# Development of Lead-Free Piezoceramics and Implementation in Multilayer Actuators

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A promising approach in the development of lead-free piezoelectric materials is to use bismuth-based materials with a perovskite structure, which can exhibit a number of non-cubic distortions allowing the presence of so called morphotropic phase boundaries (MPB), where excellent piezoelectric properties are expected due to phase instabilities. In this paper, we will introduce the material class (100-x)BNT-xBT ((100-x)$Bi_{1/2}Na_{1/2}TiO_3$-x$BaTiO_3$). Bulk properties as well as preliminary results on lead-free multilayer actuators with the composition BNT-8BT will be presented. Temperature- and frequency-dependent investigations on piezoelectric and dielectric properties, as well as studies on long term reliability will be discussed.

## Introduction

New regulations in the European Union and many other countries worldwide restrict the use of lead and other hazardous substances in electric and electronic devices. Therefore, the replacement of lead in future piezoceramics has become a key aspect of current research [Röd09]. These materials have to provide similar or even better properties and should, furthermore, be affordable and easy to manufacture. A promising approach is to use bismuth-based materials with a perovskite structure, which can exhibit a number of non-cubic distortions allowing the presence of so called morphotropic phase boundaries (MPB), where excellent piezoelectric properties are expected due to phase instabilities [Tak91, Röd09]. Up to now, basic properties of lead-free bulk material like small signal parameters have already been addressed in several papers [Hol05]. For lead-containing bulk PZT, there is a vast amount of literature available dealing with the degradation behaviour under cyclic electric field, see e.g. [Lup09] and references therein. Comparably few publications deal with the degradation behaviour of lead-containing PZT multilayer actuators [Abu94]. In the field of lead-free piezoceramics, the aspect of long term reliability and degradation has been subject to investigation in some recent work [Luo11] dealing with the cyclic electrical fatigue of bulk materials. For multilayer materials, no comparable work is known so far. In this paper, we will present first characterisation data of multilayer actuators manufactured of such lead free material.

## Experimental

### Samples

For the experiments, bulk samples made of 92BNT-8BT as well as multilayer actuators (MLA) manufactured from the same material were used.

The bulk material was manufactured by a conventional mixed oxide method using $Bi_2O_3$ (99.975% purity), $Na_2CO_3$ (99.5%), $BaCO_3$ (99.8%) and $TiO_2$ (99.9%, all powders by Alfa Aesar, Karlsruhe, Germany) as raw materials. The starting materials were weighed according to the stoichiometric formula and ball milled for 24 h in ethanol. The dried slurries were calcined at 900°C for 3 h and then ball milled again for 24 h. The powders were subsequently pressed into green disks with a diameter of 10 mm. Sintering was carried out at 1150°C for 3 h in covered alumina crucibles. To prevent evaporation of volatile elements during sintering the samples were embedded in atmospheric powder of the same composition. The purity and formation of the desired single perovskite phase in the calcined powders and sintered products was confirmed by x-ray diffraction.

The sintered samples were ground to approximately 500 µm thickness, polished and electroded with sputtered silver. An additional electrode layer of silver paste (Gwent Electronic Materials, Pontypool, UK) was fired on to assure mechanical and thermal stability.

The multilayer actuators were fabricated by Noliac A/S. Each MLA consists of 32 active ceramic layers with a thickness of 50µm and inactive covering layers of 200µm thickness. Electrical contact is provided by interdigital silver palladium alloy electrodes. All the actuators were poled for 6 min at room temperature with a field of 3kV/mm.

## Temperature dependent small signal parameters

For the bulk material, temperature dependent small signal parameters were measured.

The temperature dependent permittivity of a poled sample was measured with a HP4284A Impedance Analyzer using a Nabertherm furnace at a constant heating rate of 2 K/min and frequencies from $10^2$ Hz to $10^6$ Hz. Real part ε' and loss tangent delta of the temperature dependent dielectric permittivity were calculated from the measured capacitance using the known sample thickness h and surface area A.

