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Influence of thulium impurity on dielectric and pyroelectric properties of single crystals of Barium Strontium Niobate

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It has been shown that the introduction of thulium impurity into the crystals of strontium barium (SBN:61) niobate leads to an increase in the dielectric constant value and the blur region of the phase transition. External field polarization partially stabilizes the polar state of the samples, however, the heterogeneous distribution of polarization across the thickness of the studied samples indicates the existence of regions with a developed domain structure characteristic of highly doped crystals.

Keywords: Ferroelectrics, relaxors, pyroelectric effect, polarization distribution, single crystal, SBN.

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1. Introduction

Strontium barium niobate $Sr_xBa_{1-x}Nb_2O_6$ (SBN) single crystals of solid solutions are classified as relaxor ferroelectrics with high dielectric permittivity, pyro-, piezoelectric and electrooptic coefficients [1]. The partially filled crystal structure of these materials allows doping with a rather wide range of impurities: from ions of transition metals to rare-earth ions, thus controlling their properties including dielectric and polar ones [2–6]. SBN crystals doped with a Thulium (Tm) impurity are one of the most promising materials used in laser frequency multipliers, hologram recording, as well as a medium of optical memory because doping with this impurity results in a significant improvement of optical characteristics of crystals [4,5,7]. At the same time, it is necessary to take into account the effect of the impurities on dielectric and pyroelectric properties of materials under study, as well as their dependence on the exposure to direct and alternating fields.

In this study, we have investigated the effect of Thulium impurity on dielectric and pyroelectric properties of strontium barium niobate (SBN:61) single crystals doped with Tm^{3+} ions. The crystals were grown by a modified Stepanov technique from melts containing 0.5, 1.0 and 2.0 wt% of Tm_2O_3 [8]. Samples were shaped as plane-parallel plates cut out perpendicular to the polar axis. Silver electrodes were applied on their surfaces. We investigated as-grown and polarized samples. Crystals were polarized by applying a direct field of about 5.0 kV/cm in the paraphase at a temperature of 130°C with further cooling under a field down to the room temperature. Switchable polarization and coercive field were determined at the room temperature using a modified Sawyer–Tower circuit. Pyroelectric properties were investigated by a dynamical method with a square-wave modulation of the heat flux sourced from an IR-diode with a wavelength of 980 nm, in a frequency interval of 0.5–1000 Hz. To calculate the polarization profile, both surfaces of the samples corresponding to „–“ and „+“ outputs of the macroscopic polarization were exposed to the modulated heat flux. Dielectric characteristics of the samples were measured by a „Vektor-175“ frequency response analyzer in a wide frequency range from 10 to 10^7 Hz in the temperature range from 20 to 135°C.

2. Experimental findings and discussion

It is found that, in contrast to as-grown samples, there is almost no ε dispersion in the polarized samples in the frequency range from 10 Hz to 10 MHz (Fig. 1, *a*), and the dielectric permittivity decreases by almost two times [9]. Also, anomalies are observed in the frequency dependence of the dielectric permittivity in the polarized samples in the frequency range of 10^5-10^6 Hz. Such a behavior of the dielectric permittivity in polarized ferroelectric materials can be related to electromechanical resonances corresponding to a transverse mode (along the long side of the thin plate) [10].

With an increase in concentration of the Tm impurity, ε increases noticeably in the entire frequency range, particularly: by two times in SBN:1% Tm_2O_3 samples and by three times in SBN:2% Tm_2O_3 samples as compared with undoped crystals (Fig. 1, *a*).

In the polarized samples, the doping with Thulium does not result in a significant change in the dielectric loss angle tangent (Fig. 1, *b*). In all samples a considerable growth of the dielectric loss angle tangent is observed at a frequency

