Structural and Optical Properties of $Bi_{0.5}Na_{0.5-x}Li_{x}TiO_3$ ($x =$ 0.0, 0.05) Ceramics

Susheel Patel[a], A. Mishra and Meenu Dinesh Varshney

Materials Science Laboratory, School of Physics, Vigyan Bhavan, Devi Ahilya University, Khandwa Road Campus, Indore 452001, India.
[a]susheelpatel1990@gmail.com

Abstract: The multisite occupation of Li^+ cations in the perovskite structure of $Bi_{0.5}Na_{0.5}TiO_3$ synthesized by solid state reaction technique. The structural and optical properties were analyzed by X-ray diffraction (XRD) and UV-visible absorption spectroscopy. Stoichiometric $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) adopts the ABO_3 perovskite structure with the A-site equally occupied by Na^+ and Bi^{3+} ions. XRD patterns revealed the formation of a single phase rhombohedral structure with $R3c$ space group. The calculated average particle size of $Bi_{0.5}Na_{0.5}TiO_3$ is ~ 30.60 nm that increased slightly for Li doping as $Bi_{0.5}Na_{0.45}Li_{0.050}TiO_3$. UV-Vis studies have been carried out to check the optical band-gap which was found to be ~ 3.270 eV and ~ 3.241 eV for $Bi_{0.5}Na_{0.5}TiO_3$ and $Bi_{0.5}Na_{0.45}Li_{0.05}TiO_3$ sample.

INTRODUCTION

Bismuth sodium titanate $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is one of the most important lead- free piezoelectric materials. BNT is considered to be one of the good candidates of lead-free piezoelectric ceramics because of its large remanent polarization (Pr = 38 $(C/cm^2)^3$ and high Curie point of T_C = 540 °C [1, 2]. BNT ceramics are difficult to pole because of their high coercive field (Ec = 7.3 kV/mm) and relatively large conductivity. BNT is widely used for piezoelectric actuators, sensors, and transducers due to their excellent piezoelectric properties. The ferroelectric perovskite-type ceramic materials having general formula ABO_3 with different cationic distributions at A/B-sites are being investigated due to their important device applications such as in capacitors, piezoelectric ultrasonic transducers, electrostrictive actuators, submerged-arc-welding substrates, etc. Bi-based perovskites fall in Aurivillius family and the majority of these compounds of are ferroelectrics [3].

Sodium bismuth titanate (NBT) is a rhombohedral ferroelectric perovskite (ABO_3) originally reported as having the rhombohedral ($R3c$) crystal structure, whereas the rhombohedral to tetragonal phase transition occurs at ~ 300 °C [3]. The of NBT is particularly sensitive to the volatilization of Bi_2O_3 above 825°C and Na_2O above 1132°C, temperatures below the typical synthesis temperatures of these materials. It has been noted that Bi may be the more volatile element during processing. It is well known that the solid state reaction route requires a high calcination temperature which causes the raw materials to vaporize and induces the formation of a secondary phase. The secondary phases can be formed during the sintering process. It is important to take into account their possible influence on BNT properties [4].

A feature of the Aurivillius compounds resides in their compositional flexibility of the perovskite block, which allows the incorporation of various cations. It is thus possible to modify the dielectric and ferroelectric properties by the substitution of A-site and to some extent the B-site of Aurivillius oxides. Doping with donor cations, like Nb^{5+} to Ti^{4+} site, can reduce the conductivity and, therefore, enable the existence of higher piezoelectric response. Also, the incorporation of trivalent La^{3+} ions for divalent Ba^{2+} ions could effectively stabilize the oxygen ions in the lattice and lead to a reduction in the conductivity and dielectric loss [2]. Doping and other compositional changes in Bi-based perovskite ceramics help in the control of electrochemical, phase transition, relaxer and piezoelectric properties.

