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FERROELECTRIC PROPERTIES OF RELAXOR TYPE SBN SINGLE CRYSTALS PURE AND DOPED WITH Cr, Ni, AND Ce

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Abstract. Electric permittivity ε', conductivity and loss tangent of SBN61 strontium barium niobate single crystals obtained by the Stiepanov method: pure and doped with Cr (0.01 mol.%), Ni (0.01 mol.%), and Ce (0.01 mol.%), both as a function of temperature (290-440K, at a frequency of 1 kHz and 10 kHz) and frequency (100 Hz -1 MHz) have been analyzed. The relaxor behavior of crystals has been described by a diffuseness constant value showing a deviation of the dielectric constant from the Curie-Weiss law. The results have been compared with the results for SBN33, SBN52:Cr and SBN58:Cr, Yb samples obtained by Czochralski growth, with different Sr/Ba ratios. Owing to the obtained results it may be concluded that the relaxor behavior of the investigated samples strongly depends on the crystal growth method and the kind of doping (lattice disorder), and the dependence on the Sr/Ba ratio is smaller.

1. INTRODUCTION

SBN61 ($Sr_{0,61}Ba_{0,39}Nb_2O_6$) belongs to a tungsten bronze family of ferroelectrics and represents a typical relaxor crystal with a broad diffuse phase transition, high value and strong frequency dependence of the electric permittivity [1]. The dielectric response of relaxors is quite different than that of normal ferroelectrics. Relaxors show the occurrence of a strong dispersion in the real part of a dielectric constant, the absence of macroscopic polarization at temperatures much below the T_m temperature at which the dielectric constant shows a maximum [2]. Relaxor behavior appears due to the existence of a lattice disorder and polar nanodomains at a temperature much higher than T_m. The high dielectric constant in the vicinity of the dielectric anomaly, characteristic of the relaxors, with T_m shifted upwards with the increasing frequency, makes relaxors excellent candidates for multi-layered ceramic capacitors and other piezoelectric and ferroelectric devices [2-4]. The SBN*x* characteristics can be modified by a variation of the Sr/Ba ratio or by doping. SBN61 doped with Cr and Co are promising photorefractive materials with a sufficiently short response time [5]. These photorefractive materials are widely used in experimental studies on holographic recording, phase conjugation and wave mixing. Rare-earths (RE) and transition metals (TM) doping lowers the phase transition temperature of the crystals appreciably and broadens it without any abatement of the optical quality. Ce, Ni, and Cr (r_i<0.7 Å) dopants in SBN61 single crystals enter at octahedrally coordinated Nb^{5+} sites [6]. There are however opinions in the literature that Ni^{2+} ions enter at Sr and Ba sites [7].

When obtained by the Czochralski (CZ) method, the crystals reveal spiral growth and they are not

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transparent due to the nitrogen atmosphere during the growth, hence, they have to be annealed in the air at 1273K to be applied [8]. Optically better crystals can be obtained using the Stepanov (ST) method [5].

Although there are many researchers of these materials, there is a wide block of questions associated with the physical properties of SBN*x*.

The dielectric properties for SBN61 crystals, pure and doped with Ce, Cr and Ni (all dopants 0.01 mol.%), obtained by the ST growth method and compared to the SBN crystals obtained by the CZ method have been described in this paper.

2. EXPERIMENTAL

SBN61, pure and doped with Ce (0.01 mol.%), Ni (0.01 mol.%), and Cr (0.01 mol.%) crystals were obtained by the ST method in the A.M. Prokhorov Physics Institute, Moscow, Russia [5]. The SBN33, SBN52:Cr (0.02 mol.%) and SBN58:Cr (0.02 mol.%), Yb (0.5 mol.%) single crystals were obtained by the CZ method in the Institute of Physics, Szczecin University of Technology, Poland [8].