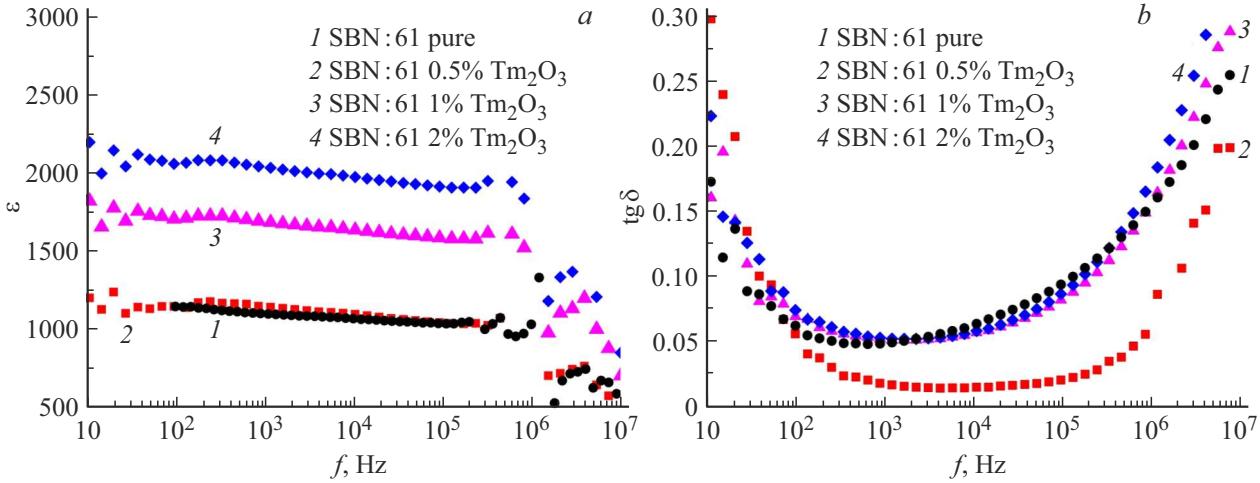

Figure 1. Frequency dependencies of dielectric permittivity (*a*) and dielectric loss angle tangent (*b*) for SBN crystals doped with Thulium ions after polarization of samples.

of 10^6 Hz, which is usually related to the presence of the bulk-relaxation polarization in the samples.

The investigations of temperature dependence of the dielectric permittivity of crystals have shown that doping with Tm impurity results in a decrease in both the temperature of maximum dielectric permittivity (T_{max}), and the ε itself at the point of maximum [9]. Also, the presence of temperature hysteresis of the maximum dielectric permittivity is found under heating and cooling, which is typical for crystals with phase transition of the first order (Fig. 2, *a, b*).

It is worth noting that ΔT decreases insignificantly with an increase in the concentration of Tm impurity.

The table represents dielectric and polar characteristics of polarized SBN crystals with different content of Thulium ions. As can be seen, an increase in the Thulium impurity concentration results in a strong spreading of the Curie range.

To determine values of the switchable polarization and coercive field of samples, dielectric hysteresis loops in an alternating field with a strength of up to 6 kV/cm were recorded. As can be seen from the table, a noticeable decrease in the polarization has been observed in the SBN:0.5% Tm_2O_3 samples in comparison with the undoped sample (almost by 7 times). However, with further increase in the impurity concentration the switchable polarization increases again.

The decrease in the switchable polarization in the samples with 0.5% concentration may be related to the fact that at a low percentage the impurity is distributed in a more uniform manner, which results in a domain wall pinning, a decrease in their mobility and, as a consequence, a decrease in polarization and an increase in the coercive field. With higher concentrations the disorder of ion arrangement increases and the doped impurity becomes the center of nucleation of new domains, which is the cause of the considerable increase in the switchable polarization and the decrease in the coercive field. It is worth emphasizing that this well matches the fact that the dielectric permittivity in samples with increased concentration is significantly higher than that in nominally pure SBN:61 and SBN:0.5% Tm_2O_3.

The investigation of pyroelectric properties of polarized samples has shown that with a change of the side exposed to radiation the direction of pyroelectric current changes depending on the direction of the spontaneous polarization in relation to the impact of the heat radiation modulated by square-wave pulses. The calculation of pyroelectric coefficient by the formula presented in [11] has shown that

Dielectric and pyroelectric characteristics of the samples

Sample	Temperature maximum ε, T_{max}, °C	Curie range θ, K	Switchable polarization P, μC/cm^2	Coercive field E, kV/cm	Pyroelectric coefficient γ, 10^{-4} C/m$^2 \cdot$ K, $+P/-P$
SBN:61 pure	85	13	50	0.7	4.5/5.0
SBN 0.5% Tm	77	18	7	2.6	2.6/3.0
SBN 1% Tm	75	24	37	0.8	3.5/4.2
SBN 2% Tm	68	30	36	0.6	4.5/5.4

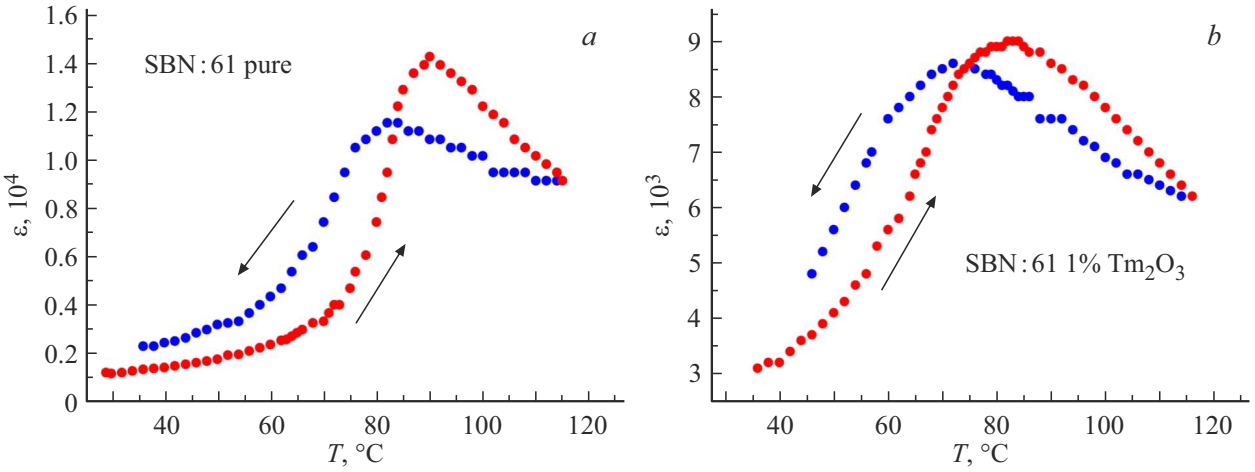

Figure 2. Temperature dependencies of the dielectric permittivity under heating and cooling: *a* — for nominally pure samples of SBN:61, *b* — for SBN:61 doped with 1% Tm_2O_3.

