Structure, morphology, and ferroelectric behavior of $Ba_{1-y}Zn_yTiO_3$ (y = 0.2, 0.4, 0.6 & 0.8) nanoceramics

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The barium zinc titanate (BZT) nanoceramic samples were prepared via the hydrothermal technique. It was found from XRD patterns that the y = 0.2 to 0.8 compositions showed the cubic perovskite structure along with some secondary phases related to the zinc titanate (Zn_2TiO_4). The surface morphology indicated the formation of nanospheres like grains/particles for y = 0.2, and 0.3 compositions while the rest of the samples showed the rods like structures. Further the P-E loops of y = 0.2-0.8 samples showed the saturation of all samples.

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1. Introduction

It was a known fact that most of ceramic titanate materials belong to the perovskite family having a general chemical formula of ABO_3, wherein, A = divalent cation, and B = trivalent cation [1-5]. Barium titanate is a well-known dielectric, and ferroelectric material due to its predominant dielectric and saturation polarization value [6-12]. In addition, it revealed the significant properties like piezoelectric, pyroelectric, memory applications upon doping/substituting other cations like Zr, Pb etc., into its perovskite system [13, 14]. Thus, it received several applications in different fields of interest.

However, the research is going on still on doping/substituting different cations into either barium titanate or its based perovskite structure. This led to achieve more advanced properties of barium titanate-based ceramics in both bulk as well as nano. In this connection, we thought of doping zinc due to its wide energy gap behavior, and with the intention to check the diffraction pattern, topographical, and ferroelectric behavior. For the synthesis of barium zinc titanate nanoceramics, we opted a low temperature hydrothermal technique due to several advantages like low operating temperatures, pure crystallinity, homogeneity, easy preparation, and inexpensive [1-5]. Moreover, in the literature also many scientists [6-15] did research work barium titanate-based materials but very limited investigations were seen for the zinc doped barium titanate nanoceramics synthesized using hydrothermal method at small operating temperatures.

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2. Experimental procedure

To prepare the nano BZT ceramic materials, we selected the raw materials in nitrate form such as barium nitrate, zinc nitrate, and titanium dioxide (99.6 % purity). Herein, titanium dioxide is in oxide form, but it could be able to form the compound as mentioned in the published work [5]. At first, these starting materials were mixed in a stoichiometric ratio and kept in a fresh glass beaker. And the beaker was again kept on magnetic stirrer with hot plate. The stirring process was continued by adding the distilled water for half an hour. Then the delicious solution was obtained, and this solution is transferred to Teflon bowl of the capacity of 300 ml. This bowl is again kept in stainless steel autoclave and positioned in a hot air oven. The hydrothermal reaction was carried out at 150 degrees centigrade for 6 hours. After completion of the reaction, the autoclave was kept in the oven only till the temperature comes to room temperature. Once it is happened, the autoclave will be removed, and solution is further shifted to fresh glass beaker. This solution is centrifuged to get the fresh BZT nanopowder. Later, this powder is processed for various characterizations such as XRD, FESEM, TEM, and P-E loop tracer. These characterizations were done for investigating the structure, surface morphology, and ferroelectric behavior.

3. Results and discussions

The X-ray diffraction patterns of BZT nanoceramics were shown in Fig.1. It was observed from the XRD patterns that the all the samples showed the well crystalline phases related to the cubic structure. Inclusively, the secondary phases were detected associated with the Zn_2TiO_4 structure. The maximum intensity was recorded for [110] reflection planes of y = 0.2-0.8. The average crystallite size of y = 0.2 to 0.8 samples was found to be increasing with zinc content from 38.2 to 85.7 nm using a formula of $0.9\lambda/\beta\mathrm{Cos}\theta$, where λ is the wavelength of X-rays, β is the full width half maxima, and θ is the diffraction angle [16-18]. The lattice parameters of cubic planes were determined using a formula of $a = b = c$: $d_{hkl}\ [h^2+k^2+l^2]^{0.5}$, where hkl are the Miller indices and d_{hkl} is the interplanar distance [19-21]. The results showed that the lattice constants were found to be increasing from 0.3979 to 0.3998 nm as a function of composition. This was attributed to the increasing ionic radii of zinc content with composition. These values were in good agreement with the standard JCPDS: 89-2475.

