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Uniaxial Stress and Temperature Dependence of Field Induced Strains in Antiferroelectric Lead Zirconate Titanate Stannat Ceramics

O. Essig,[a]* P. Wang, M. Hartweg, P. Jänker,[b] H. Näfe[c] and F. Aldinger[c]

[a]Daimler-Benz AG, Forschung und Technologie, Ulm, Germany.
[b]Daimler-Benz AG, Forschung und Technologie, Ottobrunn, Germany
[c]Max-Planck-Institut für Metallforschung, Pulvermetallurgisches Laboratorium, Stuttgart, Germany

Abstract

The electric field induced antiferroelectric–ferroelectric phase transformation of polycrystalline lead zirconate titanate stannate (PZST) was investigated under prestress conditions at various temperatures. Lanthanum- and niobium-modified compositions of PZST with varying titanium content were prepared. The field induced strains of the ceramics were studied. The measured hysteresis loops indicate that the antiferroelectric–ferroelectric phase transformation depends on temperature, as well as on mechanical stress. For example compositions of niobium-modified PZST, which are in a ferroelectric state without pressure, can be transformed progressively into an antiferroelectric phase, by a pressure up to 30 MPa. Antiferroelectric compositions of both Lanthanum and Niob modified PZST can show either increasing or decreasing strain under the influence of a compressive stress. This depends on the composition of the sample and the strength of the pre-stress. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Antiferroelectrics like lead zirconate titanate stannat (PZST) are expected to be very important for the next generation of actuators. The field induced strain is almost twice as large as that of conventional piezoelectric ceramics. In contrast to the latter the motor of the induced strain of PZST is a field induced phase transformation. A strain of 0·85% is reported to be possible for ideal single crystals.[1] Due to this property, PZST is a very interesting material for actuator applications. In addition, a large volume change and digital 'switching' makes PZST favorable for these applications.

Compositions of the PZST family are well known for the electric field induced antiferroelectric 2 (AFE) to ferroelectric (FE) phase transformation, which is also called phaseswitching.[2] The ability to switch these two phases is because the free energy of the antiferroelectric crystal is comparable to that of the ferroelectric modification. The phase transformation is accompanied by a volume expansion and the crystal structure is changed from tetragonal to rhombohedral. Both structures are related to the perovskite structure, which is obtained above Curie temperature.

The field induced strain of the antiferroelectric to ferroelectric phase transformation has been studied for various temperatures during the last years. Even though mechanical stress also affects the phase transformation there are only a few publications dealing with such measurements.

The present paper studies the field induced strain of PZST for different uniaxial stress conditions and temperatures. The induced strain of lanthanum (La)- and niobium (Nb)-modified PZST is described along with the discussion of the results.

2 Experimental

2.1 Sample preparation

The ceramics were prepared by a mixed-oxide process. Oxide powders with a high purity and small particle size were used. To increase reactivity, the starting oxides were attrition milled. After calcination and another milling process pellets with 10 mm diameter were cold isostatically pressed. The

*To whom correspondence should be addressed. Fax: +49 731 505 4106; e-mail: oliver.essig@dbag.ulm.daimlerbenz.com

samples were sintered in Al_2O_3 crucibles and PbO rich atmosphere. After grinding and polishing, pellets of 0·7 mm thickness were obtained. To avoid mechanical stress by preparation, the samples were annealed at 500°C. As an electrode, aluminium was sputtered on the ceramic surface.

The compositions of the samples used in this paper are listed in Table 1.

2.2 Field induced strain measurement

The field induced strain was measured with (i) an laserinterferometer (ii) an inductive sensor system (LVDT). The system with the LV/DT sensor was not provided with an uniaxial stress device. This system was used for electric cycling and temperature dependent measurements. The electric field was 45 kV/cm, representing a sine wave of 0·1 Hz.

3 Results and Discussion

3.1 Electric field induced strain

With an increasing electric field, the strain increases abruptly at the transformation field E_{A-F}. With decreasing electric field, the strain remains at E_{A-F} and the ferroelectric to antiferroelectric phase transformation is observed at E_{F-A} ($E_{F-A} < E_{A-F}$).

