

Structural and Optical Properties on Na Doped BaTiO₃

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Abstract: Hereby, the synthesis of Ba_{1-x}Na_xTiO₃ [$x = 0, 0.33$] perovskite has been reported. The samples were prepared conveniently by ceramic route i.e. solid state reaction method. The phase and structure of the synthesized samples were confirmed using x-ray diffraction technique. The room temperature XRD data recorded in the angular range of 2θ ($20^\circ < 2\theta < 80^\circ$) was analyzed and the analysis revealed that the prepared samples have acquired the tetragonal structure exhibiting space group (P4mm). The samples were highly crystalline and possessing larger average particle size > 40 nm. Further, the sample formation was confirmed via Fourier Transformation Infra-red spectroscopic characterization. The optical bandgap was calculated using UV-Vis technique and the values found were 3.1eV and 3.03 eV for pristine and Na Doped BaTiO₃.

Keywords: Perovskites, Structure, Optical bandgap, opto-electronics.

INTRODUCTION

Ferroelectric materials have been the centre of research in materials science, investigated and most often are exploited in the bulk form. Perovskite oxides have long been of great interest because of a large variety of phenomena that can emerge in these materials, such as ferroelectricity, ferromagnetism and superconductivity. The phenomenon gives rise to technological utilization of these materials ranging from memory to photovoltaic [1]. Ferroelectric functional materials are indispensable in various technological applications due to their electromechanical coupling properties, quick response, and compact sizes. Perovskite BaTiO₃ (BTO) has attracted researchers for its interesting optoelectronic properties. It also possess much worth dielectric, piezoelectric and ferroelectric nature [2,3]. Despite being very important in daily life based applications, it is non-hazardous and environment friendly. Because of its potential reliability and excellent performance, it further finds applications in transducers, actuators, random access memories and other integrated optoelectronic components [2-4].

BaTiO₃ undergoes structural transitions from cubic to tetragonal, tetragonal to orthorhombic, and orthorhombic to rhombohedral. Its dielectric and ferroelectric nature originates from Ti ion displacements, however interaction between B and O has no ferroelectric active component which is ionic. To enhance the device performance using BaTiO₃ based materials, higher dielectric constant, lower loss, lower coercive field, high remanent polarization and good dielectric strength is indispensable. From fundamental and commercial point of view, research has been initiated to revolutionize the dielectric and ferroelectric properties of BaTiO₃ via substitution where A-site substitution can be carried out using alkaline-earth (Sr²⁺ or Mg²⁺), alkali metals (Na¹⁺, Li¹⁺) and rare-earth ions (La³⁺ etc.) [2-5].

When it is the case of designing the optical devices, the band gap energy is the key factor. To develop the electronic band structure, the determination of band gap energy (E_g) is necessary step. It is established that direct transition occurs for maximum valence band and the minimum conduction band being at the same point in the Brillouin zone while as for an indirect transition, the minimum and the maximum conduction bands are at different places [6,7].

Dopants that can be accommodated in the BaTiO₃ lattice are decided taking into consideration the ionic radius of dopants which mainly determines the substitution site. Even on small doping, the dopants can lead to the lattice deformations and makes the material abnormal in the sense of charge neutrality. The charge compensation is met by oxygen vacancies created while sintering at high temperature which act as acceptors of dopants [4-7].

EXPERIMENTAL DETAILS

Ferroelectric Ba_{1-x}Na_xTiO₃ [$x = 0, 0.33$] perovskite was synthesized using conventional solid state reaction method to study their structural and other physical properties. BaCO₃, TiO₂ and Na₂CO₃ of analytic grade and high purity were used as the starting materials without pre-heating. The said compounds were taken in stoichiometric amounts and mixed well in an agate-mortar for 5h. The samples were calcined at 750 °C for 10h and re-calcined at a temperature of 950 °C for 10h after grinding them for 6h. Finally the samples were ground for 2h again to get the fine powder and was packed for characterization [6,8].

Phase formation, crystal structure and crystallite size of the ferroelectric compound Ba_{1-x}Na_xTiO₃ [$x = 0, 0.33$] was verified via the x-ray powder diffraction technique at room temperature employing Bruker D8-Advance X-ray diffractometer with CuK α 1 (1.5406 Å). The data was recorded with a step size of 0.02 over the angular range 2 θ (10° < 2 θ < 80°). UV-Vis spectrometer (Perkin Elmer, Lambda 950 - USA) was used to find the band gap of all the samples under investigation. Fourier Transformation Infrared Spectroscopy (FTIR) was done by Perkin Elmer FT-IR/FIR spectroscopy in the range of 400 to 4000 cm⁻¹.

