Piezoelectric coefficients of PMN-0.29PT single crystals in the temperature range of phase transitions

M. Sulc · J. Tryzna · M. Pokorny

Abstract The temperature dependencies of piezoelectric coefficients d_{33} and d_{31} for $Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.29PbTiO_3$ multi-domain single crystals, poled in [001]-direction, were investigated. The two samples had x- and y-axes identical with crystallographic [100] and [010] directions respectively, and the second two samples with [−110] and [110] directions. The laser interferometry method was used for the piezoelectrically induced displacement measurement. Piezoelectric coefficients were similar for all samples at room temperature and were roughly $d_{31}=-550$ pC/N and $d_{33}=1,100$ pC/N. Very high increase of coefficients to values about $d_{31}=-2,100$ pC/N and $d_{33}=3,900$ pC/N was observed below temperature of the first phase transition 101 °C. The coefficients exhibited only negligible frequency dependence at room temperature. But coefficient increases of about 10–30% as were observed at temperatures about 98 °C for 1 Hz applied field frequency in comparison to values received at 1 kHz. The second phase transition to cubic phase was observed at the temperature 124 °C. The temperature dependencies of dielectric and piezoelectric coefficients were compared too.

Keywords PMN-PT · Piezoelectric coefficients · Temperature dependency · Laser interferometer

1 Introduction

Relaxor ferroelectric PMN-PT single crystal have been used in various kinds of device applications, such as a piezoelectric transformer, and actuator, an ultrasonic motor, and an ultrasonic vibrator, among others, because they exhibit extremely high dielectric and piezoelectric properties [1–3]. The phase transitions between the rhombohedral R, tetragonal T, and cubic C phases were observed in these types of crystals. The presence of orthorhombic, monoclinic M_A, and monoclinic M_C phases was also verified for crystals with a composition near the morphotropic phase boundary (MTB) [4, 5]. The coexistence of the mentioned phases, especially polarization rotation induced by an external electric field between the R and T phases through intermediate M or O symmetries [2], seems to be responsible for the excellent piezoelectric response. The research on crystals with titanium content near MTB, with different crystallographic orientations and cuts, in the temperature range of phase transitions, and with applied electric field of wide frequency ranges can help to explain their characteristics.

Research on the temperature dependence of the dielectric constant has been performed for the crystals $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) of near to morphotropic phase boundary composition [6–13]. The temperatures of the phase transition to the cubic state are indicated as the temperature at which the dielectric constant exhibits a maximum value, but it is very difficult, from those measurements, to obtain the exact temperature of the R–T phase transition.

In this paper, we research the dependence of piezoelectric and dielectric coefficients on the temperature of PMN-0.29PT crystals. We performed direct measurements of the converse piezoelectric effect over a wide temperature range, and over phase transition temperatures by a laser interferometer method. The applied small electric field signal ranged between 1 and 1,000 Hz. The dielectric constant was measured too. These results can help to deepen the understanding of the microstructure and properties of PMN-PT crystals, and may be useful in their practical applications.

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2 Experimental procedure

We studied $Pb(Mg_{1/3}Nb_{2/3})O_3$-0.29PbTiO$_3$ multi-domain single crystals that were provided by Crystal Associates Inc., East Hanover, NJ, USA. The crystals were oriented and cut so that the samples' crystal structure orientation were [100]/[010]/[001] for samples A and B and of [110]/[−110]/[001] for samples C and D. The samples had a cubic shape with dimensions $4.9 \times 4.9 \times 4.9$ mm^3. All samples were painted by the room-temperature-treated silver paste on the required surfaces so the electrodes were on faces [100] and [−100] for sample A, [010] and [0−10] for B, [−110] and [1−10] for C, [110] and [−1−10] for D. The electric field of 3 kV/cm that was applied for 20 min at an ambient temperature of 21 °C poled the samples in the [001] direction. When the temperature overran the Curie point within the tests, the samples were cooled to RT at zero-field-cooling conditions. The same poling process was used before the next measurement.