Table 1. Compositions of the samples

NB1	$Pb_{0\cdot 99}Nb_{0\cdot 02}(Zr,Sn,Ti)_{0\cdot 98}O_3$;	Ti: 5 mol%
NB2	$Pb_{0\cdot 99}Nb_{0\cdot 02}(Zr,Sn,Ti)_{0\cdot 98}O_3$;	Ti:7 mol%
LA1	$Pb_{0\cdot 97}La_{0\cdot 02}(Zr, Sn, Ti)O_3$;	Ti: 9 mol%

This hysteresis is a characteristic feature of the field induced AFE-FE phase transformation.

The antiferroelectric to ferroelectric phase transformation is accompanied by a large volume expansion. This was particularly investigated for the composition LA1. To calculate the volume change, the strain was measured in the direction of the electric field (longitudinal strain) and perpendicular to the direction of the electric field (transvers strain). A volume change of 0·45% was estimated (Fig. 1).

It is necessary to remark that the ferroelectric phase of PZST shows the inverse piezoelectric effect. This results in an additional strain in the direction of the electric field, but also in a compressive deformation perpendicular to the electric field. Therefore the maximum longitudinal strain exists at the maximum electric field and the maximum transversal strain exists at the lowest electric field (Fig. 1).

3.2 Electric field

The transformation field E_{A-F} is affected by the composition, microstructure and the number of switching processes. For the composition NB1 the transformation field E_{A-F} is approximately 3·5 kV/cm and for LA1 it amounts to 40 kVmm^{-1}. The difference between these two compositions is not only related to the modification elements Nb and La but also to the Ti-concentration.

The phase stability of PZST is strongly affected by the concentration of titanium. An increasing Ti-concentration of the antiferroelectric phase results

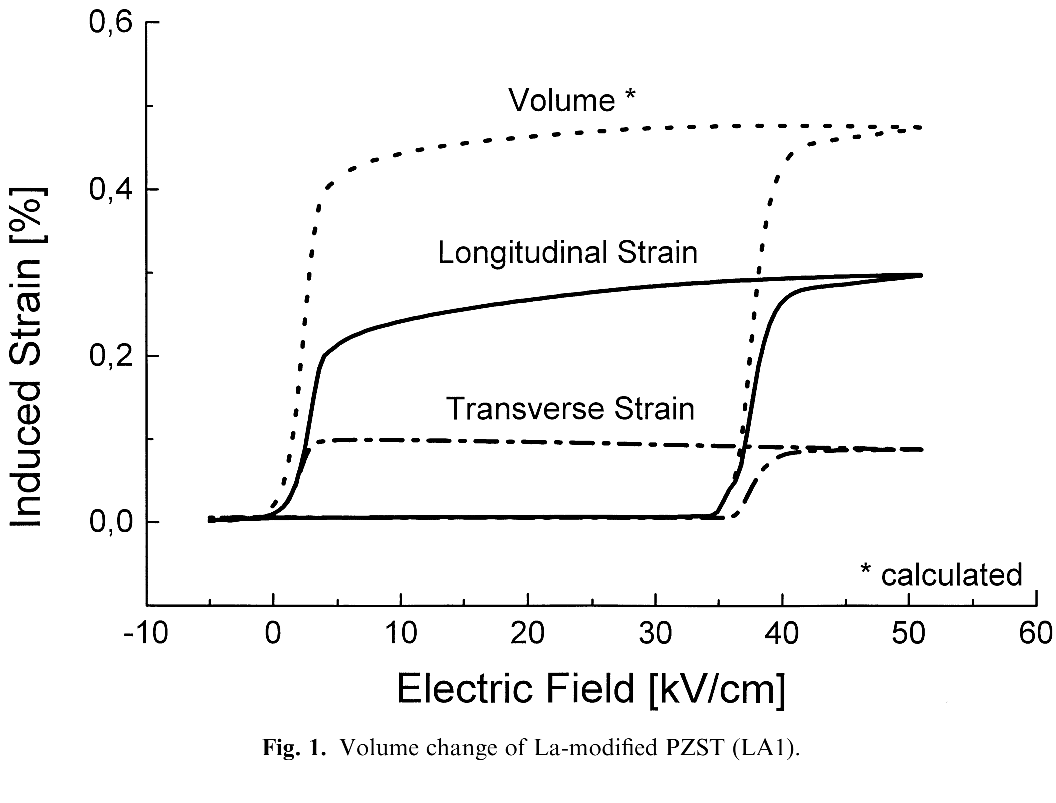

Fig. 1. Volume change of La-modified PZST (LA1).

