

# Electrostriction versus low frequency dielectric dispersion in $\text{PbZrO}_3$ and $\text{PbHfO}_3$ single crystals

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For the antiferroelectric crystals  $\text{PbZrO}_3$  and  $\text{PbHfO}_3$  pure and doped with small amount of  $\text{PbTiO}_3$  the measurements of electrostrictive strain  $e$  have been performed in paraelectric phase as a function of temperature, frequency (40–400 Hz) and strength (100–700 kV/m) of an applied electric field. In particular, compliance with quadratic relation between strain  $e$  and the electric field  $E$  ( $e = ME^2$ ) in different frequency regions was examined. The observed effects for  $\text{PbZrO}_3$  and  $\text{PbHfO}_3$  were compared and discussed with previously investigated low frequency dielectric dispersion found in those antiferroelectric materials. The experiments showed that in the frequency range where the dipolar relaxation exists, the departure from the quadratic relation ( $e = ME^2$ ) can be clearly observed for  $\text{PbZrO}_3$  and PZT single crystals. In all investigated single crystals ( $\text{PbZrO}_3$ , PZT and  $\text{PbHfO}_3$ ) the dependence of strain versus electric field obeys the electrostrictive relation in the frequency range below and above dielectric relaxation observed. For frequencies beyond dielectric dispersion the electrostrictive coefficients  $Q_{11}$  for all samples are temperature independent and take values typical for ferroelectric and antiferroelectric materials (i.e.  $Q_{11} \cong 2 \times 10^{-2} - 3 \times 10^{-2} \text{ m}^4/\text{C}^2$ ). © 2001 Kluwer Academic Publishers

## 1. Introduction

Low frequency dielectric dispersion is a phenomenon seen in a wide class of dielectric materials. It seems to be well established that the mechanism connected with it is mainly due to hopping of ionic charge carriers. Usually a source of the dispersion is ascribed to mobile charge carriers behaviour in sample volume, on the surface or across interfaces. In many cases the dispersion cannot be described by ideal Debye or Dissado-Hill response and is characterised most often using empirical functions like Cole-Cole, Cole-Dawidson, Havriliak and Negami or simple power laws ( $\chi \sim \omega^n$ ) with fractional exponent  $n$  [1]. While the functions are useful mathematical formulas to fit experimental data, the most important task is to find what physical mechanisms stand behind a dielectric dispersion. It seems that for the  $\text{ABO}_3$  oxidic perovskites this question still can be considered as a current one. Especially it is interesting in case of the antiferroelectric materials undergoing structural phase transitions and at the same time having no macroscopic polarisation.

Recently, strong low frequency relaxations in the frequency 10 Hz–1 MHz have been found in model antiferroelectric  $\text{PbZrO}_3$  and  $\text{PbHfO}_3$  single crystals [2, 3]. While in the lead zirconate only one dispersion in the range 10 Hz–20 kHz of almost ideal Debye character has been detected, the lead hafnate revealed two well-

separated strong dispersions below 1 MHz. In both materials, in spite of distinct development in technological process in last years, it is very difficult to get a stoichiometric compound. Consequently it is hard to avoid lattice defects especially in the lead and oxygen sub-lattices. In the literature data, it is well established that just these defects are responsible for low frequency relaxation observed in the investigated antiferroelectrics  $\text{PbZrO}_3$  and  $\text{PbHfO}_3$ . Fact that, similar kind of relaxations have also been detected in the crystals in which Ti ions were introduced in place of Zr supports the previous statement [3]. Details of the frequency dependencies of the real and imaginary part of the electric susceptibility can be found in papers [3, 4].

It was decided to investigate the electrostriction in the paraelectric phase (Pm3m) of the antiferroelectric materials  $\text{PbZrO}_3$  and  $\text{PbHfO}_3$  pure and doped with small amount of  $\text{PbTiO}_3$  since this is a non-linear universal effect, in particular always existing in phase with centre of symmetry and - what is the most important - related to the mechanical deformations (vibrations) of the sample. Because the appearance of polar properties of crystal lattice is connected with atomic displacements this investigations may help to understand physical mechanisms responsible for huge dielectric relaxations not only near the phase transition.

