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Thermal Energy Harvesting using BaTiO₃ Based Ferroelectric Ceramics: A Review

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ABSTRACT

Ferroelectric oxide ceramics are used in a very broad range of functional ceramics and form the materials base for the majority of electronic applications like sensors, actuators, buzzers, medical ultrasonic transducers, etc. These materials have excellent piezoelectric properties, pyroelectric properties, figure of merits (FOMs) and good temperature stability. In this context, efficient conversion of heat energy into electric signal is of great importance. Pyroelectric materials have been extensively explored for such kind of energy harvesting applications. These materials generate electrical current on the expense of input thermal energy. This property of these materials propounds ample possibilities for harnessing energy from the thermal by-products of many ferroelectric materials are also promising for efficient energy storage capacity (ESD). This study explore the knowledge about the energy storage density and thermal energy harvesting potential for Sn doped BaTiO₃ based ferroelectric material. Therefore, we can get the maximum energy storage density and maximum energy harvesting density materials.

Keywords: *Ferroelectric; Energy Storage Density; Thermal Energy Harvesting.*

1.0 Introduction

Ferroelectric ceramics are technologically important materials and widely used as sensors, actuators, buzzers, transducers and medical ultrasonic transducers. Lead-free ferroelectric ceramics providing clean alternatives to their lead-based supplement [1]. These materials have been broadly explored for their energy storage and thermal energy harvesting capabilities. Various researchers have been focused on harnessing thermal and mechanical energies using ferroelectric materials. Pyroelectric materials have been broadly explored for energy harvesting applications.

These materials convert thermal energy into electrical signals. Many electronic appliances such as refrigerator, internal combustion engines, television and microwave oven etc are having great energy harvesting scope [2-5]. From the literature, various designs for energy harvesting applications have been proposed. It is observed that the energy harvesting using direct pyroelectric effect is not compelling. In this direction, applications [14].

the concept of energy harvesting using ferroelectric hysteresis loop was explored by Olsen. So, pyroelectric coefficient is not straight touching energy harvesting capability of materials and electric field-induced polarization is used to harvest energy from ferroelectric materials [6-13]. Further, ferroelectric materials are also promising for efficient energy storage (ESD) for capacitor applications. Therefore, the materials will also be explored for high energy density capacitor The lead-free ferroelectric materials are having a great interest of researchers for the development of materials owing to environmental concerns and corresponding legislation. Hence, BaTiO₃, K_{0.5}Na_{0.5}NbO₃ and Bi_{0.5}Na_{0.5}TiO₃ based ferroelectric materials have been extensively studied [15-17]. These compositions are fabricated near morphotropic phase boundary (MPB); so, the system can exhibit high pyroelectric, piezoelectric and ferroelectric properties [17].

Lastly, Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O₃ (BCT-BZT) ceramic has reported for large pyroelectric and piezoelectric properties as compared to other lead-free and lead-based materials at lower electric field. It

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exhibits great properties of $d_{33}= 650$ pC/N, $d_{31}= 74$ pC/N, $k_p= 0.53$, $k_t = 0.38$, $k_{31}= 0.309$, $SE_{11}= 14.0 \times 10^{-12}$ m²/N, $\epsilon_r= 4500$ and $P_r = 11.69$ C/cm² [18, 19]. So, BCT-BZT also shows great dielectric properties in this direction [20, 21, 23, 24]. Therefore, it has low dielectric loss of 0.001, which is very less as compared to other ferroelectric materials [22]. It consists of high pyroelectric coefficient of 5.84×10^{-8} C/(cm² K) at room temperature, which is bigger than those reported for other BaTiO₃-based materials[21]. These enhanced piezoelectric, pyroelectric and ferroelectric properties are attaining due to the existence of MPB adjacent room temperature of ferroelectric rhombohedral and tetragonal phases. In this regard, Sn doped [(1-x)(Ba_{0.9}Ca_{0.1}TiO₃)-x(BaSn_{0.2}Ti_{0.8}O₃)], [abbreviated as BCT-BST hereafter] looks viable alternative to replace Pb based oxides for number of energy storage density and energy harvesting applications.

2.0 Materials and Method

Polycrystalline [(1-x) Ba_{0.9}Ca_{0.1}TiO₃-x(BaSn_{0.2}Ti_{0.8}O₃)] ceramic with x= 0 and 0.5 samples was prepared through solid state reaction route. The pure powders with analytical reagent grade of BaCO₃, CaO SnCl₂ and TiO₂ were used as initial precursors. The starting powders were weighed and mixed according to their stoichiometric ratio.