Further, the surface morphology of y = 0.2-0.8 nanoceramics was studied using the field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). The FESEM pictures were shown in Fig.2. It was understood from those FESEM images that the y = 0.2 samples showed the existence of clustered spheres. This clustering or agglomeration behavior of nanoparticles could be due to the interaction among those nanoparticles. In the literature also, this kind of observation was found [22-27]. However, for y = 0.4 sample, the growth of nanorods just initiated, and for y = 0.6 & 0.8, it seemed to be larger extent in nature. From these results, it was observed that the distortion was occurred in the case nanospheres like grains of y = 0.2 sample. In general, these kinds of distortions will be happened owing to the nucleation process, wherein, the distortion will be taken place either in horizontal or vertical direction or in both. Thus, the formed structures will be like nanorods either in vertical or horizontal directions. These observations were evidenced in the case of y = 0.4-0.8 samples. The similar kinds of reports were found in the literature. Besides, the grain size was determined to be altering from 98.5 to 186.2 nm as a function of zinc content. On the other hand, the TEM images of y = 0.2 & 0.8 samples clearly showed the existence of nanospheres and nanorods like particles. These results were in good comparison with the FESEM results. Herein, also the distortion occurred for y = 0.2 samples after doping high amount of zinc. Little agglomeration of nanoparticles was noticed due to some interactions among those particles. The y = 0.2 sample showed average particle size of 32.7 nm, whereas the y = 0.8 sample provided the 51.8 nm sized nanorods, and length having 168.4 nm.

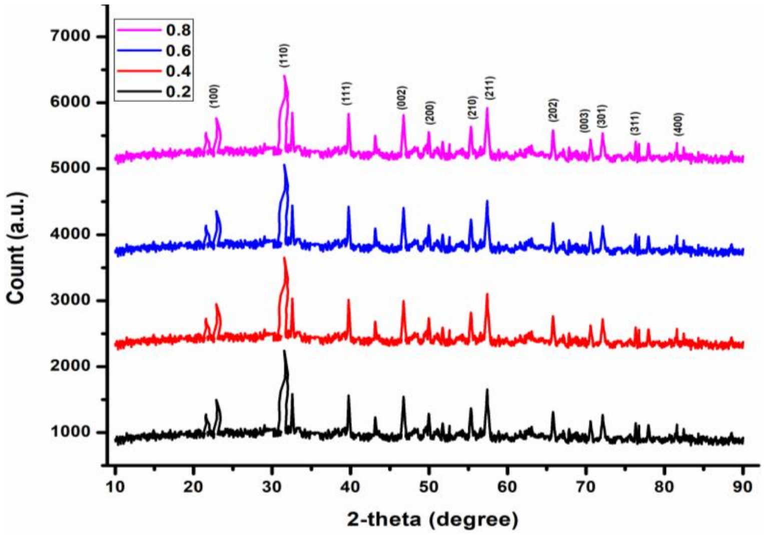

Fig.1. XRD patterns of BZT nanoceramics.

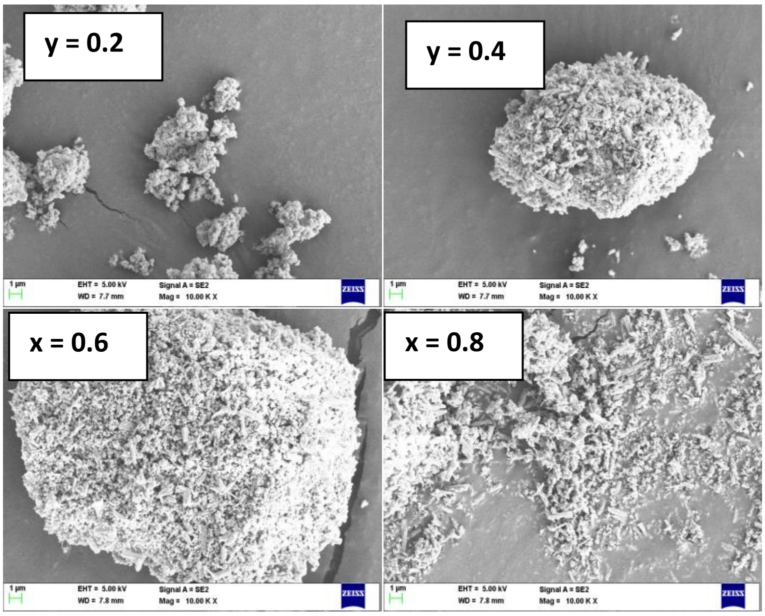

Fig. 2. FESEM images of BZT nanoceramics.

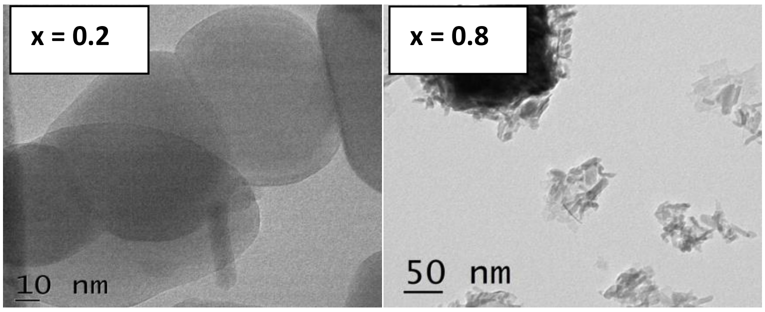

Fig. 3. TEM images of BZT nanoceramics.

