IJISET - International Journal of Innovative Science, Engineering & Technology, Vol. 4 Issue 2, February 2017
ISSN (Online) 2348 – 7968 | Impact Factor (2016) – 5.264
www.ijiset.com

Structural and Dielectrical Properties of Pure And Strontium Doped Barium Titanate Nanoparticles By Sol-Gel Auto Combustion Method

P. M. Kshirsagar [1], Pankaj P. Khirade[2], D. N. Bhoyar[2], S. J. Shukla[1], K. M. Jadhav[2*]

[1]Department of Physics, Deogiri College Aurangabad (M.S.) India.

[2]Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (M.S.), 431004, India.

Abstract

$Ba_{1-x}Sr_xTiO_3$ (x =0.0, 0.2) nanoparticles were prepared at low temperatures using the sol-gel auto combustion method. XRD analysis confirmed the formation of single phase tetragonal structure without any impurity phases. Using XRD data we have calculated lattice constant (a and c), unit cell volume (V), micro-strain (ε), X-ray density (ρ_x), bulk density (ρ_B), porosity (P%) and average crystallite size (D) was calculated. The average crystallite size (t) was recorded in the range of ~19–23 nm. Dielectrical property was measured as a function of frequency in the range 10 kHz - 1 MHz at room temperature which was found to be higher at lower frequencies. Dielectric constant (ε') shows strong compositional as well as frequency dependences.

Keywords: *Nanoparticles, sol-gel, $BaTiO_3$, dielectrical.*

1. Introduction

The barium titanate $BaTiO_3$ perovskite has been more interesting topic for researcher due to wide variety of applications. It is one of the most widely used ferroelectric materials due to its high dielectric constant and low loss characteristics [1]. Complex oxide perovskites possessing the ferroelectric property have verity of applications, as, ceramic capacitors in bulk forms and in the forms of thin films for ferroelectric random access memory, infrared pyroelectric sensors, transistors, microwave electronics, electro-optic modulators, etc. maintain to its excellent ferroelectric properties [2, 3]. $BaTiO_3$ is one of the most commonly investigated ferroelectric materials among the complex oxide perovskites. Furthermore, in the continuous advance in miniaturization of ferroelectric devices, $BaTiO_3$ fine particles as a ferroelectric material have been applied in advanced electric devices such as multilayer ceramic capacitors [4]. Their physical properties have been dramatically influenced by various effects, such as temperature, pressure, substitution, and size. Among them, due to the close relationship between ferroelectric properties and crystal structure, the size dependence of structure is presently the major research topic [5].

Barium titanate ($BaTiO_3$) is a ferroelectric oxide that undergoes a transition from a ferroelectric tetragonal phase to a paraelectric cubic phase upon heating above 130 °C. Ferroelectricity in tetragonal $BaTiO_3$ is due to an average relative displacement of titanium (Ti^{4+}) from its centro-symmetric position in the unit cell and consequently the creation of a permanent electric dipole [6]. The elongation of the unit cell and consequently the deviation of the *c/a* ratio from unity are used as an indication of the presence of the ferroelectric phase. The dielectric and ferroelectric properties of $BaTiO_3$ are known to correlate with size, and the technological trend toward decreasing dimensions makes it of interest to examine this correlation when sizes are at the nanoscale [7].

ABO_3 types of ferroelectric materials have been widely used due to their high dielectric constant and low leakage current [8, 9]. Among the materials, the most important examples of ferroelectrics are $Ba_{1-x}Sr_xTiO_3$ (BST) which is developed from $BaTiO_3$ (BT). Due to its pyroelectric, ferroelectric and piezoelectric properties, it has been widely used in technological application, such as high permeability capacitors, ferroelectric memories, pyroelectric sensors, piezoelectric sensors, piezoelectric transducers, PTC thermistors [10].

When strontium atoms were introduced to A site, it replace barium atoms and phase transition temperature decreases. In case of paraelectric phase, these materials have considerably high dielectric constant and low losses at microwave frequencies. $Ba_{1-x}Sr_xTiO_3$ (BST) ceramics possesses high dielectric constant, low leakage current and good thermal conductivity due to these properties, BST have been widely used as dielectric capacitor, PTC, random access memory, infrared detector, gas sensor, humidity sensors. These BST ceramics are also used to developed tunable oscillators and delay lines. In the present study, Sr-substituted barium titanate ceramics of the compositional formula $Ba_{1-x}Sr_xTiO_3$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were synthesized using sol-gel auto combustion method. An extensive literature survey shows very few reports are available on the synthesis of Ba_{1-}

$_xSr_xTiO_3$ by wet chemical method. This prompted us to synthesize the present composition using wet chemical sol-gel method. The structural and dielectrical properties of these compositions were investigated.
The main objective of the present work is to investigate the effect of Sr substitution on the nature of structural and dielectric properties of $BaTiO_3$ nanoparticles synthesized by sol-gel auto combustion technique.

