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Short communication

BNT-based multilayer device with large and temperature independent strain made by a water-based preparation process

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Abstract

A piezoelectric multilayer device based on bismuth–sodium–titanate ceramics (BNT) co-fired with Ag/Pd inner electrodes is described and its dielectric and piezoelectric properties are measured. The ceramic powder and tape was made by a water-based preparation process. After printing with Ag/Pd paste for inner electrodes these tapes were stacked to a multilayer device with 50 active layers. This device exhibited a large and temperature independent strain around 0.19% between 25 °C and 150 °C. The large strain is due to a field-induced phase transition. The low temperature dependence results from the broadening of the nonpolar phase by doping.

Keywords: BNT; Lead-free; Multilayer; Piezoelectricity; Actuators

1. Introduction

For decades researchers work in the field of lead-free piezoelectric ceramics to find a material that could replace lead–zirconate–titanate in piezoelectric devices. Excellent reviews on that topic are given by Rödel et al.[1] or Takenaka et al.[2]

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is one of the most promising lead free materials for actuator applications, which was first reported by Smolenskii et al.[3] It has a perovskite type structure with rhombohedral symmetry at room temperature. The depolarization temperature (T_d) is at 186 °C and the temperature at the maximum of the permittivity (T_m) at 335 °C.[3,4] Both temperatures can be shifted by doping. It exhibits a morphotropic phase boundary with tetragonal compounds, such as barium titanate[5] and bismuth–potassium–titanate.[6,7] Zhang et al.[8] found a large strain in the system $Bi_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$–$K_{0.5}Na_{0.5}NbO_3$ (BNT–BT–KNN) which is due to a field-induced nonpolar/ferroelectric phase transition. In literature the nonpolar phase is sometimes termed as antiferroelectric which is supported by the shape of the polarization curves. Structural changes at T_d, which were suggested by Hiruma et al.[7] were not confirmed by Jones et al.,[9] who performed Rietveld neutron powder profile analysis of the compound $Na_{0.5}Bi_{0.5}TiO_3$ over the temperature range from 5 to 873 K.

Key for a device fabrication is the multilayer technology, which requires co-firing of ceramics and metal electrodes, preferentially Ag/Pd-alloys. The first BNT-based multilayer actuator was presented by Takenaka et al.,[10] who used Pt-electrodes because of the concern of a bismuth–palladium reaction.[11,12] Schütz et al.[13] showed that BNT based ceramics do not interact with palladium during the sintering process as long as free bismuth oxide is not present. Hence the use of Ag/Pd-alloys for the co-fired inner-electrodes should be possible.

Other drawbacks for the use as material for piezoelectric devices are the huge intrinsic losses due to the large hysteresis and a pronounced temperature dependence of the piezoelectric properties due to the phase transition at the depolarization temperature.

To become temperature independent in dielectric and piezoelectric properties in an extended temperature range it is necessary to broaden the nonpolar phase, i.e. to lower the depolarization temperature T_d and to increase the temperature at the maximum of the permittivity T_m. This can be done in different ways. The major point is to increase the volume on the A-site of the perovskite to facilitate nonpolar ordering. This can be achieved by doping with smaller ions on the A-site[14] or larger ions on the B-site[15] of the perovskite, by the formation of vacan-

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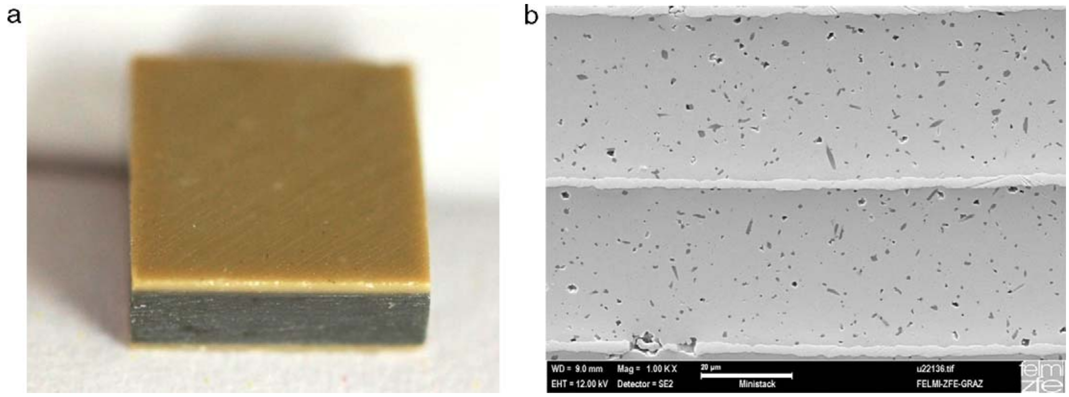