## 2. Theoretical remarks

Electrostrictive effect appears independently on crystal symmetry and follows from the second power dependence of the mechanical deformation on the electric field. The total deformation of a sample placed in an electric field can be described by the following equation [5, 6]:

$$e_{jk} = d_{ijk}E_i + M_{iljk}E_iE_l \quad (1)$$

where  $e_{jk}$  is the strain tensor and  $E_i, E_l$  - the components of electric field vector. The first term of the right side describes the linear piezoelectric effect which, disappears if centre of symmetry is present.  $d_{ijk}$  is the first derivative  $\frac{\partial e_{jk}}{\partial E_i}$  for infinitely weak fields. The second term describes the electrostrictive effect in which the  $M_{iljk}$  is equal to  $\frac{\partial^2 e_{jk}}{\partial E_i \partial E_l}$ . Coefficients  $M_{iljk}$  create fourth order tensor which is symmetrical in relation to  $i$  and  $l$  such as  $j$  and  $k$ . In crystals with point group possessing centre of symmetry the deformation is of pure electrostrictive character and can be then written as:

$$e_{jk} = M_{iljk}E_iE_l \quad (2)$$

or

$$e_{jk} = Q_{iljk}P_iP_l$$

where  $P$  denotes polarisation. For the cubic symmetry of Pm3m when no external stresses are present, the tensor  $Q_{iljk}$  has the independent components  $Q_{1111}, Q_{2211} = Q_{1122}$  and  $Q_{1212}$ . Substituting  $Q_{1111} = Q_{11}, Q_{1122} = Q_{2211} = Q_{12}$  and  $Q_{1212} = Q_{44}$  we can write one of the Equations 2 in the following contracted form:

$$\begin{pmatrix} e_{11} \\ e_{22} \\ e_{33} \\ e_{23} \\ e_{31} \\ e_{21} \end{pmatrix} = \begin{pmatrix} Q_{11} & Q_{12} & Q_{12} & & & \\ Q_{12} & Q_{11} & Q_{12} & & & \\ Q_{12} & Q_{12} & Q_{11} & & & \\ & & & Q_{44} & & \\ & & & & Q_{44} & \\ & & & & & Q_{44} \end{pmatrix} \times \begin{pmatrix} P_1^2 \\ P_2^2 \\ P_3^2 \\ P_2P_3 \\ P_3P_1 \\ P_2P_1 \end{pmatrix} \quad (3)$$

The most commonly measured are longitudinal  $x_{11}(x_1)$  strains:

$$e_{11} = Q_{11}P_1^2 \quad (4)$$

and similarly

$$e_{11} = M_{111}E_1^2 \quad (5)$$

The measurements of the electrostrictive coefficients  $Q_{11}$  and  $M_{11}$  enables the calculation of the value of the electric permittivity  $\varepsilon_{11}$ . Taking into account the relation  $P_1 = \varepsilon_0\varepsilon_{11}E_1$  and Equations 4 and 5 one obtains

that

$$M_{11} = (\varepsilon_0\varepsilon_{11})^2 Q_{11}. \quad (6)$$

Thus from independently determined coefficients  $Q_{11}$  and  $M_{11}$  the electric permittivity  $\varepsilon_{11}$  can be easily calculated.

## 3. Experimental setup

Electrostrictive strain  $e_1$  was caused by alternating electric field of frequency  $f$  and strength  $E$  applied perpendicular to the sample surface. The mechanical vibrations of frequency  $2f$  induced by this field were measured using in the frequency range 40–400 Hz. The values of coefficient  $Q_{11}$  could be easily calculated knowing the value of polarisation  $P_1$ , corresponding to applied electric field of strength  $E_1$  (Equation 4). The  $P_1$  was measured simultaneously with the measurements of the strain  $e_1$  by means of well known Sawyer-Tower system.

According to Equation 5 the magnitude of electrostrictive strain  $e_1$  should be a quadratic function of electric field strength. To determine the coefficient  $M_{11}$  a dependence  $e_1(E_1)$  was thus measured.

