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Ferroelectric and Dielectric Properties of BT based Lead Free Ceramics

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Abstract

Lead free piezoelectric ceramics $(BaTi_{1-x}Hf_x)O_3$ with x=0.00, 0.04, 0.08 (abbreviated as BT, BHT-1 and BHT-2) were prepared by ceramic method. The structural phase formation has been investigated by using X-ray diffraction. The polarization (P) versus electric field (E) i.e. P-E hysteresis measurements confirm the ferroelectric nature with sufficiently high remanent polarization, $P_r \sim 5.47 \mu C/cm^2$ and lower coercive field, $E_c \sim 1.22$ kV/cm. The temperature dependent dielectric constant measurements show dielectric maxima at the Curie temperature. The observed results suggest that the samples may be useful for ferroelectric random access memory (FRAM) for computers, piezoelectric sensors, actuators, infrared sensors, and many other applications.

Keywords - Lead free ceramics, Barium titanate, X-ray diffraction, Ferroelectrics, Dielectrics.

Introduction

$BaTiO_3$ (BT) and BT based lead free ferroelectric/piezoelectric materials are in great demand due to its eco-friendly nature. These materials find their applications such as sensors, transducers and actuators etc. Moreover, lead (Pb and PbO) based piezoelectric ceramics have been used in many electronic devices due to their better piezoelectric and ferroelectric properties. However, because of the toxicity of Pb and PbO, there is a need to develop environmental friendly Pb-free ceramics[1-3]. The available few reports suggest the better dielectric performance in BT is obtained by partially replacing Ti^{4+} by Hf^{4+} [2, 3]. In present paper, we have reported the dielectric and ferroelectric behavior of pure BT and Hf substituted barium titanate.

Methodology

$BaTi_{(1-x)}Hf_xO_3$, with x = 0.00, 0.04, 0.08 were prepared by ceramic method. The starting materials used were $BaCO_3$, TiO_2, HfO_2 (from sigma Aldrich company with purity > 99%). All the starting materials were weighed according to their stoichiometric proportions and ball milled in an ethanol medium for 10 hrs. After ball milling, mixture was dried at 110 °C for 5 hrs and then the samples were calcined at 1160 °C for 5 hrs. To make the dense pellets, polyvinyl alcohol (PVA) was used as a binder and then the mixture was grounded for 20 minutes. The powder was then pressed into pellets (1 cm diameter and 1mm thickness) with the help of hydraulic press with pressure 6 ton/cm^2 for 8 minutes. Then the pellets were finally sintered at 1300 °C for 5 hrs.

The purity and structural information of samples was examined using X- ray diffraction technique (XRD) with Cu K_α having λ = 1.5406 Å. To characterize the samples for ferroelectric and dielectric measurements with good Ohmic contact, electroding were done on both the sides of pellets by using silver paste. The dielectric measurements were performed by employing LCR (Hioki-3532-50) precision meter. Moreover, the temperature dependent dielectric properties were measured at 10 kHz. The Ferroelectric (P-E) hysteresis loop was measured at 50 Hz using Marine India PE loop tracer.

Results and Discussion

$(BaTi_{1-x}Hf_x)O_3$ with x= 0.00, 0.04, 0.08 (abbreviated as BT, BHT-1 and BHT-2) were synthesized by ceramic method. The formation of pure phase was examined using X- ray diffraction (XRD) with CuK_α radiation having wavelength λ = 1.54 Å[1-3]. XRD patterns, shown in Figure-1, confirms the pure phase formation with perovskite tetragonal structure having space group *P4mm* and the lattice parameters calculated are presented in Table 1. From the XRD patterns, it is seen that the diffraction peaks shift towards the left side with increase in Hf content, which indicates the strain is induced along the horizontal *a* direction. This results in an increase of lattice constant '*a*' which leads to the decreasing c/a ratio. Ferroelectric nature of all the synthesized samples was confirmed from P-E loop tracer and is shown in Figure 2. From the Figure-2, is observed that the remnant polarization (P_r) begins to increase up to x = 0.04 whereas the P_r decreases for the higher concentration of Hf i.e. for x = 0.08. Furthermore, the coercivity shows a linearly decreasing trend (Table-1). Temperature dependent dielectric constant measurements at 10 kHz are shown in figure 3. It is seen from Figure-3 that with increase of Hf content, the Curie temperature (T_c) decreases from 135 °C (x = 0.00) to 105 °C (x = 0.08) and the maximum dielectric constants ε'= 6872 (x = 0.00) and ε'= 7415 for (x = 0.04) were observed at their respective Curie temperatures. The decrease in Curie temperature with

Hf^{4+} content may be due to the ionic radius of Hf^{4+} (0.71Å) is greater than that of Ti^{4+} (0.605Å) and as a result shift of the tetravalent cation from the oxygen octahedra center becomes constrained, which induces lowering of the curie temperature T_c[4-5].