## Field dependent small signal parameters

For the field-dependent measurements of small signal $d_{33}$ and $\varepsilon_{33}$, which were performed at MLA samples, a DC voltage was applied to the MLA and increased stepwise according to the schematic signal wave form displayed in figure 1.The schematic shows the setup for $\varepsilon_{33}$-measurement.

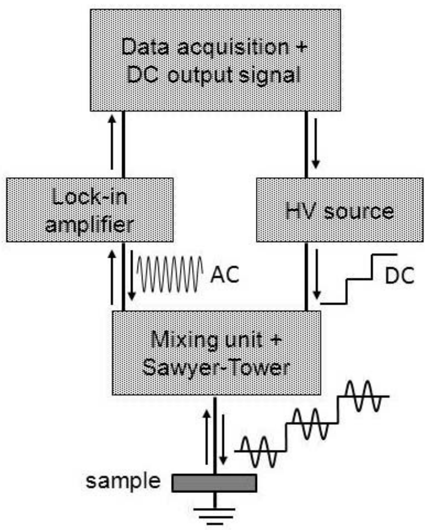



***Fig. 1*** *Test setup for determination of field-dependent small signal parameters at bulk samples.*

A second Lock-In amplifier is used for the strain measurement in combination with an optical strain sensor (not displayed in figure 1 for clarity). The same excitation frequency and field were used for $\varepsilon_{33}$ and $d_{33}$ measurements. The additional application of an AC voltage with a frequency of 1 kHz and a maximum field of 10 V/mm allowed the simultaneous detection of large signal P(E) and small permittivity $\varepsilon_{33}$(E) as well as large signal strain S(E) and small signal $d_{33}$(E).

## Large signal and reliability investigation of multilayer actuators

The multilayer actuators were first characterized in the virgin (uncycled, but pre-poled) state with respect to their large-signal performance as well as temperature development during first driving cycles. In a second step, long term reliability tests over $10^8$ unipolar cycles were done.

For the pre-characterisation, the samples were driven with a unipolar field of maximum 6kV/mm (Trek voltage amplifier PZD 700) and a frequency of 50 Hz. A minor preload of 40 kPa was applied by the sample fixture. The measurement was carried out at ambient temperature, and the temperature of the sample was measured by means of a thermocouple mounted to the sample surface. The temperature was recorded after the first cycles as soon as a stable value was reached. In a different setup, polarization and strain were recorded simultaneously at 50Hz using a Sawyer-Tower setup with a 130 µF measurement capacitance and an optical strain sensor (Philtec D63).

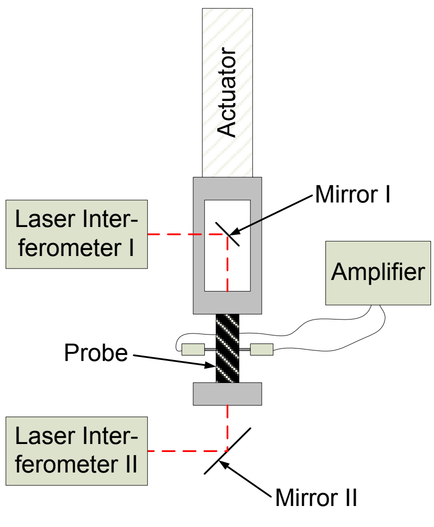



***Fig. 2*** *Principal sketch of the sample arrangement in the AixCMA test bench. The mechanical load is applied to the sample by means of a piezoelectric stack actuator. The displacement of the sample is measured via differential measurement of two laser interferometers.*

For long term reliability testing a Ceramic Multilayer Actuator test bench (aixCMA) provided by aixACCT Systems GmbH was used. The main components of this system are an SMA sample holder, which is able to carry specimens of 2 – 50 mm in length, a 400V amplifier (TFA-AMP356-6) and two Sios SP-S-2-120 Laser Interferometers. As can be seen in figure 2, the displacement of the probe is measured by a differential method using two laser interferometers. The external mechanical force for passive mechanical cycling can optionally be applied by a piezoelectric actuator (assigned as "Actuator" in the figure).