Fig. 1. Photograph of the multilayer device (a) and SEM image of the active layers with Ag/Pd inner electrodes (b). The scale bar in the SEM image indicates the length of 20 μm.

cies and the reduction of the rhombohedral distortion by adding tetragonal compounds like $BaTiO_3$ (BT)[5,16] or $Bi_{0.5}K_{0.5}TiO_3$ (BKT).[6,17]

Desirable for the replacement of PZT is a cost effective production process. PZT is made by a mixed oxide process with water as a solvent, which is comparably cheap and safe. BNT-based ceramics are usually made in ethanol because of the solubility of the alkaline raw-materials. But ethanol is very expensive in comparison with water and one has to install an explosion protection in the powder and tape production line.

In this work, we present a method to produce a cost effective lead-free ceramic multilayer device with large strain and reduced temperature dependence. Therefore we designed a ceramic material based on BNT that was prepared by using water as a solvent.

2. Experimental

The powder for the multilayer-stack is $[Bi_{0.50}Na_{0.335}K_{0.125}Li_{0.04}]TiO_3$ doped with 2 mol% Nd which was made by a modified mixed oxide process. The reagent grade raw materials were Bi_2O_3 (HEK-Oxides), Na_2CO_3 (Merck), K_2CO_3 (Merck), Li_2CO_3 (Merck), TiO_2 (Tronox) and Nd_2O_3 (Treibacher). The raw materials were ball milled for 5 h in a laboratory ball mill (Dyna-Mill Multi Lab) with water as a solvent and subsequently dried with a laboratory spray dryer. After calcination at 900 °C for 2 h a second milling for 5 h and drying took place with the same equipment. From this powder a water-based slurry was made with a binder and tape casting was done on a laboratory equipment. 50 layers were printed with Ag/Pd-metal paste (70/30), stacked in a format of 10 cm × 10 cm with additional covering layers and were pressed under uniaxial pressure of 100 tons. After dicing and binder burn out sintering took place in air at a sintering temperature of 1100 °C for 5 h. The final dimensions were 7 mm × 7 mm × 2 mm with an active layer thickness of approximately 35 μm. The sintered multilayer-stacks were contacted with silver paste (burn-in temperature 750 °C) for electric measurements. In Fig. 1 one can see the sintered multilayer-stack and the SEM-image of the active layers.

The temperature dependence of the permittivity was measured using a Novocontrol Concept 40 impedance analyzer. Measurements were performed from −100 °C to 400 °C with a heating rate of 2 K/min. The polarization and displacement curves were measured with aixPES Piezoelectric Evaluation System from aixACCT from room temperature to 150 °C. The curves of polarization and displacement shown in Fig. 3 were measured at room temperature as the last cycle of three. SEM images were taken on a FEI Quanta 600 scanning electron microscope.

3. Results and discussion

With the choice of material we considered the phase diagram published by Hiruma et al.,[18] who found for the composition $[Bi_{0.50}Na_{0.335}K_{0.125}Li_{0.04}]TiO_3$ a depolarization temperature (T_d) of 160 °C and temperature at the maximum of the permittivity (T_m) of 290 °C. The concept of broadening the nonpolar phase was achieved by doping with 2 mol% Nd. As one can see in Fig. 2 this amount of Nd has enlarged the nonpolar phase from approximately 50 °C (T_d) to 320 °C (T_m).

In Fig. 3 one can see a narrow nonpolar polarization curve with low remnant polarization and a displacement curve with no remnant displacement and a maximum strain of about 0.19%.

