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Effect of electrical poling on the structural, dielectric and photoluminescence properties of small concentration of Ho⁺³ substituted NBT

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Abstract. The effect of electrical poling on the room temperature structural, dielectric and photoluminescence properties of small concentration (i.e. 0.5 mole%) of Ho⁺³ substituted sodium bismuth titanate ferroelectric material (Na_{0.5}Bi_{0.495}Ho_{0.005}TiO₃ abbreviated as NBT-0.5Ho) has been investigated. Its crystal structure was found to be the mixture of two phases of rhombohedral (R3c) and monoclinic (Cc) in which monoclinic (Cc) coexisted as major phase. Comparative study of X-ray diffraction (XRD) patterns of electrically poled and unpoled specimens of NBT-0.5Ho revealed that electric field irreversibly transformed crystal structural of dominant Cc (~94.05% phase fraction) phase to R3c (~70.6% phase fraction) as major phase. Dielectric value and its dispersion with frequency were significantly decreased in poled specimen which is ascribed to electric field driven structural change. Two photoluminescence (PL) emissions at 655nm and 756nm were obtained in NBT-0.5Ho. PL intensity was considerably tuned in effect of electrical poling in term of quenching. Obtain quenching is correlated with induced structural ordering towards higher symmetry phase (R3c) in effect of electric poling which is confirmed from XRD analysis. Obtained additional functionality of photoluminescence in the NBT-0.5Ho ferroelectric material and its tuning in effect of electric field opens the possibility in the material for optoelectronic devices applications.

1. Introduction

Multifunctional materials, manifesting two or more properties from among ferroelectric, magnetic, and pyroelectric, piezoelectric and optoelectric properties, have drawn the remarkable attention. Among lead (Pb) free system, sodium bismuth titanate (Na_{0.5}Bi_{0.5}TiO₃ abbreviated as NBT) is considered as one of the best ecofriendly ABO₃ ferroelectric material which exhibits high remanent polarization ($P_r \approx 37 \mu\text{C}/\text{cm}^2$) and high Curie temperature ($T_c \approx 320^\circ\text{C}$) [1]. However, NBT has drawback of its low piezoelectric coefficient ($\approx 80\text{-}90 \text{ pC}/\text{N}$) and high coercive field ($\approx 70 \text{ kV}/\text{cm}$). Main reason behind this drawback is its



high leakage current and large conductivity which create difficulties in the proper electric field poling of the specimen. High leakage current are induced in the NBT due to creation of oxygen vacancies to maintain the charge neutrality due volatile nature of Bi^{+3} during heat treatment process [2,3]. To overcome the drawback, numerous attempts have been made ranging from various synthesis process to site substitution methods [4,5]. Substitution of trivalent rare earth at Bi^{+3} site is an effective method to solve the problem by reducing the concentration of Bi^{+3} at A-site[6–8]. Generally, it has been observed that small substitution of rare earth significantly improves the ferroelectric properties because of less loss of the $\text{Bi}^{+3}3p(6s2)-O^{-2}(2p)$ hybridization which is fundamentally responsible for ferroelectric properties in the NBT [9]. Since rare earths are optical active ions and they exhibit the photoluminescence properties when they are embedded in NBT type non-centrosymmetric host materials [10]. In such way, rare earth substitution in the NBT is not only improving the ferroelectric properties but also makes the material as multifunction with additional functionality of photoluminescence. Photoluminescence properties of rare earth ion is subject of interest for researcher due to huge applications in laser lightening, bio-applications and medical imaging[11]. Along with this, it is always desirable to tune or control photoluminescence properties through external stimuli, such as thermal treatment, mechanical stress and electric field around the ambient temperature and pressure conditions. Principle behind controlling or tuning the PL properties is changing of crystal structure of host and local crystal field around rare earth. The photoluminescence modulation through structural changes by external electric field has received for great deal of interest for various optoelectronic device applications. In order to this, herein, small amount of rare earth holmium (0.5 mole %) is substituted at Bi^{+3} site of NBT host material using conventional solid state sintering method. Interesting aspect of changing of the crystal structure of holmium substituted NBT by applying the electric field which in turn, effect in modification of photoluminescence intensity, has been demonstrated. Moreover, correlation among crystal structure, dielectric and photoluminescence properties of the electrically poled and unpoled NBT -0.5Ho have been established.