The specimen was tested under a maximum operational field of 6 kV/mm unipolar rectangular signal form and an excitation frequency of 500 Hz. A mechanical preload of 4 MPa was applied to the sample due to requirements of the AixCMA test bench. The fatigue treatment was interrupted three times per decade for 2 seconds, followed by 10 hysteresis measurement cycles at 500 Hz. The data points received from these 10 measurement cycles were automatically averaged and plotted as one representative hysteresis loop for polarisation and displacement at the corresponding cycle number.

## Results and discussion

### Temperature and electric field dependent small signal parameters

The small signal parameters in dependence of the ambient temperature were measured in order to identify the depolarisation temperature $T_d$ of the material.

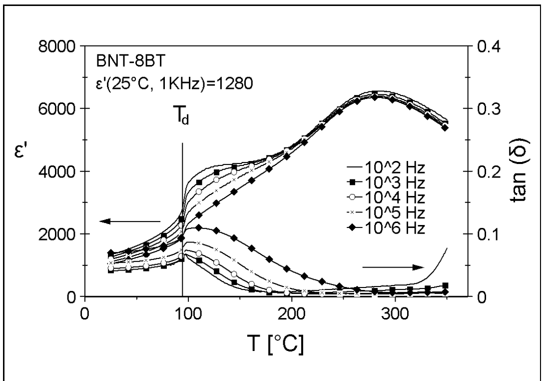
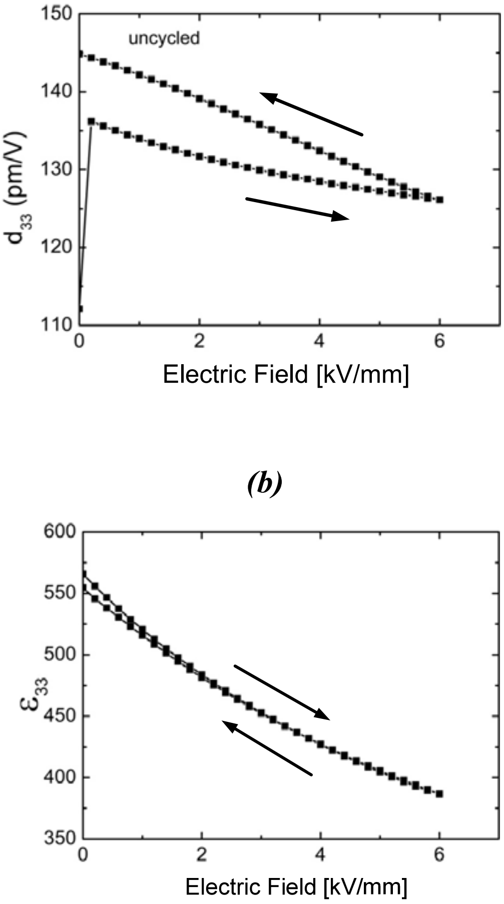



*Fig. 3 Small signal parameters of bulk material as a function of temperature and excitation frequency.*

This temperature is of interest for technical application since according to actual state of the art a safe use of a multilayer actuator is given if the temperature during dynamic operation is not exceeding ½ $T_d$ (in °C). Fig. 3 shows the result of the measurement. As can be seen, the material shows an abrupt change in the small signal values at about 100°C, as the dielectric constant ε′ strongly increases and the loss angle tan (δ) strongly decreases at this temperature. According to [Xu91], the depolarization temperature is determined as $T_d$ = 100°C. This value is considerably lower than for typical lead containing PZT materials ($T_d$ > 150°C). Further conclusions will be drawn in the context of the driving temperature of the multilayer actuators (see below in this paper).

The electric field – dependent small signal parameters of the MLA are shown in Fig. 4a) and 4b).

