Ferroelectric, dielectric and optic properties of Mn and Cr-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$ single crystals

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ABSTRACT

The results from Raman, pyroelectric, dielectric and ferroelectric investigations of Mn and Cr-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT) single crystals are presented. Influence of this substitution on the properties of NBT was observed. The influence manifests in several ways: (i) an increase of the electric conductivity, (ii) an increase of the remanent polarization and the decrease of coercive field, (iii) an improvement of pyroelectric properties and (iv) an increase of $T_m$ temperature. Raman studies showed that substitution of a small amount of foreign ions affected local structure of the material. No evidence of the antiferroelectric phase was found in NBT-doped single crystals.

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1. Introduction

In many mixed (A$^{1-x}$A$'^{x}$)BO$_3$ and A(B$^{1-x}$B$''^{x}$)O$_3$-type perovskites the diffuse phase transitions can be observed. The diffuseness demonstrates itself in a broad maximum of dielectric permittivity and a gradual change of the spontaneous polarization with temperature which cannot be described by the physics of proper or improper ferroelectrics. Some of the systems show a strong dependence on the frequency: maxima of dielectric permittivity and dielectric loss are shifted towards higher temperatures with increasing frequency - the so called relaxor behavior. Simultaneously, the value of dielectric permittivity in its maximum decreases and dielectric loss increases as the frequency increases. The broad maximum of permittivity does not correspond to any phase transition in these materials. Microscopic structure below the temperature of the permittivity peak ($T_m$) consists of polar regions with coherence length of the order of several nanometers. These polar regions persist up to temperatures far above $T_m$. It is generally accepted that the relaxational behavior in relaxor ferroelectrics results from existence of structural disorder in A or/and B sites, which leads to the appearance of polar regions. Physical properties of these materials are strongly sensitive to the structural disorder. However, the majority of relaxor ferroelectrics are based on the lead-oxide (for example...
PbZr$_x$Ti$_{1-x}$O$_3$, PbMg$_{1/3}$Nb$_{2/3}$O$_3$ and related compounds), which have some drawbacks due to the volatility and the toxicity of PbO. It is also impossible to grow single crystals of PZT of sufficient quality and size for scientific investigations and for applications. Recently, it is desirable to use low-lead or lead-free materials for the applications [1–14]. Some of the promising candidates are sodium-bismuth titanate Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT) and its modified compounds [1–8].

NBT is cubic at highest temperatures with the Curie-Weiss behavior in the dielectric permittivity. A phase transition to tetragonal phase takes place at 540–520 °C (813–793 K), and to rhombohedral phase at \( \sim 260 \) °C (533K) [15–23]. The tetragonal and rhombohedral phases are known to exhibit ferroelasticity/ferrielectricity and ferroelectricity, respectively. The broad maximum of the dielectric permittivity occurs at \( T_m \approx 320 \) °C (593K). This maximum, as in relaxors, does not correspond to a phase transition because no change in crystal structure, specific heat etc. are observed around this temperature. However, some behavior of NBT is different from that of other relaxors. For example, the distinct shift of temperature \( T_m \) with increase of frequency, typical for relaxors, does not take place. Also, the transition to a long-range ferroelectric state in NBT takes place spontaneously in contrast to relaxors where this phase must be rather induced by application of an electric field or mechanical stress. The formation of long-range ferroelectric order in NBT corresponds to a small (diffuse) bump on dielectric permittivity profile. This bump shows a small relaxor-like behavior. Regarding this contradiction, the antiferroelectric ordering has been proposed [16]. However, X-ray, neutron scattering, Raman scattering measurements deny this suggestion, and rather indicate the coexistence of the tetragonal and rhombohedral phases in a wide temperature range [15, 17–23]. This may be caused by the preexisting unstable polar regions whose correlation radii increase as temperature decreases [18]. Below 280 °C (553 K), the regions are stable and are expected to become the nuclei of low-temperature ferroelectric phase.

Recently, detailed studies of domain structure of NBT single crystals have been carried out by Viehland’s group [24]. They showed that a tetragonal ferroelastic domain structure of NBT is unchanged upon cooling from 520 °C (793 K) to 25 °C (298 K) (which is consistent with our earlier results [25]), and then polar microdomains nucleate on cooling in rhombohedral ferroelectric phase within the geometrical restrictions imposed by the inherited ferroelastic domains [24].