The temperature dependencies of the piezoelectric coefficients d_{33} and d_{31} were determined by a single beam laser interferometer [14] using a modified Michelson scheme. The sample in the probing arm and fixed mirror in the reference arm were situated in the temperature chamber. In order to suppress temperature dilatation influences of mechanical parts inside the chamber to the laser beam alignment, the piezoelectric actuator was placed outside the chamber. It constituted, together with two other beam splitters, a feedback circuit. The temperature control was realized by steps of 10 °C from room temperature up to 140 °C with a precision of 0.1 °C. There were about 10 min temperature stabilization times before all measurements. The temperature dependencies of the piezoelectric coefficients were measured with an applied a 10 V/cm, 1 kHz AC field. The frequency dependencies of the piezocoefficients were measured in the range of AC frequencies from 1 Hz up to 10 kHz when the temperature was stabilized.

The dielectric constant, the coefficient ε_{33}, was measured by the impedance analyzer HP4192A. Samples were situated in the temperature chamber and connected by a four-wire method to the measuring set outside. A small electrical test signal with an amplitude of 0.5 V and a frequency 1 kHz was applied without any bias field. The temperature inside the chamber was set, in steps of 5 °C, between 20 and 170 °C.

3 Results and discussion

All multi-domain tested crystals had their own temperature histories from previous measurements. This is why the d_{33} values were measured after every poling process by the d$_{33}$-meter before our interferometric measurements. The

values for the first-time-poled crystals were near 2,000 pC/N, but the values were stabilised at about $1,220 \pm 20$ pC/N for all samples except sample B ($1,120 \pm 20$ pC/N) at room temperature after three to four poling processes (we have been starting our experiments after this). These smaller values are close to coefficients calculated for single-domain crystals. A possible reason for the small piezoelectric response is that induced stresses between adjacent domains [15] would not be so significant after a few poling and temperature cycles.

The very large increase of both of the d_{33} and d_{31} coefficients up to $d_{33} \approx 4,000$ pC/N and $d_{31} \approx -2,000$ pC/N with increasing temperature can be seen in Fig. 1(a and b). The increase of about 100% between 20–80 °C is similar to that in the low temperature range [16, 17]. The especially high increase in the range 90–101 °C can be explained by polar vector rotation from pseudo-rhombohedral M_A, to pseudo-orthorhombic M_C, to the tetragonal T phase [18]. First-order-like phase transitions (with a sharp peak) to the T phase were observed at a temperature of 101 ± 1 °C. The

(a)