2. Experimental

The Analytical grade barium nitrate hexahydrate ($Ba(NO_3)_2 \cdot 6H2O$), tetra butyl titanate ($Ti(OC_4H_9)_4$), citric acid ($C_6H_8O_7$), ethanol (C_2H_5-OH) and ammonium hydroxide (NH_4OH) provided by Merck with ~99 % purity were used as a starting materials without further purification for the synthesis. Firstly, tetra butyl titanate solution diluted with ethanol was added into the citric acid aqueous solution with pH = 8 which is adjusted by adding the appropriate amount of ammonia. Ethanol was used to chelate tetra butyl titanate.

A yellowish transparent liquid was obtained which is marked as solution 'A' after being stirred at 80 °C for 1 h. At the same time, barium nitrate were dissolved into distilled water, accompanying continuous stirring until all salts were absolutely solved which is marked as solution 'B′. Subsequently, solutions 'A' and 'B′ were poured together. Followed by a continuous stirring for 3 h, the viscosity of solution increased gradually and then a stable transparent sol formed. Uninterrupted heating of 100 °C initiates the gel formation. Under constant stirring and heating, viscous gel transforms into dry gel. The dried gel formed from metal nitrates and citric acid exhibited self-propagating combustion behavior. The obtained powders dried, crushed and were annealed at 950 °C for 4 h in a muffle furnace in order to get the nanocrystalline powders.

Characterizations

The X-ray diffraction (XRD) patterns of samples were taken by using Phillips X-ray diffractometer (Model PW-1710) using Cu-Kα radiation (λ = 1.5418 Å). The AC parameters such as capacitance (C) of the samples were measured in the frequency range 10 kHz - 1 MHz using LCR-Q meter bridge (HP Model 4284 A). The dielectric constant was obtained using formula [11].

3. Results and Discussions

Fig.1 (a) and (b) shows the X-ray diffraction patterns of $Ba_{1-x}Sr_xTiO_3$ ceramics with x = 0.0 and 0.2 concentrations respectively.

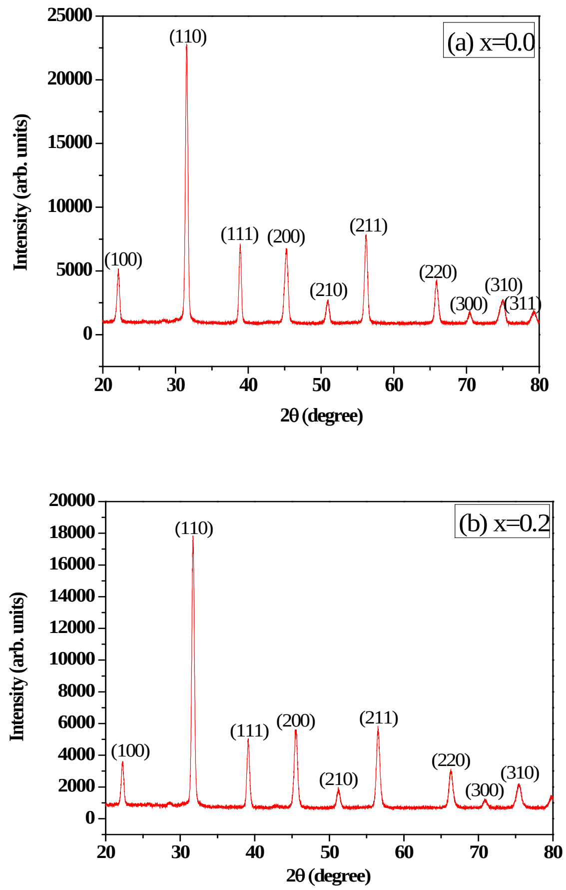

Fig. 1. XRD patterns of $Ba_{1-x}Sr_xTiO_3$
(a) x=0.0 and (b) x = 0.2

It exhibits all the characteristic peaks of perovskite structured material without any impurity peak and the most intense peak was observed at (110). The other planes observed are (100), (110), (111), (200), (210), (211), (220), (221), (300) and (310). The XRD pattern confirms the formation of perovskite tetragonal structure without any impurity peaks. The pattern shows well defined peaks and there is no any intermediate phase is formed, confirming the single phase formation of $BaTiO_3$. The occurrence of splitting of peaks with specific indices characteristic indicates the tetragonal perovskite structure in the $BaTiO_3$ ferroelectric phase. The lattice parameters are found to be a = 4.0076 Å and c = 4.0092Å with c/a = 1.0004 for pure barium titanate nanopowders [12]. This suggests that the crystal structure is tetragonal at room temperature (Table 1). It is also observed that with increase in Sr content X-ray density increases (Table 2). The average crystallite sizes were calculated by using Scherrer formula and are represented in table.2. The unit cell volume (V), bulk density (ρ_m) and porosity (P) values were also calculated for the present samples and their values are tabulated in Table 1 and 2.

