

Study of FT-IR Spectrums of Barium Zirconate Titanate Synthesized Via Sol-Gel Auto Combustion Method

Jyoti Shukla^{a)}, Mehjabeen Khan, Supriya Bisen, Ashutosh Mishra

¹School of Physics, Vigyan Bhawan, DAVV Campus, Indore India - 452001

^{a)}jyotishukla12@yahoo.com

Abstract. Barium Zirconate Titanate [Ba(Zr_xTi_{1-x})O₃] where (x = 0.00, 0.12 & 0.24) samples were synthesized through sol-gel auto combustion method. The x-ray diffraction characterization of the prepared samples revealed the phase confirmation. Also increasing the Zr concentrations would shift the diffraction patterns towards lower angle side. At 24% of zirconium concentration, the sample is converted from tetragonal to cubic. The FT-IR spectroscopy of the prepared samples demonstrated the effect of zirconium on the structure of perovskite barium titanate.

INTRODUCTION

The polycrystalline barium titanate (BaTiO₃) due to its ferroelectric characteristics seems to be very attractive material in the field of electro-ceramics and microelectronics. Its high dielectric constant results from its crystal structure. As it is well known that barium titanate belongs to the family of perovskite (*i.e.*, ABO₃) where each barium ion is surrounded by 12 oxygen ions like a dodecahedron, titanium ion is surrounded by 6 oxygen ions and is small in size so that it is stable in octahedral position. Since, each titanium ion has +4 charge *i.e.*, Ti⁴⁺, the degree of polarization is very high. When the electric field is applied, the Ti⁴⁺ ions can shift from random positions to aligned positions and result in high bulk polarization and high dielectric constant. [1]

The high permittivity of barium titanate can be further enhanced by addition of zirconium on titanium site for its application in MLCs [2]. This is because zirconium (Zr⁴⁺) is chemically more stable than that of titanium (Ti⁴⁺) due to its larger ionic radius (0.087 nm for Zr⁴⁺) than titanium ion (0.068 nm for Ti⁴⁺) which expands perovskite lattice. In paraelectric state which is just above Curie temperature (*i.e.*, T_c = 120° C) barium zirconate titanate (BZT) ceramics are attractive candidate for dynamic random access memory (DRAM) and tunable dielectric devices. [3]

Addition of dopants plays a vital role in performance of any structure including perovskite. They can alter the microstructure of the material and therefore can change its physical properties. The physical properties in ferroelectric materials such as barium titanate are associated with defects, dipole moments, crystal structures and so on. Thus it is important to know the impact of dopants to the vibration of crystal lattice. Fourier Transform Infra-red (FTIR) spectroscopy is an effective technique to monitor the reaction process of preparation of material because it is sensitive to chemical bonds and it is also used to characterize the functional materials. [4]

In the present work, barium zirconate titanate [Ba(Zr_xTi_{1-x})O₃] samples with different Zr concentrations (*i.e.*, x = 0.00, 0.12 and 0.24 respectively) have been prepared through chemical route sol-gel auto combustion method. The structural analysis viz. XRD of the prepared samples has been carried out and phase transformation from tetragonal to cubic for 24% zirconium doped barium titanate has been observed. The FTIR spectroscopy of the prepared samples has been done in order to see the influence of Zr concentrations on the vibrations of crystal lattice and hence physical properties of the materials.

EXPERIMENTAL TECHNIQUES

The powdered samples of barium zirconate titanate [$\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$] where $x = 0.00, 0.12$ and 0.24 respectively have been prepared through sol-gel auto combustion synthesis. The precursors were barium nitrate [$\text{Ba}(\text{NO}_3)_2$], zirconyl oxy-nitrate [$\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$], titanyl oxy-nitrate [$\text{TiO}(\text{NO}_3)_2$], and citric acid. All the precursors were dissolved with minimum amount of distilled water to make a mixed solution. Now small amount of ammonia solution (NH_4OH) was introduced to maintain the pH 7 and to make the clear solution. The prepared solution was then put into magnetic stirrer at 90°C for conversion into gel form and after that a further heat treatment was accomplished for auto combustion. Here citric acid promotes auto combustion process. Now the obtained xerogel was calcined at around 900°C for 2 hours to obtain the desired oxide.

