Structural, optical, and electrical properties of Nd-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$

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**Abstract**

The effects of Nd$^{3+}$ addition on structure and functional properties of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT) are examined. X-ray crystallography has allowed the identification of a continuous solid solution with the general formula Na$_{0.5}$[Bi$_{1-x}$Nd$_{x}$]$_{0.5}$TiO$_3$. In the composition range $0 \leq x \leq 0.25$ the structure was found to crystallize in rhombohedral symmetry while for higher Nd$^{3+}$ concentrations tetragonal symmetry is favored. The functional properties are investigated in more detail for the solid solution containing 5% Nd$^{3+}$ where an overall improvement of the ferroelectric properties and a rather high pyroelectric coefficient could be obtained. The fluorescence behavior of this composition is also reported. It is thought that Nd$^{3+}$ doped NBT may be highly promising for a range of applications requiring lead-free ferroelectrics with improved properties.

**Keywords:** NBT, Nd-doping, Microstructure, Ferroelectric properties

1. Introduction

Most of the piezoelectric ceramics used in industry and research belong to lead-containing perovskites. However, it is well recognized that lead is one of the most significant harmful element to environment and health. It ensuèd that research and development of lead-free materials have gained momentum in order to develop a range of materials that could replace the current industry standard materials (mostly based on PZT). Sodium bismuth titanate, Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT), is one of the most promising lead-free ferroelectric materials with a perovskite structure discovered by Smolenskii et al. in 1960 [1]. Because of its high Curie temperature ($T_C = 325$ °C), and piezoelectric coefficient ($d_{33} = 73$ pC/N), comparable to that one of BaTiO$_3$ [2], the NBT is considered as a good candidate for lead-free piezoelectric ceramics. However, the main drawback of pure NBT is its high conductivity that prevents proper poling.

Numerous alkali metal and lanthanide as doping elements were tried in order to improve the electrical properties of NBT [3–8,29–32]. For example, an exceptional change was observed by Xiao et al. with the use of Li$^+$ and K$^+$ co-doping on the Na$^+$ site [29,30]. Xiao et al. were able to increase the piezoelectric and coupling coefficients of NBT to 146 pC/N and 36%, respectively, and reduce the coercive field to $3.7 \, \text{kV \, mm}^{-1}$ while maintaining a high depolarization temperature to produce a lead-free middle frequency filter which performed comparable to a Pb-based one [29,30].

However, a systematic analysis of how such doping affects microstructure, optical and electrical properties is still lacking.

The purpose of the present study is to determine the effects of the addition of Nd$^{3+}$ on microstructure, dielectric, ferroelectric, and optical properties of NBT.

2. Experimental procedure

The polycrystalline samples with various composition of the solid solution Na$_{0.5}$[Bi$_{1-x}$Nd$_x$]$_{0.5}$TiO$_3$ ($0 \leq x \leq 0.35$; xNBTN) were synthesized by the solid-state reaction method. Stoichiometric amounts of Na$_2$CO$_3$ (99.8%), Bi$_2$O$_3$ (99.7%), TiO$_2$ (99.99%), and Nd$_2$O$_3$ (99.99%) powders were thoroughly mixed with alcohol in agate mortar for 2 h, then dried, and calcined for 3 h at 800 °C. The ground powders were pressed into disks of 8 mm in diameter and 1 mm in thickness. The pellets were sintered between 1100 °C and 1130 °C for 3 h in air. The density of all samples was analyzed by Archimede’s method and the obtained values were found to be higher than 95%.

The phase purity of xNBTN solid solution was checked using X-ray diffraction (XRD) analysis (PanAnalytical X’Pert PRO, CuK$_\alpha = 1.5406$ Å) and the microstructure of the sintered ceramics was characterized by a high resolution SEM (Zeiss Ultra...
plus 40, Germany). The Raman and photoluminescence spectra were recorded at room temperature using a SENTERRA spectrometer (Bruker, Germany) with laser excitations at 532 and 785 nm, while, the absorption spectrum was obtained by diffuse reflection on opaque ceramics using Perkin Elmer Lambda 35 UV–VIS Spectrometer. Ferroelectric polarization was investigated at room temperature using a ferroelectric test system (TF Analyzer 2000, aixACCT, Germany and a voltage amplifier). The dielectric properties were studied using (Agilent 4284A) from 20 Hz to 1 MHz on ceramic discs, after deposition of gold electrodes on the circular faces by cathodic sputtering. The pyroelectric coefficient for 5NBNT was measured by a dynamic technique using sinusoidal temperature change with amplitude of 1 °C at 20 mHz.

3. Results and discussion

3.1. Crystal structure and microstructure

Fig. 1 shows the X-ray diffraction patterns of sintered ceramics for all prepared compositions. Two structure types were identified. In the range 0 ≤ x ≤ 0.25, the whole compositions were found to crystallize in rhombohedral symmetry with the space group R3c, while for x ≥ 0.3 a tetragonal structure could be asserted.