An electric field of amplitude  $E_1$  and frequency  $f$  was applied to the sample. In a sufficiently strong electric field of strength  $E = E_1 \sin \omega \cdot t$ , electrostrictive vibrations of the sample proportional to  $E_1^2 \sin^2 \omega \cdot t$  and cause a change in distance between the plates of the coupled measurement condenser and hence a change of its capacity. The strength of electric field was limited in this experiment to  $10^6$  V/m to protect the sample from the electric break-down. To measure value of  $e_1$  of the electrostrictive vibrations of the tested sample the measurement condenser  $C$  was connected up to a resistance  $R$  and a constant voltage source  $U$  (Fig. 1). Electrostrictive vibrations of the sample cause variations in charge of the condenser  $C$  and an alternating current  $I = dq/dt$  then flows in circuit RC with. The magnitude of strain  $e_1$  was calculated on the basis of potential drop at resistance  $R$  measured with a selective nanovoltmeter.

$$e_1 = \frac{l_0}{d_0} \frac{U_x}{\omega RUC_0} \quad (7)$$

where  $l_0$  is the distance between measurement condenser plates when sample is not vibrating,  $d_0$  is the thickness of the sample and  $C_0$  – the capacity of the measurement condenser when there are no electrostrictive vibrations.

Further details of measurement of the electrostrictive strain are described in paper by Roleder [6].

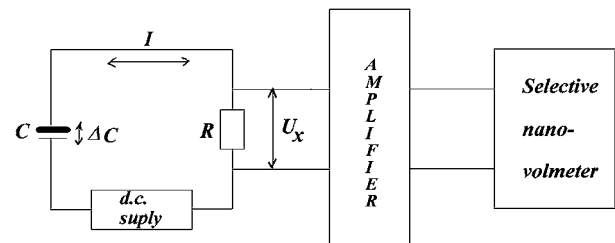


Figure 1 Measurement system for determining magnitude of electrostrictive strain [6].

#### 4. Experimental results

The flux grown crystals  $\text{PbHfO}_3$ ,  $\text{PbHf}_{0.98}\text{Ti}_{0.02}\text{O}_3$ ,  $\text{PbZrO}_3$  and  $\text{PbZr}_{0.97}\text{Ti}_{0.03}\text{O}_3$  in form of thin, as grown plates of dimensions  $3 \times 3 \times 0.05 \text{ mm}^3$  have been used in experiments. The samples were of high quality and polishing of surfaces was not necessary. The opposite faces were electroded using silver paste.

In the  $\text{PbHfO}_3$  and  $\text{PbHf}_{0.98}\text{Ti}_{0.02}\text{O}_3$  two phase transitions are observed. The first one between two antiferroelectric phases ( $A_1$ - $A_2$ , at 443 K) and the second one between antiferroelectric  $A_2$  and paraelectric  $P$  phase at  $T_c = 485 \text{ K}$ . While  $\text{PbZrO}_3$  undergoes one transformation at about 500 K, in the  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  with small Ti content a transient ferroelectric phase just below  $T_c$  appears. More information about phase transitions in the investigated samples can be found in [8]. Because of the as-grown crystal habit, only the longitudinal  $e_1$  strain was measured and thus  $Q_{11}$  and only  $M_{11}$  coefficients were calculated.

#### 5. Strong low frequency electrostrictive strain in $\text{PbZrO}_3$ and $\text{PbZr}_{0.97}\text{Ti}_{0.03}\text{O}_3$ single crystals

Measurements of electrostriction for pure  $\text{PbZrO}_3$  were made previously and are reported in paper [9]. It was demonstrated that the low frequency relaxation has a marked influence both on the value of induced polarisation and electrostrictive strain. The strong increase of  $P_1$  and  $e_1$  below 100 Hz corresponds to the strong increase of the dielectric permittivity due to the dispersion process found. It should be noted that for frequencies from the relaxation region, departure from the quadratic relation (5) was observed. Similar behaviour has revealed for the  $\text{PbZr}_{0.97}\text{Ti}_{0.03}\text{O}_3$  single crystal (Fig. 2). At given temperature this departure depended on the frequency of the electric field inducing electrostrictive strain with respect to the relaxation time. For example, close to  $T_c$  the frequency 300 Hz lies outside the dispersion region and thus the departure is absent. However, at higher temperatures, the relaxation time diminishes and at the same measuring frequency, a stronger deviation of the theoretical line from the experimental points is observed. This behaviour is shown in the inset in Fig. 2. Hence, one can conclude that in the samples under consideration the changes of the electrostrictive deformation are strictly connected with the low frequency relaxation.