The structural disorder in A and/or B-sites can result from a heterogeneous positional distribution of the ions, from off-center location of ions, and from chemical heterogeneity connected with different ionic polarizability, radii and valence. It was shown by Petzelt et al. [26] that the dynamics of bismuth ions are responsible for the unique properties of sodium bismuth titanate. Therefore, we can expect that doping of NBT with ions of different ionic radius and/or different valence than those of (Na, Bi) and/or would change its properties (especially ferroelectric and relaxor behavior). The large coercive field and relatively large electric conductivity make NBT difficult to pole. We expect that doping of NBT might decrease both the coercive field and the electric conductivity. In present paper, Cr or Mn (Jahn-Teller configuration cations) ions were chosen for the modification of NBT and they are expected to affect structural disorder.
To the best knowledge of the authors, there is a lack of data in the literature about the doping of NBT by Mn and Cr ions (some information on doping with Mn has been reported in Refs. [27] and [28]). The aim of this study is to investigate optical, dielectric, pyroelectric and ferroelectric properties of Mn and Cr-modified NBT single crystals.

2. Experimental procedure

2.1. Preparation of the samples

Single crystal samples were grown by Czochralski method. Single crystals of NBT, NBT doped with Mn (0.05% mol) and Cr (0.05% mol) have been obtained. Stoichiometric amounts of initial compounds (Na$_2$CO$_3$, Bi$_2$O$_3$, and TiO$_2$) were weighted and homogenized in agat mortar using alcohol for 24 h. The mixed powders were then dried and calcined at 800 °C (1073 K) for 2 h. The calcined powders were reground and calcined again under the same conditions. The crystal growth was performed at 1300–1350 °C (1573–1623 K). Slightly yellowish (NBT) and light-brown (Mn and Cr-doped NBT) crystals of 1.5 cm diameter were obtained. Relative density which was obtained by Archimedes method is 99%. Polished (001) cuts of the crystals have been used for the present experiments.

2.2. X-ray diffraction analysis

X-ray diffraction analysis was performed on powder samples using Seifert powder diffractometer (XRD 3000 TT). The Cu K$_\alpha$ radiation was filtered. The samples were annealed at 600 °C (873 K) for half an hour. The temperature was stabilized with the accuracy equal to ±0.1 °C (± 0.1 K).

2.3. Raman spectroscopy

The Raman spectra were recorded in Bio-Rad FTS 6000 spectrometer with Nd-Yag laser system for powder samples, where the 1064 nm line was used as excitation line. The laser power was 200 mW. The spectra were collected with 4 cm$^{-1}$ resolution.

2.4. Dielectric measurements

Dielectric properties were investigated in 10 Hz–500 MHz in transmission regime from 27 °C to 727 °C (300 K to 1000 K). Agilent E5071C vector network analyzer was used to measure complex transmission coefficient. The detailed description of an experimental procedure can be found in Ref. [29]. Silver electrodes were used for all the crystals.

2.5. Pyroelectric and hysteresis loops measurements

Pyroelectric measurements were done by a quasistatic method at heating rate of 10 °C/min (10 K/min). Poling was performed on cooling from 250 °C (523 K) down to room temperature at D.C. electric field up to 20 kV/cm. The hysteresis loops were measured
by low-frequency triangular signal method [30] using the field up to 60 kV/cm at 0.25 Hz.

3. Results and discussion

Figure 1 shows the X-ray diffraction pattern of the NBT. The diffraction patterns for other compositions are not shown because they exhibit a similar behavior as observed in undoped NBT. All specimens have pure perovskite structure at room temperature, and no secondary phases could be detected within the error-limits of the XRD machine. This means that all doped ions have diffused into the lattice of NBT host. It should be pointed out that Mn and Cr ions have mixed valence states of $\pm 2$ or $\pm 3$ which can be incorporated into either A-site or B-site of NBT. Ions with valence state $\pm 2$ incorporated into the Bi$^{3+}$ or Ti$^{4+}$ sites would act as a lower valent species on higher valent site. In this case oxygen vacancies would be created for the charge compensation.

