International Advance Journal of Engineering, Science and Management (IAJESM)
ISSN -2393-8048, January-June 2018, Submitted in May 2018, iajesm2014@gmail.com

Phase formation mechanism in ferroelectrics

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Abstract

In the present work thermal analysis has been used to determine the phase transition characteristics of well known ferroelectric material Barium Titanate. Differential Scanning calorimeter assisted to determine the temperature range from disordered to ordered transition. Thermal analysis is found to have significant key role in phase formation of the material. Crystallization temperature can be easily determined. The difference in ionic radii of $Ba^{+2}$and Sr^{+2}ionic was responsible for reduced *c/a* ratio and shifting of tetragonal symmetry to cubic structure.

Keyword: Phase Transition, Ferroelectrics

Introduction

Perovskites are the most important class of ferroelectric materials in advanced material research. Ferroelectric ceramics are intensively studied in the scientific community for electrical applications [1]. Barium titanate ($BaTiO_3$, BT) is one of the most important perovskite materials, which has high research interest because of its excellent ferroelectric properties, high dielectric constant and low loss [2-4]. It is an environment friendly material and provides an alternative for Pb based materials [2]. BT has the tetragonal phase at room temperature. BT shows three phase transitions at different temperatures, from rhombohedral to orthorhombic around -80 ^oC, from orthorhombic to tetragonal around 5 ^oC and from tetragonal to cubic around 130 ^oC [5-7] and this temperature is called Curie temperature T_c [1].

Further extensive studies have been done to know the effect of doping in this system. Both A and B site substitution has been done and explored the possibility in various fundamental applications [7-8].

Thermal analysis is an essential tool to explore the phase formation temperature range. Different techniques can be employed to know the behavior of the material with respect to temperature.

In this study, solid-state method (SS) and sol-gel synthesis methods (SG) are used for synthesis of barium titanate ceramics (BT). Thermal analysis has major role to determine glass transition, crystallization and melting temperature. With the help of differential scanning calorimetry these temperatures can be easily determined.

Experimental Details

The two methods were adopted to prepare barium titanate. First one is solid-state method, which is easy conventional mixture method but a high temperature synthesis method. The second method is sol-gel by which good control over composition, high purity and homogeneity can be achieved. Also this is low sintering temperature and low cost synthesis method. Sr-substitution was done in A-Site to observe the structural changes.

Differential scanning calorimetry (DSC) is useful tools to investigate the changes in physical or chemical properties of the samples with variation of temperature. DSC is a helpful method to study the melting point, oxidation, heat flow into or out from the sample, crystallization of a sample with temperature change. DSC properties were characterized in temperature range from 15 ^oC to 1000 ^oC by differential scanning calorimetry (STA8000, Perkin Elmer Ltd.). The structure of the calcined powders were analyzed by X-ray powder PANalytical diffraction spectroscopy with Cu K_α radiation (1.540598 $\dot{A}$) at 45 kV and 30 mA in the 2θ range of $20^0 \leq 2\theta \geq 80^0$. The morphology of the samples was characterized by the field emission scanning electron microscope (FESEM: Jeol JSM-7600F).

Results

Thermal Analysis of Barium Titanate ceramics prepared by solid-state method

The possible decomposition temperature and structural phase changes or crystallization of BT can be analyzed with using the DSC thermographs. It is used to measure the heat of transition or heat

capacity and detects the percentage of the tetragonal phase in BT [9]. DSC thermographs are plotted between heat flow rate and temperature. Figure 1 shows the DSC curve of the solid state prepared Barium titanate. Three exothermic peaks are observed in DSC thermograph at 458 ºC, 627ºC and 832 ºC respectively and these are non-perovskite peaks or unreacted phases [10]. The exothermic peaks between 458 to 832ºC are arising due to decomposition of solvent and intermediate phases. It can be seen from the DSC curve that the perovskite formation may maintain upto more than 900 ºC temperature. Due to the limitation of temperature range from room temperature to 900ºC of DSC characterization instrument, the calcination at 1100 ºC and sintering at 1300 ºC temperature of Barium Titanate samples are confirmed only by the expert's views and from the various reported data [9-13].