#### 6. Dielectric relaxations and electrostriction in $\text{PbHfO}_3$ and $\text{PbHf}_{0.98}\text{Ti}_{0.02}\text{O}_3$

Different behaviour of the electrostrictive effect and dielectric properties than that existing in the  $\text{PbZrO}_3$  and  $\text{PbZr}_{0.97}\text{Ti}_{0.03}\text{O}_3$  was observed for single crystals of the lead hafnate  $\text{PbHfO}_3$  and lead hafnate doped by small amount of the lead titanate  $\text{PbTiO}_3$  -  $\text{PbHf}_{0.98}\text{Ti}_{0.02}\text{O}_3$ . For lead hafnate in the range of 10 Hz–1 MHz the frequency dependence of the imaginary part of the capacitance equivalence of the complex permittivity is presented in Fig. 3. This quantity was used since in the problem of low frequency dielectric relaxation the relevant geometry of the sample in fact is not known i.e. the formula  $\epsilon' = (C * d)/(\epsilon_0 * S)$ , where  $C$  is ca-

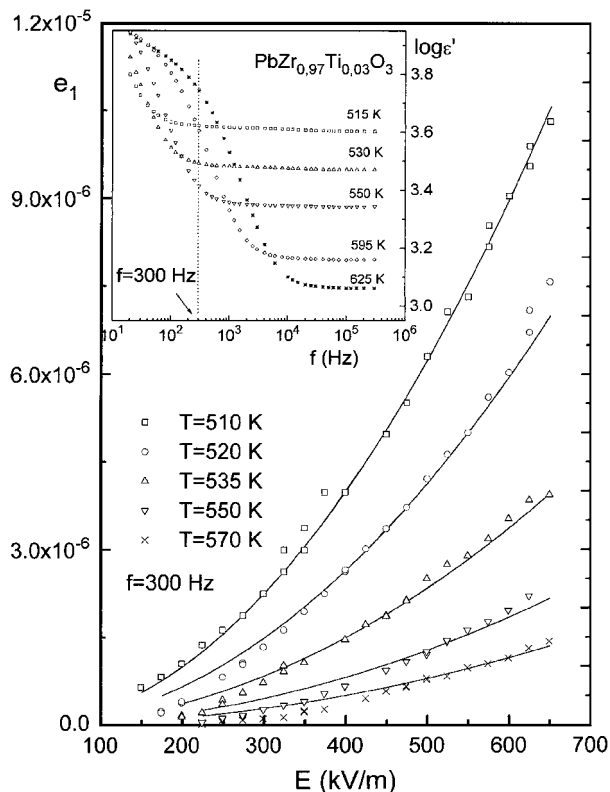


Figure 2 Strain as a function of electric field strength for the  $\text{PbZr}_{0.97}\text{Ti}_{0.03}\text{O}_3$  single crystal measured at different temperatures in the paraelectric phase and at the frequency 300 Hz. Solid lines in the figure represent the fit of the  $e_1 = M_{11} E_1^2$  relation to the experimental points. Inset shows the frequency dependence of the real part of  $\epsilon'$  of the electric permittivity.

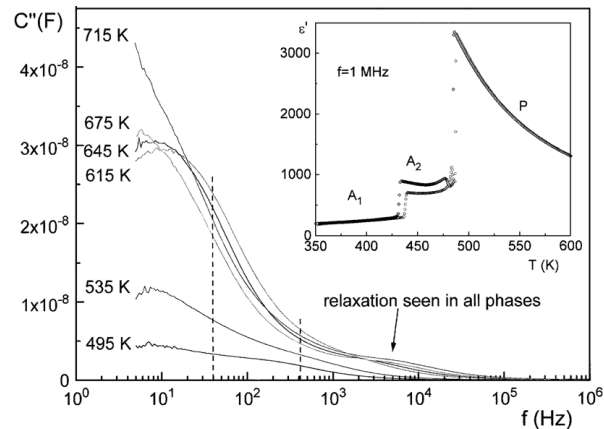


Figure 3 Temperature/frequency evolution of the imaginary part of the capacitance ( $C''$ ) measured for  $\text{PbHfO}_3$  in the paraelectric phase. Inset presents temperature dependence of the  $\epsilon'$  phase transitions in  $\text{PbHfO}_3$ .

pacitance,  $\epsilon_0$  - vacuum susceptibility,  $d$  - thickness of sample and  $S$  surface of electrodes, lead to a huge value of the electric susceptibility. In particular, the  $S$  value is difficult to calculate because the intimate contact with metallic electrode is not flat. Reason for that is not only non-perfect polishing or a process of deposition of electrodes but also electromechanical processes taking place near surface of crystal [10].