Table 1 lists the values of lattices parameters of the investigated ceramics and the octahedral distortion (c/a). As can be seen, a steady decrease of both a and c with increasing Nd3+ was observed (the lattice parameters were calculated using the program Fullprof [9]). This behavior is directly associated with the substitution of Bi3+ by the smaller size ion Nd3+ (r(Bi3+) = 1.03 Å; r(Nd3+) = 0.983 Å, according to the Schanon’s table [10]). For the tetragonal phase, the lattice parameters obtained are in good agreement with those reported for tetragonal NBT [11].

The grain morphology is shown in the SEM secondary electron micrographs, Fig. 2, for different compositions. Fig. 2 shows the large equiaxed grains obtained for pure NBT with a mean grain size of approximately 2 μm. The microstructure is fairly pore-free, and corroborates the density measurements. The grain size decreases with increasing Nd, and some faceting is well visible (Fig. 2b). In the region of the tetragonal phase (x ≥ 25%), the whole grain morphology is square-shaped and a rather porous structure is obtained (Fig. 2c).

3.2. Raman spectroscopy analysis

The Raman spectra of xNBNT recorded at room temperature are shown in Fig. 3. The deconvolution of spectrum at room temperature using Lorentzian functions, shows six vibration modes for NBT situated at 135, 276, 514, 582, 767 and 845 cm−1. These results are in good agreement with the published literature [12–16].

For 5NBNT a smearing of the bands in a Gaussian like curve was observed. This behavior is directly imputed to optical phenomena.

![Fig. 1. X-ray diffraction patterns of Na0.5[Bi1−xNdx]0.5TiO3 sintered ceramics.](image-url)
caused by the introduction of Nd$^{3+}$ in the NBT matrix, and is discussed below. For other compositions, the bands observed are rather characterized by large HWTM values, and are in this respect similar to those generally observed in glassy materials or in disordered host lattices [17,18].

We note that the vibration modes at low frequency cannot be obtained because device limitation, and because of this the Bi–O band positions that are located at very low frequencies, due to the high mass of bismuth atom, cannot be investigated, particularly in terms of Nd effects. Nevertheless, the vibration mode at 138 cm$^{-1}$, assigned to A-site vibration of the perovskite and more specifically to Na–O bonds [13], seems to become broader with the introduction of Nd$^{3+}$ and merges with the one at ca. 277 cm$^{-1}$. Such mode was reported to become overdamped in tetragonal NBT and appeared only as a diffusive quasielastic scattering [14]. The peak position of the band situated at about 277 cm$^{-1}$ in pure NBT that is attributed to the Ti–O vibration [12,13] shows a slight blue-shift with increasing Nd, and is stabilized at 255 cm$^{-1}$ for 30NBNT (see Fig. 3). Further, the doublet observed at high frequency (767, 845 cm$^{-1}$) in pure NBT becomes indistinguishable in a flat and broader band upon doping. This is similar to what was reported in complex perovskite like PMN-PT where the doublet was attributed to some additional bands related to Ti–O bonds [19]. In our case, the reduction of such doublet is a signature that the oxygen network has been affected, which tends to confirm the existence of a phase transition around this composition, already evidenced by XRD.

3.3. Optical investigation

Since the Raman spectroscopy tends to indicate the presence of only a Gaussian like spectrum for 5NBNT under green laser excitation (532 nm), it is worth to investigate the optical properties for such composition. The absorption spectrum at room temperature is shown in Fig. 4a. All observed lines have been indexed with the corresponding electronic transition from the ground $^4I_{9/2}$ manifold to the higher excited states. As a matter of fact, the recorded spectrum at 300 K clearly shows unresolved structure with broad peaks similar to those observed in disordered materials [20]. At closer look to the absorption spectrum, the wavelength of 532 nm is located in the band corresponding to $^4I_{9/2} \rightarrow ^2K_{13/2}, ^2G_{9/2}, ^4G_{7/2}$ transition, and should correlate with the Raman spectrum profile depicted above for 5NBNT.

To investigate the photoluminescence at room temperature, red laser has been used to excite $^4F_{3/2}$ level of Nd$^{3+}$ ($\lambda_{\text{ext}} = 785$ nm). Fig. 4b shows the emission expected for $^4F_{3/2} \rightarrow ^4I_{15/2}$ transitions. For such transition we expected five lines for one Nd$^{3+}$ site, experimentally we observed six peaks (see Fig. 4b). In the case of the transition $^4F_{3/2} \rightarrow ^4I_{11/2}$ (see Fig. 4c) characteristic of laser emission, we expected to get two lines for one Nd$^{3+}$ site, experimentally we observed a large peak centered at 1064 nm with a shoulder at ca. 1056 nm, and a less intense peak at around 1074 nm, which let us surmise that two individual Nd$^{3+}$ sites have been excited. This suggests a distribution of Nd$^{3+}$ over the Na- and Bi-sites. This assumption is compatible with structure disorder evidenced by Raman investigation. We notice that the highest emission was observed for 5% Nd-doped NBT, then
decreases with further increase of Nd (Fig. 4d). This quenching effect is a direct result of cross relaxation interactions between Nd ions [21].

