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Fabrication and Structural Analysis of Barium Titanate-Doped Niobium Pentoxide Ceramics for Energy Storage System

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***Abstract*:** Dielectric materials are gaining attention for energy storage due to their high power density. However, their low energy density limits their applications. This paper explores dielectric materials with suitable permittivity and breakdown strength. It focuses on enhancing the energy storage capabilities of Barium Titanate-based ceramics by adding Niobium Oxide. The study investigates the effects of Nb_2O_5 addition on 0.98BT-0.02BMC ceramics. XRD analysis confirms a single perovskite phase for all compositions. The addition of Nb_2O_5 significantly improves dielectric and energy storage properties. The composition with x=4 exhibits a high dielectric constant (~2200), high energy density (1.40 J/cm³), high recoverable energy density (~1.10 J/cm³), and high efficiency (78.8%). This material shows promise for a power pulse system. The Barium titanate can be used as a component in radiation detectors, such as ionization chambers and scintillation detectors. Its high density and atomic number contribute to its radiation-stopping ability.

Keywords: *Dielectric materials, Energy storage, High power density, Low energy density, Permittivity, Breakdown strength, Barium Titanate, Niobium Oxide, Perovskite, Energy density, Structural Analysis*

Introduction

Materials science is the study of the properties of solid materials and how their properties are determined by a material's composition and structure [1]. A dielectric (or dielectric material or dielectric medium) is an electrical insulator that can be polarized by an applied electric field. When a dielectric material is placed in an electric field, polarization take place [2]. Anything in the universe needs the energy to live and to do some useful work. Without the availability of energy, life is impossible. Keeping in view the importance of energy, Scientists trying to discover and explore new resources and enhance the capacity, efficiency of the already known source of energy [3]. Nowadays, throughout the world, scientists are trying to improve and enhance the capacity of renewable energy production. The literature reveals that up to 2019, the global renewable energy production capability was recorded to 2536 GW (wind energy=622 GW, solar energy=585 GW, bio energy=125 GW, geo-thermal energy=14GW, and ocean energy=500MW). But renewable energy is not available every time. Now to provide a steady supply there is

a high demand for energy storage systems. Based on energy storage time the storing system is broadly divided into long-term and short-term [4]. Out of the many long-term systems, the fascinating one is the batteries. Two kinds of batteries are available in the market, primary and secondary. The primary batteries are non-rechargeable, lightweight, and low-cost. The common types of primary batteries are alkaline, zinc-carbon (Z-C), lithium (Li), mercury oxide (Hg-O), silver oxide (Ag-O), and zinc-air [5]. The secondary batteries can recharge and store a large volume of energy. The most famous types of secondary batteries are Li-ion, NIMH, NiCD, and lead-acid batteries. Generally, the batteries have a high density of energy storage ranging from 10 Wh/kg to 300Wh/kg. While the slow-motion of the charged particles in the batteries reduces its power density (500 W/kg) [6]. The capacitors are mainly considered as the short-term energy storage system. Capacitors may be polar and non-polar, also fixed and variable. The power densities of the capacitors are very high ranging from 10^1 to 10^8 W/kg and the density of energy storage is small mostly less than 30 Wh/kg. The below Figure 1 shows the power density of various energy storage systems[7].

