

SYNTHESIS AND CHARACTERIZATION OF CATION DEFICIENT DIELECTRIC RESONATOR PEROVSKITE ELECTROCERAMICS



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DOI: <https://doi.org/10.29121/granthaalayah.v8.i12.2020.2731>

Article Type: Research Article

Article Citation: Anand K Tyagi, and Karamveer Kaur. (2020). SYNTHESIS AND CHARACTERIZATION OF CATION DEFICIENT DIELECTRIC RESONATOR PEROVSKITE ELECTROCERAMICS. International Journal of Research - GRANTHAALAYAH, 8(12), 1-9. <https://doi.org/10.29121/granthaalayah.v8.i12.2020.2731>

Received Date: 11 December 2020

Accepted Date: 31 December 2020

Keywords:
Resonator
Electroceramics
Circuit
Ceramic Materials

ABSTRACT

Electroceramics are the ceramic materials that have been specially designed for specific electrical, electronic, optical or magnetic properties. The futuristic demands of Communication Technology require the advanced electroceramics that may efficiently perform the functions of various circuit elements. The performance of electroceramics and their devices is primarily dependent on the three factors namely; complex interplay between processing & chemistry, structure at many levels and device physics. This paper describes the Nano Science assisted synthesis of application grade complex titanate based electroceramics that are presently being used or have futuristic potential to be used in communication technology. A preparative scheme using Nano-powders generated by Auto-ignition method has also been outlined and phase development investigated. The optimized preparational conditions have also been studied and complex titanates to be used as Dielectric Resonators (DR) are specially tailored to meet the demand and requirement of microwave applications for high performance and low-cost devices. The dielectric constants measured by sandwich method were found to be around 39 at 5 MHz frequency and all the samples were found to have Q-factor larger than 3500 that make the synthesized materials suitable to be used as DR in Microwave Communication Technology.

1. INTRODUCTION

Barium titanates are widely used in fabrication of dielectric resonators (DRs) for microwave communication technology applications. These materials possess promising dielectric properties, low power losses, good mechanical strength; high thermal stability [1] and in addition, these systems are environment friendly. Major phases of these complex titanates include barium titanate (BaTiO_3), barium tetra titanate (BaTi_4O_9), barium nona titanate ($\text{Ba}_2\text{Ti}_9\text{O}_{20}$) and cation deficient perovskite ($\text{A}_6\text{B}_5\text{O}_{18}$) etc. The cation deficient perovskites belonging to this family have emerged as a leading candidate as ceramic material used in the fabrication of DRs because of their best suited dielectric properties. The properties of barium titanates can be tuned by doping other elements at barium or titanium sites. This helps to tailor out the materials with desired micro-structural properties; like level of porosity, grain size, core-shell structures, secondary phases etc. The dielectric properties of these titanates are largely dependent on the growth of the grains during sintering and on the type and concentration of the dopants that are to be added [2]. It has been reported that the homo-valent or hetero-valent replacement of Ba or Ti ions in Barium

titanates lead to significant variations in material properties [3]. Zr^{4+} (Zirconium ion) can replace Ti^{4+} ions in $BaTiO_3$ (BTO) as it is iso-valent with Ti^{4+} . It has been reported that Zr addition to BTO shows shift in Curie point, notable depression in the dielectric peak and formation of core shell grains that lead to desired temperature stability of dielectric properties and enhancement in dielectric properties [4].

In the present work, we have attempted to dope Zr^{4+} to cation deficient perovskite $Ba_6Ti_5O_{18}$ of $(A_6B_5O_{18})$ family with an objective to have similar improvement in properties of this highly promising DR material. The samples with nominal composition $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$; ($0.0 \leq x \leq 0.25$) have been synthesized by Sol-Gel Auto Combustion method and the effects of substitution of titanium by zirconium on phase development, structural, micro-structural, morphological and dielectric properties have been investigated in this report.