The investigated samples with the dimensions of 6×4×1 mm were cut from the crystals perpendicularly to the polar axis. One sample of each SBN crystal type was polished on both sides and next investigated for its optical absorption. The silver paint electrodes of the second sample were deposited on parallel planes. Before measurements were taken each sample had been heated to the temperature above the dielectric constant maximum temperature to remove any memory effect, and then it was cooled down. The following parameters: $\varepsilon'(T)$, $\varepsilon''(T)$ – the dielectric constant real and imaginary components, and, $\sigma(T)$ – conductivity were measured. The dielectric losses were calculated as being equal to $\mathrm{tg}(\delta(T))= \varepsilon''(T)/\varepsilon'(T)$. Quantities of the above parameters were examined also as field frequency functions in the range of 100 Hz -1 MHz. The experimental setup for dielectric measurements comprised a Hewlett Packard Impedance Analyzer HP4192A, a Shimaden SR-30/Pt 100 temperature controller, a sample chamber with nitrogen atmosphere and a PC.

3. RESULTS AND DISCUSSION

The dependences of ε' on temperature for SBN61, SBN61:Ni, SBN61:Ce and SBN61:Cr samples at two different frequencies (1 kHz and 10 kHz), on heating and on cooling, are shown in Figs. 1a– 1d. The figures reveal a broad dielectric maximum indicating that the measured samples undergo a relaxor-type dielectric anomaly. In Fig. 1a two different SBN crystals are compared. As can be seen, the SBN33 CZ crystal reveals a much higher dielectric constant as compared to SBN61 ST. The positions of temperature T_m were derived from the temperature dependences of the inverse ε' plotted for 10 kHz. They were registered for the above mentioned SBN61 samples at 370, 362, 358, and 347K on heating, and at 377, 360, 358, and 345K on cooling, respectively, at the measuring frequency of 10 kHz.

Hence, the T_m of SBN61 samples changes within 23K or 2-8K depending on the kind of doping (for RE and TM doping kept on the level of 0.01 mol.%) or the temperature change direction. Larger reducing of T_m, is observed for a pure SBN61 crystal. We have measured larger T_m values in crystals obtained by the CZ method: 389, and 386K for SBN33 and SBN52:Cr, respectively [8]. Moreover, the value of ε_m', the value of ε' at T_m, have been found to be at least 10 times larger for the latter. The ε'_m value is suggested to be determined by competition between the reduction of the polarization due to the substitution of Cr for Nb and the enhancement of the polar moment arising from the weakening of Nb–O bonds due to the creation of oxygen vacancies [9]. It is only in the case of an SBN61:Ni sample that the measured dielectric constant value has been detected to be much higher (see Fig. 1b). It should be mentioned that, as a result of an increase in the dielectric constant, all other constants (pyro- and piezoelectric and electrooptic coefficients) are also increased with respect to a pure SBN61 crystal. In the case of SBN61:Ni, the increase in the dielectric constant is probably due to an essential change in the crystal microstructure due to doping [10]. Indeed, a substitution of Ni^{2+} (r_i=0.7 Å) for Sr^{2+} or Ba^{2+} (r_i = 1.12 Å and 1.34 Å, respectively), if real, results in some distortions in the SBN61 lattice.

The dielectric behavior for a normal ferroelectric, above the Curie temperature, T_C, follows the Curie-Weiss law:

$$1/\varepsilon = (T - T_0)/C, \tag{1}$$

where T_0 is the Curie-Weiss temperature and C the Curie-Weiss constant.