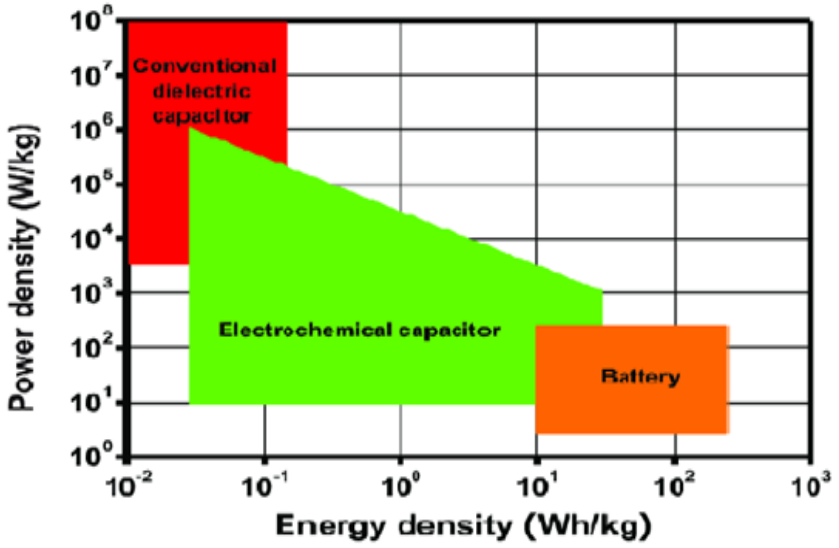

Figure 1: Diagram of power density as a function of energy density in various storage devices.

Dielectric-based HED capacitors are suitable sources of energy used in military applications such as electric armor, in medical just like X-ray equipment and power storage modules, etc. So, to construct smaller, lighter, and less expensive High Energy Density capacitors have long been area of intense research field for both academics and industry communities [8]. High Energy Density capacitors should be able to have a fast charge-discharge response, high-temperature stability, high breakdown strength, and high-power density. Operating temperatures of up to 250°C are also required for some particular applications. The dielectric materials must meet these demanding standards. This section gives a quick rundown of the several types of materials that are regularly utilized or promising for High Energy Density capacitor applications [9]. Ceramics dielectrics possess high dielectric constants, low dielectric loss, fast charge-discharge response and can also sustain long-term performance at higher operating temperatures making them superior to polymer dielectrics for energy storage applications [10]. Generally, in ceramics on opposite tendency exists between the dielectric constant and breakdown strength. Nano crystallites embedded in glass matrix heating at certain temperatures formed glass ceramics. The crystalline phase in glass ceramics may result in a greater dielectric constant than the glass matrix's permittivity. The sample Na_2O-PbO-Nb_2O_5-SiO_2 handled under optimum processing conditions, reported that dielectric constant value at 8239 frequency 1 kHz is (650-850), low tangent loss ~ 0.02 in the temperature (25-150°C) [11].

X-Ray Diffraction

Crystallography is important tool to find inter planer space (d), phase analysis, theoretical density and size of the ceramics crystal [12]. The bending of waves through sharp edges of an obstacle or an opening is known as diffraction. As for diffraction, the size of the obstacle is comparably equal to the wavelength of the given wave. To study crystals, x-rays are used because their wavelength (~1Å) is comparably equal to the lattice constant of the crystals. So for phase analysis x-ray powder diffraction technique is used which is given by the following equation [13].

$$2d\sin\theta = n\lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where 'θ' represent Bragg's angle, the x-rays wavelength by "λ", "n" order of diffraction and "d" is the inter planer space.

Only those X-rays are diffracted from the crystal planes and gives sharp distinctive diffraction pattern which satisfying the Braggs diffraction law. A graph can be drawn between the intensity of diffracted X-rays and angle "2θ" by using an X-Ray diffract meter. Now this pattern is compared to reference model for phase analysis which gives information about phase formation and its structure of the given ceramics in detail.

The schematic diagram is given in Figure 2 for this analysis (JDX 3532 Jeol XRD) is used [14].

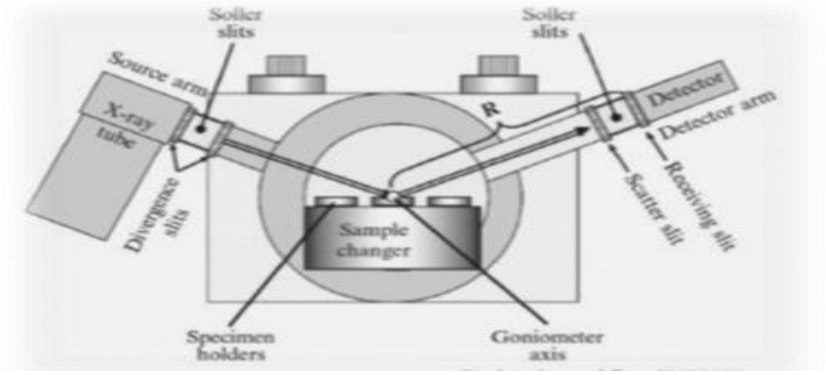

Figure 2: The schematic diagram of X-ray Powder Diffraction technique.