The difference in the chemical nature of cations is known to lead to the different types of A-O bonding with different stretching frequencies. Therefore, observed change of Raman spectra can be attributed to the formation of new bonds and change of A-O strength. The Raman spectra of all the crystals are given in Figure 2. The Raman spectrum of unmodified NBT is consistent with published data [19, 31], where it was assigned as belonging to the rhombohedral R3c phase, for which 13 Raman-active modes ($I_{\text{Raman}, \text{R3c}} = 4A_1 + 9E$) are expected. The Raman bands are rather broad, which can be connected with the cation disorder on the A-site and with some overlapping Raman modes. Five main ranges that exhibit scattering effect located at $\sim 142, 280, 530, 585$ and above 700 cm$^{-1}$ can be discerned. The low-frequency one is associated with Na-O vibrations, the second one-with Ti-O vibrations, whereas the higher frequency bands can be assigned to vibrations of the TiO$_6$ octahedra (superposition of transverse optical (TO) and longitudinal optical (LO) bands of $A_1$ character). The high-frequency range above 700 cm$^{-1}$ can be caused by the vibrations resulting from the shift of oxygen and also correlated to the presence of oxygen vacancies [32]. This range has been linked to $A_1$ (LO) and $E$ (LO) overlapping bands [33]. Due to the high mass of the bismuth atom, a Bi-O band would be located at very low frequencies below 50 cm$^{-1}$ [26] and was not possible to observe in our experimental conditions. It is clearly seen from
Figure 2 that the modified NBT spectrum is similar to the unmodified NBT one indicating there is no significant change of the crystal structure in accordance with XRD data. However, a small variations in the peak position were observed, which is consistent with the small difference in atomic mass on the A/B site Mn/Cr substitution. Moreover the shape of 142 cm\(^{-1}\) mode is very similar for undoped and Cr-doped NBT, but it is different from Mn-doped NBT. However the shape of the 280 cm\(^{-1}\) mode change after both Mn and Cr ions substitution to the NBT (most after Cr ions substitution). Thus we can conclude, that Mn ions occupies both A and B-sites, but Cr ions occupies B-site. Also small changes of 585 cm\(^{-1}\) and 700 cm\(^{-1}\) bands occur. The small evolution of 585 cm\(^{-1}\) band can be caused by the change of the average ionic radius of cations in sublattice A/B (after Mn or Cr doping). However, the small evolution of above 700 cm\(^{-1}\) band can be caused by the change of vacancy concentration [32]. Although the observed Raman spectra change cannot be precisely assigned, there are detectable variations in local symmetry (in short range crystalline order).

Temperature dependences of complex dielectric permittivity at 10 MHz frequencies are depicted in Figure 3. The experiments were carried out on heating and cooling cycles during the same experiment.

The dielectric data for NBT single crystals is consistent with previously published results in the literature. The most important result here is the dielectric data above 1 MHz in a broad temperature range. Our experimental results show that the dispersion
below 227°C (500 K) is observed at frequencies only below 1 MHz. We show that the
dispersion disappears at microwave frequencies and we do not observe the kink in the
vicinity of room temperature (Figure 4). This result does not allow to categorize sodium
bismuth titanate strictly as a relaxor because the main feature of relaxors is very broad
dispersion expanding 10–12 orders of magnitudes. In earlier investigations it was shown
that this dispersion is strongly affected by the poling of the sample [34]. It suggests that
this dispersion might be related to domain wall motion. Furthermore, it is known that
domain wall dispersion usually lies at frequencies below 1 MHz. Another important
matter is that sodium bismuth titanate has well defined phase transition from ferroelectric phase to nonpolar one. This structural phase transition distinguishes this material from canonical relaxors thus the dispersion which is observed in the ferroelectric phase can be attributed to the peculiarities of this phase transition.

The temperature dependences of complex dielectric permittivity of pure sodium bismuth titanate single crystal is represented in Figure 4 (temperature dependences of doped crystals can be found in the Supplementary Material, available online). The anomaly in $227^\circ\text{C} - 527^\circ\text{C}$ ($550^\circ\text{C} - 800^\circ\text{K}$) temperature region does not exhibit the shift of dielectric maxima at different frequencies. It is clear evidence that this anomaly cannot be attributed to the relaxor behavior either. To the best of our knowledge this is the first time this temperature region was probed at the microwave frequencies (up to 500 MHz) in single crystals. Ceramics exhibit qualitatively similar behavior [26].

Another interesting feature that is observed in the temperature dependence of the imaginary part of complex dielectric permittivity is the hysteresis on heating and cooling cycles. The thermal hysteresis occurs at temperature region where the paraelastic-ferroelastic phase transition takes place. The anomaly is more pronounced on heating cycle but it still exists on cooling as well. This anomaly can be related to the ferroelastic domain walls and the scattering of the charge carriers. Indeed, existence of ferroelastic domains in tetragonal phase of NBT was observed [24, 25]. On cooling into rhombohedral phase, ferroelectric domains then form within the ferroelastic tetragonal domains [24], however complete stress accommodation is not achieved [24, 25].

The addition of Chromium and Manganese increase the dielectric permittivity of NBT single crystal (Figure 3). This substitution leads to higher $T_m$ as well. The increase is observed both in real and imaginary parts. Both dopants modify the properties in a similar fashion. The increase in real and imaginary part of dielectric permittivity might be closely related to the additional charges appearing with the new dopants in the single crystals. The results of Mn doped crystals are consistent with Ge et al. (although the concentration of Mn in the mentioned work is fairly larger) [27]. According to the

![Figure 5. Temperature dependence of DC conductivity of the investigated crystals.](image)

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study of Nagata et al. [29] Mn ions occupy the A-site in the perovskite lattice. Our results are consistent with these previous works.