The modified Curie-Weiss law has been proposed by Uchino and Nomura [11] to describe the dielectric anomaly diffuseness observed for relaxors as:

$$1/\varepsilon' - 1/\varepsilon'_m = (T - T_m)^{\gamma}/C_1, \tag{2}$$

where ε'_m and T_m represent a dielectric constant maximum and the corresponding temperature,

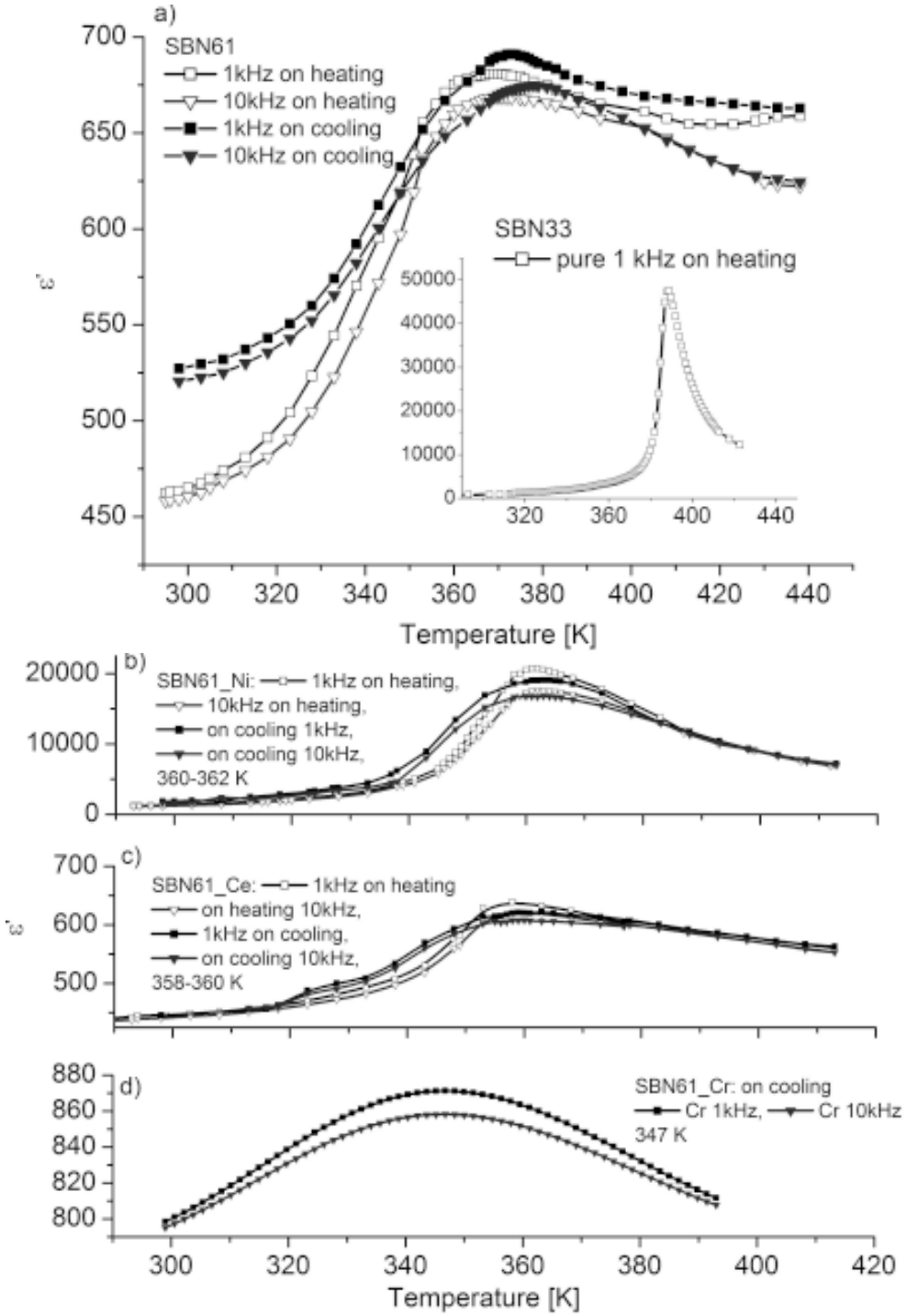

Fig. 1. Dependences of a relative dielectric constant on temperature for SBN61 and SBN33 (a), SBN61:Ni, SBN61:Ce and SBN61:Cr samples (b-d), at two different frequencies (1 kHz and 10 kHz) on heating and on cooling.

moreover γ and C_1 are assumed to be constant. The parameter γ gives information on the nature of the dielectric anomaly: a normal Curie-Weiss law is followed for $\gamma = 1$, whereas $\gamma = 2$ describes a complete diffuse anomaly (diffuse phase transition).