Methodology

Solid state reaction route is very effective technique used to manufacture ceramics. Some important steps of this method are:

Appropriate Raw Materials Selection:

From the literature, the appropriate raw materials are selected for this project. Highly pure raw materials are weighted in stoichiometric ratios and mixed together. In the present study to prepare Nb_2O_5 doped $0.98BaTiO_3$-$0.02Bi(Mg_{0.5}Ce_{0.5})O_3$ ceramics requires highly pure raw materials of MgO, TiO_2, Ba_2CO_3, NbO_5, Bi_2O_3 and CeO_2. The chemical name, formula, purity level, and sources of the selected raw materials for this composition are shown in Table 1.

Table 1: List of purified raw materials

Chemical Name	Chemical formula	Purity (%)	Sources
Magnesium Oxide	MgO	>99	Sigma-Aldrich
Titanium Oxide	TiO_2	>99	Sigma- Aldrich
Bismuth oxide	Bi_2O_3	>99	Sigma- Aldrich
Barium carbonate	$BaCO_3$	>99.5	Sigma- Aldrich
Niobium Oxide	NbO_5	>99.9	Sigma- Aldrich
Cerium Oxide	CeO_2	>99.9	Sigma- Aldrich

The purity level of MgO, TiO_2, and Bi_2O_3 is greater than 99% whereas $BaCO_3$, NbO_5, and CeO_2 is greater than 99.5%.

Stoichiometric Ratios:

Another important step after the selection of raw materials is the stoichiometric ratios because any small error occurring in stoichiometric ratio can alter the required results. Isopropanol is used as a lubricant and zirconia balls as a grinding media to get proper grain size. The resulting composition was dried in an oven at a temperature of 95°C for 24 hr to get homogenous powders.

Mixing of raw materials:

The next step is the mixing of raw materials for which ball milling machine is used. This process is important as it affects the dielectric properties of solid solution. In the current study to synthesize $0.98BaTiO_3$-$0.02Bi(Mg_{0.5}Ce_{0.5})O_3$ the compounds MgO, TiO_2, Ba_2CO_3, NbO_5, Bi_2O_3 and CeO_2 are weighted and mixed them in stoichiometric ratio.

Results And Discussion

Phase Examination:

The X-ray diffraction pattern of $0.98BT–0.02BMC+xwt\%Nb_2O_5$ (x=0, 2, 4) samples are displayed in Figure 3. In the present study, for x=0, a single perovskite phase is observed. The XRD pattern at around 2θ=45° exhibiting peak splitting (002)/(200) peaks matched with card # 70-4760 for x=0 composition demonstrating tetragonal structure and is reported for different BT-based ceramics. The split peaks merged for 2wt% and above, demonstrating the formation pseudo-cubic phase. Further, within no secondary phase has been observed for all the compositions in the present study.

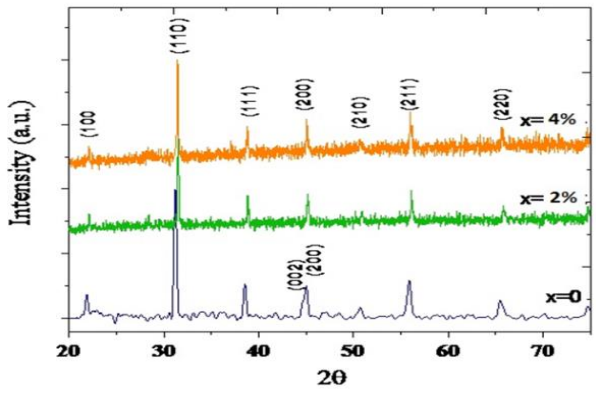

Figure 3: XRD patterns of $0.98BT–0.02BMC+xwt\%Nb_2O_5$ (x=0, 2, 4) ceramics

Microstructure Examination:

