Dielectric Investigations and Birefringence of PbNi$_{1/3}$Nb$_{2/3}$O$_3$ Single Crystals

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Abstract. The results of studies of dielectric response and birefringence in the PbNi$_{1/3}$Nb$_{2/3}$O$_3$ (PNN) single crystal are presented. An anomaly in the temperature dependence of the complex dielectric permittivity in the vicinity 153 K has been observed. It is shown that the anomaly is attributed to the transition relaxor ferroelectric state. The presence of slightly noticeable anomaly in permittivity in the temperature range of 200-210 K has been confirmed by means of optical birefringence microscopy.

1. Introduction

Complex perovskites with a common formula AB’B”O$_3$ (A = Pb; B’= Mg, Co, Ni etc.; B”=Nb) and solid solutions based on them form a large family of crystals and demonstrate a large diversity of physical properties [1]. This family includes dielectrics, anti- and ferroelectrics, relaxor ferroelectrics, and multiferroics. Such compounds as PbMg$_{1/3}$Nb$_{2/3}$O$_3$ have giant piezoelectric coefficients, which makes them attractive for industry. They are characterized by a diffuse phase transition which is not always associated with structural transformations. During this phase transition, a frequency-dependent anomaly of the dielectric response stretched for hundreds of degrees is observed. A wide frequency-dependent anomaly in the vicinity of the maximum permittivity is also typical of many physical parameters of these materials [1]. Studies of the phase transformations which give rise to the ferroelectric relaxor state are significant for the condensed matter physics. Of special interest in the large family of relaxor ferroelectrics is a group of multiferroics-relaxors in which one of the ions in the B position is magnetic. A typical representative of this group is the PbFe$_{1/2}$Nb$_{1/2}$O$_3$ compound [2]. The combination of magnetic, polar and piezoelectric properties of single crystals, ceramics, and films of multiferroics-relaxors makes them promising multifunctional materials for electronics, spintronics, and other technical applications.

PbNi$_{1/3}$Nb$_{2/3}$O$_3$ (PNN) can be regarded as a multiferroic-relaxor. A feature of the PNN, which distinguishes it from the model ferroelectric relaxor PMN, is the existence of a structural phase transition from the paraelectric cubic phase Fm3m to the ferroelectric rhombohedral P31m at 153 K [3]. The possibility of the existence of an antiferromagnetic phase below 100 K is discussed in the literature [4]. In [5] a diffuse phase transition which manifested itself as an anomaly in the temperature dependence of the permittivity in the form of a wide frequency-dependent maximum $\varepsilon_m$(1kHz) = 2400 - 3800, in the vicinity of $T_m$ = 120 - 155 K was reported. A difference in the dielectric properties is probably due to specific features of the crystal growth technology.

The other feature of the PNN is a wider maximum in the real part of dielectric response compared to the model relaxor PMN. It is possible that in the temperature range 200-210 K there is another
slightly noticeable anomaly in the permittivity. Therefore, this publication focuses on a detailed study of the dielectric and optical properties of the PNN single crystals in this temperature range.

2. Materials and methods
Single crystals of PNN were grown by the method of solution in the melt. The phase composition of the crystals was controlled by the X-ray diffraction technique; the quantitative elemental composition was examined by the X-ray fluorescent technique. The samples were green transparent single crystals with a thickness of 0.27 mm and an area of 2 mm². The surfaces (001) were covered with gold electrodes by the thermal sputtering.

The dielectric response was measured by a GoodWill LCR-819 impedance meter, the measuring voltage amplitude was 1 V and frequency range was from 10 Hz to 100 kHz. The studies were performed from 77 up to 750 K at a rate of 1–3 K/min.

The birefringence was investigated by microscope system equipped with polarizers and a high-resolution CCD camera.

3. Results
Figures 1 and 2 show the temperature dependences of the real and imaginary parts of the complex permittivity \( \varepsilon^*(T) = \varepsilon'(T) - i\varepsilon''(T) \). A wide maximum of the real permittivity at a frequency of 1kHz reaches \( \varepsilon'_{\text{max}} = 5500 \) at a temperature of \( T_{\text{max}} = 153 \) K (for comparison in PMN: \( \varepsilon'_{\text{max}} = 11400 \) and \( T_{\text{max}} = 265 \) K [1]). The width of the half maximum level is 145 K (PMN – 80 K [1]). The temperatures of the maxima depend on the frequency and there is a shift to higher temperatures by 17 K in the frequency range from 100 Hz to 100 kHz (PMN – 18 K [1]). Figure 1 inset also demonstrates a slightly noticeable anomaly in permittivity in the temperature range of 200-210 K. The analysis of the temperature dependence of the reciprocal value of the permittivity show that for the linear sections described by the Curie-Weiss law is not fulfilled (figure 3). The deviation from the Curie-Weiss law and a wider maximum in comparison with PMN are apparently associated with the presence of another anomaly in the temperature range of 200-210 K.

![Figure 1](image_url)  
**Figure 1.** Temperature dependence of the real part of the dielectric permittivity in PNN.
Figure 2. Temperature dependence of the imaginary part of the dielectric permittivity in PNN. Inset shows the frequency dependence of the $\varepsilon''$ maxima temperature positions in Arrhenius coordinates.

Figure 3. Reciprocal permittivity fitted by Curie–Weiss law (dashed lines).
The anomaly in this temperature range can be revealed by means of the temperature dependence of the intensity of the polarized light passing through the sample (figure 4). In this figure one can see that the crystal becomes optically isotropic above 210 K.

Figure 2 also shows the frequency-dependent maxima of the imaginary part of the permittivity in the vicinity of the temperature 138 K (1 kHz). The width of maximum is the same as that one in PMN. The temperature and frequency dependences of maxima were checked for correspondence of Arrhenius equation $\omega = \omega_0 \exp \left( \frac{-E_a}{kT_{\text{max}}} \right)$ (where $\omega_0$ and $E_a$ are the constant and activation energy) (figure 2 inset). For the imaginary part the approximation does not give reasonable values of the parameter $\omega_0 = 2 \times 10^{31}$ s$^{-1}$. At high temperatures, above 400 K, an increase in dielectric losses and their frequency dispersion is seen and this behavior can be attributed to Maxwell-Wagner relaxation (figure 2).

![Figure 4](image1.png)

Figure 4. Temperature dependence of the intensity of the polarized light passing through the PNN crystal.

4. Conclusion
The anomalies of the dielectric response in the form of frequency-dependent maxima are observed at the temperature region near 150 K. It is shown the presence of anomaly in dielectric response in the range of 200-210 K that can be also revealed by optical birefringence microscopy.

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