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Effects of Ni doping on properties of strontium–barium–niobate crystals

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Abstract

Doping congruently melting crystals of SBN with Ni results in a strong lowering of the phase transition temperature and a significant smearing of the phase transition. As a consequence such parameters as the dielectric permittivity, the pyro-, piezo- and the electrooptic coefficients are remarkably increased at room temperature and show relatively weak temperature dependencies. The Ni-induced optical absorption is interpreted as crystal field transitions.

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Ferroelectric strontium–barium–niobate SBN- x ($\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$) crystals are attractive for various applications because of high values of important parameters (optical, pyro- and piezoelectric, etc. [1]). An appropriateness of these crystals for both applications and fundamental studies in relaxor ferroelectrics [2] is particularly due to a significant dependence of these parameters on the phase transition temperature T_c and its diffuseness induced by the [Sr]/[Ba] ratio or various dopants. An increase in the Sr content, as well as doping with rare-earth (RE) impurities [3–5] lowers T_c and smears out the phase transition, which leads to an increase in all parameters at ambient conditions. Similar effects were achieved by doping SBN-0.61 with a transition metal (TM) impurity Cr [6].

We report on the effects of another TM impurity—Ni—on ferroelectric and related properties of SBN-0.61. We show that Ni doping strongly affects the phase transition and

permits to vary efficiently a variety of important parameters in SBN. Recently two- and four-wave mixing was demonstrated in SBN:Ni when recording a grating at $\lambda = 476.5$ nm with a two-beam coupling gain factor Γ of 19 cm^{-1} and a rather fast response [7]. So the data presented here provide particularly the characterization of a new photorefractive composition based on SBN-0.61.

The crystals were grown by a modified Stepanov technique [8] from a congruent melt, the Ni impurity was introduced into the melt as the ‘black oxide’ Ni_2O_3 . The crystals with 0.05, 0.5 and 1 wt% in the melt were grown.

Fig. 1 presents the temperature dependence of the dielectric permittivity ϵ_{33} in a Ni-doped and an undoped SBN-0.61. The temperature T_m of the maximum of ϵ_{33} in SBN:Ni is strongly lowered and the phase transition noticeably smeared. This effect of doping with 1% Ni is comparable with an increase in the content of the host ion Sr from 61 to 75 mol%. Preliminary estimates show that the shift of the maximum per 1 at.% Ni in the crystal is not less than 20° . As a result, all parameters (dielectric permittivity, pyro- and piezoelectric and electrooptic coefficients) are increased. Table 1 summarizes these data obtained at

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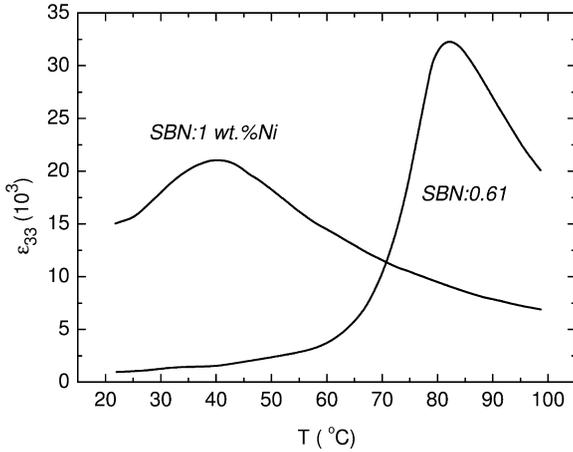


Fig. 1. Temperature dependencies of the dielectric permittivity ϵ_{33} in SBN-0.61 and SBN-0.61:1 wt% Ni at a measuring frequency of 1 kHz and voltage of 3 V/cm (polydomain crystals).

room temperature for SBN:Ni samples in comparison with SBN-0.61 and SBN-0.75 crystals grown from the same charge under the same growth conditions [8]. The parameter ϵ_{33} was measured in poly-domain crystals at 1 kHz. The pyroelectric coefficient γ was determined in single-domain crystals by means of a static integrating technique. The piezoelectric coefficient d_{33} was obtained by means of a resonance–antiresonance technique [9] in the frequency range from 100 kHz to 5 MHz in single-domain samples with sizes $3 \times 3 \times 10 \text{ mm}^3$, the edges of the parallelepiped being parallel to the crystallographic axes.

Calculations were done with the use of the well-known formula [9]

$$d_{33} = \frac{\pi}{4} \sqrt{\frac{\epsilon_{33} \epsilon_0 (f_a - f_r)}{\rho f_r^3 h^2}} \quad (1)$$

where f_r, f_a are the resonance and antiresonance frequencies corresponding to the maxima and minima of the total impedance, ρ is the crystal density for the undoped SBN-0.61 [10], h is the crystal thickness in the direction of the polar axis. The half-wave voltage $V_{\lambda/2}$ was measured for $\lambda = 476.5 \text{ nm}$ with an Ar-ion laser by a dynamical method under a sinusoidal field of 50 Hz. The electrooptic coefficient r_{33} in SBN-0.61 and SBN:0.5% Ni were measured by an optical compensator technique under a

quasi-static field. Additionally, it was calculated for SBN:0.05% Ni and SBN:0.5% Ni on the base of combined data of $V_{\lambda/2}$ and Γ . The accuracy of γ, d_{33}, r_{33} was not worse than 10%. For SBN-0.61 the values of d_{33}, r_{33} and $V_{\lambda/2}$ are in good agreement with literature data [1,10].

