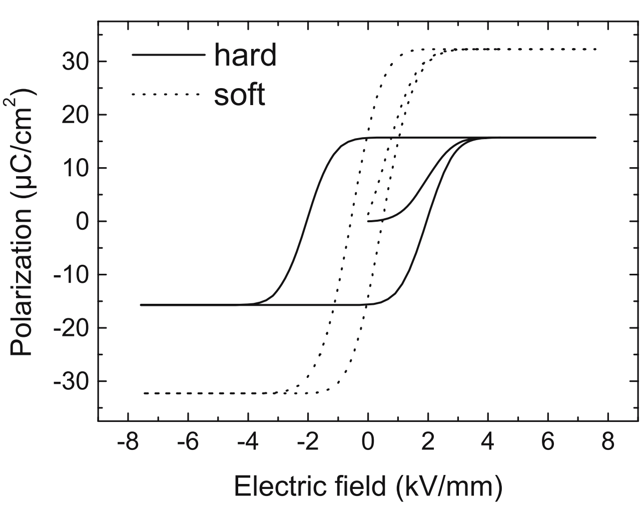

Fig. 3 Hysteresis loops of ferroelectric soft and hard materials modelled by the Preisach model

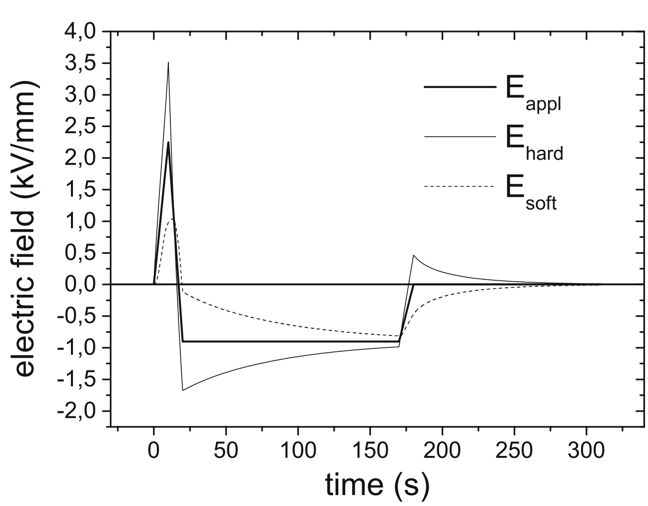

Fig. 4 Time-dependence of the local electric field in hard and soft layers during the poling process

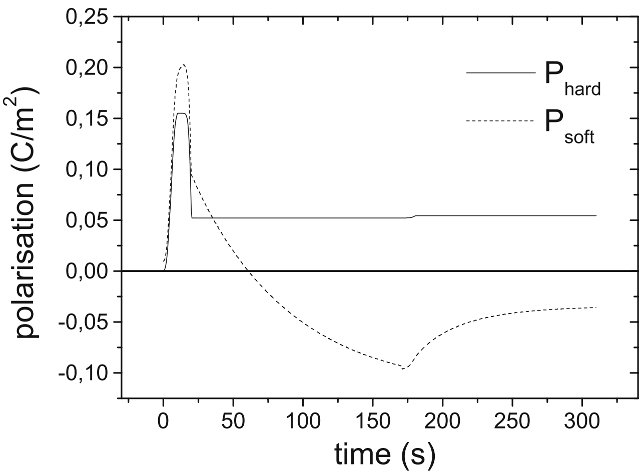

Fig. 5 Time-dependence of the polarization of hard and soft layers during the poling process