The x-ray diffraction (XRD) patterns for the prepared samples were recorded using Bruker D8 Advanced X-ray Diffractometer with $\text{Cu-K}\alpha 1$ radiation ($\lambda = 0.15406\text{ nm}$) with a step size of 0.019° over the range 2θ range (20-80).

The FTIR spectroscopy of prepared samples were carried out using Perkin Elmer, in wave number ranges from 400 cm^{-1} to 4000 cm^{-1} with 0.5 cm^{-1} resolution in transmission geometry in mid infrared region.

RESULTS AND DISCUSSIONS

The structural confirmation of the barium zirconate titanate (BZT) samples with different zirconium concentration is given by x-ray diffraction. FIGURE 1 illustrates the x-ray diffraction patterns for various BZT samples. From the figure it is concluded that as the zirconium concentration in the sample is introduced more there is a shift of peaks towards the lower angle side because ionic radius of zirconium is more than that of titanium.[5] Here, with the addition of 24 wt% of zirconium at titanium site, the structure has been transformed from tetragonal to cubic phase (JCPDS file no. 31-0174).[6] The values of lattice parameter, volume and average crystallite size of barium zirconate titanate samples are depicted in TABLE 1.

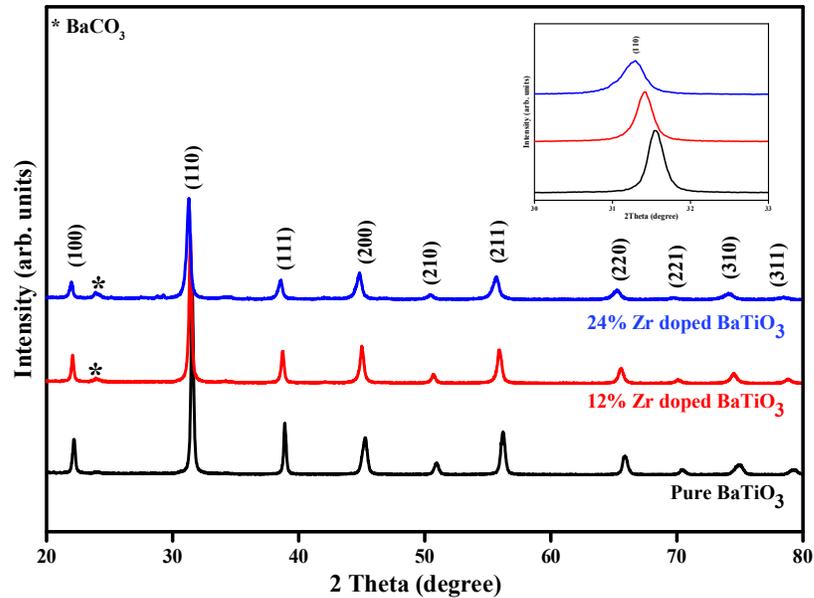


FIGURE 1. X-Ray Diffraction Patterns for Barium Zirconate Titanate at Various Concentrations

FIGURE 2 represents the FTIR spectrums of barium zirconate titanate for different concentrations. The absorption bands in the wave-number range 1500 cm^{-1} to 400 cm^{-1} are known for skeletal vibrations. From the figure it is concluded that a strong absorption peak appears at 504.27 cm^{-1} for pure barium titanate which is attributed to the crystal lattice vibration specifically the vibration of Ti-O bond. All the samples have a fingerprint of Ti-O-Ti and Ti-O bonds between 500 cm^{-1} and 800 cm^{-1} which is the molecular fingerprint of

barium titanate. As zirconium is added the peak is shifted to 497.23 cm^{-1} for 12% concentration and 496.05 cm^{-1} for 24% concentration which indicates that there is a change in lattice parameter. The bands in the region from 1430 cm^{-1} to 1435 cm^{-1} are mainly attributed to BaCO_3 phase present in the sample as impurity. [7]