in the phase transformation to the ferroelectric state. If the antiferroelectric composition is close to the AFE–FE phase equilibrium, the transformation field decreases.[2]

The measurements show that the transformation field of the first switching is always higher than the E_{A-F} of subsequent switching processes (Fig. 2). The reason is that the field induced strain of antiferroelectric to ferroelectric phase transformation is not only due to a structural deformation, but also related with a reorientation of domains.[3–5] In an electric field, ferroelectric domains are reorientated in the direction of the applied field. If the ferroelectric to antiferroelectric phase transformation occurs, antiferroelectric domains remain orientated. For the subsequent switching process less energy is required for domain reorientation. After approximately 10 switching cycles there is a constant transformation field. Because of the elongation of the ordered antiferroelectric phase into the direction of the electric field, the overall induced strain decreases. Figure 2 shows decreasing strain and transformation field with increasing number of switching processes.

3.3 Temperature

The field induced strain was studied at 20, 50 and 100°C with an electric field of 40 kV/cm. With increasing temperature, Nb-modified PZST of the composition NB1 shows a significant change of the hysteresis loop. Without uniaxial stress, there is a non-reversible antiferroelectric to ferroelectric phase transformation at 20°C. Figure 3 illustrates the ferroelectric hysteresis loop. At 50°C the hysteresis describes an antiferroelectric to ferroelectric switching with remanent strain at zero field (Fig. 4). On the other hand at 100°C there is an ordinary antiferroelectric to ferroelectric switching which leads to an induced strain of only 0·15%.

The previous observation can be explained by the fact that the occurrence of the prevailing phases depends on the temperature. That means the phase boundary is shifted with the temperature and thus the energy necessary to transform one phase into the other must be different at different temperatures. Simultaneously the effect of non-reversible switching, which is observed for compositions near the phase boundary, disappears.

The non-reversible antiferroelectric to ferroelectric switching is known as the shape memory effect.[3] There are two kinds of shape memory behaviour. In the first case, a slightly reverse bias field is required for recovering the strain (Fig. 4). In the second case the ferroelectric state exists during the following cycles of the electric field (Fig. 3). Both effects are temperature dependent and disappear with increasing temperature. This can be explained by the temperature dependence of the AFE–FE phase equilibrium. An increasing temperature favours the antiferroelectric phase of Nb-modified PZST. The reason is that the phase equilibrium is shifted to higher Ti-concentrations.[5,6]

The Curie temperature of the composition NB1 is 160°C. This was determined by the measurement of the temperature dependence of the dielectric