2. EXPERIMENTAL WORK

The low temperature synthesis of $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$ ceramics has been realized by using Barium Nitrate $\{Ba(NO_3)_2\}$ (S A), Zirconium Oxy-nitrate $\{ZrO(NO_3)_2\}$ (S A) and Titanium Iso-propoxide $[Ti\{OCH(CH_3)_2\}_4]$ (S A) as starting chemicals. Nitric Acid (HNO_3) (F S), Citric Acid Monohydrate ($C_6H_8O_7 \cdot H_2O$) (C D H) and Ammonia (NH_3) (RFC) are used as solvents. In all six samples corresponding to $x=0, 0.05, 0.1, 0.15, 0.2$ and 0.25 have been synthesized in accordance to the metallurgical reaction given below and the obtained ceramics are termed as BZT0, BZT05, BZT1, BZT15, BZT2 and BZT25 respectively.

$$54 Ba(NO_3)_2 + 45x ZrO(NO_3)_2 \cdot H_2O + 45(1-x) TiO(NO_3)_2 + 53 C_6H_8O_7 \cdot H_2O \rightarrow 9 Ba_6(Ti_{1-x}Zr_x)_5O_{18} + 99 N_2 + 318 CO_2 + (265+45x) H_2O$$

The starting AR grade chemicals $Ba(NO_3)_2$, $TiO(NO_3)_2$, $ZrO(NO_3)_2$ and citric acid are taken in a molar proportion of 6: 5-5x: 5x: 5.88 for synthesizing one mole of $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$ ceramic according to above equation maintaining the total metal ion to citric acid molar ratio to 1:0.534. Firstly, a clear solution of titanyl nitrate $TiO(NO_3)_2$ is prepared from titanium iso-propoxide $\{Ti\{OCH(CH_3)_2\}_4\}$ under ice cold conditions using the method reported in our earlier report [5]. Separately, an aqueous solution of Ba^{2+} cations is formed by dissolving weighed amount of $BaNO_3$ in minimum amount of distilled water at $40^\circ C$ by continuous stirring. The weighed amount of $ZrO(NO_3)_2$ is dissolved in hot distilled water under continuous stirring to obtain an aqueous solution of Zr^{4+} cations. $TiO(NO_3)_2$ solution, aqueous Zr^{4+} solution and aqueous Ba^{2+} solution is mixed together under vigorous stirring to obtain clear solution. The citric acid solution, prepared separately in distilled water, is then added to the above prepared solution under vigorous stirring to obtain transparent aqueous solution having citrate and nitrates. The solution is named Citrate - Nitrate (CN) solution.

Dilute ammonium hydroxide NH_4OH is added drop wise to the CN solution to adjust the pH value ~ 6 that leads to clear yellow transparent solution. The obtained solution is heated on a hot plate at $\sim 90^\circ C$ till the formation of yellow transparent gel. Then temperature of the hot plate is raised and at $\sim 240^\circ C$, the gel swells and gets ignited. The ignition takes place for approximately 5 seconds with evolution of large volume of gaseous products. As a result, black voluminous powder containing carbon residue is produced. The obtained powder is then calcined at $600^\circ C$ to remove the carbon residue. The pellets of the powder, so obtained, are prepared using PVA (poly vinyl alcohol) as binder and then, calcined at $600^\circ C$ to expel the binder. The sintering of pellets is done at $1250^\circ C$ for 2 hours at heating rate of $3^\circ C/minute$. All the six samples were synthesized using the aforesaid method in a single go.

X ray diffraction of the sintered pellets is done with the help of Bruker D8 Advance diffractometer using $Cu K_\alpha$ radiation. FESEM/EDS analysis of sintered pellets is done using using Nova Nano FE-SEM (FEI) for morphological and elemental analysis. FTIR analysis is carried out using FT-IR Spectrum 2 (Perkin Elmer). Dielectric properties are measured using Hioki impedance analyzer in frequency range 100 Hz to 5 MHz at room temperature.

3. RESULTS AND DISCUSSION

3.1. XRD CHARACTERIZATION

The XRD patterns for $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$; ($0.0 \leq x \leq 0.25$) ceramics sintered at $1250^\circ C$ are shown in figure1(a). Clearly, all the XRD peaks are well defined and can be indexed on the basis of hexagonal symmetry of the structure. The XRD patterns observed are similar to the XRD pattern of $Ba_6Nb_4TiO_{18}$ ceramic reported in literature [6],[7]. All Zr doped $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$ ceramics show nearly identical XRD patterns with no detectable impurity phases.

However, the peaks show a shift toward smaller angle side which may be attributed to intake of relatively larger ion Zr^{4+} (0.72\AA) as a replacement of Ti^{4+} (0.605\AA) ions in the ceramic matrix. The indexing of peaks and calculation of lattice parameters are done using the analytical method for non-cubic crystals [8]. The lattice parameters 'a' & 'c' values are 5.67, 5.69, 5.69, 5.71, 5.72 and 5.72\AA ('a'); 41.62, 41.78, 41.83, 41.98, 42.06 and 42.00\AA ('c') for BZT0, BZT05, BZT1, BZT15, BZT2 and BZT 25 respectively. Both the parameters are found to increase with the increase in value of x. This is due to the replacement of Ti^{4+} (0.605\AA) ions with larger Zr^{4+} (0.72\AA) ions [9],[10]. $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$ ($0 \leq x \leq 0.25$) ceramics with densities above 93% have been obtained after sintering at 1250°C for 2 hours. The crystallite sizes, as calculated for (110) reflection for BZT ceramics, lie in the range 30-40 nm[9].