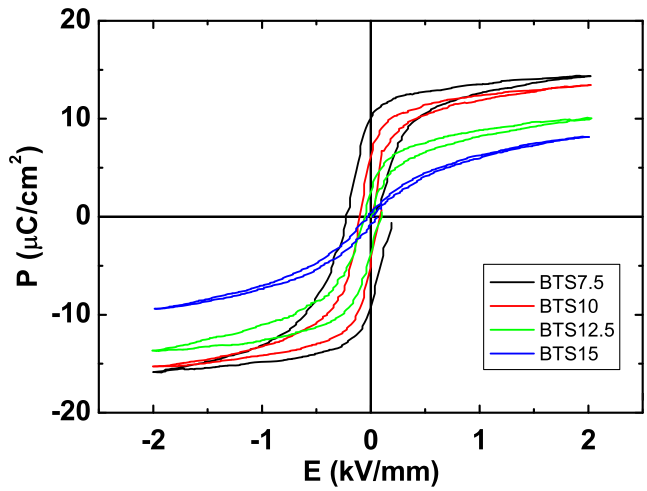

Fig. 6 Virgin loops of $Ba(Ti,Sn)O_3$ ceramics in dependence on the tin content

the conductivity of the materials. When the saturation is achieved the voltage is switched off. The remnant polarizations show different signs after a short relaxation time. This simulation demonstrates the possibility of polarizing parts of a layered system in antiparallel directions (Fig. 5).

3 Sample preparation

The symmetry of barium titanate—barium stannate changes at room temperature depending on the tin content. $BaTi_{0.925}Sn_{0.075}O_3$ (BTS7.5) has a rhombohedral structure. The ceramics with 15% Sn (BTS15) are at the phase boundary to the cubic phase [7]. Correspondingly, the dielectric properties change from ferroelectric to electrostrictive. The virgin loops of the polarization of BTS ceramics with different Sn content are shown in Fig. 6. The ferroelectric BTS7.5 reaches a higher maximum polarization. The P(E) curve has a hysteretic shape. The polarization of BTS15 depends also nonlinear, but nearly non-hysteretic on the applied electric field.

Monolithic ceramics with a gradient of the tin content were prepared by pressing powder 2, 3 or 4 layers with different amount of tin. The overall thickness of the samples was about 1.1 mm. In dependence on the number of the used powder layers the chemical gradient can be influenced. Fig. 7 shows the tin gradient after sintering. The tin results were measured by electron probe microanalysis (EPMA). An approximately linear gradient can be prepared using 4 layers. Other authors used up to 21 layers to prepared a functionally graded structure [8].

The powders were prepared by the conventional mixed-oxide technique. The pressed green body was sintered 1 h at 1400 °C. After sintering the samples were polarized with a poling field strength of about 2 kV/mm for 4 min. The time should be enough to reach the saturation of polarization described in the section before.

The ceramic sheets for the model system of soft and hard ferroelectrics have an homogeneous chemical composition. The preparation route is the same as described for the BTS ceramics. Oxides of barium and titanium were mixed for the pure $BaTiO_3$ ceramics. Manganese oxide were added in the stoichiometric relation to prepare $BaTi_{0.995}Mn_{0.005}O_3$ ceramics. The sintered ceramic sheets were metallized with aluminium electrodes and connected by a thin wire of tin foil. The samples have a diameter of 10 mm and a thickness of 0.5 mm.

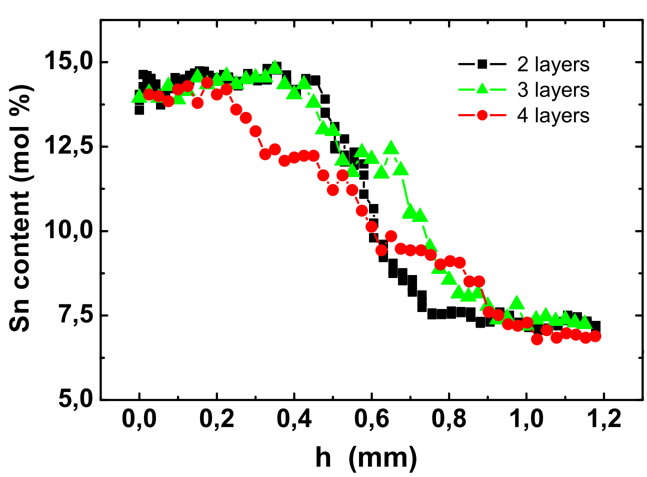

Fig. 7 Tin gradient along the thickness of samples prepared with 2, 3 or 4 powder layers