The scanning electron microscope images from etched surfaces of 0.98BT–0.02BMC+xwt% Nb_2O_5 (x=0, 2, 4) ceramics are given in Figure 4, 5 and 6. The composition x=2 shows very porous microstructure while x=4 shows dense microstructure. Further the average grain size of x=2 is greater than 1 nm while that of x=4 is less than 1 nm

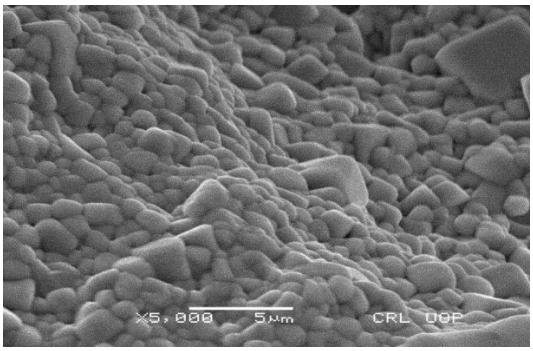

Figure 4: Scanning Electron Microscopy of Barium Titanate

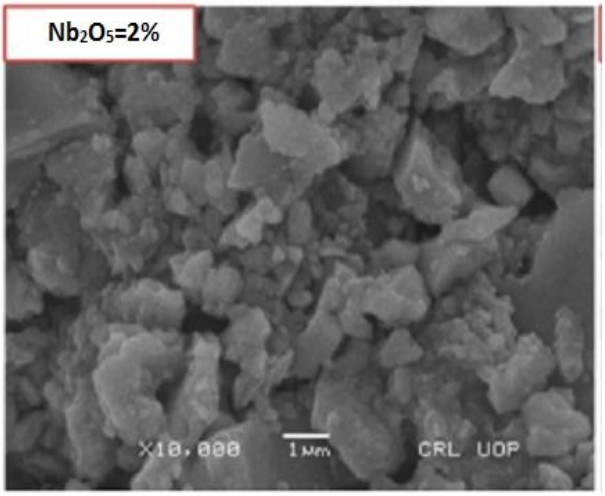

Figure 5: Scanning electron microscope image of 0.98BT–0.02BMC+xwt%Nb_2O_5 (x=2) samples

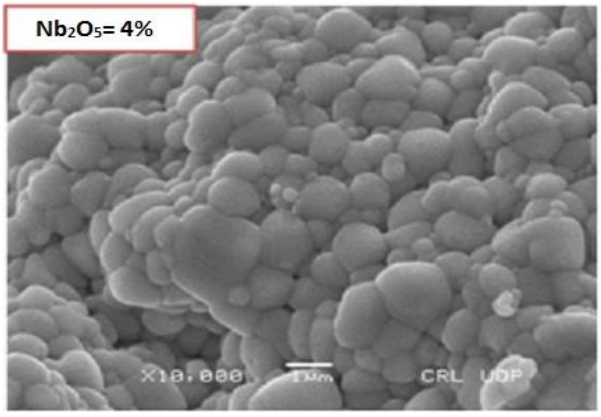

Figure 6: Scanning electron microscope image of 0.98BT–0.02BMC+xwt%Nb_2O_5 (x=4) samples

Dielectric Properties Measurement:

