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DIELECTRIC PROPERTIES OF $Pb(Fe_{1/2}Ta_{1/2})O_3$ CERAMICS OVER 70–300 K TEMPERATURE RANGE

K. Bormanis [a], A. Kalvane [a], A.I. Burkhanov [b], and A.M. Serezhkin [b]

[a] *Institute of Solid State Physics, University of Latvia, Riga, Latvia*

E-mail: bormanis@cfi.lu.lv

[b] *Volgograd State Architectural and Engineering University, Volgograd, Russia*

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The studies of dielectric response in ferromagnetic lead ferrotantalate $Pb(Fe_{1/2}Ta_{1/2})O_3$ are reported over a wide range of temperature under the applied bias field. The features of dielectric nonlinearity deduced from behaviour of reverse $\varepsilon'(E_=)$ curves at different temperatures, including regions of ferroelectric phase transition and vicinity of the Néel point, are examined. Obtained results indicate a substantial broadening of the ferroelectric phase transition. The results are discussed with respect to effects of ferroelectric ordering in relaxor materials of such kind.

Keywords: ferroelectrics, ceramics, ferrotantalate, dielectric properties, polarization

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1. Introduction

Materials exhibiting coexisting electric and magnetic ordering are of increasing interest. The interaction between electric and magnetic subsystems allows one to control the magnetic properties of ferroelectric-ferromagnetic materials by the electric field and, conversely, to modify electrical properties by the magnetic field, thus making this multiferroics appealing to basic and applied research. A large group of these materials have the ABO_3 perovskite structure containing magnetic ions. Lead ferrotantalate $PbFe_{1/2}Ta_{1/2}O_3$ (PFT) is one of the group. The compound is a ferroelectric exhibiting a diffuse phase transition. An antiferromagnetic ordering occurs at low temperatures [1–3]. Despite rather abundant studies of the material, a number of questions concerning physical properties (such as regularities of the effect of structural disorder on phase transitions in the magnetic subsystem) are still waiting for answer.

The purpose of the present study is to obtain experimental data on dielectric response of PFT ceramics to low and infra-low frequencies over a range of temperatures, including ferroelectric and antiferromagnetic phase transitions (PT) and the dielectric nonlinearity under conditions of a strong bias field.

2. Experiment

The $PbFe_{1/2}Ta_{1/2}O_3$ (PFT) ceramics was obtained by a conventional ceramic technology. The lead ferrotantalate powder was synthesized from the corresponding oxides by solid phase thermal chemical reactions. The initial material was homogenised in ethanol in agate ball mills for 24 h, dried and calcinated at 1000 °C for 1 h after which repeatedly calcinated for 4 h at the same temperature. The structure of ceramics was sintered at 1150 °C for 1 h, after grinding and cold-pressing the obtained substance was 95% perovskite. The samples of the PFT ceramics for dielectric measurements were prepared of the size of $8 \times 6 \times 0.5$ mm^3 and supplied with silver electrodes fired at 700 °C.

A bridge set-up providing connection to the bias field $E_=$ was used to measure the complex dielectric permittivity $\varepsilon^* = \varepsilon' + i\varepsilon''$ in a 1–1000 Hz frequency range at low electric field intensities $E_o < 5$ V/cm. Measurements were performed in the range of liquid nitrogen to room temperatures. The real part of dielectric permittivity $\varepsilon'(E_=)$ was measured at weak fields E_o of 1 kHz frequency with the bias field being applied by steps during the measurements.

3. Results and discussion

The ferroelectric phase transition in $PbFe_{1/2}Ta_{1/2}O_3$ (Fig. 1) is seen as a broad peak at T_m on the $\varepsilon'(T)$ curve (220 K < T_m < 270 K). The broadening of the ferroelectric phase transition may be related to local fluctuations of composition [1], the PT being observed without any relaxor shift (Fig. 1).

The thermal behaviour of the real and imaginary components of the dielectric response $\varepsilon'(T)$ and $\varepsilon''(T)$ were studied at frequencies of 1, 10, 100, and 1000 Hz. The thermal range below T_m includes