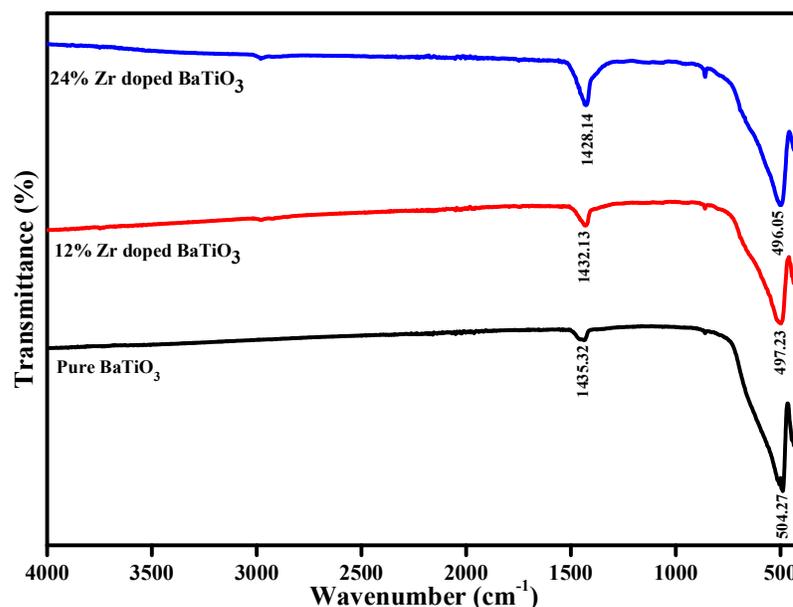


FIGURE2. FTIR Spectrums of Barium Zirconate Titanate at Different Concentrations

TABLE 1. Lattice Parameters, Volume and Average Crystallite Size for BZT Samples

Sample	Lattice Parameter (in Å)		Volume (in Å ³)	Average Crystallite Size (in nm)
	a	c		
BZT00	4.0016	4.0224	64.4078	24.61
BZT12	4.0292	4.0194	65.2514	25.17
BZT24	4.0465	4.0465	66.2591	17.62

CONCLUSIONS

The barium zirconate titanate samples in different Zr concentrations have been prepared through sol-gel auto combustion synthesis process. The x-ray diffraction of the prepared samples confirms all the samples are in phase. At 24% zirconium concentration, the structure has been transformed to cubic. The FT-IR spectrums of different samples reveal the absorption bands as well as the effect of zirconium on the vibrations of crystal lattice.

ACKNOWLEDGMENTS

The authors are thankful to Dr. Mukul Gupta, UGC-DAE-CSR Indore for providing X-ray diffraction facility and Dr. Pratibha Sharma, School of Chemical Science for FT-IR facility.

REFERENCES

1. G. Arlt, D. Hennings, and G. de-With, Dielectric Properties of Fine-Grained Barium Titanate Ceramics, *Journal of Applied Physics*. 1985, 58(4), 1619-1625.
2. X. Tang, K. Chew and H. Chan, *Acta Mater.* 52, 5177 (2004).

3. W. Chaisan, R. Yimnirun, S. Ananta, Effect of vibro-milling time on phase formation and particle size of barium titanate nanopowders, *Ceram. Int.* 35 (1) 173-176 (2009).
4. R. Asiaie, W. Zhu, S.A. Akbar and P.K. Dutta, *Chem Mater.* 8, 226 (1996).
5. T. Tsurumi, T. Hoshina, H. Takeda, Y. Mizuno, H. Chazono, Size effect of barium titanate and computer-aided design of multilayered ceramic capacitors, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* 56 (8) 1513–1522 (2009).
6. N. Nanakorn, P. Jalupoom, N. Vaneesorn, A. Thanaboonsombut, Dielectric and ferroelectric properties of Ba(ZrxTi1-x)O3 ceramics, *Ceram. Int.* 34 (4) 779–782 (2008).
7. R. Ashiri, A. Nemati, *Mater. Res. Bull.* 46 2291-2295 (2011).