The plot of $\ln(1/\varepsilon'-1/\varepsilon'_m)$ as a function of $\ln(T-T_m)$ (see Figs. 2a and 2b) gives the diffuseness constant (γ) (the slope). For the investigated samples (see Fig. 2a), we have obtained the following γ: SBN61 – 1.89 and 1.40; SBN61:Ni – 1.73 and 1.98;

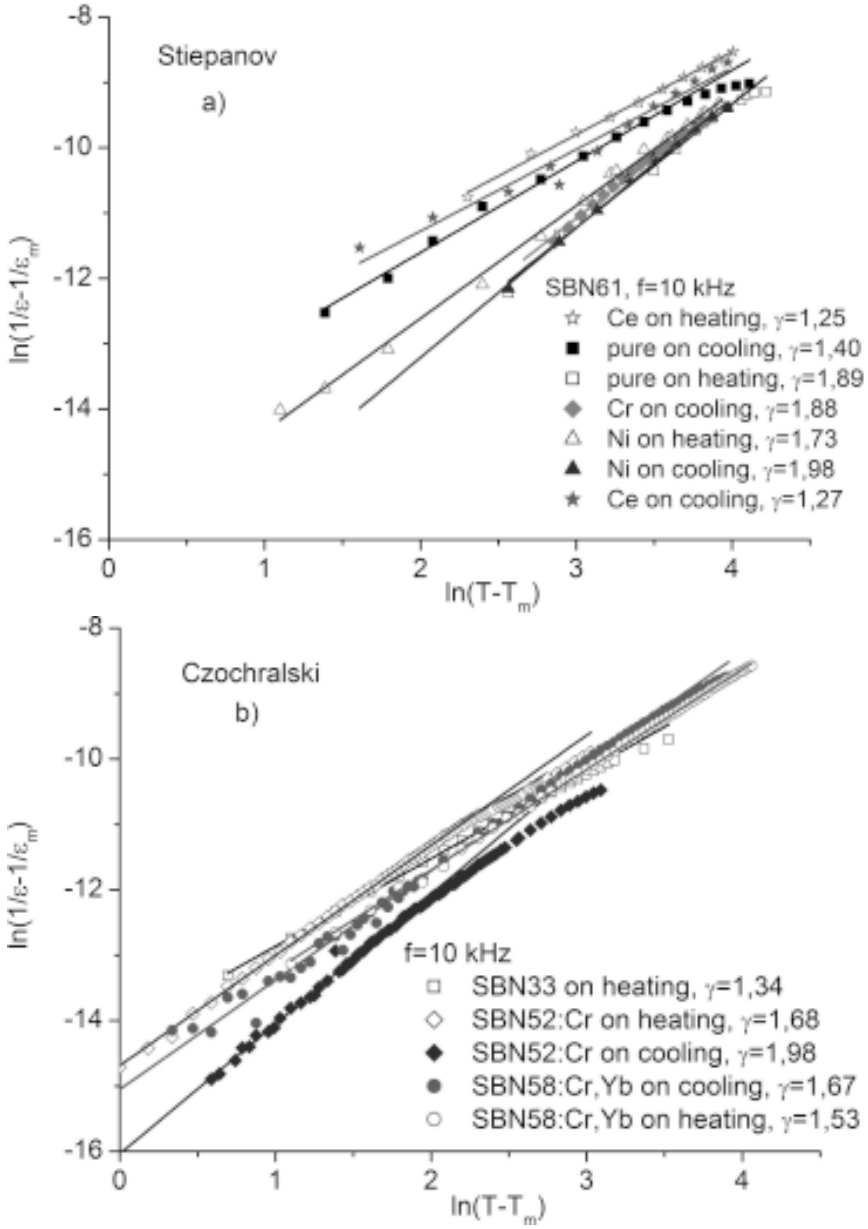

Fig. 2. a) $\ln(1/\varepsilon-1/\varepsilon_m)$ versus $\ln(T-T_m)$ for SBN ST crystals, b) $\ln(1/\varepsilon-1/\varepsilon_m)$ versus $\ln(T-T_m)$ for SBN CZ crystals.

SBN61:Ce – 1.25 and 1.27 and SBN61:Cr – 1.88 on heating and on cooling, respectively. We have obtained 1.34, 1.68 (1.98 on cooling) and 1.53 (1.67 on cooling), respectively on heating in case of SBN33, SBN52:Cr and SBN58:Cr, Yb, (see Fig. 2b). As can be seen, the largest value of γ has been registered for the samples doped with Cr and Ni.