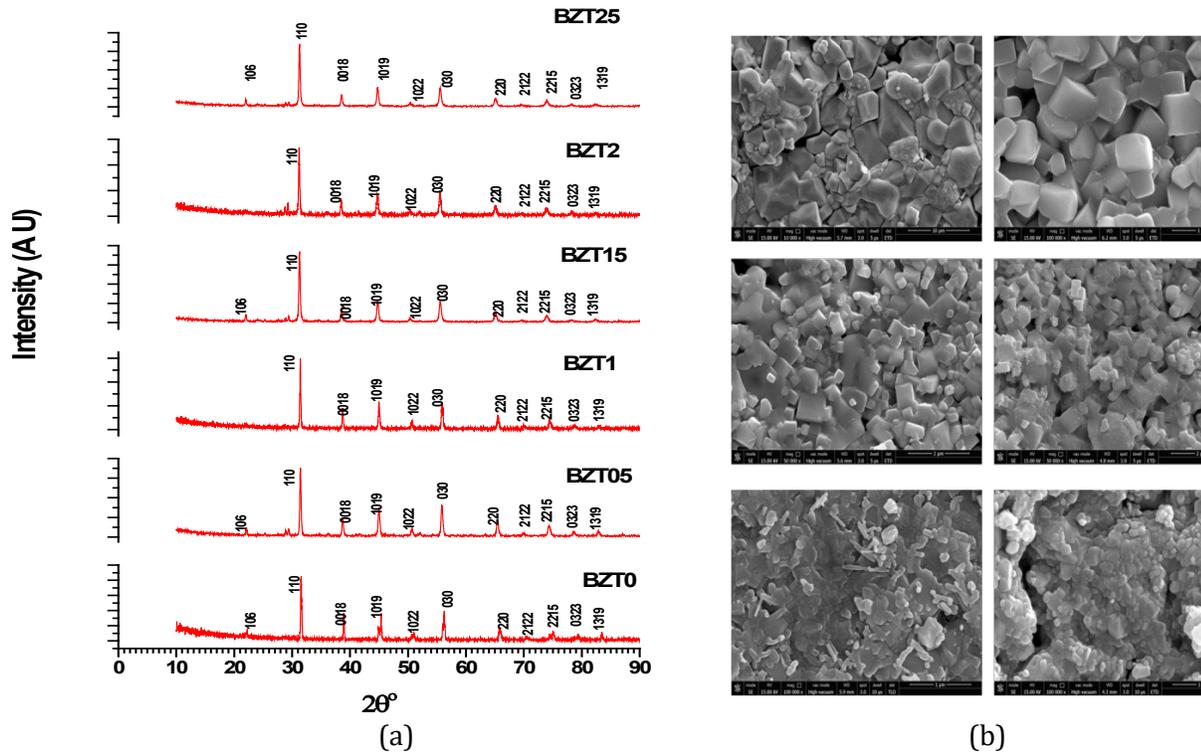


Figure 1: (a) XRD patterns of $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$ ceramic samples ($0 \leq x \leq 0.25$) sintered at 1250°C . (b) FESEM images of $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$ ceramic samples ($0 \leq x \leq 0.25$)