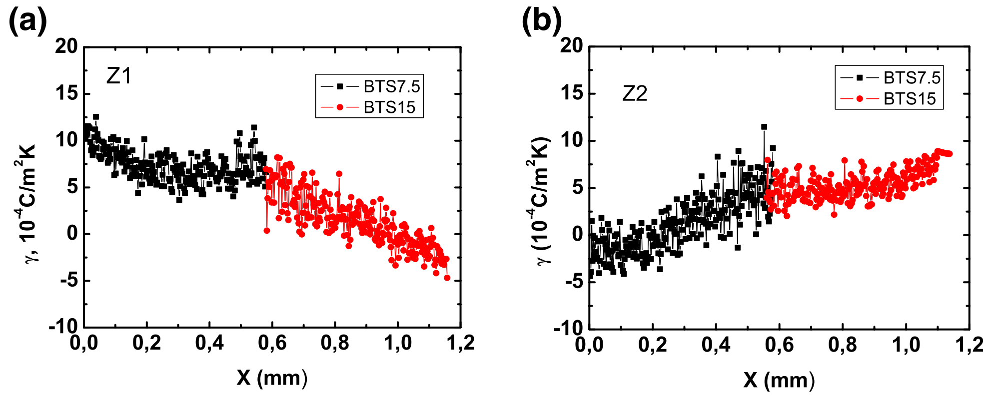

Fig. 8 Thickness profile of the pyroelectric coefficient of BTS samples with a Sn gradient poled in opposite directions. (**a**) Prepared with BTS7.5, (**b**) prepared with BTS15

4 Experimental results

The polarization distribution along the thickness was characterized by the thermal wave method. A intensity modulated laser beam is focussed on the sample surface. The laser heats the sample at some mK and a pyroelectric current can be measured. The penetration depth of the laser depends on the modulation frequency. Thus, a profile of the pyroelectric coefficient can be determined.

The pyroelectric coefficient profiles of two samples of BTS are shown in Fig. 8(a) and (b). Both samples are prepared from two powder layers with BTS7.5 and BTS15, respectively. The samples were polarized in different directions. Sample Z1 was poled by a positive DC voltage applied to the electrode at the BTS7.5 surface. Sample Z2 was poled with a negative voltage applied to this surface, respectively. The BTS15 electrode was connected to the ground in both cases.

The induced gradient of the polarization is proportional to the measured pyroelectric signal. The negative values of the pyroelectric coefficient do not correspond to a local negative polarization. They are rather connected with space charges predicted also by the theory. However, the sign of the gradient of the pyroelectric coefficient along the thickness is in a good agreement with the poling conditions. A vanishing polarization is expected at the BTS15 surface because of the nearly zero remnant polarization of the bulk ceramics. Since the maximum of the polarization at the other surface (BTS7.5) is positive or negative, the slope of the polarization gradient is negative or positive, respectively, as well as the slope of the measured pyroelectric current profile.

Ferroelectric soft and hard materials based on $BaTiO_3$ are needed for the preparation of a gradient from positive to negative polarization. $BaTiO_3$ doped with 0.5 mol% Mn (BTMn) was used instead of the hard material. The non-poled ceramics show antiferroelectric behavior of the polarization (Fig. 9). The strain is constant below a threshold value of 0.5 kV/mm. The sample was polarized with 2 kV/mm for 30 min at 80 °C. After poling the strain has a small hysteresis with a shift to negative voltage (Fig. 10). Thus, the remnant piezoelectric response $d_{33} = dS_3/dE_3$ at small voltages remains positive after a short-time high field strength of 2 kV/mm. The strain loop was measured at 10 Hz by a capacitive displacement sensor.

We used a model structure to investigate the poling process and to characterize the local piezoelectric coefficients. Two single layers of $BaTiO_3$ and $BaTiO_3$ + 0.5 mol% Mn were connected by a wire and poled together. This allows measuring the piezoelectric coefficients d_{33} of each single layer at several instances during the poling process. After 30 min poling at 80 °C both layers were completely poled. The piezoelectric coefficients of $d_{33,BT}$=198 pm/V and $d_{33,BTMn}$=175 pm/V were measured. After cooling down to room temperature a negative electric field strength of 2 kV/mm was applied for a few seconds. After 20 s, the $BaTiO_3$ layer