2. Experimental

Polycrystalline $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) and $\text{Na}_{0.5}\text{Bi}_{0.495}\text{Ho}_{0.005}\text{TiO}_3$ (NBT-0.5Ho) have been synthesized by using conventional solid sintering rout method. Dried oxides of high purity reagent grade Bi_2O_3 (Alfa Aesar, 99%), Na_2CO_3 (Alfa Aesar, 98%), TiO_2 , (Alfa Aesar, 99.8%), and Ho_2O_3 (Alfa Aesar, 98%) have been used for preparation of the materials. Detailed synthesis process can be found elsewhere [12]. Room temperature frequency dependent dielectric constant (ϵ') was measured by using the impedance analyzer (Wayne Kerr 6500 B). Photoluminescence measurement at room temperature has been recorded by using the spectrofluorometric (FLS1000 spectrometer, Edinburgh Instrument). Phase analysis of the specimen has been confirmed by X-ray diffractometer (Panalytical X'pert Pro) with $\text{Cu } K_{\alpha} \approx 1.5406 \text{ \AA}$). Electrical poling on the specimen has been carried out in a silicon oil (DOW CORNING 704) bath by applying a DC electric field of 55 kV/cm for 40 min.

3. Result and discussion

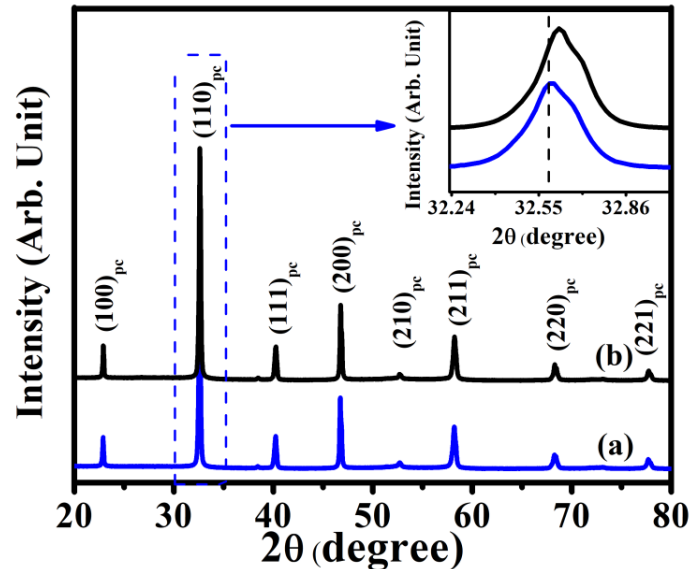


Figure 1. X-Ray diffraction (XRD) patterns of (a). Pure NBT (b) NBT-0.5Ho. Inset shows the close observation of $(110)_{pc}$ Bragg peak

The room temperature X-Ray diffraction (XRD) patterns of the unpoled NBT and NBT-0.5Ho are shown for range of 20° to 80° in Figure 1. Sharp peaks of Bragg reflection of both the compositions are confirming the formation to perovskite structure without secondary phases. In inset of Figure 1, higher intense $(110)_{pc}$ Bragg peak of NBT-0.5Ho seems to be shifting towards higher angle which occurs due to reduction of size of unit cell due to partial replacement of Bi^{+3} (1.37 \AA , Coordination Number=12) by smaller ionic radius ion Ho^{+3} (1.18 \AA , Coordination Number =12) [13]. This observation depicts that the holmium is successfully substituted at the Bi^{+3} site of NBT.