Two relaxations can be recognised in Fig. 3. The first one seen at frequency range of 10 kHz is a relaxation of nearly monodispersive character which well obey Arrhenius law. Since dielectric step was independent on temperature up to about  $300^\circ\text{C}$  and then decreased

with increasing temperature it can come from an accumulation of charges at the vicinity of electrodes. This kind of charge accumulation may lead to appearance of relaxing “large” dipole, as if the sample is macroscopically polarised. This relaxation was observed at each phase of the materials under consideration.

The second relaxation seen in Fig. 3 below 100 Hz starts to play important role just at higher temperatures. This effect is related with response of mobile space charges in the bulk of sample to external alternating electric field. This relaxation appears to be of distinct polydisperse character. Moreover around frequency 6 Hz some deviations of the  $C''(f)$  run from Debye-like shape could be interpreted as due to electrochemical processes. More information about parameters of the relaxations observed can be found in [4].

Measurements of the electrostriction phenomena in the frequency range indicated in the Fig. 3 showed that the electrostrictive strain is not correlated to any of the observed relaxations. For both samples the  $e_1(E_1)$  function well obeys quadratic relation (Fig. 4) and polarisation  $P_1$  does not depend on frequency (Fig. 5). It is important that values of the electric susceptibility calculated directly from capacity compensated linear  $P_1(E_1)$  dependence - related to the frequency 40–400 Hz and strong electric field of strength of the order of  $10^6$  V/m - were comparable with those found from the  $\varepsilon'(T)$  run at 1 MHz and much weaker electric field strength  $0.02 \cdot 10^6$  V/m. Having measured mechanical strain  $x_1$  it was possible to determine the electrostrictive coefficients  $Q_{11}$  which dependencies are presented in

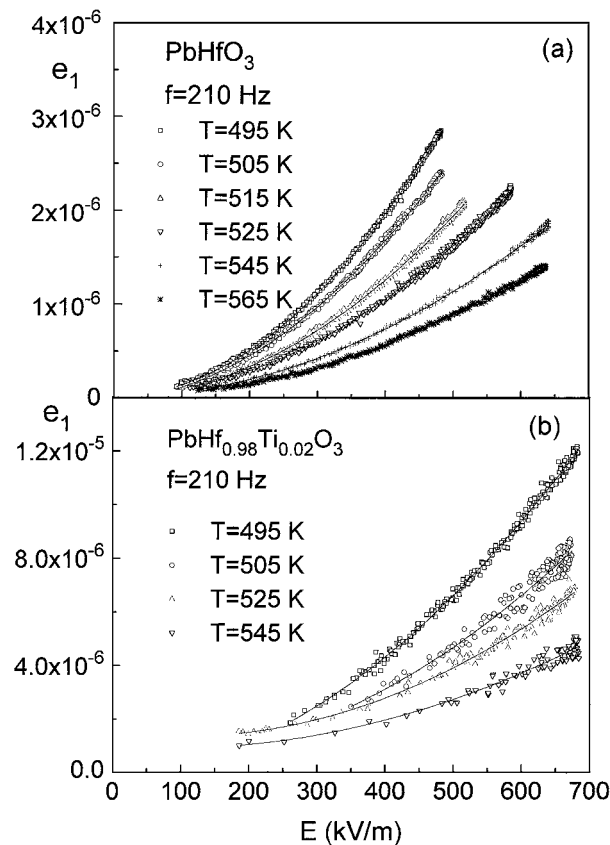


Figure 4 Strain as a function of electric field at frequency 210 Hz for  $\text{PbHfO}_3$  (a) and  $\text{PbHf}_{0.98}\text{Ti}_{0.02}\text{O}_3$  (b) and at different temperatures in the paraelectric phase. Solid lines represent the fit to the relation  $e_1 = M_{11}E_1^2$ .