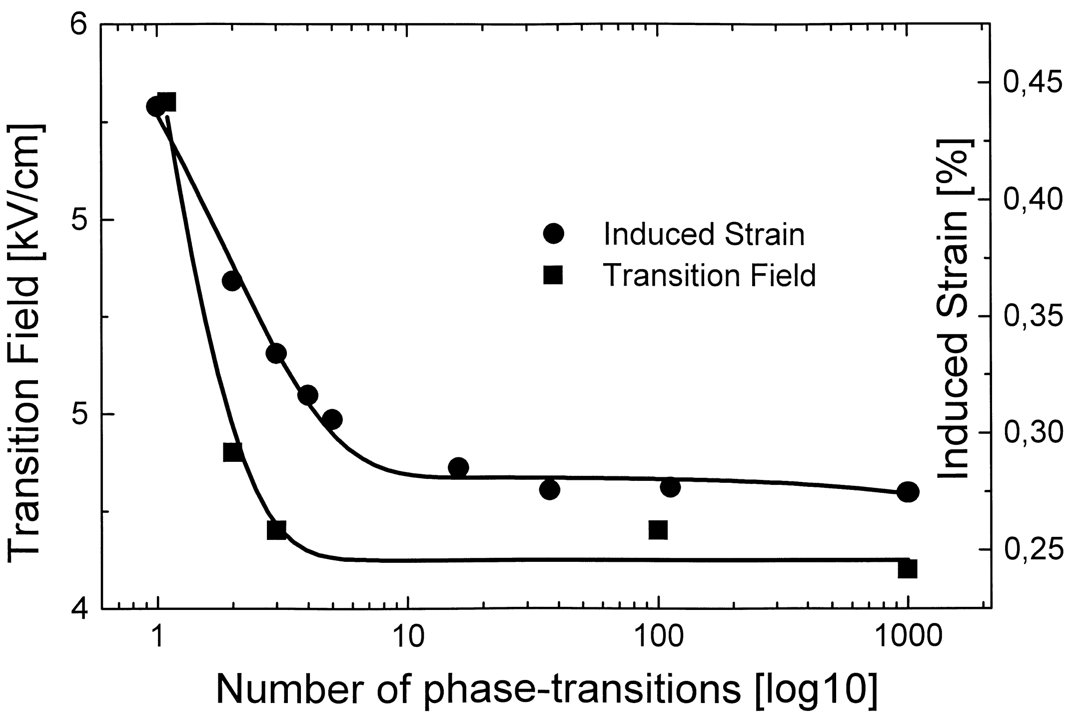

Fig. 2. Cyclic switching of PZST (LA1).

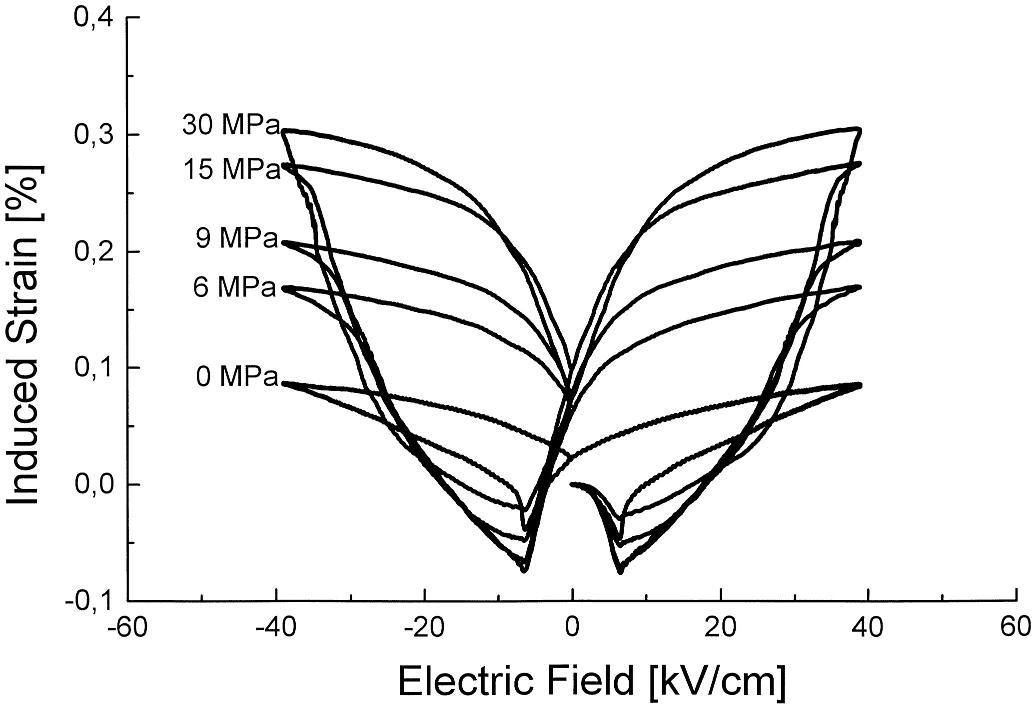

Fig. 3. Induced strain for various electric fields, Nb-modified PZST (NB2), 85°C.