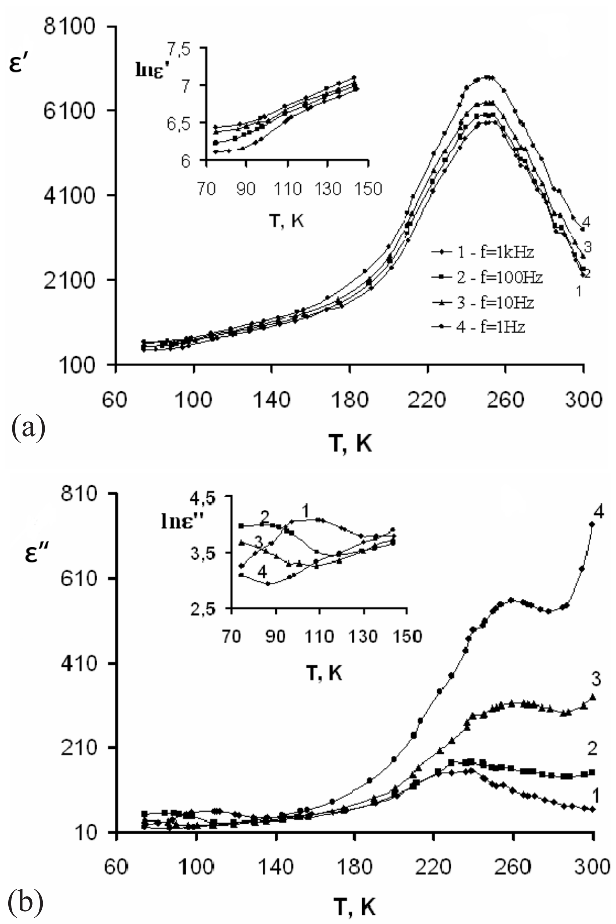

Fig. 1. Thermal behaviour of the real ε' and imaginary ε'' components of dielectric permittivity in the $Pb(Fe_{1/2}Ta_{1/2})O_3$ ceramics at frequencies of (1) 1000 Hz, (2) 100 Hz, (3) 10 Hz, and (4) 1 Hz.

the Néel temperature T_N as estimated in the studies of other authors to be 180 K [1, 3].

As to the character of $\varepsilon'(T)$ at $T \ll T_m$, a small deviation from monotonicity in $\varepsilon'(T)$ is seen below $T \approx 110$ K in the form of a "shoulder". The relaxation of the anomaly, a shift of the "shoulder" to lower temperatures with decreasing frequency are shown in the inset in Fig. 1(a), where the values of ε' are presented in the logarithmic scale.

From the behaviour of the dielectric loss factor $\varepsilon''(T)$ at the ferroelectric PT (Fig. 1(b)) the anomaly seen as a maximum appears at all frequencies. Thus, at frequencies of 100 Hz and 1 kHz the temperature $T_{m\varepsilon''}$ (corresponding to the maximum on the $\varepsilon''(T)$ curve) is located below T_m, while at frequencies of 1 Hz and 10 Hz the temperature is almost identical to T_m. In the first case, at $T_{m\varepsilon''} < T_m$, the behaviour of the dielectric response at 100 Hz and 1 kHz is characteristic of ferroelectrics with a diffuse phase transition. The reason of temperature $T_{m\varepsilon''}$ at frequencies of 10 Hz and 1 Hz being higher than at higher frequencies is likely to be a contribution of conductivity in the dielectric response of the material almost completely screening the anomaly of $\varepsilon''(T)$ associated with the PT.

The maximums of $\varepsilon''(T)$ with a significant shift in frequency (Fig. 1(b), inset) appear at 77–150 K, where the "shoulder" on $\varepsilon'(T)$ is observed (Fig. 1(a), inset). The growth of $\varepsilon''(T)$ at frequencies of 10 and 1 Hz with decreasing temperature suggests that maximums of $\varepsilon''(T)$ at these frequencies exist as well, possibly being located at still lower temperatures.

The activation energy U of polarization estimated under assumption of the Arrhenius thermal relaxation is expressed by

$$U = \frac{k \cdot T_1 \cdot T_2}{T_1 - T_2} \cdot \ln(\omega_2/\omega_1),$$

where k is Boltzmann constant, T_1 and T_2 are temperatures of maximums of $\varepsilon''(T)$ at the appropriate frequencies ω_1 and ω_2. The activation energy was found to be $U \approx 0.07$ eV. The pre-exponential factor in the Arrhenius equation was estimated to be of the order of $2 \cdot 10^7$ Hz.

A similar low-temperature relaxation is rather frequently observed in ferroelectrics and is associated with "freezing" of domain boundaries [4]. In a number of other materials (e. g. crystals of the potassium–tungsten bronze structure [5, 6]), the low-temperature relaxation is ascribed to manifestation of glass properties. A minimum of dispersion $\Delta\varepsilon(T) = \varepsilon'_{1Hz}(T) - \varepsilon'_{1kHz}(T)$ observed within the range of 70–110 K is due to an abrupt decrease of ε' at 1 kHz, while at the frequency of 1 Hz the value of ε' monotonously decreases down to lower temperatures (Fig. 1, inset). Under the bias field $E_=$, the temperature corresponding to the minimum of $\Delta\varepsilon(T)$ decreases [7]. Since the bias field mainly affects the infra-low part of the dispersion while the "step" at 1 kHz stays in the same position, the minimum of the total decrease of $\Delta\varepsilon(T)$ under the applied bias field must move to a lower temperature.