The loss tangent, tanδ, for all samples, measured at 10 kHz, is presented in Fig. 3. The curves were obtained on heating of the samples. The maxima of the tanδ versus temperature, except for the SBN61 sample, are shifted by only a few K with respect to T_m. Higher losses are observed for the SBN61:Ni sample, while lower losses are seen for SBN61:Cr sample.

A variation of lnσ where σ denotes the electrical conductivity, versus the inverse of the absolute temperature at 1 and 10 kHz, measured for pure SBN61, SBN61:Ni and SBN61:Ce samples, is plotted in Fig. 4. In the inset of the figure we have shown a comparison of lnσ versus temperature between pure SBN61 and SBN33 samples for 1 kHz. When comparing the values of lnσ for CZ and ST grown crystals, it can be seen that higher values are revealed

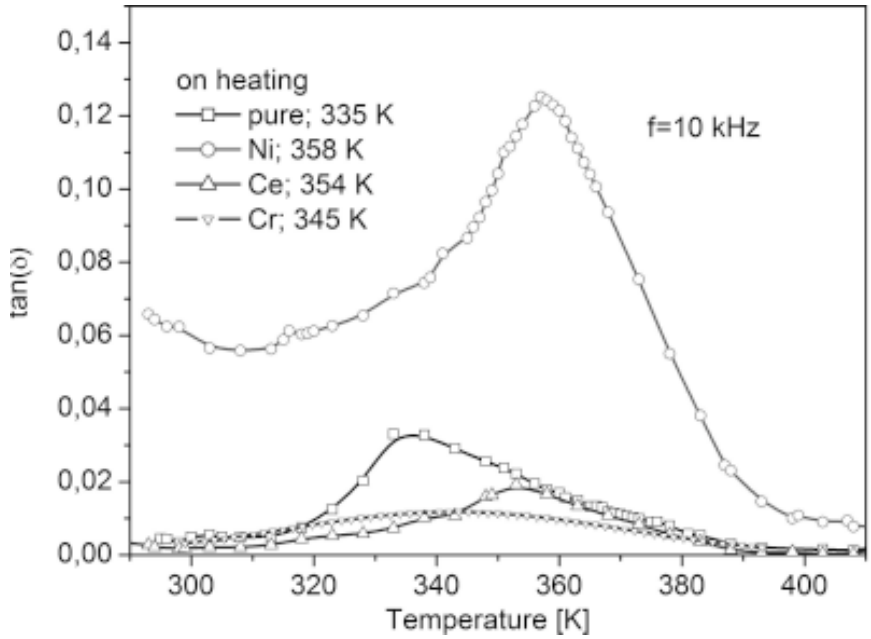

Fig. 3. The loss tangent of SBN61 pure, SBN61:Ni, SBN61:Ce and SBN61:Cr samples measured at a measuring frequency of 10 kHz.