Pure $BiTiO_3$ is difficult to prepare by any means under ordinary conditions, however, relates titanate is formed with different formula when doped with rare earth, mono and divalent elements [4]. The materials can be doped at B-site by transition metals too. The materials and their characteristics depend on the preparation process and the heat

treatment. The crystallite size all influences the properties of the material. Therefore, several methods are used for the preparation of these materials to control properties as required. However, we are using solid state reaction route which if followed carefully assures of the quality through higher particle size which itself is important from the characteristic and application point of view [5]. The focus of the present work is to present a simple method to prepare $Bi_{0.5}Na_{0.5-x}Li_xTiO_3$ with $x = 0.0$ and 0.05 piezoelectric ceramics through the solid-state reaction route and the study of its structural and Optical properties.

EXPERIMENTAL DETAILS

Ceramic powders were prepared by solid state reaction technique. Oxides and carbonates of the raw materials Bi_2O_3, Na_2CO_3, Li_2O_3 and TiO_2, were weighed according to the stoichiometric formula $Bi_{0.5}Na_{0.5-x}Li_xTiO_3$ with $x = 0.0$ and 0.05, (BNT and BNLT). The mixture was grounded in motor pestle for 6h and calcined at 800 °C for 4h. The phases purity of the samples were checked using X-ray diffraction (XRD) analysis which was carried out using X-ray diffractometer with Cu $K\alpha$ ($\lambda = 1.5406$Å) radiation from a Bruker *D8* Advance X-ray diffractometer with a step size of 0.02^0 in the range of 2θ (20^0- 80^0) at room temperature. UV-Vis spectrometer (Perkin Elmer, Lambda 950 - USA) was used to find the band gap of the sample.

RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns of Li-doped $Bi_{0.5}Na_{0.5-x}Li_xTiO_3$ ($x = 0.0$ and 0.05) perovskite samples. Both the samples were prepared using solid state reaction technique and sintered at $800^\circ C$ for 4h. A pure perovskite phase was obtained for BNT sample while a very small secondary phase is observed in the BNLT. The very small secondary phase in BNLT might be due to the volatilization of Bi_2O_3 and Na_2CO_3 with high lead vacancies concentration (Li = 0.05) marked by (*). The crystallite size was calculated using Scherer formula $D = k\lambda/\beta\cos\theta$, here '*D*' is crystallite size, λ is the wavelength of x-ray (1.5406 Å), k is a constant (shape factor ≈ 0.9), θ is the angle of diffraction and β is the full width at half maximum in radians. The average crystallite size was found to be equal to ~32 nm. The observed peaks are indexed as (101), (110), (021), (202) (211), (112), (204), and (311) which are the characteristics planes of single-phase rhombohedral structure (space group $R3c$). The average particle size, lattice parameter and X-ray density of samples are observed and shown in Table 1. There is variation in the lattice parameters because of the different ionic radius of Bi^{3+} (1.36 Å), Na^+ (1.39 Å) and Li^+ (1.41 Å) [4-6]. Since ionic radii of Li^+ (1.41 Å) is smaller than Na^+ (1.39 Å) [6], we can thus speculate that lattice parameters decrease with increasing Li^+ contents.
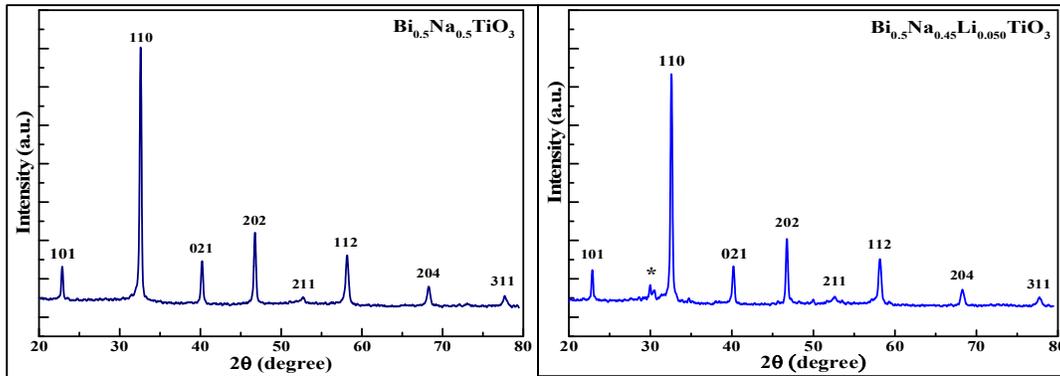

FIGURE 1 XRD patterns of BNT and BNLT.