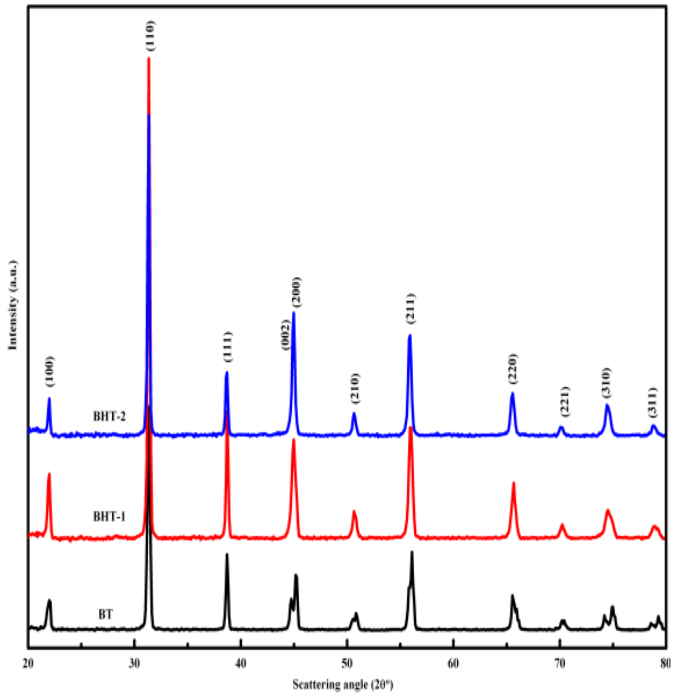

Figure-1
XRD patterns for BT and BHT ceramics.

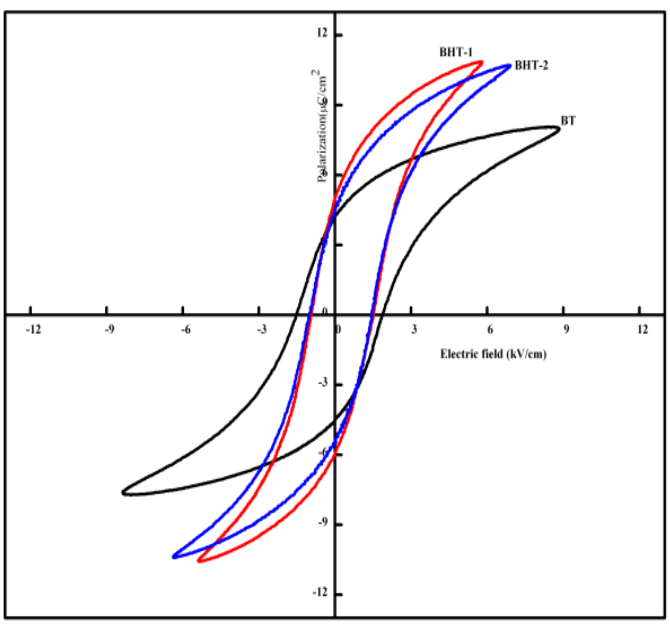

Figure-2
PE hysteresis loops for BT and BHT ceramics.

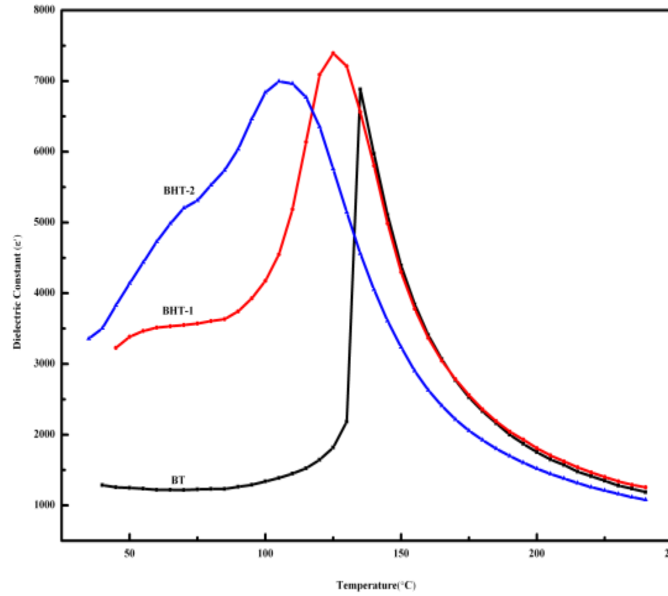

Figure-3
Dielectric constant vs. temperature for BT and BHT ceramics

Table-1
Structural and ferroelectric Parameters of BT and BHT Ceramics

Sample	BT	BHT-1	BHT-2
a (Å)	4.015	4.045	4.046
c (Å)	4.035	4.029	4.035
c/a	1.005	1.003	1.002
E_c (kV/cm)	1.69	1.22	1.23
P_r (μC/cm^2)	4.35	5.47	4.93
E_{max} (kV/cm)	7.99	5.79	6.91
P_{max} (μC/cm^2)	8.84	10.85	10.71

Conclusion

All the BT and BHT lead-free piezoelectrics were prepared by ceramic method. The XRD study confirms the formation of pure tetragonal phase of BT, BHT-1 and BHT-2. Typical ferroelectric nature has been observed for all the samples. The enhancement in the magnitude of dielectric constant is observed with Hf^{4+} content in pure BT content, whereas the Curie temperature tends to decrease with respect to pure BT. The observed systematic decrease in E_c and increase in P_r with Hf substitution at Ti site in BT indicates the samples may be useful for FRAM, memory storage applications. Furthermore, the samples may be utilized for the lead-free ferroelectric applications.

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