***(a)***




***(b)***

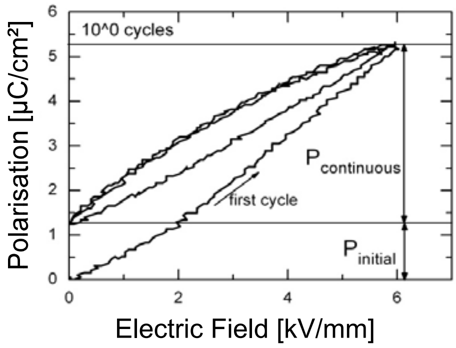
*Fig. 4 Field – dependent small signal parameters. (a) Piezoelectric coefficient $d_{33}$, (b) dielectric constant $\varepsilon_{33}$.*

The small signal $d_{33}$ and $\varepsilon_{33}$ respectively, which are shown for uncycled but pre-poled samples, are in the same order of magnitude as similar BNT-6BT compositions [Luo11]. Increasing field strength leads to lower $d_{33}$ and $\varepsilon_{33}$ values, what is expected since lead-containing PZT showed the same qualitative behavior during our previous yet unpublished experiments. In conventional ferroelectrics this is attributed to reduced domain wall density as well as domain wall clamping with increasing external field.

## Characterisation of the lead free multilayer actuator (MLA)

In order to characterize the multilayer actuators, unipolar hysteresis loops of polarization P(E) and strain S(E) were recorded at the virgin, pre-poled actuator, Fig. 5a) and b).

***(a)***




***(b)***

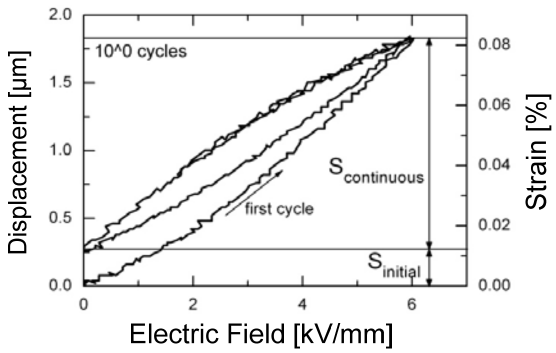



***Fig. 5*** *Hysteresis loops measured at virgin pre-poled MLA sample. (a) Polarization, (b) displacement/strain.*

Both loops exhibit a pronounced run-in effect during the initial cycle, although the actuator was prepoled. After the first cycle, the hysteresis loops are closed at E = 0kV/mm as expected. It is assumed that the run-in effect does not affect the technical exploitability of the MLA, nevertheless this effect may give insights into the dynamic properties of the domain wall system of the basis material. The initial polarisation is also very pronounced during all hysteresis measurements received from the fatigue experiment shown in the next section. One possible explanation for this finding is an incomplete poling of the sample, which reaches a saturated polarization only after several cycles [Ver03]. Another possible reason is the relaxor nature of BNT-8BT. In the unpoled state, no ferroelectric macrodomains can be observed in BNT-8BT [Ma10]. Instead, polar nanoregions exist, which are characteristic relaxor features. Applying sufficiently high electric fields leads to a structural phase transition from rhombohedral to tetragonal in BNT-7BT [Dan09] which is accompanied by the evolution of a long-range order, similar to that in conventional ferroelectrics. For other BNT-xBT compositions the coexistence of polar and non-polar nanoregions with different structures has been found [Dan11]. Upon poling, the volume fractions of these regions change. A possible model is that only one type of polar nanoregion increases in volume fraction during poling and is responsible for polarization and strain during cycling. A second phase persists but reacts only after a larger cycle number.

The maximum strain reached at the stable hysteresis cycles was about $S_{continuous}$ = 0.07%, what is in the same range of strain reached by PZT. During the first measurement cycles, the sample temperature did not exceed the ambient temperature of 25°C by more than 3°C. At 50 Hz cycling frequency, the temperature of the actuator therefore remained well below the depolarization temperature determined from temperature dependent permittivity (see previous section).