As seen from Table 1, a relatively low Ni doping leads to a strong enhancement of all parameters. Particularly, ϵ_{33} grows essentially and for 1% Ni it is as high as 14 000, which can be of practical interest, for example, for layered structures. However, for SBN:1% Ni we do not show data γ, d_{33}, r_{33} , because owing to the closeness of T_c to room temperature, the single-domain state in this crystal is unstable. As a result, these parameters, as well as Γ [7], are unstable, too, and lower than in SBN:0.5% Ni.

Fig. 2(a) and (b) presents the temperature dependencies of the resonance–antiresonance frequencies and calculated from them the temperature dependence of d_{33} in SBN:0.5% Ni. In Fig. 2(a) we show $f_r(T)$ and $f_a(T)$ both at temperatures below and above T_c in order to demonstrate their anomalous temperature behavior. Namely, both $f_r(T)$ and $f_a(T)$ in the range of the smearing phase transition increase with temperature and a stable piezoelectric resonance exists deeply in the centro-symmetric paraelectric phase, where it is symmetrically forbidden. (In model ferroelectrics like TGS only a weak non-zero piezo-effect is detected in a narrow temperature range above T_c). Similar ‘long tail’ of piezoelectric resonance into the non-polar phase was observed in SBN:Ce [11] and was accounted for by relaxor features of SBN [2], namely by a non-zero polarization caused by polar clusters far above T_c . Actually, a strong smearing of the ϵ_{33} peak in SBN:Ni (Fig. 1) indicates an enhancement of relaxor features.

The dependence $d_{33}(T)$ calculated in the temperature range of a ‘classical’ behavior of $f_r(T)$ and $f_a(T)$ in the ferroelectric phase, is presented in Fig. 2(b). As seen from Table 1 and Fig. 2, d_{33} in SBN:Ni is essentially increased in the whole temperature range. A similar increase in the piezoelectric effect is caused in SBN by some RE doping [3,5].

To characterize the optical properties we present optical absorption spectra in SBN:1.0% Ni (Fig. 3) calculated from the transmission spectra with an account for multiple reflection. The spectra show two absorption bands, the one at higher energy with no symmetrical shape has a shoulder at its low energy side. The intensity of these bands scales

Table 1

Ferroelectric and related parameters of SBN-0.61:Ni crystals, for details see the text. T_m means the maximum temperature for ϵ_{33}

Crystal	wt% Ni in the melt	T_m (°C)	ϵ_{33} (1 kHz)	$V_{\lambda/2}$ (V)	$\gamma \times 10^{-3}$ (C m ⁻² K ⁻¹)	$d_{33} \times 10^{-12}$ (C N ⁻¹)	$r_{33} \times 10^{-12}$ (mV ⁻¹)
SBN-0.75		50	3500				
SBN-0.61		82	950	250	0.75	140	260
SBN-Ni ₂ O ₃ :0.05	0.05		1700	235			265
SBN-Ni ₂ O ₃ :0.5	0.5	60	5200	125	12.3	270	495
SBN-Ni ₂ O ₃ :1.0	1.0	40	14 000				

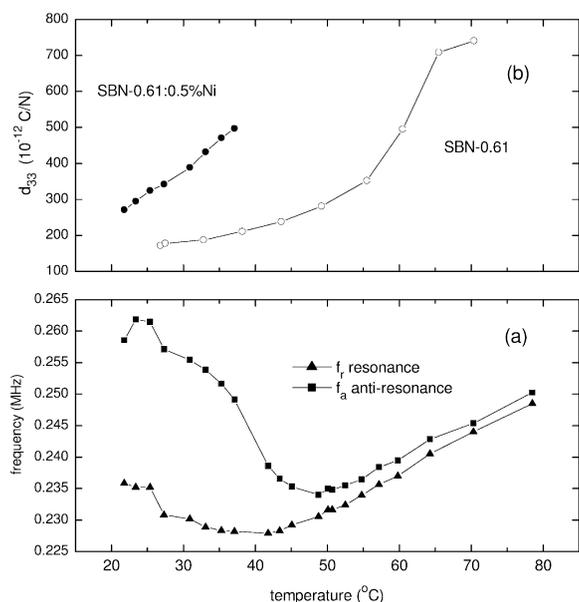


Fig. 2. Temperature dependencies of the resonance–antiresonance frequencies in SBN-0.61:0.5 wt% Ni (a) and of the piezoelectric coefficient d_{33} in SBN-0.61:0.5 wt% Ni in comparison to an undoped SBN-0.61.