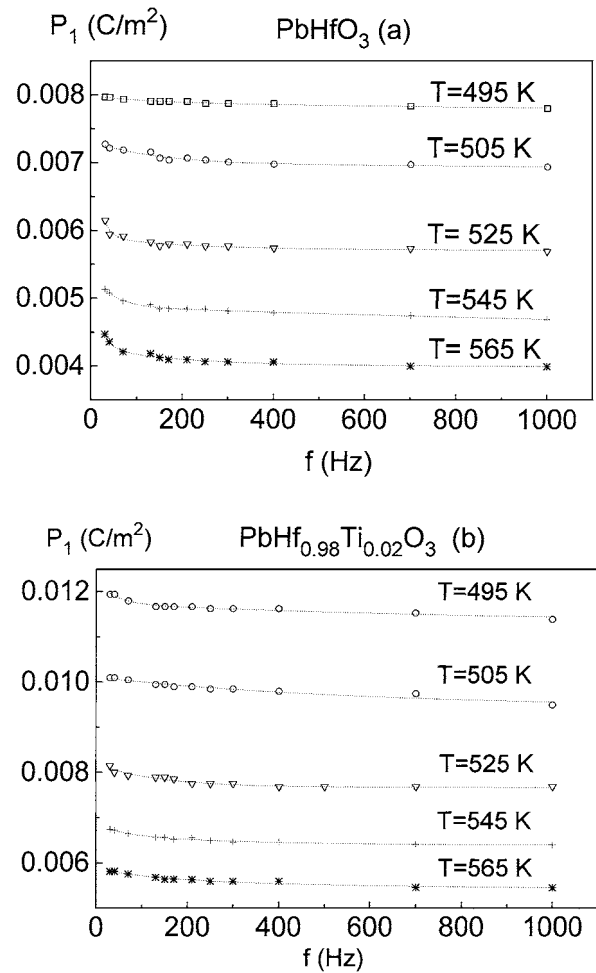


Figure 5 Temperature-frequency dependence of the dielectric polarization  $P_1$  for  $\text{PbHfO}_3$  (a) and  $\text{PbHf}_{0.98}\text{Ti}_{0.02}\text{O}_3$  (b) measured in Sawyer-Tower setup at the electric field strength  $E = 10^6$  V/m.

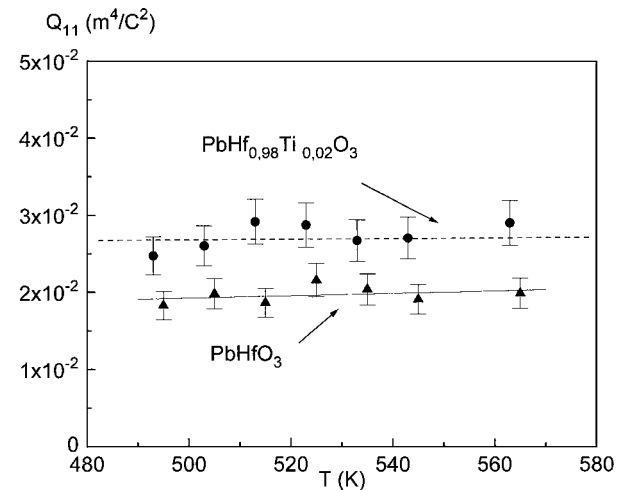


Figure 6 Temperature dependence of the electrostrictive coefficients  $Q_{11}$  in the paraelectric phase measured at electric field frequency 210 Hz for  $\text{PbHfO}_3$  and  $\text{PbHf}_{0.98}\text{Ti}_{0.02}\text{O}_3$  single crystals.

Fig. 6 as a function of temperature. According to theoretical predictions, the coefficient  $Q_{11}$  for both samples is temperature independent and it takes values typical for ferroelectric materials of perovskite type [11]. Moreover the  $M_{11}(T)$  dependence has the same type of anomaly as the electric permittivity above transition point from the antiferroelectric to paraelectric phase (Fig. 7).