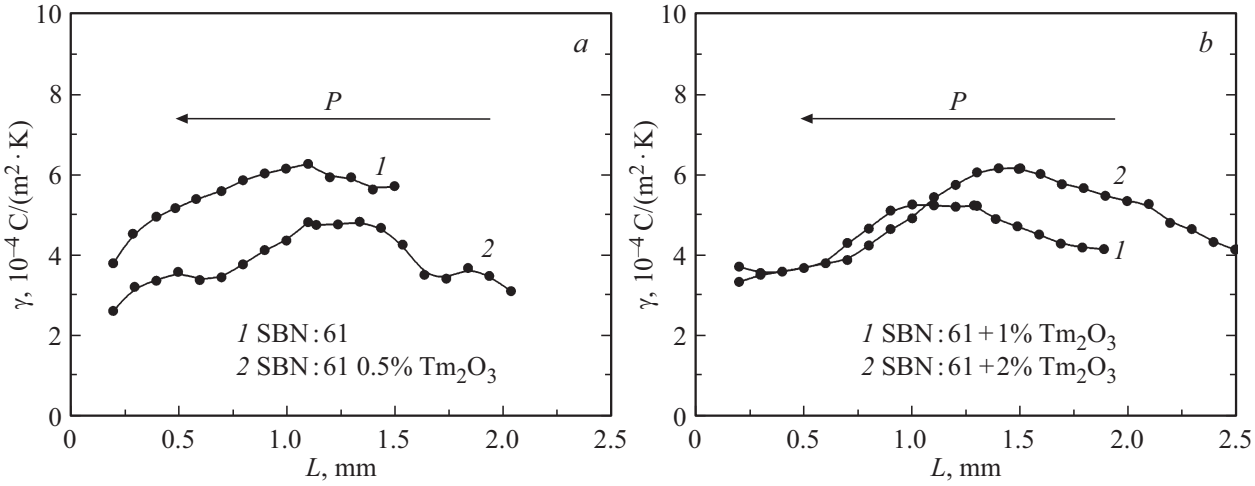

Figure 3. Distribution of the pyroelectric coefficient over the thickness of SBN and SBN:Tm samples.

this coefficient depends on the amount of the Thulium impurity introduced into the SBN crystal. For the SBN:0.5% Tm_2O_3 doped crystal, the coefficient depends on the Thulium impurity concentration in the SBN:61 crystal. For the SBN:0.5% Tm_2O_3 crystal, the pyroelectric coefficient decreases abruptly as compared with the nominally pure SBN:61 sample, then it grows again with increase in the Thulium concentration. It should also be stated that pyroelectric coefficients calculated for different radiation-exposed surfaces of samples are different, i.e. they depend on the direction of the polarization vector in the crystal in relation to the heat flux (see the table).

The investigation of frequency dependencies of the pyroelectric response in SBN and SBN:Tm samples has shown the presence of dispersion and a change in the response shape at modulation frequencies from 100 Hz to 1 kHz, which is indicative of the impurity charge state contribution to the pyroelectric response and the presence of a layer with highly nonuniform distribution of the polarization near the crystal surface.

With consideration to the depth of heat flux penetration into the sample and using the technique described in [12,13], the distribution of the pyroelectric coefficient over the thickness of samples under study was calculated, which corresponds to the polarization profile in the crystals (Fig. 3).

It can be seen, that for the undoped SBN and SBN:0.5% Tm_2O_3 the pyroelectric coefficient and, as a consequence, the polarization in the volume are quite uniform, especially under the irradiation from the side with the output — *P*. With an increase in the Thulium ion concentration the pyroelectric coefficient becomes more nonuniform.

As it is shown in [1], the Tm^{+3} ions can occupy different positions in the SBN crystallographic lattice. With an increase in the Thulium concentration the structural disorder of the crystal increases, which makes the introduced

impurity a center of nucleation of new domains and, as a consequence, leads to a significant increase in the switchable polarization, a growth of the dielectric permittivity and a decrease in the coercive field as compared to the crystals with low content of impurity (0.5% Tm_2O_3).

We assume that doping of the congruent composition of SBN:61 with Thulium ions makes the domain structure more developed, which is an obstacle for the uniform distribution of polarization in heavily doped crystals and, as a consequence, results in different pyroelectric coefficients calculated for different sides of samples exposed to a heat flux.

Conflict of interest

The authors declare that they have no conflict of interest.

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