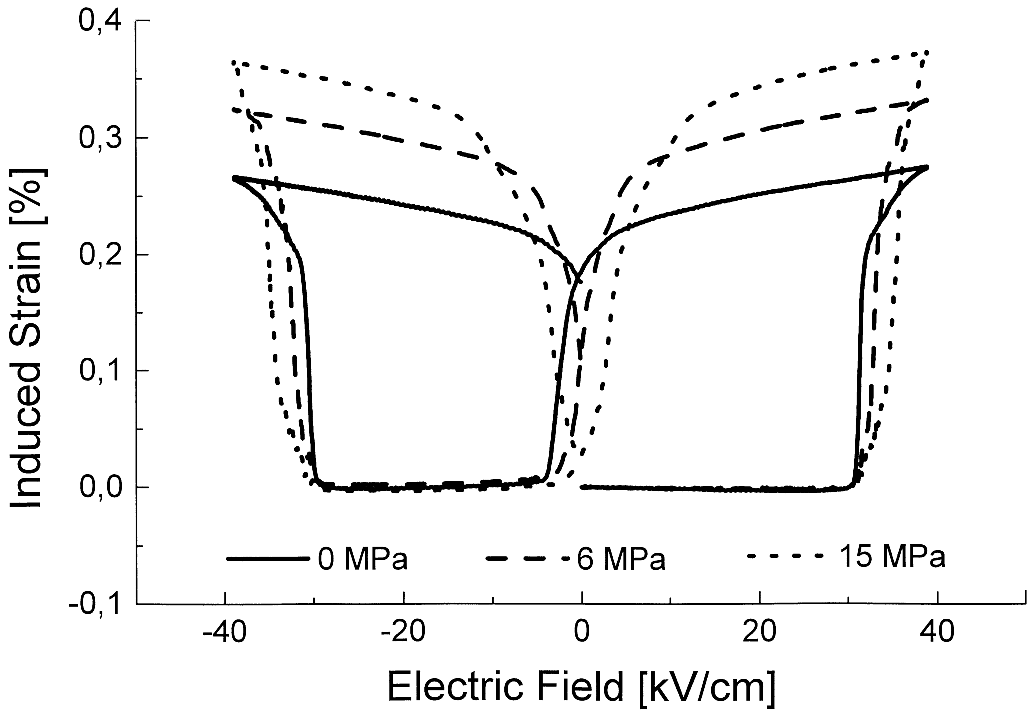

Fig. 4. Hysteresis loops of the induced strain for Nb-modified PZST (NB1), 50°C.

constant. Nevertheless, the induced strain is only 0·15% at 100°C. This is due to the increasing transformation field, which is necessary at a higher temperature. The influence of the electric field on the induced strain is demonstrated in Fig. 5 for the composition NB2. The La-modified PZST of the composition LA1 shows antiferroelectric to ferroelectric switching at 20, 50 and 100°C. With an electric field of Eappl = 45 kV/cm, an increasing temperature reduces the strain from almost 0·4 to 0·3%. Simultaneously the hysteresis gets smaller. The increasing transformation field E_{FE-AFE} is related to an increasing atomic mobility.

3.4 Uniaxial mechanical stress

Compressive stress favours the antiferroelectric phase. The crystal structure of antiferroelectric PZST is tetragonal and the volume of a primitive cell is smaller than the volume of a rhombohedral cell.[1,2,7] An uniaxial compressive stress can transform the ferroelectric phase into the antiferroelectric state. Figure 3 shows the hysteresis of the induced strain for NB1 at 20°C. Without prestress the hysteresis loop looks like that of a ferroelectric material. With increasing uniaxial stress the field induced strain is increasing too. Then the character of the hysteresis loop changes to an antiferroelectric–ferroelectric switching type.

This shows that pre-stress can transform the ferroelectric phase into the antiferroelectric state. After that an electric field can transform the mechanically induced antiferroelectric phase back into the ferroelectric state.

In the same way as described before, the decreasing remanent strain in Fig. 4 can be explained by a mechanically induced ferroelectric to antiferroelectric phase transformation. This is because the remanent strain is caused by the occurrence of the ferroelectric state at zero field ($E = 0$). This remanent strain does not disappear at once. For polycrystalline materials, the stress induced transformation is a gradual process, which leads to the coexistence of antiferroelectric and ferroelectric domains in the material.