The variation of dielectric constant (ε_r) and tangent loss (tanδ) of 0.98BT–0.02BMC+xwt% Nb_2O_5 (x=0, 2, 4) samples with temperature in a range of 25 to 500°C at various frequencies of 1 KHz, 10 KHz, and 100 KHz and 1 MHz are shown in Figure 7 (a–c). A very sharp Curie temperature (T_c) is observed at ~125°C (Figure 7-a), revealing the ferroelectric to paraelectric transition for *x*=0. The maximum dielectric constant (ε_{rmax}) of 3400 is obtained for x=0 at 1 kHz. The addition of Nb_2O_5 shifted the Curie temperature below room temperature. The maximum dielectric constant (ε_{rmax}) of 670 and 2200 at 1 kHz for x=2 and 4. The lower dielectric constant of x=2 is related to its porous microstructure indicative of lower density in comparison to x=4. Further, the lower dielectric constant of Nb_2O_5 addition is related to the less dielectric constant of Nb_2O_5 in comparison to the base material (i.e. x=0). The shifting of Curie temperature towards lower temperature and decrease in dielectric constant due to Nb_2O_5 has also been observed in other studies. A decrease in the tangent loss has also been observed by Nb_2O_5 in the present study.

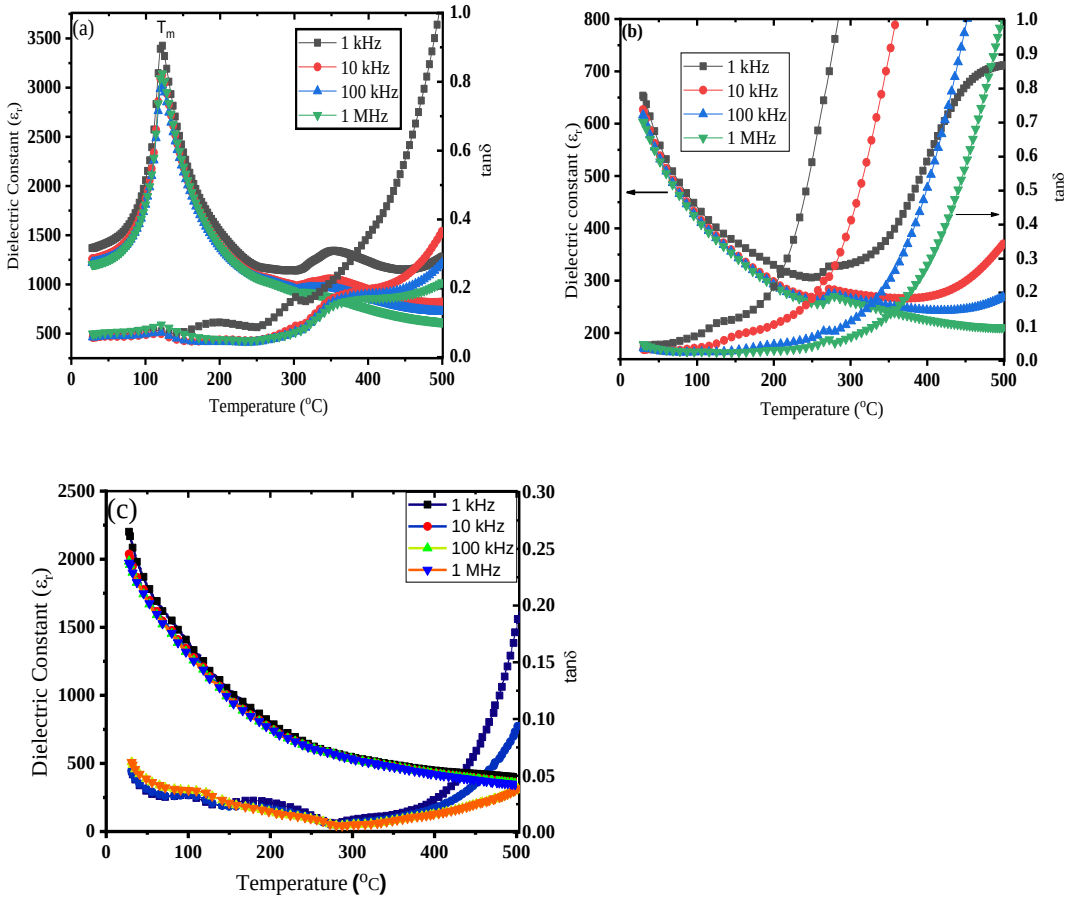

Figure 7: The variation of ε_r of 0.98BT–0.02BMC+ xwt%Nb_2O_5 (x=0, 2, 4) samples as a function of temperature at different frequencies (a) x=0, (b) x=2 and (c) x=4

Figure 7-(a): reveals the ferroelectric transition to paraelectric transition for x=0%. The maximum dielectric constant 3400 is observed at 1 KHz.