The effect of field on the dielectric response was studied from the behaviour of the reverse $\varepsilon'(E_=)$ dependence. As follows from Fig. 2, no hysteresis of $\varepsilon'(T)$ is observed at temperatures (294 K) well above T_m indicating the paraelectric phase. Hysteresis appears at temperatures closer to T_m. Such a nonlinear

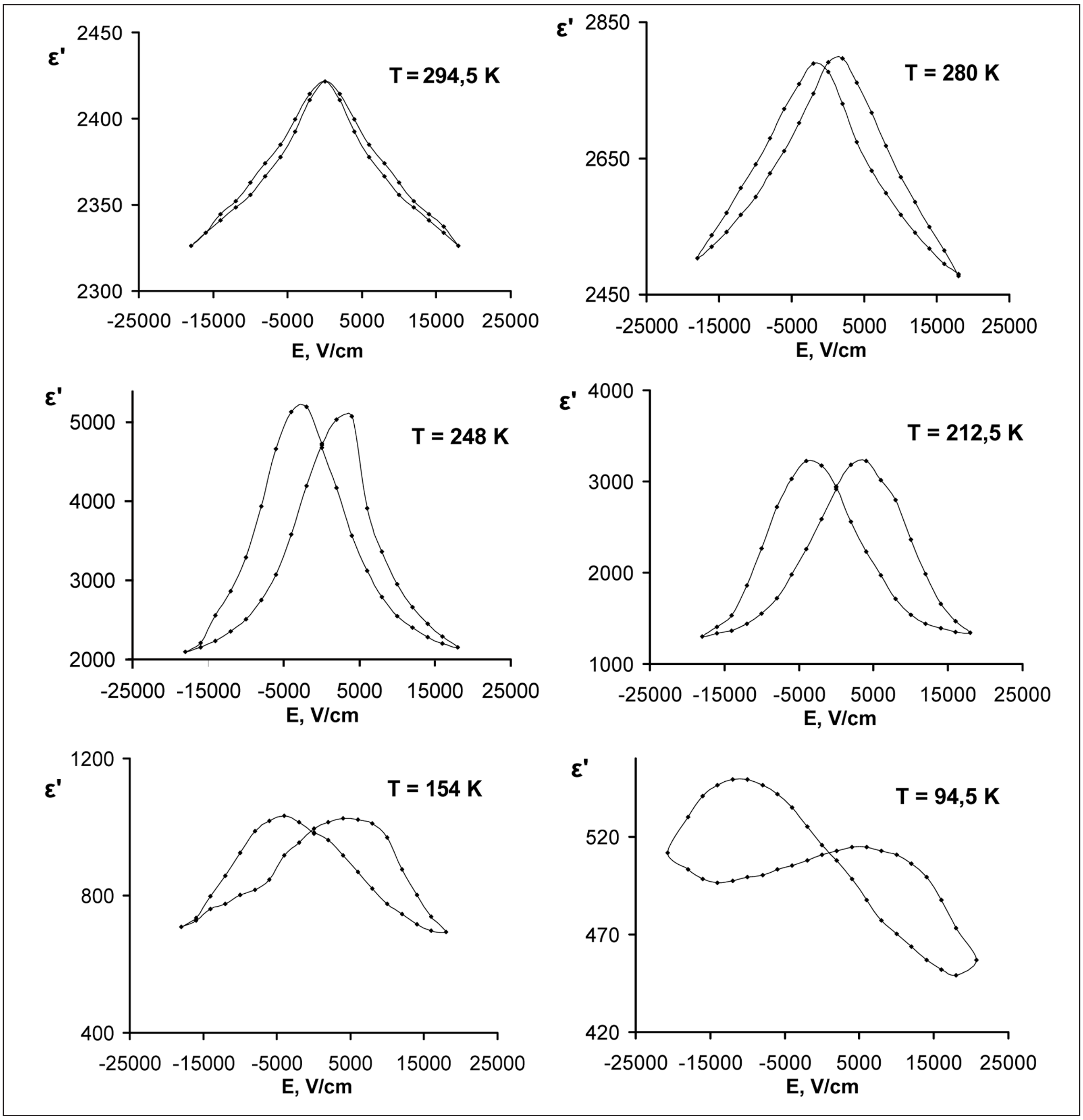

Fig. 2. Reversed dielectric permittivity $\varepsilon'(E_=)$ curves at different temperatures.