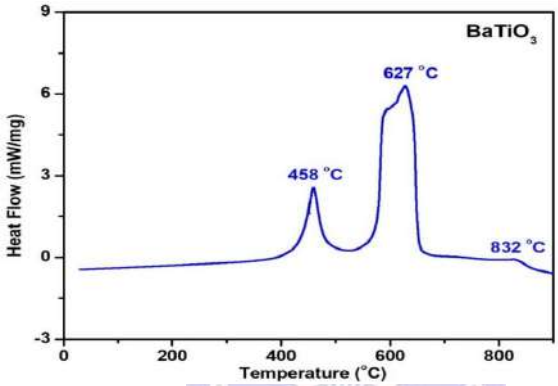


Figure 1: DSC thermograph of BT ceramic prepared by Solid State method

2. Thermal Analysis of Barium titanate ceramics prepared by sol-gel method

DSC curve of sol-gel prepared BT is shown in figure 2. Five peaks are observed in DSC thermograph and clearly indicates the change from non-perovskite to perovskite phase formation. First peak at 91 ºC occurs due to vaporization of water. The decomposition of solvent and the intermediate phases arises as a exothermic peak at three temperatures 309 ºC, 477 ºC and 645 ºC. The perovskite formation and exothermic peak occurs at 825 ºC temperature. Above this the melting temperature of material will occur and phase structure of material will be distorted. For pores elimination sintering has to be done at relatively higher temperature than crystallization temperature.

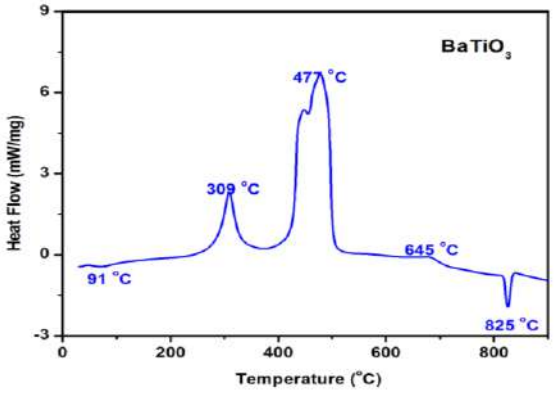


Figure 2: DSC thermograph of BT ceramic prepared by Sol-gel method

X-Ray Diffraction

XRD is a non-contact and non-destructive method for structural characterization of the samples. This method commonly used to determine the crystal structure, phase structure, the distance between the planes of the crystal, average grain size, lattice strain and crystal defects . Based on the result of thermal analysis these perovskite have been calcined and sintered at respective temperatures. For crystal structure determination X-ray diffraction studies has been performed.

The XRD graph (Fig.3) shows the major peaks with Miller indices (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0), (2 1 1) and (2 2 0). All the peaks were found to match well with the JCPDS file (space group*P4mm*) and confirms the tetragonal crystal structure. There is no evidence of non-perovskite secondary phase in XRD graph.

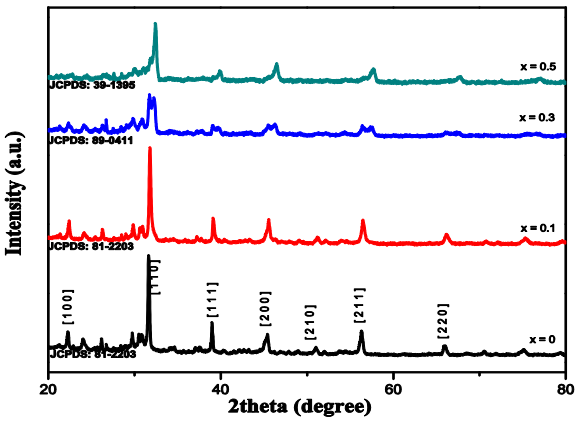


Figure 3: The XRD patterns of $Ba_{1-x}Sr_xTiO_3$ for x = 0, 0.1, 0.3 and 0.5, calcined at 1100 ºC

With increasing concentration of Sr into BST ceramics, the unit cell tetragonality is reduced due to contraction of both '*a*' and '*c*' values which leads to the shifting of the tetragonal structure towards cubic in nature [14] as shown in Fig.4 .