(b)
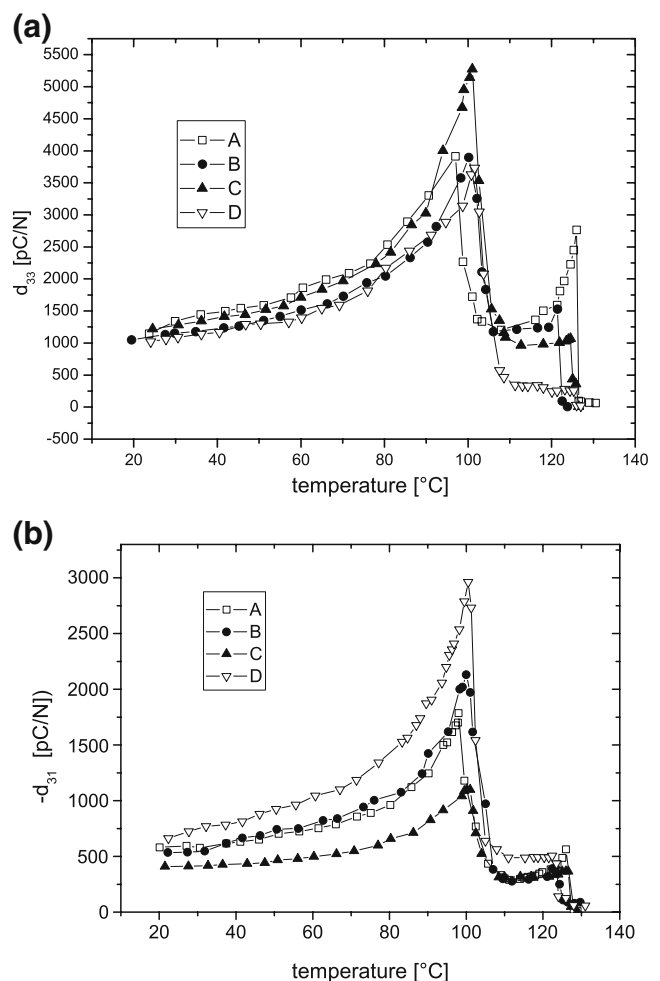
Fig. 1 Temperature dependence of (**a**) d_{33} and (**b**) d_{31} coefficients for PMN-0.29PT crystals
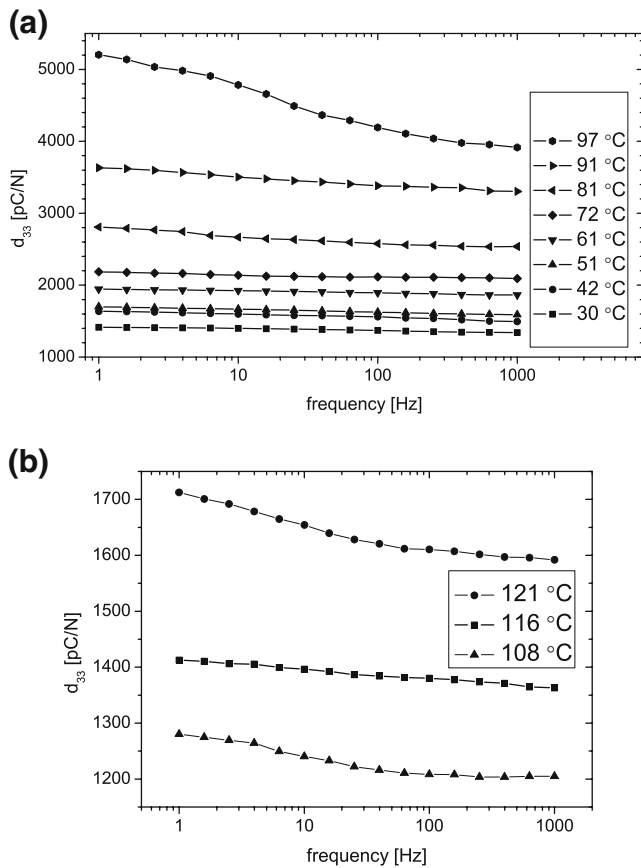
Fig. 2 Frequency dependence of d_{33} coefficient at various temperatures for PMN-0.29PT at (**a**) rhombohedral and (**b**) tetragonal phases, crystal A

piezoelectric response in the tetragonal phase is not negligible, and d_{33} reaches 2,800 pC/N in the case of sample A. The temperature of the phase transition to the cubic phase is about 124 ± 1 °C, and the temperature dependency of the piezoelectric coefficients is a steep jump function here. Small differences between the temperatures of the phase transitions can be caused by different PT contents in crystals because similar differences were observed both for d_{33} and d_{31} independent measurements for the same crystals. The biggest difference was measured for sample A. The temperature of the R–T transition is lower by about 2.5 °C and, for the T–C transition, it is higher by about 1.5 °C than the average from other samples. The piezoelectric coefficients are significantly higher in the rhombohedral phase than in the tetragonal one. The high piezoelectric-induced strain in R has an origin not only from elongation of the polar vector, but also from tilting under the electric field.

The frequency dependence of the coefficients was measured too. As you can see in Fig. 2(a) (for sample A), a very small increase (2%) of d_{33} was observed at decreasing frequencies from 1 kHz to 1 Hz at room temperature. But, an increase of about 33% was observed

with decreasing frequency at temperatures near the phase transition. Four equivalent domain families exist in the [001] poled R phase, so this increase cannot be explained by domain motion. The increase of d_{33} with decreasing frequency is observed at the low frequency range at a temperature range where monoclinic phase can appear too. Most probably, the induced dynamic stresses (rather than the tilt of the polar vector in four monoclinic phases) can be a possible reason for this property.

A similar frequency dependency was observed at the tetragonal phase (increase 9%), see Fig. 2(b). There are six domain families that are not all equivalent. This is why the contribution of the domain wall motion is most likely the reason why the piezoelectric response increases at low frequencies, and it can be interpreted as the wall mobility increase due thermal activation.