with the doping rate. At about $20\,000\text{ cm}^{-1}$ a strong absorption feature is observed for both ordinary and extraordinary polarization. This absorption has to be attributed to the Ni doping, because first the bandedge absorption of pure SBN appears at several thousand wavenumbers shifted to the blue (see right side in Fig. 3), second the dichroism is about two times stronger in SBN:Ni than in pure SBN, and third the stoichiometry [Sr]/[Ba] ratio of SBN does not change the dichroism for these absorption strengths [12]. Although there are no clearly visible strong differences in

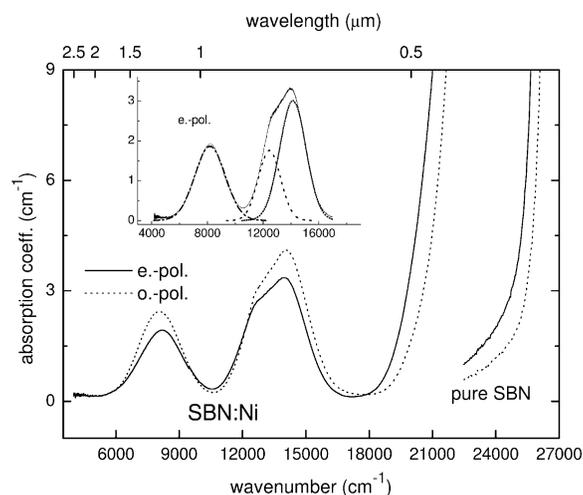


Fig. 3. Polarized optical absorption spectra in SBN-0.61:1 wt% Ni.

the spectral shapes of the spectra, a decomposition shows that the low energy transition can be well described by a Gaussian, while for the asymmetric band two Gaussians are needed, see the inset in Fig. 3. In Table 2 the energies obtained with these fits are presented, and it is obvious that the low energy absorption is due to two different transitions.

Although Ni has been added as Ni_2O_3 , we have so far no unambiguous proof for its charge state in the crystal. The usually performed electron paramagnetic studies failed or were not conclusive. Because of the high dielectric constant we observed only a broad unstructured signal at He temperature far from the maximum T_m . This result is not surprising, because Wingbermühle et al. [13] have shown that even for the closed shell rare-earth ion Ce^{3+} the open tungsten bronze structure causes a broad signal with no fine structure. The situation is more unfavorable for TM elements like Ni and thus, as far as we know, no detailed EPR studies are known for transition metal element in SBN. Therefore, we have to argue by comparison with typical Ni spectra. As pointed out by Lever [14], Ni^{3+} generally, only exhibit charge transfer spectra, and thus only a few examples for d–d transitions have been reported. Much more likely is Ni^{2+} , because first our bands are not very broad, second many examples of crystal field spectra are known and third substituting for Ba or Sr causes no charge compensating problems. The free Ni^{2+} ion forms a ${}^3\text{F}$ state which is split in cubic symmetry into the three levels ${}^3\text{A}_2$, ${}^3\text{T}_2$, and ${}^3\text{T}_1$ and further into $({}^3\text{B}_1)$, $({}^3\text{E}, {}^3\text{B}_2)$, and $({}^3\text{A}_2, {}^3\text{E})$ in tetragonal symmetry, respectively. Transitions between the ground state ${}^3\text{A}_2$ and the excited ones are spin-allowed in cubic symmetry but forbidden in tetragonal one. Thus we have to assume vibronically allowed transitions. Then under weak tetragonal splitting the bands 1 in Table 2 may be assigned to transitions ${}^3\text{B}_1 \rightarrow {}^3\text{E}$, ${}^3\text{B}_2$ and bands 2, 3 to ${}^3\text{B}_1 \rightarrow {}^3\text{A}_2, {}^3\text{E}$. But we cannot exclude that the splitting of the bands 2, 3 is due to an admixture of the transitions ${}^3\text{A}_2 \rightarrow {}^3\text{T}_2, {}^1\text{E}$, due to the large spin–orbit-interaction of Ni. The absorption close to the bandedge may be attributed to a transition to a level derived from ${}^3\text{P}$. Finally, we mention that the energies given in Table 2 are in good agreement with data compiled by Lever [14] for Ni^{2+} .

In summary, we characterized properties of a new photorefractive composition, SBN:Ni, and showed that doping SBN with a relatively low Ni concentration in the range of 1 wt% (in the melt) provides an efficient tool for enhancing important practical parameters, which is due to a strong lowering of T_c and a simultaneous smearing of the

Table 2
Energies in cm^{-1} obtained by fitting the spectra with Gaussians

Light pol.	Band 1	Band 2	Band 3
Ordinary	8105	12 540	14 185
Extraordinary	8190	12 450	14 130

phase transition. The optical absorption was interpreted as crystal field transitions of Ni^{2+} .

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