Table 1: Lattice constant (a and c), c/a ratio and unit cell volume (V) of $Ba_{1-x}Sr_xTiO_3$ nanoparticles

x	a (Å)	c (Å)	c/a	$V(Å)^3$
0.0	4.0076	4.0092	1.0004	64.3925
0.2	3.9874	3.9858	0.9996	63.4997

Table 2: Average crystallite size (D), X-ray density (ρ_x), bulk density (ρ_m) and porosity (P) of $Ba_{1-x}Sr_xTiO_3$ nanoparticles

x	D (nm)	ρ_x (g cm^{-3})	ρ_m (g cm^{-3})	P (%)
0.0	23.36	4.733	3.638	23.135
0.2	19.75	5.066	3.617	28.597

Fig. 2 shows the variation of dielectric constant (ἐ) with the frequency. It is observed that with the increasing frequency the dielectric constant decreases rapidly and remains constant at higher frequencies. The high value of dielectric constant observed at low frequencies is explained on the basis of space charge polarization due to inhomogeneous structure i.e. porosity, grain structure and impurities. At higher frequencies dielectric constant remains independent of frequency due to inability of dipoles to follow the applied field.

The electronic exchange between Ti^{4+} and Ti^{3+} ions give rise to n-type carriers, however, mobility of p-type carrier is smaller than that of n-type carriers. It is also observed that with increase in Sr content dielectric constant increases. At higher frequencies dielectric loss is reduced and the dipole contributes to the polarization. The dielectric behaviour of pure barium titanate is similar to that of reported in the literature [13].

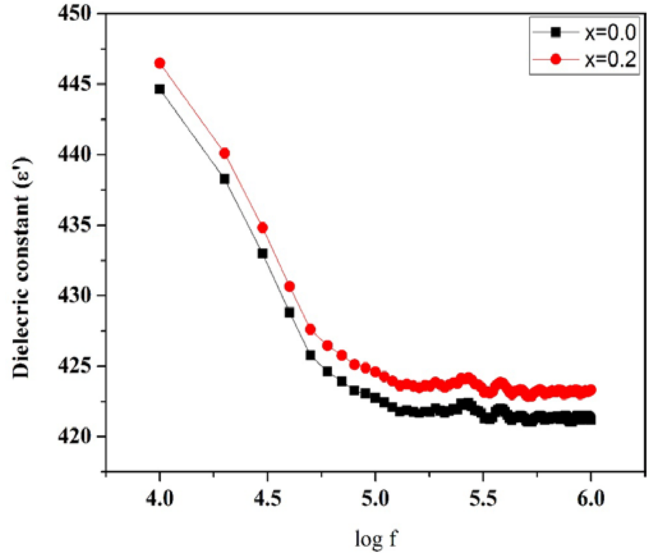

Fig. 2. Dielectric constant of $Ba_{1-x}Sr_xTiO_3$ (x = 0.0, 0.2) nanoparticles

4. Conclusion

$Ba_{1-x}Sr_xTiO_3$ (x = 0.0, 0.2) nanoparticles were successfully synthesized by sol-gel auto combustion method. XRD patterns confirmed the formation of tetragonal perovskite structure. Using XRD data, unit cell volume (V), X-ray density (ρ_x), bulk density (ρ_B), porosity (P%), and average crystallite size (D), porosity value changes when Sr ions are substituted in $BaTiO_3$ lattice, resulting in the structural variation. The dielectric behavior has shown strong frequency as well as composition dependence. As the Sr content increases ε' increases significantly. It was observed that the dielectrical constant was high at lower frequencies.

References

[1] P.P. Khirade, S.D. Birajdar, A. Raut, K. Jadhav, Ceramics International, 42 (2016) 12441-12451.
[2] R. Ramesh, Thin film ferroelectric materials and devices, Springer Science & Business Media, 2013.
[3] D. Gill, C. Conrad, G. Ford, B. Wessels, S. Ho, Applied Physics Letters, 71 (1997) 1783-1785.
[4] J.Y. Lee, J.H. Lee, S.H. Hong, Y.K. Lee, J.Y. Choi, Advanced Materials, 15 (2003) 1655-1658.
[5] H. Irie, M. Miyayama, T. Kudo, Journal of Applied Physics, 90 (2001) 4089-4094.
[6] S. Pillai, New age international publishers, New Delhi, (2005).
[7] M. Kamalasanan, N.D. Kumar, S. Chandra, Journal of applied physics, 74 (1993) 5679-5686.

[8] P.P. Khirade, S.D. Birajdar, A.V. Humbe, K. Jadhav, Journal of Electronic Materials, 45 (2016) 3227-3235.
[9] P.P. Khirade, A. Shinde, A. Raut, S.D. Birajdar, K. Jadhav, Ferroelectrics, 504 (2016) 216-229.
[10] J. Liou, B. Chiou, Materials Chemistry and Physics, 51 (1997) 59-63.
[11] V. Vinayak, P.P. Khirade, S.D. Birajdar, R. Alange, K. Jadhav, Journal of Superconductivity and Novel Magnetism, 28 (2015) 3351-3356.
[12] H. Terauchi, Y. Watanabe, H. Kasatani, K. Kamigaki, Y. Yano, T. Terashima, Y. Bando, Journal of the Physical Society of Japan, 61 (1992) 2194-2197.
[13] P.P. Khirade, S.D. Birajdar, A. Raut, K. Jadhav, Journal of Electroceramics, 37 (2016) 110-120.