3.2. FESEM ANALYSIS

The microstructures of all the $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$ (BZT) ceramics as obtained by FESEM are shown in figure 1(b). BZT0 ($x=0$) ceramic has homogeneous microstructure with smaller grains having size range from 37.58 nm to 75.54 nm and larger grains having size range from 703.5 nm to 4.813 μm . The grains have the polyhedral shape with clear, well defined edges, corners, faces and grain boundaries. It has good sinterability and the low amount of inter-granular porosity. The microstructures of $x=0.05$ (BZT05) and $x=0.1$ (BZT1) samples have identical features, differing only in grain sizes; from 68.78nm to 600nm for BZT05 and 129.9 nm to 806.6 nm for BZT1. Both these samples have cuboidal shape grains in comparison to polyhedral shape for BZT0 ceramics. The grains are having clear, well defined edges, faces and grain boundaries. These ceramics possess less inter-granular porosity in comparison to BZT0 ceramic. The microstructure for BZT15 ceramic is homogeneous having size ranging from 24.43 nm to 568.2 nm. The grains have the cuboidal shape and initiation of the coalescence process can be clearly seen in the FESEM image of BZT15 ceramic[11]. This leads to coarsening of grains and thus increase in densification. The grain boundaries have started merging each other due to coarsening of grains and intergranular porosity has decreased much in comparison to BZT0, BZT05 and BZT1 ceramics. Similarly, it can be observed that coalescence process and agglomeration of grains goes on for BZT2 and BZT25 ceramics, as a result inter-granular porosity is further reduced to the large extent. The agglomeration of grains at higher Zr content is due to the nano-metric size of these grains. As the grains having small dimensions have the large surface area and are thus thermodynamically

unstable. These have large surface energies and thus tend to agglomerate [9]. The sample BZT2 is unique in itself as it has bimodal distribution of grains having rod shaped, as well as, the polyhedral shaped grains with grain size lying in the range from 30.52 nm to 176.4 nm. However, the sample BZT25 showed grains of sizes ranging from 48.56 nm to 343.9 nm. The decrease in grain size at higher Zr content is due to the reduced grain growth rate owing to slow diffusion of Zr^{4+} ions having larger ionic radius [12].

From analysis of EDX spectra for all the BZT compositions, it was observed that only Barium, titanium and oxygen elements are present in BZT0. There are no traces of any other element. For all other compositions from BZT05 to BZT25, the presence of zirconium was observed along with barium, titanium and oxygen elements. The atomic composition obtained for BZT ceramics from EDX spectra and that calculated theoretically match well and amount of zirconium increases from BZT0 to BZT25 ceramics, as expected. However, the amount of oxygen was little deficient for $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$ ceramics in comparison to theoretical value.

3.3. FTIR ANALYSIS

FTIR absorption spectra was almost same for all the compositions showed almost same FTIR spectra, wherein the absorption peaks between 3777cm^{-1} to 2823.21cm^{-1} have been identified as the stretching vibration of hydrogen bonded OH (hydroxyl) bond of water (H_2O) absorbed on the surface [13],[14]. The absorption peaks at around 1600cm^{-1} and 1400cm^{-1} correspond to bending mode of absorbed water (H-O-H bending) and the OH bond of the water molecule respectively [13],[15]. The presence of water can be due to absorption of moisture from the environment. The absorption peaks having very small intensity at 1052.38cm^{-1} and 1059.14cm^{-1} for BZT05 ($x=0.05$) and BZT1 ($x=0.1$) samples may be due to stretching vibration mode of the C-O bond [16]. The absorption peak at 858.25cm^{-1} , 858.70cm^{-1} and 859.62cm^{-1} for BZT0 ($x=0.0$), BZT1 ($x=0.1$) and BZT2 ($x=0.2$) may be due to stretching vibration mode of distorted TiO_6 octahedral[17]. The highly intense absorption peaks between 540.07cm^{-1} and 573.06cm^{-1} for BZT ceramics correspond to the stretching vibration of TiO_6 octahedral connected to Barium ion [13],[18]. The absorption peaks between 410.57cm^{-1} and 436.55cm^{-1} for BZT ($0 \leq x \leq 0.25$) compositions have been identified as bending vibration mode of Ti-O bonds [14],[16]. The stretching vibration of TiO_6 octahedral and Ti-O bending vibration confirms the presence of TiO_6 octahedral; the face sharing of these TiO_6 octahedral leads to the formation of hexagonal closed pack structures.