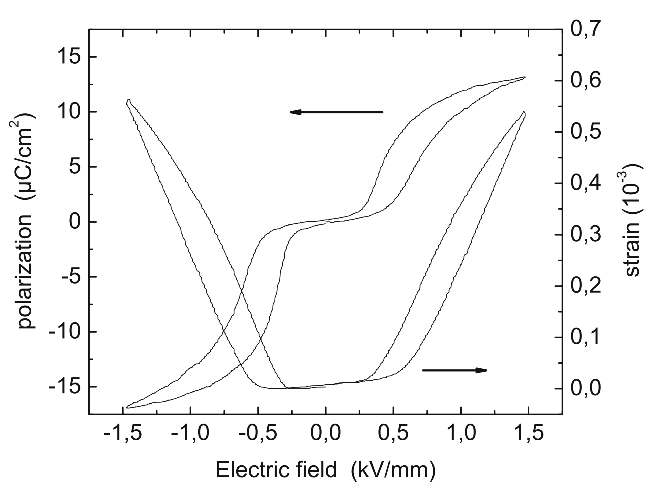

Fig. 9 Polarization and strain of unpoled $BaTiO_3$ + Mn in dependence on the electric field

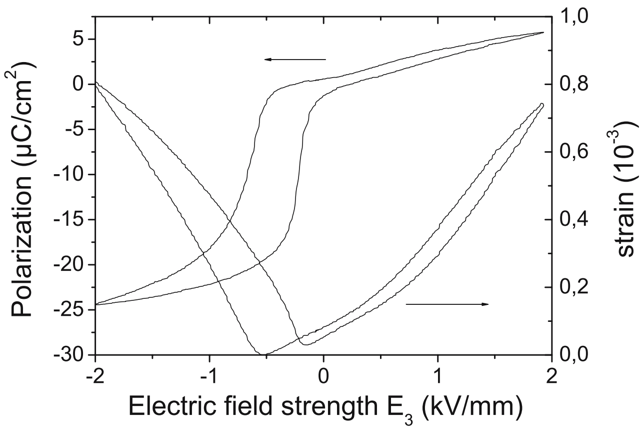

Fig. 10 Polarization and strain of poled $BaTiO_3$ + Mn in dependence on the electric field

was nearly completely depolarized. That means the absolute value $d_{33,BT}$ was about zero. The piezoelectric coefficient of BTMn decreases to half the original value. After another 30 s poling at −2 kV/mm the polarization switched back in the $BaTiO_3$ layer and was still remain in BTMn. The piezoelectric coefficients $d_{33,BT} = -200$ pm/V and $d_{33,BTMn} = 80$ pm/V were measured. The negative sign means that the piezoelectric response is in the opposite direction to the first poling field direction. Thus, we could demonstrate that it is possible to prepare a piezoelectric gradient where the sign of d_{33} switched from positive to negative.

The investigation of the time-dependence of the poling process described in the model in Section 2 are still in work. The conductivity of the Mn-doped $BaTiO_3$ ceramics is not measured yet.

5 Conclusion

Gradients of the piezoelectric coefficient and the corresponding gradient of the electric polarization in monolithic ceramics can be induced by a poling process. This is a nontrivial result because the local different remnant polarizations should be compensated due to the continuity of the dielectric displacement. If they are not compensated inner electric fields occur. If these fields are not stabilized by space charges they should occur very quickly and are not be stable in time. Since the poling processes are long time processes (several minutes) we assume that the different local polarization states are compensates by space charges. We described this by a simple multilayer model. The value of the local polarization depends on the ferroelectric properties of the local chemical composition, especially on the remnant polarization. The time-dependence of the poling process is determined by the conductivity of the used materials.

It was shown that a gradient of polarization from a maximum value to zero can be prepared in monolithic $Ba(Ti,Sn)O_3$ ceramics with a tin gradient. Furthermore, we suggest a monolithic FGM based on soft and hard ferroelectrics with a gradient from positive to negative values of the polarization. The theoretical prediction was checked by a model system consisting of two sheets of pure and Mn-doped $BaTiO_3$, respectively. It was possible to polarize the wire-connected layers that the final piezoelectric coefficients d_33 of the layers have opposite directions (signs). Of course, it is necessary to demonstrate this behavior for monolithic FGM, too.

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