The Polarization versus electric field (P-E loop) tracer, Marine India Co., was used for studying the ferroelectric behavior of y = 0.2-0.8 samples. In order to conduct the experiment, the pellet was coated with silver on onside (half) and inserted parallel to 4 μF capacitor for the compensation. All these P-E loops of y=0.2-0.8 were recorded under an applied frequency of 600 Hz at an operating voltage of 600 V. It was observed from the Fig.4 that the P-E loops were of little bit saturated containing the "banana" shape [26]. These loops were seemed to be well defined but distorted into banana shape. Due to the banana shape, the current leakage or eddy current loss or dielectric loss will be very high. Actually, this kind of trend will be noticed owing to the formed oxygen vacancies on the surface of grains rather than polarization. Hence, the small saturation polarization and retentivity values were found for all samples. Moreover, the absence of 180^{o} ferroelectric domains, the response of electric dipoles will be less for all samples [26]. The result expressed that the saturation polarization P_s values were almost constant noting it as ~0.0418 μC/ cm^2, and the retentivity P_r of y=0.2 sample was identified to be ~0.012 μC/ cm^2. In case of y =0.4-0.8, it was found to be increasing from 0.008-0.0247 μC/ cm^2, respectively.

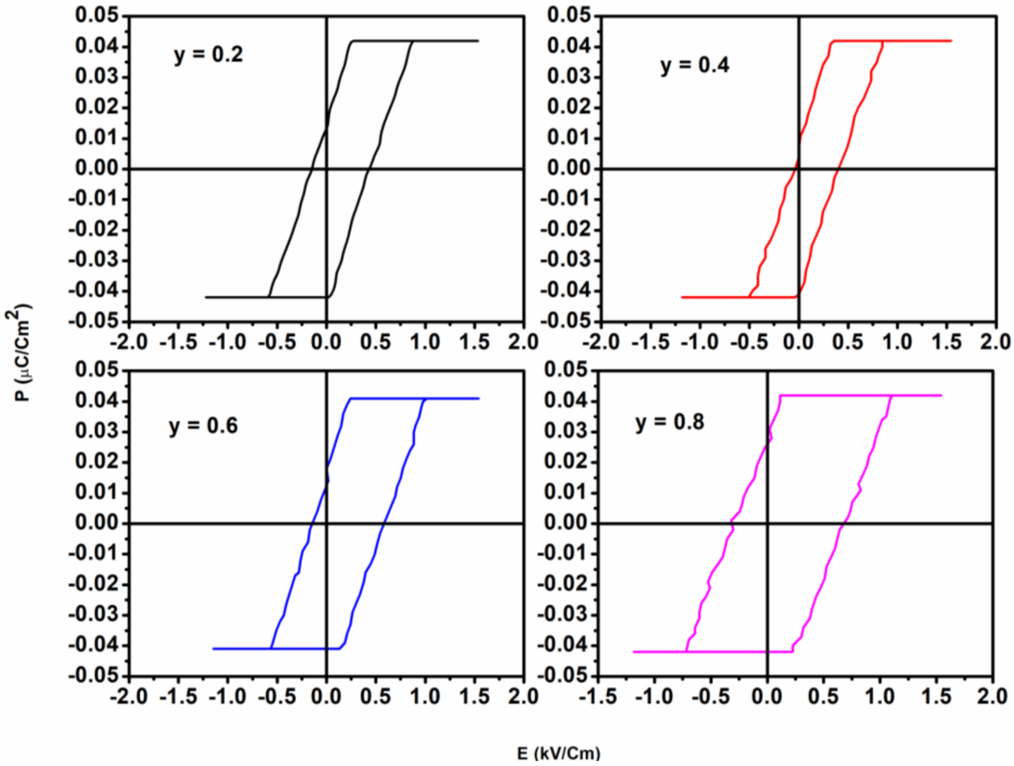

Fig. 4. P-E loops of BZT nanoceramics.

4. Conclusions

The BZT nanoceramic samples with varying composition from y=0.2-0.8 were synthesized via the low temperature hydrothermal technique. The diffraction study showed the cubic phase structure of samples pertaining some Zn_2TiO_4 phases as the secondary peaks. The FESEM and TEM images evidenced the nanospheres for y =0.2 sample while y=0.4-0.8 samples offered the nanorods like structures. Thus, the nucleation process was clearly noticed. Furthermore, the P-E loops indicated the well-defined hysteresis behavior and the distortion into banana shape due to surface oxygen vacancies.

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