Figure 7-(b): shows the shifting of Curie temperature below the room temperature by addition of 2% of Nb_2O_5.The maximum dielectric constant of 670 at 1 KHz is obtained.

Figure 7-(c): tells about maximum dielectric constant of 2200 at 1 KHz frequency. By addition of Nb_2O_5 decrease in tangent loss also observed.

P-E loops Analysis:

The Polarization versus Electric field (P-E) hysteresis loops of 0.98BT–0.02BMC+ xwt% Nb_2O_5 (x=0, 2, 4) samples are depicted in Figure 8. The P-E loops were measured at 10 Hz for each 0.3 mm thick ceramics pellet. Significant variations are observed in the maximum polarization (P_{max}) and critical or breakdown electric fields (E_b) for sample. Energy-storage parameters such as charge energy density (W_{ch}), recoverable or discharge energy density (W_r), and efficiency (η) of each sample are determined from its P-E hysteresis loop. Each sample has its own breakdown voltage that related to the average grain size and density. The P-E loop of each composition is taken at its breakdown voltage. The P-E loop of composition x=0 is very broad and has maximum and saturation polarization of 16.92C/cm^2 is observed for x=0 in the present study with large remnant polarization of 15.85 C/cm^2. For x=2, the PE loop became slim with P_{max} to 8.59 and very low remnant polarization of 1.55C/cm^2 at breakdown field of 9 kV/cm. Similarly, a maximum polarization of 16.82 C/cm^2 with remnant polarization of 2.21C/cm^2 is obtained for x=4 at breakdown field of 107 kV/cm. The charging and recoverable energy densities depend on the maximum polarization, the breakdown voltage and low remnant polarization. P_{max}-P_r is also higher for x=4. Pmax, lower Pr and large P_{max}-P_r value of x=4 are beneficial for obtaining high density and recoverable energy density.

