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THE PERMITTIVITY – THICKNESS RELATIONSHIP OF A PMN (111) SINGLE CRYSTAL

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Abstract. In this work, the permittivity measurements of lead magnoniobate PMN (111) single crystals with thicknesses of 400 μm, 25 μm and 10 μm have been carried out at a frequency of 0.1 Hz. The samples in the form of plane-parallel plates were prepared by hand grinding and then their sides were coated with 80 nm CrAu electrodes. The topography of the sample surfaces was controlled by AFM. The temperature dependences of the complex permittivity were obtained in the range from 150 to 350 K. The changes in the temperature dependences of ε with varying the thickness of the single crystals were analyzed. It The peak on the temperature curve of ε' was shown to shift to a higher temperature with a decrease in the sample's thickness, and its width increasing significantly. A phenomenological expression was proposed to describe the permittivity-thickness relationship of a single crystal.

Keywords: ferroelectric, relaxor, lead magnoniobate, permittivity, temperature dependence, single-crystal thickness

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ЗАВИСИМОСТЬ ДИЭЛЕКТРИЧЕСКОЙ ПРОНИЦАЕМОСТИ МОНОКРИСТАЛЛА PMN (111) ОТ ТОЛЩИНЫ

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Аннотация. В работе проведены измерения диэлектрической проницаемости монокристаллов магнониобата свинца PMN (111) с толщинами 25 ,400 и 10 мкм на частоте 0,1 Гц. Образцы имели форму плоскопараллельных пластин, полученных шлифовкой вручную и были покрыты металлическими электродами CrAu толщиной 80 нм. Топография поверхностей образцов контролировалась методом атомной силовой микроскопии. Были измерены температурные зависимости комплексной диэлектрический проницаемости в диапазоне от 150 до 350 K. Проанализировано изменение температурных зависимостей ε′ при варьировании толщины монокристалла. Показано, что при уменьшении его толщины пик на температурной кривой ε′ смещается в сторону более высокой температуры, а его ширина значительно увеличивается. Предложено феноменологическое выражение для описания зависимости величины диэлектрической проницаемости от толщины монокристалла.

Ключевые слова: сегнетоэлектрик, релаксор, магнониобат свинца, диэлектрическая проницаемость, температурная зависимость, толщина монокристалла

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Introduction

Devices such as ultrasonic motors, micropumps, accelerometers, sonars are based on ferroelectric materials [1–3]. Materials with high dielectric permittivity and a high electromechanical coupling coefficient are required for developing these and similar devices [4–6]. Solid solutions of relaxors with ferroelectrics are an example of such materials. Development and applications of several generations of similar materials are considered in detail in [4]: these are binary compounds of relaxors with lead titanate (PMN-PT, PZN-PT) and ternary PIN-PMN-PT compounds. The remarkable characteristics of these materials can greatly expand the capabilities of piezoelectric converters in various fields [7]. The thickness of the piezoelectric material depends on the operating frequency of the piezoelectric element used [7] (for example, in the range of

1–20 MHz for medical imaging) and is generally in the range from 100 to 1000 μm. Extensive research is underway to explore the influence of geometric dimensions on the properties of these materials both in the form of single crystals or ceramics [8, 9] and in the form of thin films [10]. Different assumptions are made about the reasons for the relationship between the main characteristics of piezomaterials with their thickness. For example, the deterioration in the characteristics of the PMN-PT material is associated in [8] with a damaged near-surface layer formed by preparing samples with a thickness of about tens of micrometers, as well as with the characteristic sizes of ferroelectric domains. On the other hand, it is reported in [7] that permittivity increases with a decrease in the thickness of a PZN-PT single crystal (12%) from 750 to 75 μm. Various factors affecting the properties of piezomaterials and methods for estimating them are considered in [11].

Even though a large number of papers discuss two- and three-component piezoelectric materials, lead magnoniobate relaxor $Pb(Mn_{1/3}Nb_{2/3})O_3$ that these materials are based on has received virtually no attention.

The goal of this study was to measure, analyze and provisionally interpret the permittivity dependence of a PMN(111) single crystal on its thickness over a wide temperature range.