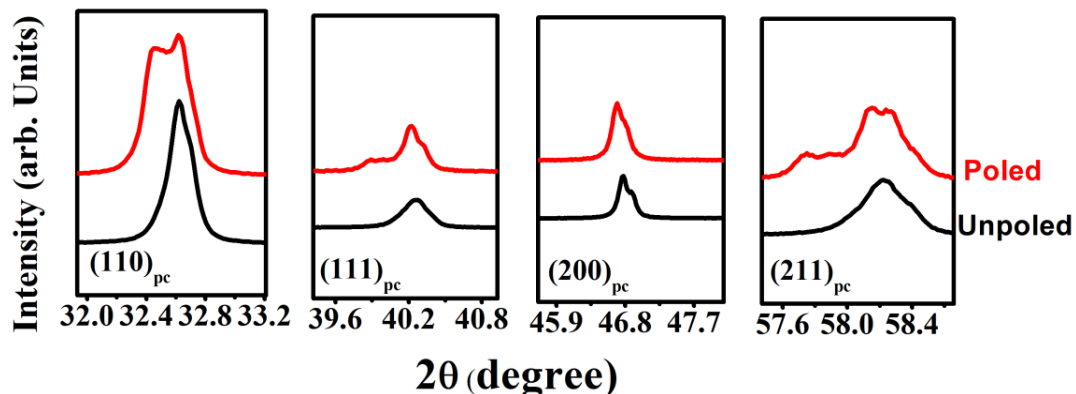


Figure 2. Close observation of selected pseudocubic Bragg reflections corresponding to $(110)_{pc}$, $(111)_{pc}$, $(200)_{pc}$ and $(211)_{pc}$ of poled and unpoled NBT-0.5Ho.

In order to study electric field driven effect on the crystal structure of holmium substituted NBT, electrical poling has been done by applying optimum DC electric field of $\approx 55 \text{ kV/cm}$ (near coercive field of ≈ 54

kV/cm of 0.5 mole %Ho⁺³ substituted NBT) for 40 minutes on the sintered pellet, and the XRD measurement has been taken on the crushed powder of poled specimen similar to the unpoled specimen to avoid preferred orientation effect. Close observation of the selected pseudocubic Bragg reflections corresponding to (110)_{pc}, (111)_{pc}, (200)_{pc} and (211)_{pc} have been plotted in Figure 2 for electrically poled and unpoled specimens of Ho⁺³ substituted NBT. It is interesting to note that except (100)_{pc}, the XRD profile of poled specimen shows drastically changes in comparison to unpoled. Among diffraction peaks in the diffraction pattern, remarkable changes are observed in strong pseudocubic reflection (110)_{pc} pattern which is split in the two defined doublet. Similarly, Bragg peak (211)_{pc} is split in the doublet with some additional peaks at right side. Shape change in term of additional peak at right side is appeared in (111)_{pc} Bragg peak. Similar type of variation in shape of Bragg peaks is reported for the electrically poled specimen of pure NBT in comparison to its unpoled specimen due to electric field driven irreversible structural transformation of monoclinic (Cc) distortion of unpoled to rhombohedral (R3c) distortion of poled specimen. [14,15]. Thus, it implies that observed shape changes in the form of splitting or additional peak in poled specimen of NBT-0.5Ho are related to rhombohedral distortion whereas unpoled specimen belongs to mainly monoclinic distortion. However, it should be noted that splitting of strong pseudocubic reflection (100)_{pc} into doublet is not much sharp with two equal peaks unlike it is reported by B. N. Rao et al. for pure NBT for rhombohedral distortion[14]. Thus, it suggests that monoclinic distortion (Cc) is not completely vanished after the electric poling and there is still possibility of the coexistence of monoclinic (Cc) phase along with rhombohedral (R3c) phase in the poled specimen of Ho⁺³ substituted NBT.