RESULTS AND DISCUSSIONS

The Perovskites of the type Ba_{1-x}Na_xTiO₃ [$x = 0, 0.33$] have been synthesized conveniently employing the high temperature solid state reaction technique. The formation of the desired materials and hence their structure was verified via the most reliable x-ray diffraction characterization technique. The data obtained in the angular range of

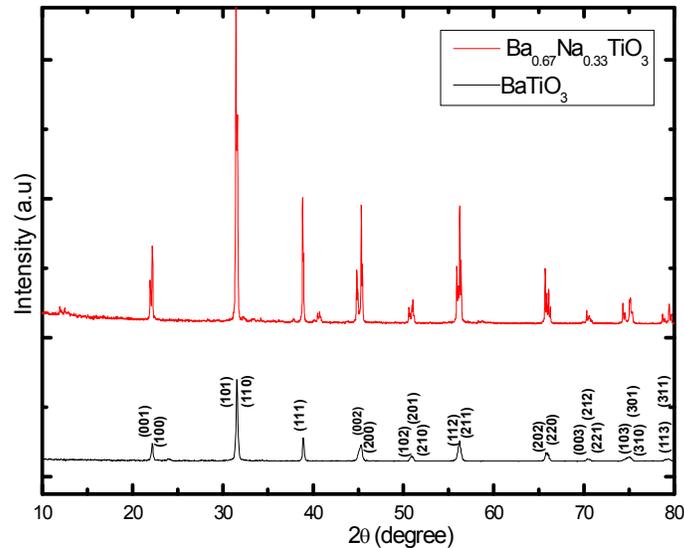


FIGURE 1: X-ray diffraction spectra of Ba_{1-x}Na_xTiO₃ [$x = 0, 0.33$] perovskite.

10° < 2 θ < 80° has been plotted and depicted in Figure 1. The XRD data analysis confirms tetragonal structure of the so synthesized samples with the space group P4mm. From Figure 1 one can interpret that within the bounds of the experiment, the structure has been retained at the higher doping of volatile Na metal. Furthermore, the crystallinity of the Na doped BaTiO₃ has been observed to be enhanced compared to the pristine BaTiO₃. Also, in the Ba_{0.67}Na_{0.33}TiO₃, the obvious peak splitting is due to temperature effect. The calculated lattice parameters are $a = b =$

3.9689 Å, $c = 3.9948$ Å with cell volume of 62.9267 Å³ for parent and that for Na doped BaTiO₃, $a = b = 3.8977$ Å, $c = 3.8938$ Å with cell volume of 62.7267 Å³. The decrease in the lattice constants and hence volume is attributed to the

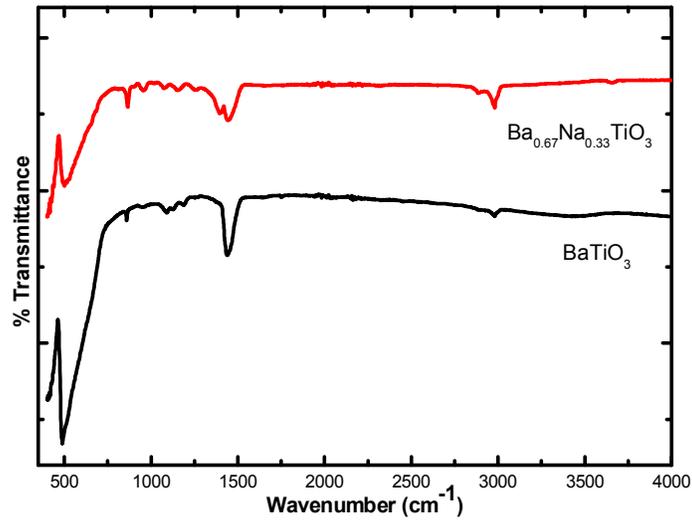


FIGURE 2: FTIR spectra for Ba_{1-x}Na_xTiO₃ [$x = 0, 0.33$] titanates.

larger ionic radii of Ba (1.34 Å) compared to Na (0.97 Å). Further, the narrowness of the FWHM is indicative of the crystallite size [8, 9] confirmed from the manual calculation using the classical Scherer's equation, $t = k\lambda / \Delta \cos\theta$, where

k is called shape factor and $k = 0.9$, $\lambda = 0.546$ Å, is the wavelength used, θ is the Bragg's angle and Δ is the full width at half maximum. The calculated particle size was found 42 and 51 nm for BaTiO₃ and Ba_{0.67}Na_{0.33}TiO₃ respectively.