effect at $T > T_m$ is likely to be due to the field-induced polar state characterising the PT in PFT as strongly broadened. The maximums of the $\varepsilon'(E_=)$ curve go with coercive field values E_c. The $E_c(T)$ curve is shown in Fig. 3. However, taking into account the strong contribution of conductivity in PFT at $T > T_m$ (Fig. 1(b)), the effects of dielectric nonlinearity (appearance of hysteresis) may be associated with the phenomena the nature of which is not related to ferroelectricity. The reduction of temperature in the range of 300–270 K does not change E_c substantially, this result being consistent with other studies of $\varepsilon'(E_=)$ in the PFT [8] also describing the PT in this material as strongly broadened. A distinct increase of the coercive field starts at 248 K, i. e. near T_m. The appearance of the $\varepsilon'(E_=)$ maximum at E_c points to polarisation switching related to restructuring (reorientation) of domains at temperatures of the region of PT. In this case, due to increasing dielectric viscosity E_c should increase significantly as temperature decreases. It should be noted that the increase of E_c with decreasing temperature is particularly pronounced below the Néel temperature. At $T = 94$ K ($T < T_N$) only a partial cycle of polarisation switching on the $\varepsilon'(E_=)$ curve is observed at the highest bias field intensity $E_=$ suggesting a significant unipolarity. The marked increase of E_c and the emerging unipolarity are possibly associated with the freezing of the domain structure at $T < T_N$ being consistent with the features revealed by relaxation at temperatures close to T_N (Fig. 1, inset).

Evaluating the data of ε^* with regard to the results of dielectric nonlinearity and dispersion at low frequencies, the low-temperature dielectric relaxation in the case of PFT can be attributed to oscillations of ferroelectric domain boundaries. The importance of contribution of magneto-electric interaction to the low-temperature relaxation in this material requires further studies.

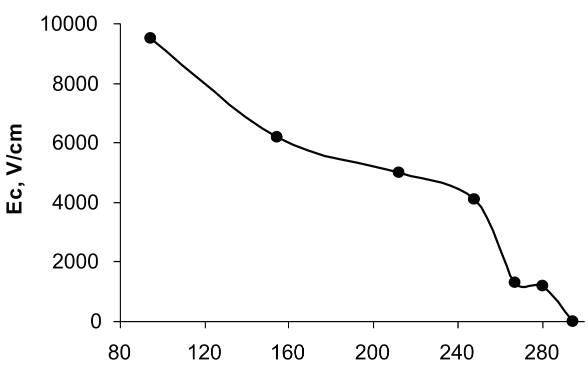

Fig. 3.Thermal dependence of the coercive field $E_c(T)$.

4. Conclusions

A broad maximum of dielectric permittivity of lead ferrotantalate ceramics is observed within the 220–270 K range of temperature and it does not display any realoxor shift. Anomalous behaviour with the temperature of the dispersion of dielectric permittivities ε' and ε'' is observed in the low-temperature range of 70–110 K. The dependence of ε' on the bias field $\varepsilon'(E_=)$ indicates a "freezing" of polarisation at 94 K, the activation energy of which is estimated to be 0.07 eV. The coercive field of the material is observed being strongly dependent on the temperature over the whole range examined.

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$Pb(Fe_{1/}Ta_{1/2})O_3$ KERAMIKOS DIELEKTRINĖS SAVYBĖS ESANT 70–300 K TEMPERATŪRAI

K. Bormanis [a], A. Kalvane [a], A.I. Burkhanov [b], A.M. Serezhkin [b]

[a] *Latvijos universiteto Kietojo kūno fizikos institutas, Ryga, Latvija*

[b] *Volgogrado valstybinis architektūros ir inžinerijos universitetas, Volgogradas, Rusija*

Santrauka

Aprašomi feromagnetinio švino ferotantalato $Pb(Fe_{1/2}Ta_{1/2})O_3$ dielektrinio atsako tyrimai plačiame temperatūros intervale esant išoriniam laukui. Nagrinėtos dielektrinės skvarbos netiesiškumo savybės, nustatytos iš grįžtamosios dielektrinės skvarbos $\varepsilon'(E_=)$ kreivių skirtingoje temperatūroje, įskaitant feroelektrinio fazinio virsmo sritis ir Nejelio (Néel) taško aplinką. Gauti rezultatai rodo, kad feroelektrinis fazinis virsmas yra pastebimai išplitęs. Rezultatai aptariami lyginant su feroelektriniu susitvarkymu panašiuose feroelektriniuose relaksoriuose.