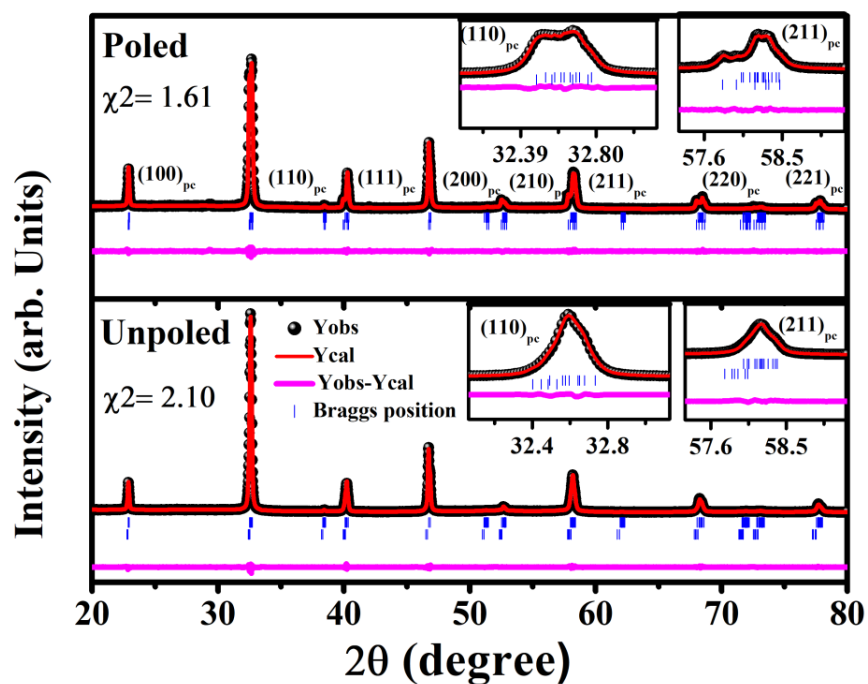


Figure 3. Fitted Rietveld refined x-ray diffraction patterns using Cc+R3c model of unpoled and poled NBT-0.5Ho. Inset shows close observation of selected pseudocubic Bragg reflections corresponding to (110)_{pc} and (211)_{pc} of unpoled and poled NBT-0.5Ho.

In order to detailed quantitative structural analysis of the poled and unpoled specimens of NBT-0.5Ho, the Rietveld refinement has been carried out by using FULLPROF software using mix phase of R3c+Cc phase [16]. In Figure 3, perfect fitting is obtained for the poled and unpoled XRD profile with acceptable

goodness of fitting (R_p : 7.93 R_{wp} : 6.60 and χ^2 : 2.10 for unpoled and R_p : 10.7, R_{wp} : 8.37 and χ^2 : 1.61 for poled). For unpoled specimen, Cc space group of monoclinic is dominating with $\approx 95.4\%$ of phase fraction and R3c space group of rhombohedral is coexisting with minor phase fraction of $\approx 5\%$ whereas after electric poling, Cc space group is diminished to $\approx 29.4\%$ and R3c space group is reasonably increased to $\approx 70.6\%$. The detailed refined parameters of the poled and unpoled are listed in Table 1-2. Thus, it can be concluded that, along with visual inspection of XRD patterns of the electrically poled and unpoled specimens, Rietveld refinement also reveals the electrical poling transfers the crystal symmetry of holmium substituted NBT from dominant monoclinic phase (Cc) to rhombohedral (R3c) as major phase.

Table 1. Refined parameters for unpoled specimen of NBT-0.5Ho

Cc	X	Y	Z
Na/Bi/Ho	0	0.25096	0
Ti	0.25402	0.24789	0.75514
O1	0.00881	0.20351	0.47802
O2	0.21189	0.51696	-0.07447
O3	0.23596	-0.00191	-0.03626
Lattice Parameters	a = 9.53118	b=5.48090	c =5.50917
(Å)	$\alpha = \gamma = 90^\circ$	$\beta = 125.41861^\circ$	
Na/Bi/Ho	0	0	0.32962
Ti	0	0	0.05919
O	0.15101	0.32372	0.08330
Lattice Parameters	a =b=5.49904	c=13.55101	
(Å)	$\alpha = \beta = 90^\circ$	$\gamma = 120.00000^\circ$	
Phase fraction	Cc(94.05%) +R3c(5.95 %)	R_p : 7.93 R_{wp} : 6.60 χ^2 : 2.10	

Table 2. Refined parameters for poled specimen of NBT0.5-Ho

Cc	X	Y	Z
Na/Bi/Ho	0	0.24361	0
Ti	0.25504	0.23901	0.71666
O1	-0.01337	0.29507	0.54933
O2	0.25464	0.48963	0.48963
O3	0.24935	0.03552	0.11692
Lattice Parameters	a = 9.52519	b=5.47402	c =5.50123
(Å)	$\alpha = \gamma = 90^\circ$	$\beta = 125.40123^\circ$	
Na/Bi/Ho	0	0	0.27241
Ti	0	0	0.00906
O	0.13062	0.33975	0.08047
Lattice Parameters	a =b=5.47714	c=13.53507	
(Å)	$\alpha = \beta = 90^\circ$	$\gamma = 120.00000^\circ$	
Phase fraction	Cc (29.4 %) +R3c (70.6 %)	R_p : 10.7 R_{wp} : 8.37 χ^2 : 1.61	