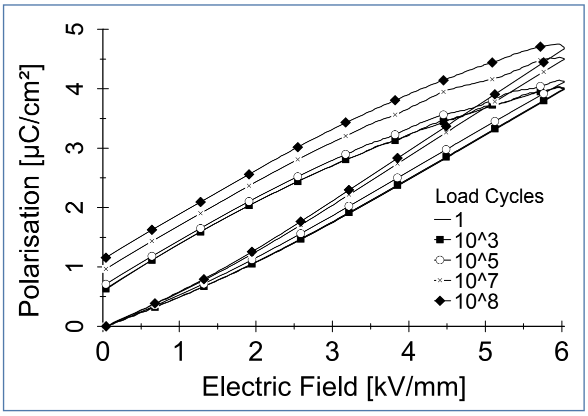
## Long term reliability of the multilayer actuator

Figure 6a and 6b provide the displacement and polarisation hysteresis of the tested actuator recorded at different cycle numbers. The maximum values for polarization measured during this long term experiment are in the same order of magnitude as measured before in the pre-characterisation. The displacement, however, is lower during the long term experiment, possibly due to the higher driving frequency (500Hz instead of 50 Hz).

Both displacement and polarisation increase slightly with cycle number. A maximum displacement of about 0.9 µm was measured before cycling. A maximum displacement of about 1.1 µm, which corresponds to a relative strain of about 0.55 ‰ was reached after $10^7$ cycles. The maximum displacement then decreases again to about 0.9 µm after $10^8$ cycles. Maximum polarisation before cycling was 4µC/cm², after $10^8$ cycles a maximum of 4.7 µC/cm² was reached. The observed changes took place continuously with logarithm of cycles.

The main result of the long term reliability experiment is that, despite the above described slight changes of the maximum polarization and strain with cycle number, there is no severe degradation during the first $10^8$ unipolar cycles. In a previous study, it was already shown that it is possible to manufacture mechanically stable multilayer actuators from a comparable material [Kra11]. In our paper, we have shown that beyond that the mechanical stability is also given after $10^8$ unipolar driving cycles. Furthermore, it was shown that the device additionally exhibits excellent resistance against electrical fatigue as well.

***(a)***




***(b)***

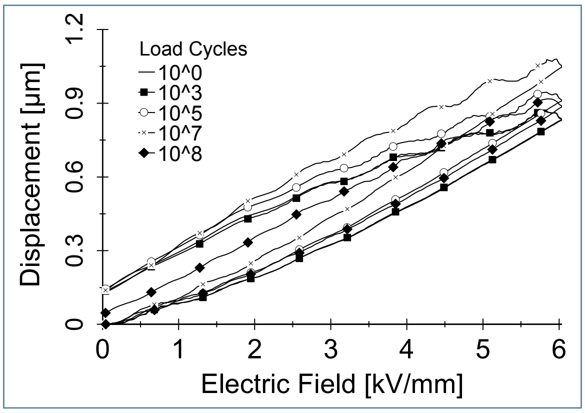



***Fig. 6*** *Polarization and displacement hysteresis loops of the tested MLA at different cycle numbers.*

## Conclusions

In this paper, we analysed bulk ceramics as well as multilayer actuators manufactured from BNT-8BT lead free piezoelectric material. From the bulk ceramic, we determined the depolarization temperature. The multilayer actuators were characterized with respect to their large signal behaviour (i.e. polarization and displacement hysteresis loops) and for the first time for their long time reliability. The latter revealed that there is no observable degradation in properties up to $10^8$ unipolar cycles when driven with 6kV/mm peak electric field at 500 Hz. This result is encouraging in view of future application in adaptronic application, e.g. for vibration reduction.

In future work, it is planned to address other cycling scenarios for reliability tests as well (e.g. superimposed temperature and moisture, different frequencies).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