3.4. DIELECTRIC CHARACTERIZATION

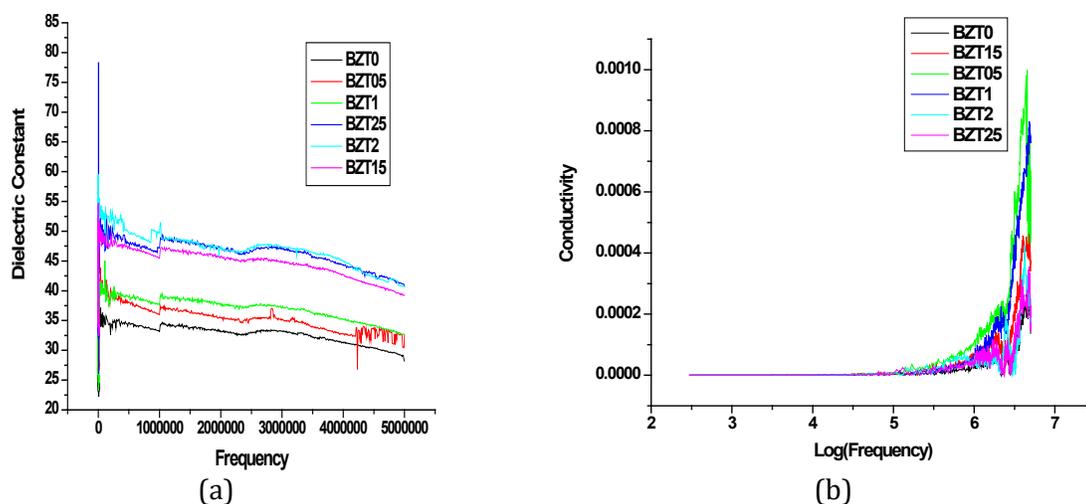


Figure 2: (a) Variation of dielectric constant (b) conductivity with the frequency for $Ba_6(Ti_{1-x}Zr_x)_5O_{18}$ ($0 \leq x \leq 0.25$) samples.

The variation in the values of dielectric constant as a function of frequency has been shown in figure 2(a) for all the BZT samples synthesized. In general, its values are observed to decrease with rise in frequency. These values were determined to be 37.26, 43.70, 42.03, 53.71, 59.20 & 54.29 at 1 KHz, 33.19, 36.01, 37.61, 45.47, 49.72 & 47.24 at 1 MHz and 28.22, 32.49, 32.70, 39.26, 40.75 & 40.72 at 5 MHz for BZT0 ($x=0$), BZT05 ($x=0.05$), BZT1 ($x=0.1$),

BZT15 ($x=0.15$), BZT2 ($x=0.2$) & BZT25 ($x=0.25$) respectively. It can be observed from here, as well as, from figure 2(a) that dielectric constant values increase with enhancement in the amount of zirconium [4],[9]. The calculated values of electrical conductivity for all the samples have been plotted against log (frequency) in figure 2(b). The conductivity is observed to increase with the rise in the frequency. The maximum values of conductivity for all BZT samples synthesized; BZT0, BZT05, BZT1, BZT15, BZT2 and BZT25 are respectively 2.65×10^{-4} , 9.15×10^{-4} , 8.26×10^{-4} , 4.67×10^{-4} , 4.25×10^{-4} and $3.56 \times 10^{-4} \text{ Sm}^{-1}$. The maximum values of quality factor for these samples are 12500, 2941.176, 7142.857, 2173.913, 100000 and 9091 respectively.

4. CONCLUSION

$\text{Ba}_6(\text{Ti}_{1-x}\text{Zr}_x)_5\text{O}_{18}$ ($0 \leq x \leq 0.25$) ceramics with densities up to 93% have been successfully synthesized using sol gel combustion method. All BZT compositions show similar, well defined and indexed XRD peak patterns with no detectable impurity phase. The peaks shift toward smaller angle with increase in amount of zirconium. The lattice parameters 'a' and 'c' increased with substitution of titanium by zirconium as expected. The crystallite size is almost same for all the compositions in the range 30-40 nm. XRD, FESEM/EDS and FTIR analysis confirm the formation of $\text{Ba}_6(\text{Ti}_{1-x}\text{Zr}_x)_5\text{O}_{18}$ with little deficiency of oxygen. The decrease in grain size and agglomeration of grains is evidenced with increase in amount of zirconium by FESEM analysis. The dielectric properties show enhancement with increase in substitution of titanium by zirconium. The investigation of dielectric constant, conductivity and quality factors reveal that $\text{Ba}_6(\text{Ti}_{1-x}\text{Zr}_x)_5\text{O}_{18}$; ($0 \leq x \leq 0.25$) ceramics are suitable to be used as dielectric resonators.

SOURCES OF FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICT OF INTEREST

The author have declared that no competing interests exist.

ACKNOWLEDGMENT

Authors highly acknowledge I.K. Gujral Punjab Technical University, Kapurthala, for its valuable inputs in course of this work. The authors are also very grateful to TEQIP, MHRD/World Bank Project for providing the necessary research facilities. Furthermore, authors appreciatively acknowledge IIC, I.I.T. Roorkee, MRC, MNIT Jaipur and S B S State Technical Campus, Ferozepur for support in characterization of samples.

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