The mixture was then ball milled using acetone as wetting agent to have physical homogeneity. The powder was then calcined at 1300°C for 4h in air.

PVA binder (2% by weight) was added to the calcined powder. The resultant mixture was compressed under a uniaxial pressure of 5.5 ton/cm² into pellets. Conventional sintering is done at 1480°C with 5h dwell time. Silver paste was used as electrodes.

The phase formation was confirmed using X-ray diffraction technique. Scanning electron microscope (SEM) measurements were done to study the microstructure of the prepared samples. Archimedes principle was used to measure the density of samples.

The polarization versus electric field hysteresis loops were recorded at different magnitude of electric field and temperatures using a modified Sawyer Tower circuit.

3.0 Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) trends for [(1-x)Ba_{0.9}Ca_{0.1}TiO₃-x(BaSn_{0.2}Ti_{0.8}O₃)] ceramics with x= 0 and 0.5 samples. It confirms the formation of a single phase with perovskite structure. No secondary peaks were recognized, it indicates that the Sn ions have dissolved into the B site to form a homogeneous solid solution.

Fig 1: X-Ray Diffraction Patterns for [(1-X)BCT-X(BST)] Ceramics for X= 0 And X = 0.5 Samples

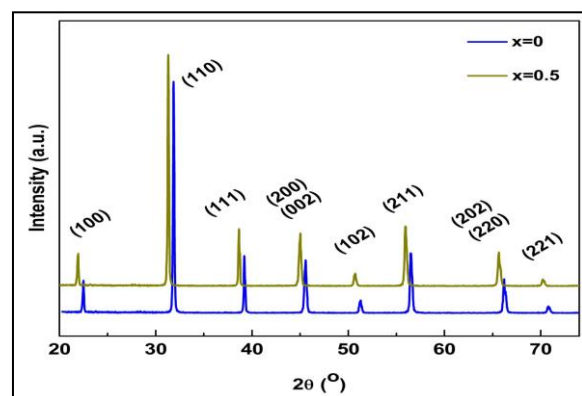


Figure 2 displays the scanning electron microscopy (SEM) images recorded on the sintered surface of both the compositions. The surface of the both compositions was free from any big porosity as visibly dense microstructures are seen for the composition under study. It has been verified by measuring the density using Archimedes principle which gives relative density ~94% of the theoretical density.

Fig 2: SEM Images of Sintered Sample (A) X=0 and (B) X=0.5

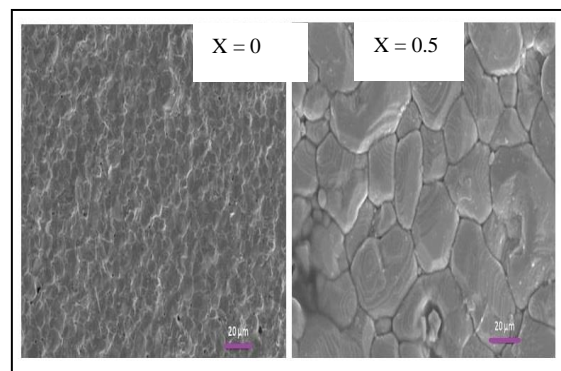
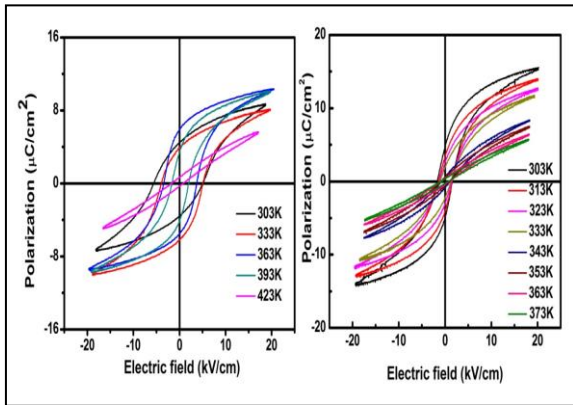