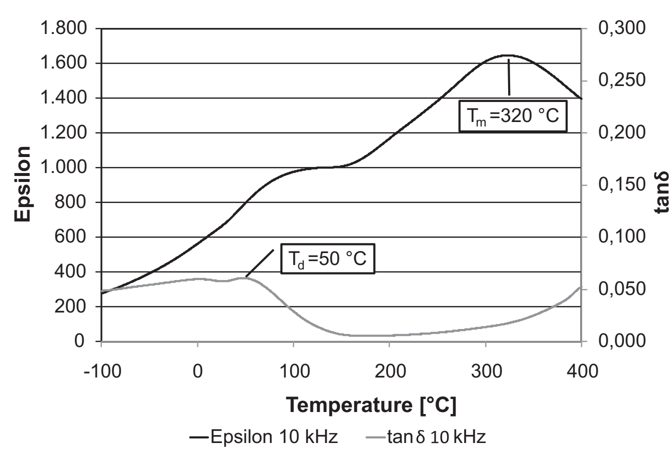

Fig. 2. Temperature dependence of permittivity (epsilon) and loss factor (tan δ) for $[Bi_{0.50}Na_{0.335}K_{0.125}Li_{0.04}]TiO_3$ doped with 2 mol% Nd.

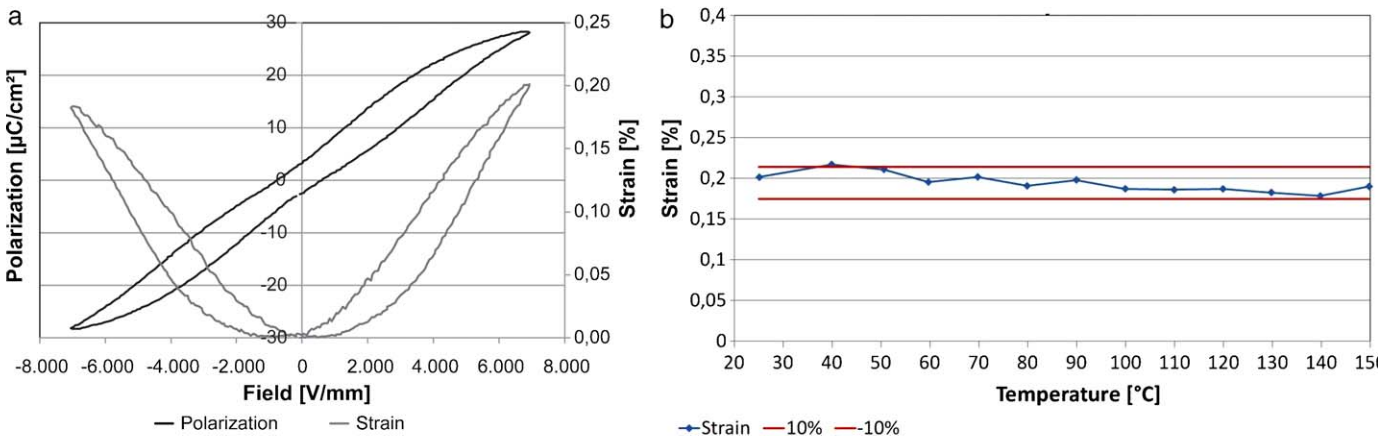

Fig. 3. Field dependence of polarization and displacement of the multilayer stack at room temperature, third cycle of three (a) as well as strain at 7 kV/mm vs. temperature measured with a frequency of 0.1 Hz (b).

Due to the dependence of T_d on frequency (which accounts only for a minor part of the shift) and electric field the above mentioned phase transition can be shifted from 50 °C (under small signal conditions of 10 kHz and 1 V) to below room temperature under large signal conditions (0,1 Hz and 200 V), which is the reason for the observed shape of the polarization and strain curves at room temperature. As we have shown in a previous work on solid solutions of BNT with $SrTiO_3$[19] there is a shift of about 75 K to lower temperatures from the small signal data to the high signal data. Further this concept yields a nearly constant strain of about 0.19% at 7 kV/mm with a tolerance of about ±10% in a temperature interval ranging from 25 °C to 150 °C.

4. Summary

We have shown that by enlarging the nonpolar phase in BNT-based piezoelectric ceramics by doping with Nd we are able to obtain a ceramic material with low intrinsic losses, low remnant polarization and a temperature independent strain in the desired operating temperature range.

Furthermore we have demonstrated the processing of a multi-layer device with a water based route using Ag/Pd inner electrodes. SEM images prove that the inner electrodes do not exhibit any delaminating, and there is no indication of a bismuth–palladium reaction. The actuator dimensions were 7 mm × 7 mm × 2 mm containing 50 active layers with approximately 35 µm layer thickness. The obtained strain at a field of 7 kV/mm gained the value of 0.19% with a variation of ±10% in the temperature range between 25 °C and 150 °C.

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