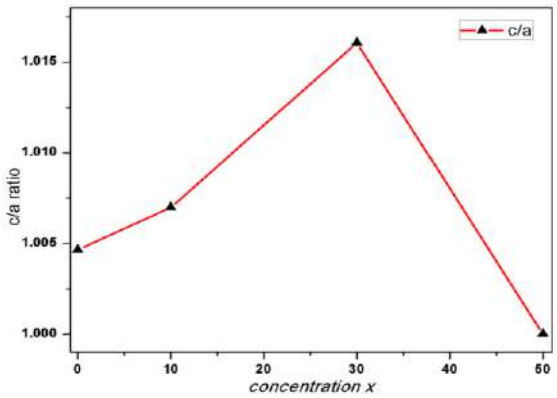
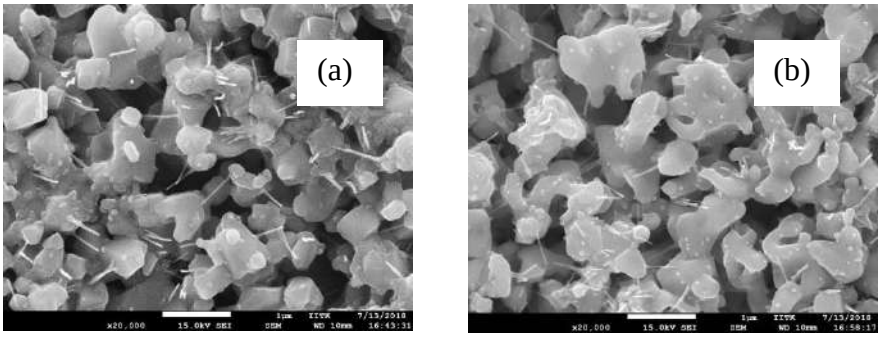


Figure 4: The c/a ratio variation with concentration x for $Ba_{1-x}Sr_xTiO_3$, calcined at 1300 ºC

The average grain size of $Ba_{1-x}Sr_xTiO_3$ ceramic samples for x = 0, 0.1, 0.3 and 0.5 obtained by SEM images by IMAGE J software. Average grain size is increased from 0.41***μm*** to 0.54 for x = 0 to 0.1 and decreased for x = 0.3 but again increased up 0.56*μm* for x = 0.5 **.**It can verify from FESEM micrographs of $Ba_{1-x}Sr_xTiO_3$ ceramic samples for x = 0, 0.1, 0.3 and 0.5 are presented in Fig. 5.



(c) (d)

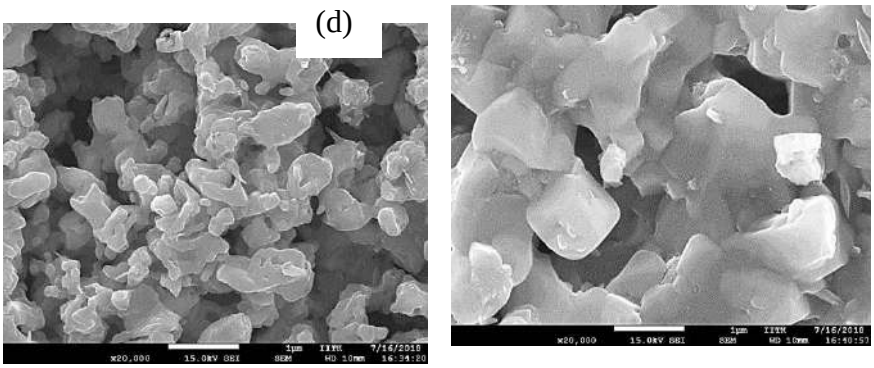


Fig. 5. FESEM images of $Ba_{1-x}Sr_xTiO_3$ ceramics, synthesized by solid state method for (a) x = 0 (b) 0.1 (c) 0.3 and (d) 0.5, sintered at 1300 ºC for 3 hr.

Conclusion

In the present work $BaTiO_3$ ceramics were successfully synthesized using solid state method and sol-gel method separately. Thermal properties were analyzed with using DSC characterization data and observed that the samples synthesized by sol-gel method required low calcination temperature as compare with the samples synthesized by solid-state method. Effect of Strontium doping was studied by X-ray diffraction and the tetragonal phase was confirmed. In the present study, $Ba_{(1-x)}Sr_xTiO_3$ ceramics for x = 0, 0.1, 0.3 and 0.5 were successfully synthesized using solid state reaction technique and structural characterization were measured. Powder X-ray diffraction investigated at room temperature and found that the crystal structure is tetragonal for x = 0, 0.1 and 0.3 and cubic structure for x = 0.5. The peaks were shifted toward higher angle and the decreasing of the unit cell volume with x. The lattice constant decreases linearly with increasing of x value, due to the Sr ions are substituting Ba ions into the lattice. The unit cell tetragonality is reduced due to contraction of both *a* and*c* values which leads to the shifting of the structure towards cubic in nature.

Acknowledgments

The authors are grateful to Prof Kantesh Balani, IIT Kanpur and Dr. A. M. Awasthi and Mr. Suresh Bhardwaj, UGC-DAE Consortium for Scientific Research Center Indore, for their valuable discussion and assistance during this work.

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