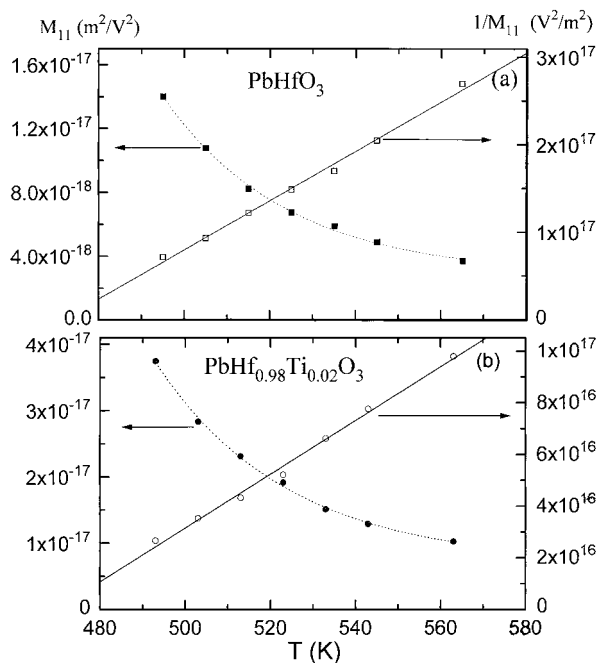


Figure 7 Temperature dependencies of the electrostrictive coefficient  $M_{11}$  and its inverse  $1/M_{11}$  in the paraelectric phase measured at electric field frequency 210 Hz for  $\text{PbHfO}_3$  (a) and  $\text{PbHf}_{0.98}\text{Ti}_{0.02}\text{O}_3$  (b) single crystals.

## 7. Discussion

Near the phase transition point in the lead hafnate, the coefficients  $Q_{11}$  and  $M_{11}$  takes the following values:  $Q_{11} = 2 \times 10^{-2} \text{ m}^4/\text{C}^2$  and  $M_{11} = 1.4 \times 10^{-17} \text{ m}^2/\text{V}^2$  (see Figs 6 and 7). The value of  $Q_{11}$  is similar to that found for lead zirconate and other perovskite ferroelectrics and antiferroelectrics using other experimental methods [12]. It means that the measured strain  $x$  fully corresponds to polarisation  $P$ , which was measured in Sawyer-Tower set-up. Thus directly from the relation  $P_1 = \epsilon_0 \epsilon_{11} E_1$  or introducing the values  $Q_{11}$  and  $M_{11}$  to relation (6) one gets that  $\epsilon_{11}$  is nearly 3000 which is of the same order as that obtained from temperature dependence of the electric permittivity in  $\text{PbHfO}_3$  at 1 MHz (see inset in Fig. 3). It proves once again that the strong low frequency dielectric relaxation does not influence changes of the electrostrictive strain and origin of this relaxation comes from the mobile (hopping) ionic charges having no contribution to mechanical deformation of crystal lattice.

Questions arise as to why in case of the lead zirconate crystals the electrostrictive strain was affected by the low frequency dielectric relaxation observed. We believe that this is connected with the concentration of point defects i.e. vacancies in the Pb and O sublattice. If the concentration is not high, the crystal is still rigid enough that movement of this kind of defects in an external electric field strongly influences the global lattice deformation induced. Hence if the measuring frequency of the electrostrictive strain was near the dispersion region there was clear discrepancy from the power 2 in the relations (4). For strongly defected crystals mobile defects (hopping ions) can move without disturbances of surrounding lattice, even at high electric field strengths. This leads to the low frequency dispersion with high electric conductivity accompanying normal mechanical

lattice deformation. The Sawyer-Tower set-up having the possibility to compensate the conductivity allowed to determine induced polarisation connected with independently measured mechanical strain. This would account for the behaviour of electrostrictive strain in lead hafnate in which the stoichiometry is more difficult to attain than in lead zirconate.

In case of  $\text{PbHfO}_3$  single crystal a second dielectric relaxation registered at higher frequency range was also observed and attributed to surface layer (Fig. 3) [13]. This relaxation, in our opinion does not influence the electrostriction, because from one hand the measuring frequency of electrostrictive strain lied beyond this relaxation area and on the other hand it is difficult to suppose that "thin" surface layer would have a considerable contribution to the total strain.

In our recent paper on the dielectric spectroscopy in the  $\text{PbHfO}_3$ , mechanisms responsible for peak of  $\epsilon$  at  $T_c$  were considered [13]. In the frequency range  $10^6$ – $10^9$  Hz a polar relaxation mode has been found and associated with a disorder in the Pb sublattice. Because of this disorder there are clusters in crystal lattice with correlated Pb displacements which behaviour in an  $ac$  electric field is responsible for this relaxation. Its dielectric strength constitutes almost the whole peak of the  $\epsilon \sim 3000$  at  $T_c$ . As we shown here from the electrostrictive strain investigations the same value of  $\epsilon$  has been found. It would thus mean that mechanical reorientation of such polar clusters (dipoles), which also takes place at doubled frequency as that of the electric field applied, should account for the electrostrictive properties in the paraelectric phase of investigated antiferroelectrics.

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