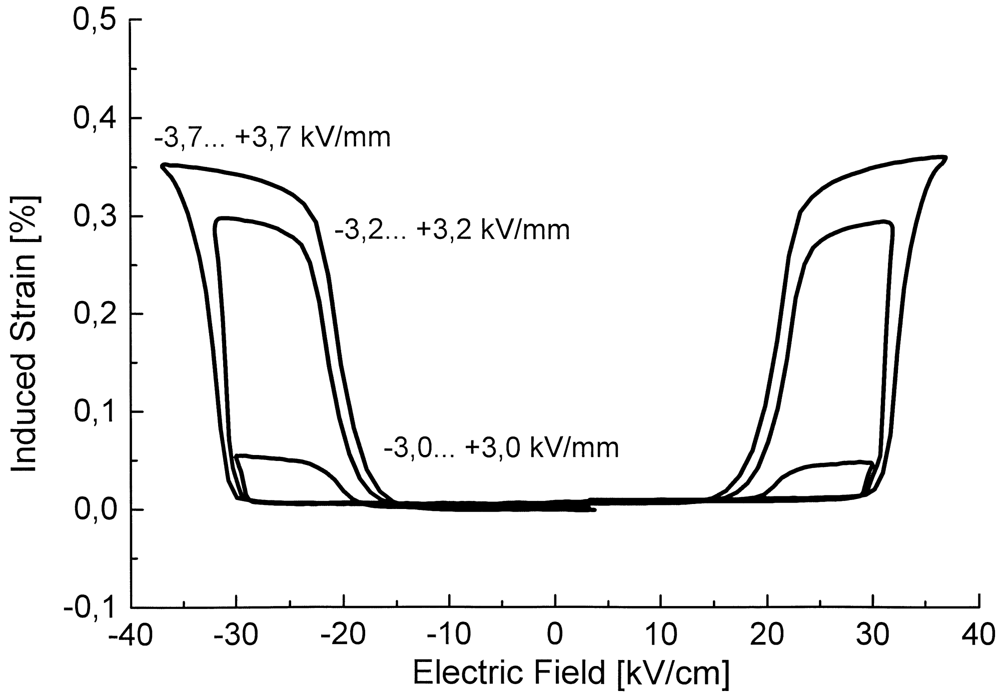

Fig. 5. Hysteresis loops of the induced strain for Nb-modified PZST (NB1), 20°C.

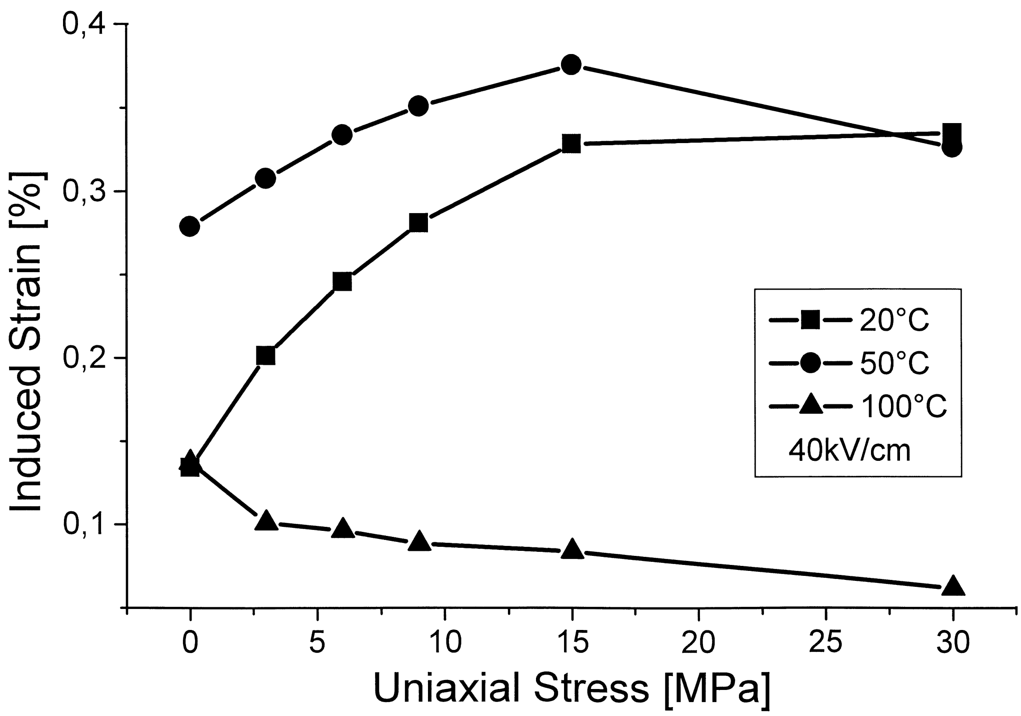

Fig. 6. Uniaxial stress—temperature dependence of the induced strain for Nb-modified PZST (NB1).