TABLE 1 Structural parameter, Energy Band gap (eV) of $Bi_{0.5}Na_{0.5-x}Li_xTiO_3$ (x = 0.0, 0.05).

S.No.	Material	Particle Size (nm)	Lattice Parameter (Å)		X- ray Density (gm/cm³)	Energy Band gap (eV)
			a(Å)	c(Å)		
1.	$Bi_{0.5}Na_{0.5}TiO_3$	30.60	5.482	13.471	3.183	3.270
2.	$Bi_{0.5}Na_{0.45}Li_{0.050}TiO_3$	31.70	5.486	13.479	11.317	3.241

Figure 2 The optical band gap Eg was estimated by plotting the square of the Kubelka-Munk function $(F(R) \, h\nu)^2$ versus photon energy. The Kubelka-Munk method is used to analyze the reflection spectrum of the scattered light. It is widely used for semi-reflective materials in the visible field. The Kubelka-Munk equation [8-9].

$$F(R) = (1-R)^2/2R$$

where R is the reflectance of light. The energy gap value can be determined by Tauc relation.

$$F(R) \, h\nu = B \, (h\nu - E_g)^n$$

where E_g is the bandgap energy, B is a constant reflecting the degree of disorder of the amorphous solid structure, n = 2 for indirect allowed transition, n = 1/2 for direct allowed transition and $h\nu$ is the photonic energy expressed in eV.
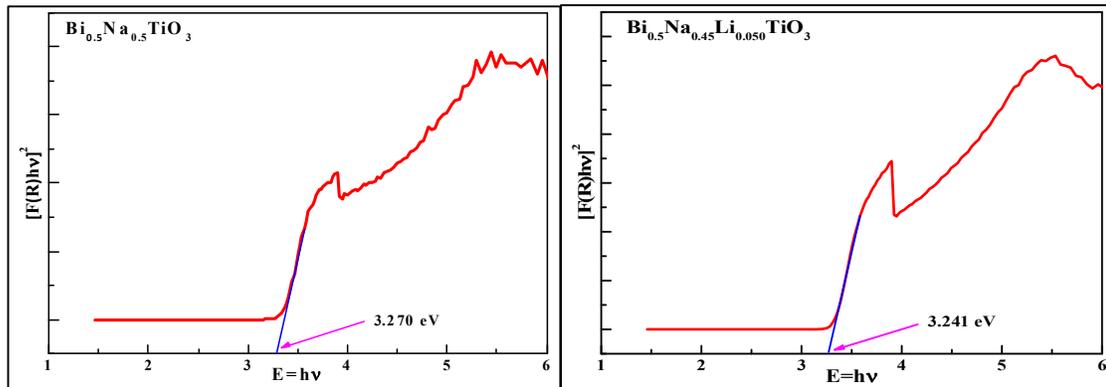

FIGURE 2 Energy Band gap $(F(R) \, E)^2$ versus E(eV) for BNT and BNLT.

In general, good fits to the experimental curves were obtained for the both samples $Bi_{0.5}Na_{0.5-x}Li_xTiO_3$ (x= 0.00, 0.050,). In these cases, the employed determination of the band gap values with good accuracy [7]. The consisted of small size particles has a higher value of Eg, which is typical in case of crystalline size shows in Table 1.

CONCLUSIONS

Lead-free piezoelectric $Bi_{0.5}Na_{0.5}TiO_3$ and $Bi_{0.5}Na_{0.45}Li_{0.05}TiO_3$ ceramics were synthesised by solid state reaction technique. The crystalline phases and optical properties of these ceramics were investigated. The results of XRD patterns showed that the ceramics possess a single perovskite rhombohedral structure with a space group $R3c$. However, a small amount of the secondary phase was caused by the volatilization of Bi_2O_3 and Na_2CO_3 with high lead vacancies concentration. UV-Vis spectroscopy confirmed the dual band-gap nature, which is reduced due to the higher crystallite size when compared to the earlier reports.

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