The room temperature dielectric measurement has been performed in range of 1000 Hz to 1 MHz for poled and unpoled specimen of NBT-0.5Ho as shown in Figure 4. Obtained electromechanical resonance peaks (resonance, f_r and anti-resonance, f_a) in higher frequency region (100 kHz-1000 kHz) for poled specimen is attribution of poling.

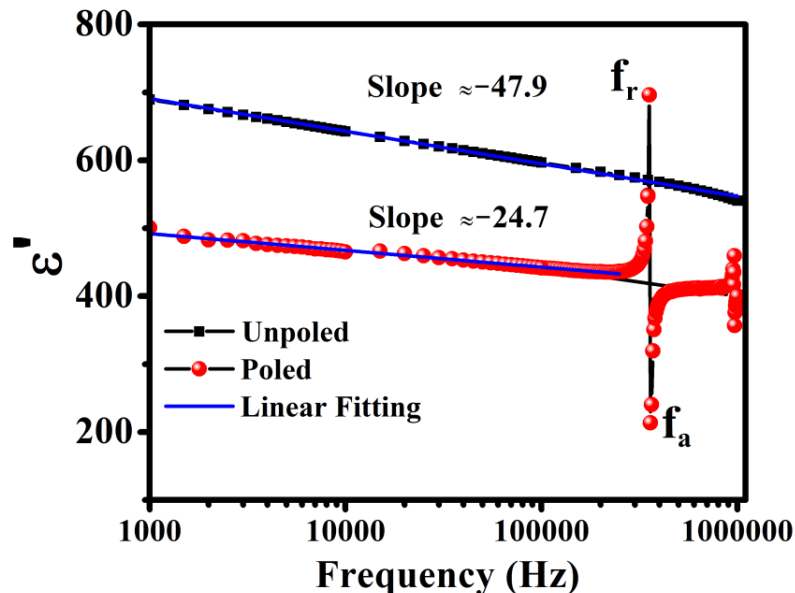


Figure 4. Real part of dielectric permittivity (ϵ') Vs frequency plot of unpoled and poled NBT-0.5Ho

Decrement in the dispersion of dielectric value of the poled specimen is observed. Quantitatively, dispersion of dielectric values is quantified by slope of liner fitting. Negative slope ≈ -24.7 of poled specimen is almost two times lesser than ≈ -47.9 of the unpoled. Moreover, dielectric values are also decreased in the poled specimen. These features are reflecting decrement of disorder and enhancement of long range ferroelectric order in the poled specimen. Observed dielectric properties can correlate with structural analysis. i.e. in unpoled sample, monoclinic (Cc) space group is dominant which is related A-site disorder due to substitution of multi-ions Na^{+1} , Bi^{+3} and Ho^{+3} of different radii and charges at A-site of the NBT-Ho perovskite. These ions Na^{+1} , Bi^{+3} and Ho^{+3} remain displaced away from the [111] polar direction of the rhombohedral (R3c) and result in positional disorder on local level which result in relaxor ferroelectric type behavior with dispersion of dielectric values [6]. In the poled specimen, electric field induce structural transformation from monoclinic dominant Cc space group to rhombohedral R3c space group as major phase with wiping away the atomic positional disorder which result in long range ferroelectric ordering with reduced dielectric dispersion [17]. Thus, electric field driven structural transformation towards rhombohedral (R3c) space group from monoclinic Cc space group are the responsible for reduction of dispersion in dielectric behavior in the poled spaceman in comparison to unpoled.