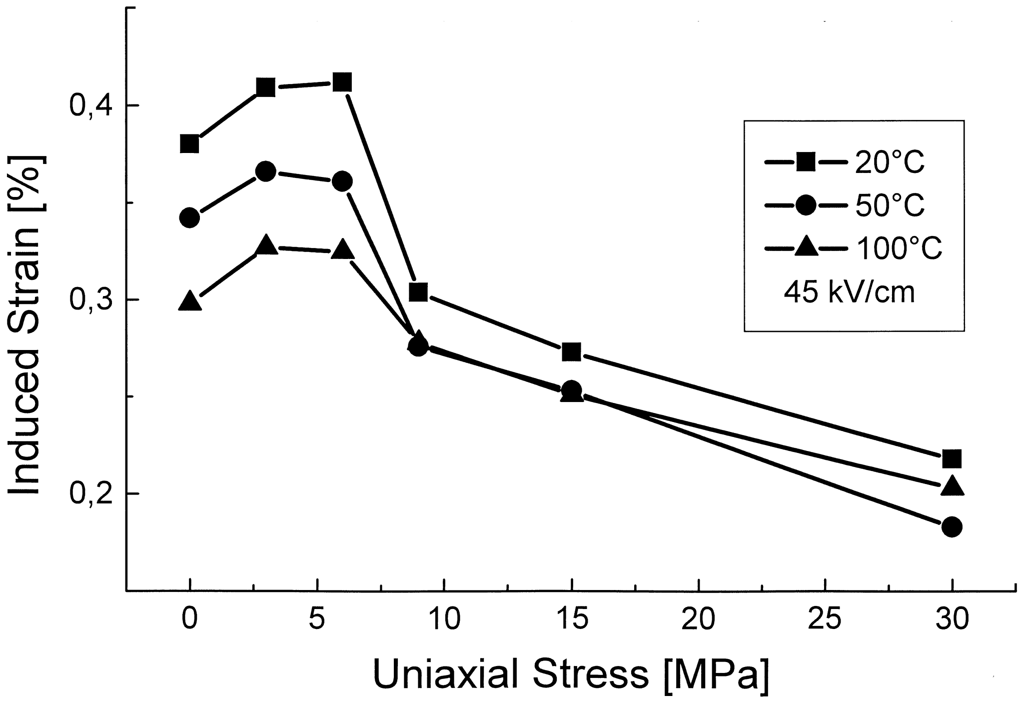

Fig. 7. Uniaxial stress–temperature dependence of the induced strain for La-modified PZST (LA1).

The overall field induced strain increases with increasing prestress as can be seen in Fig. 4. This is due to the deorientation of antiferroelectric domains. The domains are now orientated perpendicular to the direction of the mechanical stress. A 90° antiferroelectric domain deorientation and elastic deformation is observed.[8] It is known that the field induced antiferroelectric to ferroelectric transformation of a compressive-deformed sample requires more electric energy. In addition, the compressive deformation of a sample in the AFE state is responsible for the larger dimensional change during tetragonal–rhombohedral switching. The induced strain is higher than without prestress.

Figures 6 and 7 show the induced strain under uniaxial stress conditions in combination with temperature.

4 Conclusions

For the compositions under consideration, the antiferroelectric to ferroelectric phase transformation results in a strain of a maximum value of 0·4%. This depends on the application conditions with respect to prestress and temperature. Although the material is sensitive to stress and temperature, the phase switching is feasible within the temperature range of 20°C to 100°C. This is particularly appropriate for La-modified PZST. Nb-modified PZST shows excellent properties under the condition of an uniaxial stress. The hysteresis loops indicate that the induced strain of samples under uniaxial stress conditions is not only a function of the phase transformation, but also of the reorientation of AFE-domains. So a prestress can effect a gain of the field induced strain. This is due to the deformation of the antiferroelectric phase. Simultaneously the uniaxial stress stabilises the antiferroelectric phase by shifting the phase-equilibrium.

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