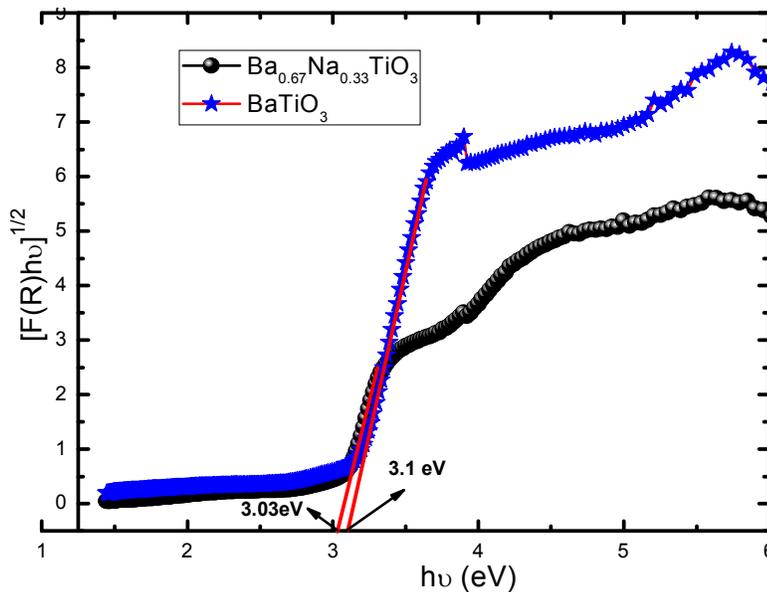


FIGURE 3: UV-Vis spectra for Ba_{1-x}Na_xTiO₃ [$x = 0, 0.33$] titanateperovskite.

The reliable characterization technique FTIR has been further exploited to confirm the required oxide formation. Both the samples exhibit strong absorption bands around 550 cm⁻¹ and 450 cm⁻¹, which can be assigned to the

stretching and bending vibrations of the Ti-O bond in $[\text{TiO}_6]^{2-}$ octahedron. The characteristic absorption at 1440 cm^{-1} is assigned to the stretching vibrations of carboxylate as there is a small amount of BaCO_3 in the samples, which is in agreement with the XRD patterns. Further, the peaks at 868 cm^{-1} were assigned to stretching vibrations of metal-oxygen. The clearly observable peak at 2924 cm^{-1} is symmetric stretching vibration of carbon hydrogen bonds [10,11].

While the designing, the band gap energy concept is the fundamental concern. Different techniques have been developed to determine the optical bandgap of a synthesized sample among which the optical approach is accurate and is precisely accurate. To determine the optical band gap of solid state synthesized $\text{Ba}_{1-x}\text{Na}_x\text{TiO}_3$ [$x = 0, 0.33$] perovskites, the optical diffuse reflectance spectra was recorded. The data was plotted after applying Schuster–Kubelka–Munk function, $F(R) = (1-R)^n/2R$ where R is the reflectance, exponent 'n' 0.5, 2, 1.5 and 3, is constant dependent on transition type. The value $n = 0.5$ corresponds and $n = 2, 1.5, 3$ corresponds to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. Among these values of 'n', we obtained the best fit of $F(R)$ versus energy (E_g) for $n = 1/2$. The values of bandgap determined were 3.1 eV and 3.03 eV obtained by extrapolating the linear portion of the $F(R)^{1/2}$ versus E_g in the plot displayed in Figure 3. The results are supported by the reports elsewhere [12-14].

The decrease in the optical bandgap of the Na doped BaTiO_3 when compared to the pristine one, has been attributed to the increase in average particle size as particle size is inversely proportional to the bandgap. Also, the reduction in the band gap on Na doping in the matrix BaTiO_3 is believed to be due to the creation excess of hole carriers in the neutral BaTiO_3 upon doping of monovalent Na^+ replacing trivalent Ba^{2+} . To understand this character, the concept of electronic interactions and scattering by impurities is indispensable. In this phenomenon, bandgap shrinks when impurity band mixes with conduction band [13-15].

In Conclusion, we synthesized the solid solution of $\text{Ba}_{1-x}\text{Na}_x\text{TiO}_3$ [$x = 0, 0.33$] perovskites materials. Through XRD characterization technique, it was established that both the samples have crystallized into the tetragonal structure (P4mm). FTIR spectroscopic measurement confirmed the XRD result i.e. the formation of the required sample. Optical bandgap was determined through UV-Vis spectroscopic technique and the value of $E_g > 3\text{ eV}$ for both the samples establishes their importance in the opto-electronic applications.

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