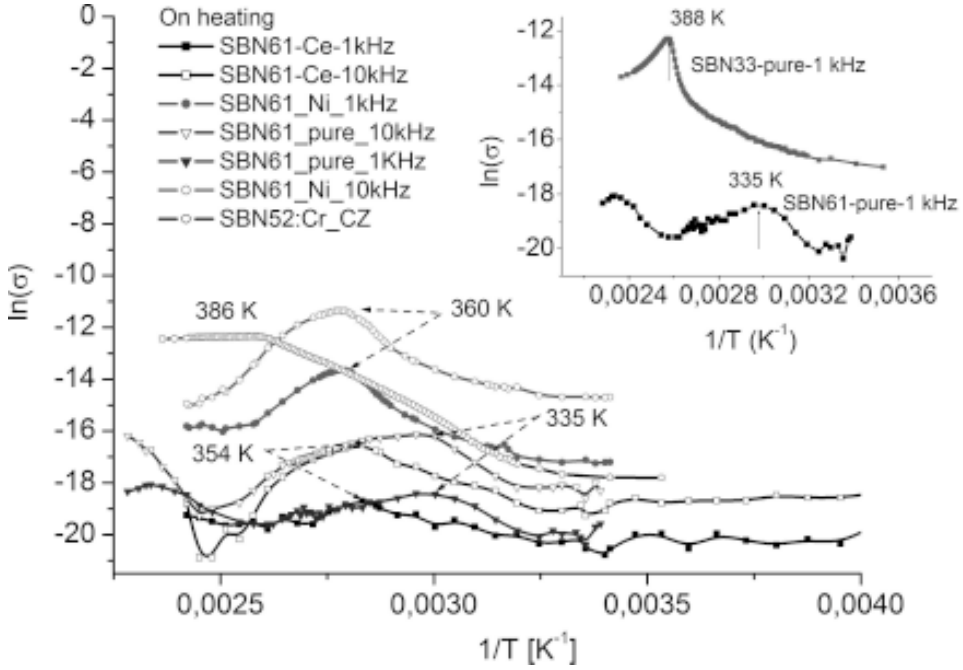

Fig. 4. Variation of lnσ versus the inverse of the absolute temperature at 1 and 10 kHz, measured for pure SBN61, SBN61_Ni, SBN61:Ce and SBN52:Cr samples. A comparison of lnσ vs. 1/*T* is made in the inset for SBN61 and SBN33 pure samples at 1 kHz.

by the former. The maxima of ln(σ) versus temperature observed near an anomaly (i.e. slope change), similarly as in tanδ, are shifted by only a few K with respect to T_m values (see arrows).

The frequency dependence of ε' (T = 300K) and tanδ (T = 358-372K) for all SBN61 samples in the range of 0,1 kHz-1 MHz can be seen in Figs. 5 and 6. As can be seen, a strong drop of ε' with a frequency in the range of 0.1-200 kHz is observed for SBN61:Ce and SBN61:Ni samples. Pure samples and samples doped with Cr show a much lower drop. All the measured samples, except of SBN61:Ni,