Temperature dependences of DC conductivity of all the crystals are depicted in Figure 5. The results were fitted with Arrhenius law at the highest temperature. It seems that the activation energies of conductivity are different for all the crystals and decrease with the dopant concentration. Pure sodium bismuth titanate has activation energy of 1.6 eV and is in good agreement with earlier investigations on ceramics [35]. Thus, the conductivity of undoped crystal is intrinsic: the value of activation energy is half of a band gap [36, 37]. Crystals with dopants exhibit lower activation energies. This means that these dopants create impurity levels in the energy band gap. Unfortunately, wider theoretical studies must be carried out in order to determine actual energy band diagram. Furthermore, changes in the slope of conductivity vs. temperature plot can be observed in the vicinity of phase transition (320 °C (593 K)) in the doped samples. The change of this slope might be related to the changes of band gap between two different
phases. Another reason for such a change might be related to the different scattering mechanisms at different temperature regions.

The current hysteresis loops of Mn and Cr modified NBT single crystals at various temperatures are shown in Figure 6. The shape of these hysteresis loops exhibits the characteristic ferroelectric current peaks separated by $\sim 2E_c$ ($E_c$ is coercive field) up to temperatures of about 200 °C (473 K) (for Mn-doped NBT single crystals) and about 130 °C (403 K) (for Cr-doped NBT single crystal). At higher temperatures these loops start to deform. Deformed hysteresis loops are characteristic for region of phase coexistence of polar and macroscopically nonpolar phases [38, 39]. The occurrence of these loops is the evidence of instabilities of local phase transitions induced by an electric field (the induction and then disappearance of polar regions [39]). These processes are accompanied by coupling of mechanical stress induced by electrostriction effect and elastic properties of polar regions. Namely, the electric field can both deform and reverse the polar regions, which due to their elastic properties, do not come back to their initial shapes. The results presented in Ref. [24] and significant influence of external compressive stress on the shape of hysteresis loops of NBT [4, 40] and NBT-based materials [41] seem to support this conclusion. Coercive field of Mn and Cr-doped NBT single crystals is lower in comparison to pure NBT (about 60 and 70 kV/cm at

Figure 7. Temperature dependence of the pyroelectric coefficient $\gamma$ (a) and temperature dependence of the remnant polarization (b) for NBT, Mn and Cr-doped NBT single crystals.
Deformed current hysteresis loops presented in Figure 6 are quite different from those displayed by the well-studied antiferroelectric materials, such as lead zirconate PbZrO$_3$ [42]. Thus, no conclusive evidence has been found in present measurements for the presence of antiferroelectric state in NBT-doped materials, similarly as that for pure NBT. Such kind ferroelectric hysteresis loops are similar to ones observed in canonical relaxors. It seems that NBT shares this feature with the lead-based relaxors despite completely different behavior in the temperature dependences of dielectric permittivity.

Pyroelectric coefficient $\gamma$ is higher for Mn and Cr-doped NBT in comparison to the pure NBT (in temperature range from room temperature up to approximately 160°C (433 K), (Figure 7a). This may be due to the fact that substitution of foreign ions to NBT creates the defects to compensate the charge equilibrium. This gives rise to local distortion of the structure. It is easier for dipole to vibrate with the change of temperature. So the pyroelectric properties are enhanced after the addition of foreign ions to NBT. This leads to increase of the remanent polarization (Figure 7b).

4. Conclusions

Single crystals of NBT and NBT-doped with Mn or Cr were fabricated by the Czochralski method. X-ray investigations showed that all samples have pure perovskite structure.

The microwave dielectric spectroscopy revealed that there is no dispersion at least up to 500 MHz frequency range and no well pronounced relaxor properties can be observed in the experimental data. This is consistent with results obtained in the ceramics samples by Petzelt et al. [26] showing that central peak in the THz region is responsible for high permittivity in sodium bismuth titanate.

The Raman data revealed that the dopants of Mn and Cr were incorporated in the perovskite lattice. It was evident from the change in Raman bands. There are evidence that Mn occupies both A-site and B-site positions with possibly different valence while Cr favors the occupation of B-site.

The conductivity studies of the doped crystals confirm that Cr and Mn ions have occupied different sites in the lattice while creating the impurity levels which increases the conductivity and in turn increase the dielectric response of the doped single crystals of NBT.

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