3.4. Electrical investigation of Na0.5(Bi0.95Nd0.05)0.5TiO3

Attention is primarily devoted to 5NBNT as this composition shows interesting optical properties. Detailed electrical investigation for all compositions will be published elsewhere.

The dielectric constants, $\varepsilon_{\text{max}}$ of pure NBT and 5NBNT vs. temperature are shown in Fig. 5. A maximum could be observed around 600 K which may be attributed to the phase antiferroelectric–ferroelastic phase transition [35]. This maximum may originate from relaxation process connected with both electrical and mechanical interaction between polar regions and nonpolar matrix [34]. The NBT exhibits a high dielectric constant with diffuse phase transition (see Fig. 5a) that is in good agreement with earlier reports [22,23,27,33–35]. In comparison 5NBNT is characterized by smaller $\varepsilon_{\text{max}}$ and the peak becomes sharp (see Fig. 5b). For NBT and 5NBNT, a bump at around 450 K could be seen. It could be attributed to depolarization temperature which was explained in some literatures by the presence of an intermediate antiferroelectric phase [24].

The room temperature $P–E$ hysteresis loops for NBT and 5NBNT are shown in Fig. 6. A larger polarization could be observed for NBT in comparison to the reported value of 38 $\mu$C cm$^{-2}$ [24], although there might be some contribution of leakage to the ferroelectric hysteresis curve as evidenced by it somewhat open shape at maximum field. In contrast 5NBNT shows a well-shaped hysteresis curve with saturation of polarization at maximum field. This behavior may be rationalized in terms of reduction of oxygen vacancies that are eventually created due to Bi volatility (for each Bi-vacancy $(V_{\text{Bi}})^{3/2}2V_{\text{O}}^-$ are created). The replacements of Bi by nonvolatile Nd$^{3+}$ should therefore compensate this loss and reduce the number of vacancies, according to the following equation (using Vink–Kröger notation):

$$\text{Nd}_2\text{O}_3 + 2V_{\text{Bi}}^- + 6h^+ \rightarrow 2\text{Nd}_{\text{Bi}}^3 + \frac{3}{2}\text{O}_2^-$$

The addition of Nd$^{3+}$ thus reduces leakage in NBT which in turns leads to ferroelectric property improvement, substantiated in the nearly square-shaped hysteresis obtained for 5NBNT.

The pyroelectric properties of 5NBNT were also investigated. Before measuring, the ceramic was poled in a silicon oil bath at room temperature under an electric field of 3 kV cm$^{-1}$ for 30 min. The measurement method of the pyroelectric current and extraction of the pyroelectric coefficient from a fast-Fourier-transform analysis of the signal amplitude is described in our previous work [25], and is similar to that described by Garn and Sharp [26]. The pyroelectric coefficient of the test sample is found to be equal to 451 $\mu$C m$^{-2}$ K$^{-1}$. This value is higher than that reported for pure NBT or BNT–BiFeO$_3$ [27] but is comparable to that reported by Zhang et al. on MnO doped NBT thick films [28]. The present results may be explained in terms of the beneficial effect neodymium on the electrical properties, consequently leading to a better poling efficiency of the ceramic.
investigations revealed both morphology and structure changes depending on Nd$^{3+}$ concentration. In particular it is shown that between $x = 0$ and $x = 0.25$ a rhombohedral symmetry with space group R3c is obtained, and above it the symmetry changed to tetragonal. The optical properties revealed a specific behavior of 5NBNT that was also observed in the Raman spectrum. The electrical properties are shown for 5NBNT in comparison to pure NBT ceramic. A sharper dielectric transition with a lower dielectric peak value was obtained for NBT, but the ferroelectric properties were improved over pure NBT. The pyroelectric properties were also characterized, and a fairly high value of the pyroelectric coefficient was obtained for 5NBNT. These overall properties show the potential of Nd-doped NBT for a number of applications such as temperature sensors (pyroelectric properties), Ferroelectric Random Access Memory (FRAM) for its ferroelectric properties, laser fusion drivers, etc.

4. Conclusion

$\text{Na}_{0.5}[\text{Bi}_1-x\text{Nd}_x]_0.5\text{TiO}_3$ $(0 \leq x \leq 0.35)$ solid solutions were processed using the conventional reaction method. Microstructural

Fig. 5. Variation of the dielectric constant ($\varepsilon_r$) versus temperature for NBT (a) and 5NBNT (b) at 1 kHz.

Fig. 6. Room temperature hysteresis loops of the NBT and 5NBNT.

References