Contrary to d_{33}, the transversal piezoelectric coefficient d_{31} seems not to be so dependent on the frequency, especially in the rhombohedral phase, see Fig. 3(a). A small increase of about 3% is observed in the tetragonal phase, see Fig. 3(b).
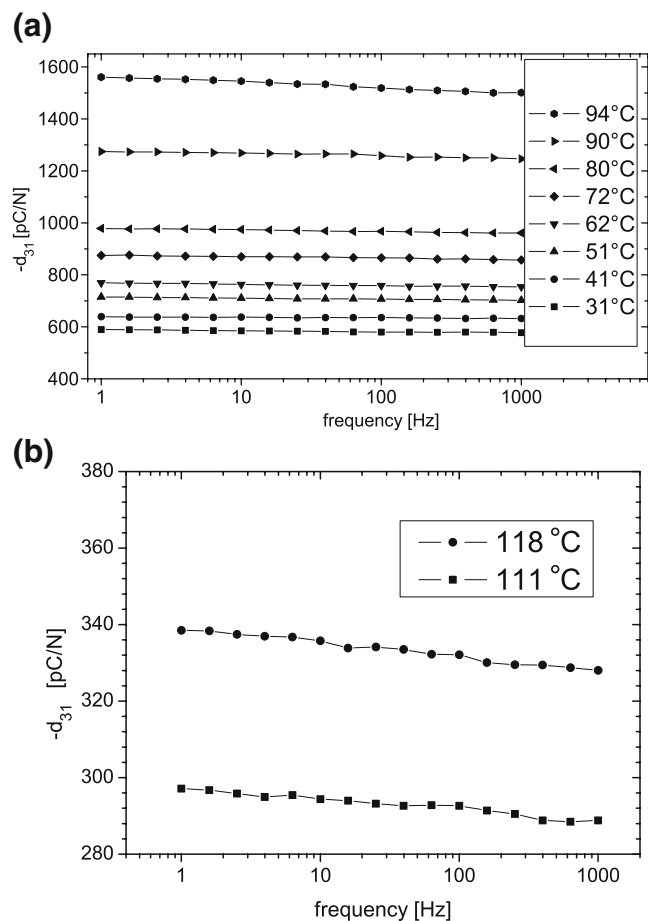
Fig. 3 Frequency dependence of d_{31} coefficient at various temperatures for PMN-0.29PT at (**a**) rhombohedral and (**b**) tetragonal phases, crystal A

The resulting piezoelectric coefficient of the multi-domain crystal with a rhombohedral phase is a combination of four states at the [001] poled crystal, and the relative fraction of each domain family can vary. The conclusion follows from a theoretical analysis [15]: the values of the transverse piezoelectric coefficient d_{31} in single domain state, calculated to measurement directions [100] or [010], are a little different from these ones for [110] and [−110] axes. The contribution of all four domain states to effective d_{31} coefficient measured along [100] or [010] is, in practice, the same. So, we expected only a small difference between the effective d_{31} measurement of samples A and B—cut [100]/[010]/[001], see Fig. 1(b). For samples C and D—cut [110]/[−110]/[001], see Fig. 1(b), the larger difference was observed. The main contribution to effective d_{31} originates from domains, where spontaneous polarization is parallel to direction of measurement. Smaller contribution can be expected from domains with perpendicularly oriented spontaneous polarization. So the effective d_{31} can vary with relative fraction of both types of domains. The contribution to d_{33} of each domain in multi-domain crystal is the same, so d_{33} depend only on poling direction [001], and the differences of the d_{33} coefficient values are duly small for samples A,B,C,D.

The measurement of the temperature dependence of the dielectric constant brought similar results, as are published [6] for PMN-0.30PT. The dielectric constant ε_{33} was about 4,800 at room temperature. The dielectric peak ε_{33} at 43,000 indicates a phase transition to a paraelectric (cubic) state and the shoulder at the dielectric curves was observed for a rhombohedral–tetragonal phase transition.

4 Conclusion

The temperature dependence of the piezoelectric coefficients d_{33} and d_{31} was measured for PMN-0.29PT crystals and a first order phase transition to a tetragonal phase was observed at a temperature of 101 °C. The rotation of the polar vector is a reason for the high piezoelectric response below this temperature. The coefficients are still high in the tetragonal phase, but their values depend on the relative fraction of each domain. The transition to cubic phase was observed at 124 °C. The results are in agreement with dielectric measurements. The first-order phase transitions are more evident in the case of a jump change of the piezoelectric coefficients.

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