Sample preparation

PMN single crystals with the surface orientation [111] and thicknesses ranging from 10 to 400 μm were prepared for measurements via dielectric spectroscopy and atomic force microscopy.

The single crystal samples were plates with a surface area of the order of 1–2 mm^2, prepared by plane-parallel hand grinding.

An Oxford Diffraction SuperNova X-ray diffractometer (manufactured by Agilent Technologies, USA) was used to measure the crystallographic orientation of the samples. Single crystals were cut by an Accutom 50 machine (Struers, Denmark) to a plate thickness of about 0.5 mm. Next, the resulting plates were ground by hand to the required thickness using sandpaper with a grain size from P500 to P4000 and polished with a DiaPro Nap R diamond suspension (Struers, Denmark).

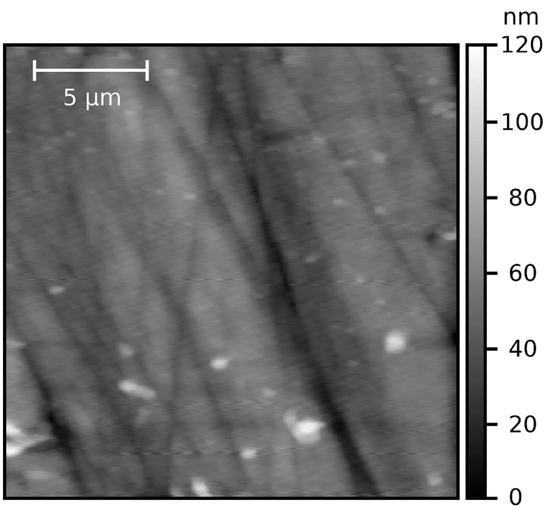

Fig. 1. AFM image of surface topography in a PMN single crystal with a thickness of 10 μm

To precisely measure the size, the sample was attached to a plane-parallel glass prism with a thin resin layer during grinding. The thickness of the resin layer and the thickness of the processed sample were monitored with a Micron SR-25 passameter (Czech Republic) and a set of gauge blocks. The measurements were carried out with a maximum absolute error of ±1.5 μm. All measuring instruments used in the work are included in the National Register of Measuring Instrument Certificates.

Both surfaces of each of the plates were coated with 84 nm thick chromium-gold electrodes (4 nm Cr, 80 nm Au). The electrodes were sputter-deposited at a residual gas pressure of 10^{-6}torr using a Minilab 080 system for vacuum deposition of thin films (Moorfield, UK). The sample was connected to the measuring circuit via conductive silver paste and gold wires 25 μm in diameter.

The permittivity was measured with a Concept-80 dielectric spectrometer (Novocontrol, Germany) equipped with a temperature control system. The measurements were carried out in the temperature range from 150 to 350 K; the sample temperature was varied and maintained by modulating the gaseous nitrogen flow with a given temperature. The presence of polar structures in ultrathin PMN crystals was studied experimentally by modified piezoresponse force microscopy (PFM). An attoAFM I atomic force microscope (Attocube, Germany) was used, equipped with a set of external measuring instruments for PFM.

Results and discussion

AFM was used to obtained topographic images for the surface of a PMN single crystal (Fig. 1); the surface roughness Ra amounted to no more than 15 nm in an area of 20 × 20 μm.

AFM measurements were carried out at room temperature. The measurement procedure combined two methods: PFM and contact-mode Kelvin probe [12]. This combination allows to measure ferroelectric hysteresis loops, detecting the cases when such loops are induced by the motion of a charge across the surface of the sample rather than by ferroelectricity.

Measurements by this combined method at room temperature revealed that a PMN single crystal with the surface orientation (111) and a minimum thickness of 10 μm has no polar regions and is not in a ferroelectric state.