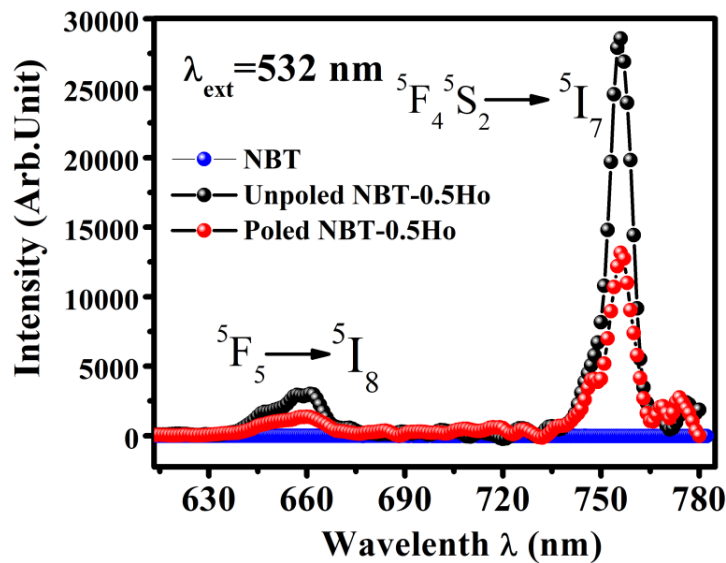


Figure 5. Photoluminescence spectra of NBT, poled and unpoled of NBT-0.5Ho ceramic under excitation of 532 nm.

Room temperature photoluminescence (PL) emission spectroscopy is recorded in range of 600 nm to 800 nm on the pellets NBT and NBT-0.5Ho by excitation of 532 nm wavelength as plotted in Figure 5. NBT is optically inactive material and no PL emission is observed. Down-conversion PL emission is observed for the NBT-0.5Ho. The emission spectrum exhibits two emissions, a weak one at 655 nm and strong at 756 nm corresponding to transition from 5F_5 to 5I_8 and transition $^5F_4, ^2S_2$ to 5I_7 transitions respectively. It is in good agreement with reported PL emission spectroscopy for Ho^{+3} -doped perovskite materials [10,13]. Thus, substitution of holmium in the NBT adds extra-functionality of photoluminescence along with ferroelectric properties. Photoluminescence intensity of the poled NBT-0.5Ho is quenched as shown in Figure 5. Significance quenching ($\approx 46\%$) is recorded from high intensity peak. Theoretically, photoluminescence emission in rare earth substituted NBT occurs due to electronic dipole transition within 4f shell. Emission from rare earth is very sensitive to its local host symmetry. According to Judd-Ofelt (J-O) theory, lower symmetry is advantageous for strong photoluminescence [15,18]. Thus, the obtained reduction or quenching in intensity of photoluminescence emission of poled specimen of NBT-0.5Ho is due to enhancement of phase fraction of higher symmetry rhombohedra (R3c) and suppression of lower symmetry monoclinic (Cc) phase in effect of electric field poling.

4. Conclusion

In this study, systematic investigation on the effect of electrical poling on the room temperature structural, dielectric and photoluminescence properties of small amount of Ho^{+3} (0.5 mole%) substituted NBT (NBT-0.5Ho) has been done. Visible inspection of X-ray diffraction (XRD) Bragg peaks and further Rietveld refinement of XRD patterns of poled and unpoled specimens of Ho^{+3} substituted NBT reveal that electrical poling transforms the crystal structure from lower symmetry of dominant monoclinic Cc phase to higher symmetry of rhombohedral R3c phase as major phase. Dielectric curves of poled and unpoled specimens of NBT-0.5Ho exhibits that dielectric value and its dispersion with frequency are significantly decreased which is ascribed to electric field driven structural change. The photoluminescence emission spectrum exhibits a weak emission at 655 nm and a strong emission at 756 nm. Emitted intensity is significantly tuned in effect of the electric poling in term of quenching. Based on the Judd-Ofelt (J-O) theory, here

quenching is associated with structural transformation from lower symmetry of dominant Cc to higher symmetry of R3c as major phase in effect of external electric field that has been confirmed from XRD of poled and unpoled specimen. Tuning of photoluminescence intensity in the effect of poling in NBT-0.5Ho ferroelectric ceramic opens up the possibility for designing the electric field controlled ecofriendly optoelectronic switchable devices. Moreover, obtained result manifests that photoluminescence emission Ho⁺³ is structurally sensitive which suggests that Ho⁺³ can be also used as structural transitional probe for the ferroelectric.

Acknowledgments

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