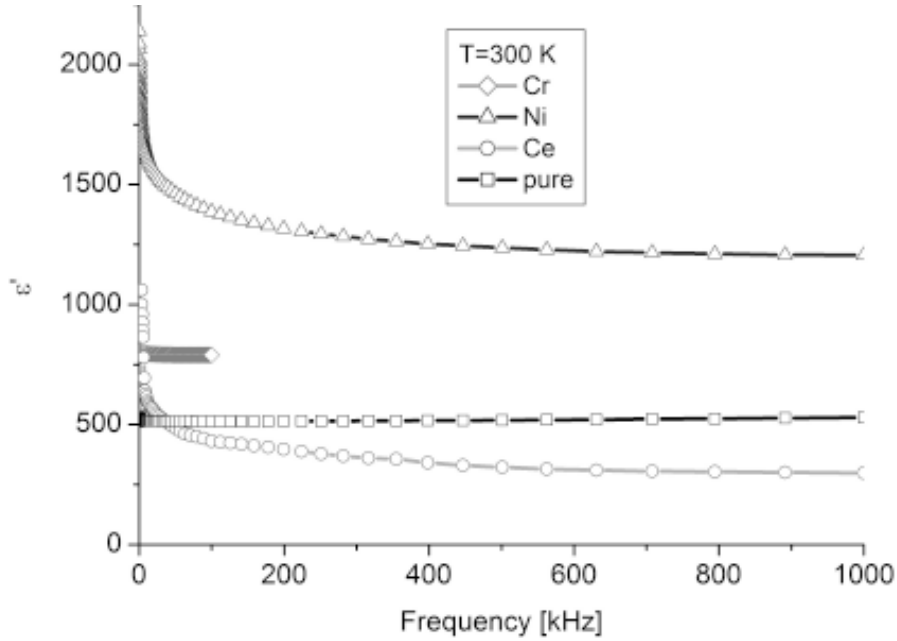

Fig. 5. Frequency dependence of electric permittivity for SBN61 ST samples at 300K.

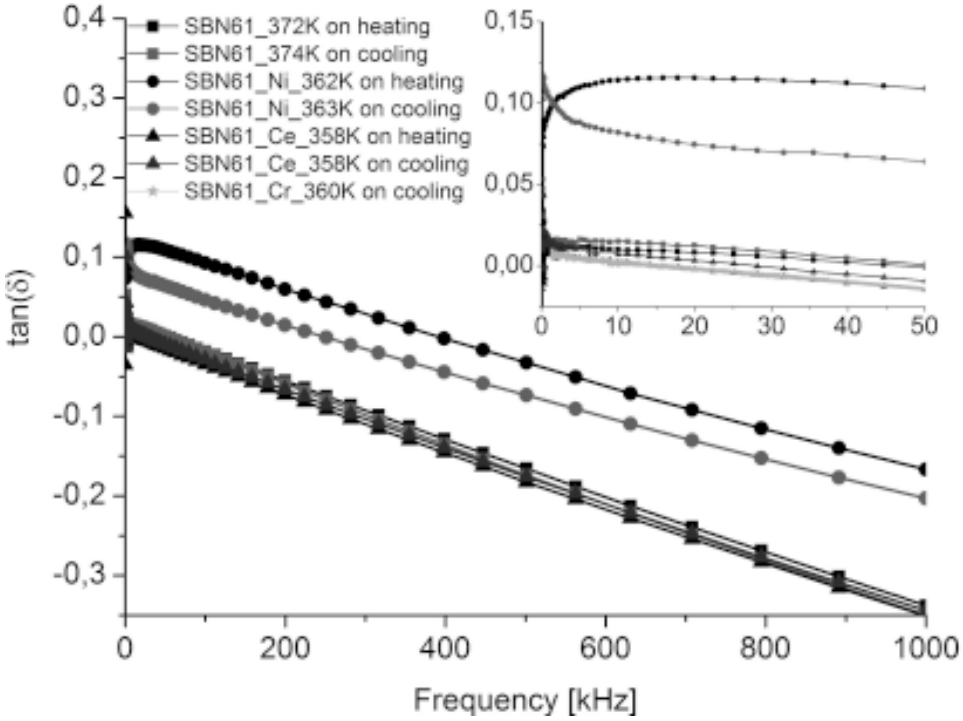

Fig. 6. Frequency dependence of tanδ for SBN61 ST samples on heating and on cooling at temperatures in the range of 358-372K.