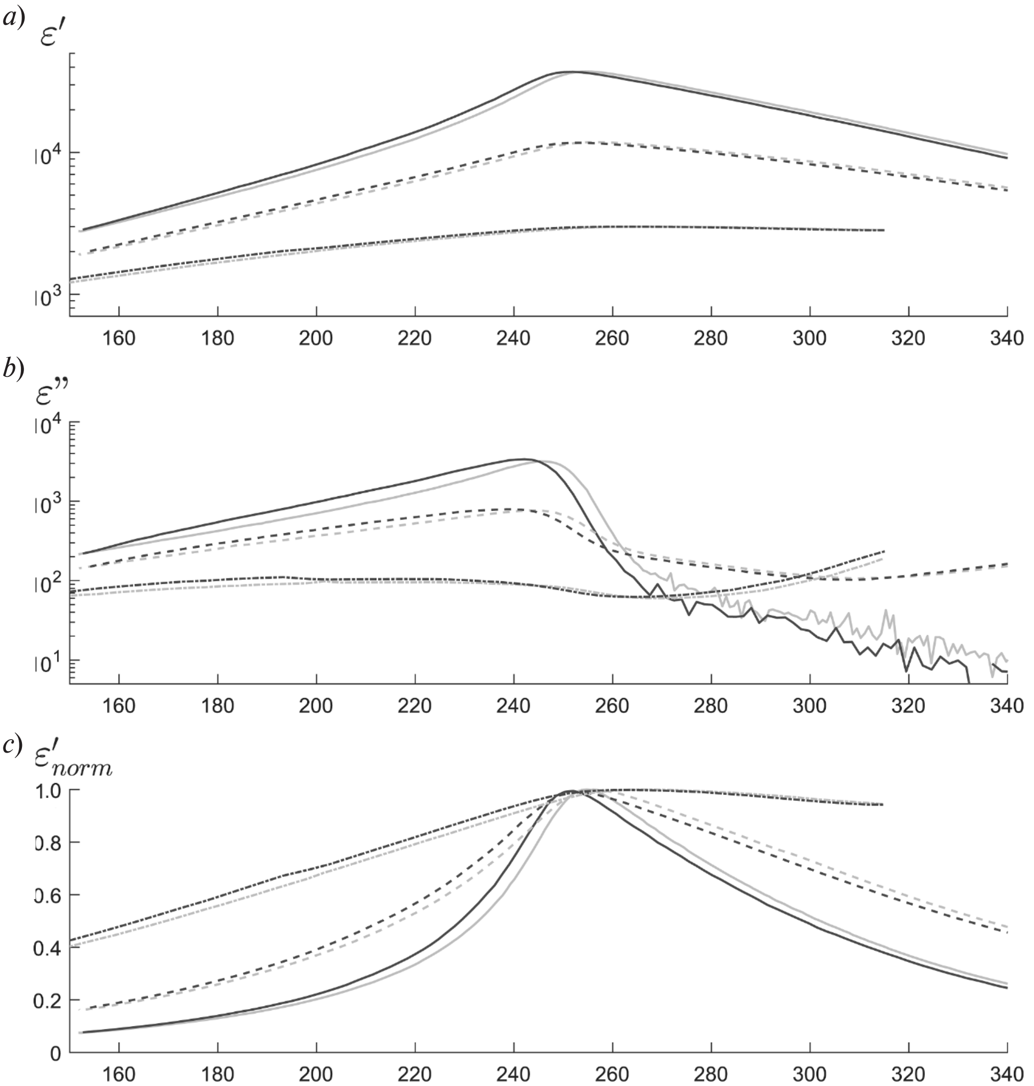

Fig. 2. Temperature dependences for real (*a*) and imaginary (*b*) parts of complex permittivity, as well as quantity $\varepsilon'_{norm} = \varepsilon'/\varepsilon'_{max}$ (*c*) for PMN single crystals with different thicknesses, μm: 400 (solid lines), 25 (dashed lines) and 10 (dotted lines). The data were obtained at a frequency of 0.1 Hz under heating (black curves) and cooling (gray curves)

Fig. 2 shows the dependences of permittivity on temperature for PMN single crystals of different thicknesses, μm: 400, 25 and 10, at a frequency of 0.1 Hz. Furthermore, a graph for the quantity $\varepsilon'_{norm} = \varepsilon'/\varepsilon'_{\max}$ is given to visually illustrate the broadening of the peak on the measured dependence $\varepsilon(T)$. The results for single crystals 25 and 10 μm thick were obtained by averaging over several measurements. The total absolute error of the experimental data is estimated at a value not exceeding 15%, including both the inaccuracies in the dimensions resulting from sample preparation and the contributions from the measurement error (contact effects and instrument error).