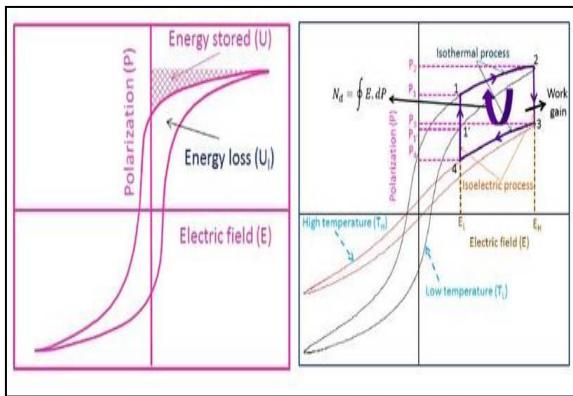
Figure 3 shows polarization versus electric field (P-E) loops for both the samples under study.

Fig 3: Polarization-Electric Field (P-E) Hysteresis Loops of Sintered Sample With X=0 And X=0.5



Figures 4 (a) & (b) show the characteristic for energy storage density and thermal energy harvesting. However, it gives the idea about the process by which we can find out the energy storage density and energy harvesting capacity.

Fig 4: (A) Energy Storage Characteristic and (B) Thermal Energy Harvesting Cycle



As indicated in figure 4(a), we have to find out the energy storage density from P-E loops. During the study, we have found that the energy storage density is more with the Sn content $x = 0.5$ with respect to $x = 0$. The maximum energy storage capacity found 63.5 kJ/m^3 for $x = 0.5$ sample of Sn doped BCT-BST. In figure 4(b), it is recorded that the reversible polarization can be made to get a clockwise loop in the middle of two different temperatures. This cycle is known as Olsen cycle, which basically is used to

convert thermal energy into electricity. This cycle have two isothermal and two iso-electric field processes. The processes 1-2-3-4-1 represent the electric analog of the Olsen cycle, whereas corresponding embedded area shows the maximum electric energy conversion per unit volume per cycle. The area enclosed (1-2-1-1) represents the hysteresis loss when Olsen cycle is operated in bipolar P-E loop. However, in the unipolar P-E loop, hysteresis loss is very small. So, for unipolar condition hysteresis loss, these can be neglected and the enhanced energy conversion is expressed by the shifted loop (1-2-3-4-1), which is considered in the current study. Process 1-2 is performed at a constant lower temperature (T_L) as electric field increases from lower limit (E_L) to higher limit (E_H), and correspondingly material polarization also increases. In process 2-3, heat (Q_S) is given to the material, which increases the temperature and produces lattice vibration. Therefore, material depolarizes at constant electrical field E_H . So, this develop a large depolarization current, which can be used or stored for powering electronic equipment using suitable circuit. Moreover, temperature of the material increases from lower temperature (T_L) to higher temperature (T_H). In the process 3-4, the electric field reduces from E_H to E_L at constant temperature T_H . Therefore, the polarization also decreases due to lack of electric field, which developed a weak depolarization current. Finally, in process 4-1, extraction of heat from the system at constant electric field (E_L) is done so that the material reaches to its initial state and finishes the cycle. Energy density (N_D) per unit volume of the material can be estimated. Olsen cycle-based energy conversion in BCT-BST as a function of applied higher electric field (E_H) at various higher temperatures (T_H). It indicates that as the temperature and electric field span are increased, energy also increases. The maximum energy 130 kJ/m^3 at $x = 0.5$ sample, is observed when the cycle is operated between 303 K-343 K and 13-19 kV/cm. We can say that for small value of electric field and temperature change, BCT-BST Sn doped is a good candidate for thermal energy conversion.

4.Conclusions

In this present study, environmental friendly ferroelectric ceramics $[(1-x)\text{Ba}_{0.9}\text{Ca}_{0.1}\text{TiO}_3-$

$x(\text{BaSn}_{0.2}\text{Ti}_{0.8}\text{O}_3)$] for $x=0$ and $x=0.5$ samples were explored in detail with the help of Olsen cycle. The samples were sintered at 1480°C for time interval 5 hr to study the energy storage density and thermal energy harvesting applications.

During investigation, we have found that when doping with Sn had done in BaTiO_3 based ferroelectric ceramics then energy storage density and thermal energy harvesting improved with respect to pure sample.

The maximum energy storage density and thermal energy harvesting are found 63.5 kJ/m^3 and 130 kJ/m^3 at $x=0.5$ for cycle operating at $303\text{K} - 343\text{K}$ and $13\text{-}19 \text{ kV/cm}$.

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