show a linear decrease of tanδ with an increase in frequency. The SBN61:Ni sample reveals some deviation from the law. It shows nonlinear behavior for frequencies lower than 10K. Czochralski grown samples reveal the same kind of a drop with frequency. We have also observed, an increase in the electric field frequency shifted T_m towards higher temperatures (by about 5K in the range of 1-10 kHz) as usually for relaxors [2]. The frequency variation of ε' and tanδ of SBN61 at room temperature reveals that both ε' and tanδ decrease with the increasing frequency, which indicates that ε' has a major contribution from dipoles at low frequency and at low temperature [12,13]. Moreover, the temperature de-

pendent dielectric studies at various frequencies show that the permittivity maxima are diffusive and dispersive.

In case of Cr or Nd doping of an SBN crystal, an increase in the dopant content leads to the shifting of T_m towards lower temperatures [9,14]. Doping may shift the band gap energy of a crystal. We have measured the optical absorption of the investigated samples and calculated the optical band gap, using the following equation:

$$(\alpha \cdot h\nu)^2 = (h\nu - E_g), \quad (3)$$

where α – the absorption coefficient of the investigated sample, $h\nu$ – the photon energy.

The calculated energy gap, E_g, has been found to be equal to 3.24 eV and 3.29 eV for SBN33, Cr doped SBN52 and Cr, Yb codoped SBN58, respectively, while 3.28 eV (pure and Ce doped), 3.24 eV (Ni doped) and 3.17 eV (Cr doped) SBN61 single crystals. The observed shifts in the T_m, diffuseness (γ) and changes in ε'_m values correlate to some extent with changes in the E_g value.

When reflecting on the occurrence of the relaxor behavior in any kind of oxide, it appears due to the existence of a lattice disorder and polar nanodomains at a temperature much higher than T_m [2]. A random lattice disorder produced by a chemical substitution in SBN can lead to the formation of dipolar impurities and defects that have profound influence on the static and dynamic properties of these materials. Enhanced relaxor behavior of Cr doped SBN52 crystals has been reported in [8]. The EPR investigations have confirmed the presence of Cr ions, except for Nb positions, also at interstitials. The nanopolar domains that may play an important role in the occurrence of relaxor behavior have been analyzed in papers [15-16]. Hysteresis loops have been analyzed for the above materials in [8,16-18]. It has been found that the domain contribution in polarization mechanisms becomes more significant at temperatures $T \geq 263$K [18].

4. CONCLUSIONS

The T_m temperatures for SBN61, SBN61:Ni, SBN61:Ce, and SBN61:Cr, have been found to be equal to 370, 362, 360, and 347K on heating, and, to 377, 360, 358, and 345K on cooling, respectively, at the measuring frequency of 10 kHz. The ε'_m and T_m values have been observed to be much higher for the SBN samples obtained by the CZ method. The SBN samples obtained by the CZ method have revealed also higher conductivity probably due to greater amounts of oxide vacancies. The diffuseness constant, characterizing the relaxor type anomaly of dielectric constant, has been found to change from 1.25 for Ce doped (1.34 for pure SBN) to 1.98 for Cr and Ni doped samples. It seems that the Ce dopant plays the role of a dopant improving lattice ordering.All the investigated samples have shown a decrease in the value of ε' with an increase in frequency. The largest decrease in the quantity has been observed for the Ce and Ni doped samples. Higher dielectric losses have been observed for the SBN61:Ni sample, while the lowest losses have been seen for the SBN61:Cr sample. All the SBN crystals, apart from the Ni doped SBN61, have revealed a linear drop of tanδ with frequency. In case of the Ni doped SBN61 sample nonlinear behavior of the above quantity has been observed in the range of 0.1-10 kHz.

Owing to the obtained results it can be concluded that the relaxor behavior of the investigated samples strongly depends on the kind of doping (lattice disorder), but less on the Sr/Ba ratio. The observed shifts in the T_m, diffuseness (γ) and changes in the ε'_m values have been to some extent correlated with the changes in the E_g value.

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