Analyzing the data, we found that the value of the dielectric constant for pure PMN decreases by an order of magnitude with a decrease in the crystal thickness from 400 to 10 μm. The position of the maximum on the $\varepsilon(T)$ curve is shifted by several degrees towards an increase in temperature. In addition, comparing the graphs of the $\varepsilon_{norm}(T)$ dependences for samples with different thicknesses, we established that the peak of the dielectric constant broadens considerably with a decrease in the crystal thickness.

Fig. 3 shows the dependence of the dielectric constant at the maximum of the temperature curve $\varepsilon'_{\max}$ on the sample thickness h. To quantify this dependence, we propose the following phenomenological expression:

$$\varepsilon'_{\max}(h) = A \cdot [1 - \exp(-h/B)], \quad (1)$$

where B is a constant characterizing the decrease rate of the quantity ε' with a decrease in the sample thickness; A is a dimensionless constant.

The constants of this expression were found by approximation of the experimental results, taking the following values:

$$A = 37500 \pm 830,\ B = (70 \pm 44)\ \mu\text{m}.$$

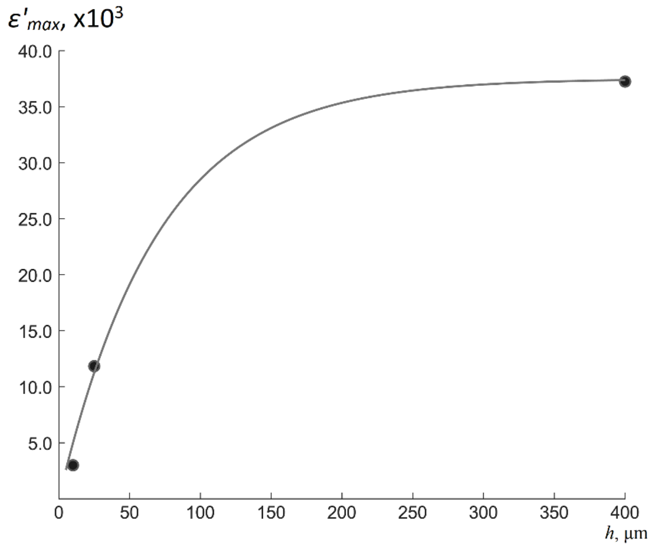

Fig. 3. Dependence of the quantity $\varepsilon'_{\max}$ on sample thickness (dots) and its approximation by phenomenological expression (1) (solid line)

We can see a similarity between the results we obtained and the data available from the literature for crystals with larger thicknesses. We checked the applicability of the phenomenological expression we formulated for the data given in [8] for the PMN-PT relaxor (see Fig. 1). Despite a large difference in the values of quantity $\varepsilon'_{\max}$ (the value of $A \approx 6000$ for the data from [8]), the constant B has a value close to the one we obtained for PMN: $B = (57 \pm 20)$ μm.

Conclusion

We prepared samples of ultrathin single crystals of (111) lead magnoniobate with the thicknesses ranging from 400 to 10 μm, measuring their temperature dependences of permittivity (real (ε') and imaginary (ε'') parts) in the range from 150 to 350 K. We found that as the thickness of a single crystal decreases, the position of the peak on the $\varepsilon'(T)$ curve shifts towards an increase in temperature, while its width increases considerably. We formulated a phenomenological expression $\varepsilon'_{max}(h)$ to describe the dependence of the dielectric constant on the thickness of a single crystal. It was established that the obtained expression can also be used to describe the permittivity of another ferroelectric, PMN-PT.

Our findings make a further step towards understanding the relationship between the main characteristics of piezo materials and their thickness, which is very useful for potential applications in ferroelectric-based devices.

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