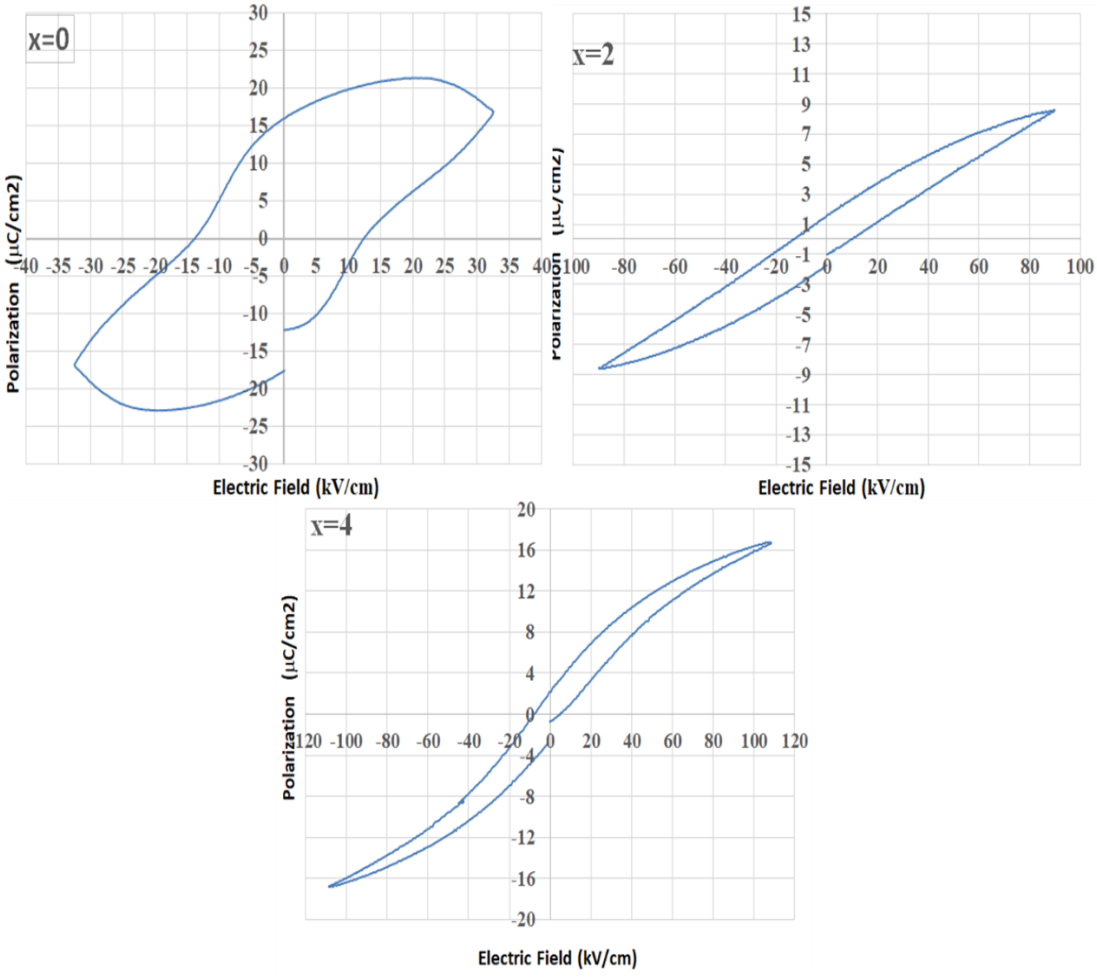

Figure 8: Polarization versus Electric field Hysteresis loops of 0.98BT–0.02BMC+xwt% Nb_2O_5 (x=0, 2, 4) samples as a function of electric field.

Energy Density Analysis:

Energy-storage parameters such as charge energy density (W_{ch}), recoverable or discharge energy density (W_r), and efficiency (η) of each sample and are determined from its P-E hysteresis loop.

$$W_{ch} = \int_0^{P_{max}} EdP \quad \ldots\ldots (2)$$

$$W_r = \int_{P_r}^{P_{max}} EdP \quad \ldots\ldots (3)$$

The efficiency of the capacitor can be determined by the following Eq 4.

$$\eta = \frac{W_{rec}}{W_{ch}} \times 100 \quad \ldots\ldots (4)$$

In this study, W_{ch}~ 1.40 J/cm^3, W_{rec}~1.10 J/cm^3 and efficiency (η) of 78.8%, has been obtained for x=4. The large value of W_{rec} and W_{st} for x=4 could be related to the high values of P_{max} and P_m-P_r to other compositions in this study. In the present study an efficiency of 78% is obtained for x=4.

All the energy storage characteristics are given in Table 2.

Table 2: Polarizations, and energy storage characteristics of 0.98BT–0.02BMC+ xwt%Nb2O5 (x=0, 2, 4) samples.

Composition (x)	**P_{max}**	**P_r**	**P_{max}-P_r**	**W_{ch}**	**W_r**	Η%
0	**16.85**	**15.92**	**0.9**	**0.50**	**0.13**	**28**
2	**8.59**	**1.55**	**7.04**	**0.95**	**0.60**	**71**
4	**16.62**	**2.21**	**14.41**	**1.43**	**1.10**	**78**

We have calculated maximum polarization, charge energy density (W_{ch}), recovrable or discharge energy density (W_r) and effieciency of each sample. For x=0, maximum polarization of 16.85 is obtained but recoverable energy is low as well as efficiency is remains to 28%.On the other hand for composition x=4, high value of P_{max} 16.62 is obtained,recoverable energy is also increased to 1.10 as well as high effieciency of 78% is obtained.

Conclusion

$Nb/BaTiO_3$ powders have been successfully synthesized by the Solid-State rout. XRD results show no reaction products other than Nb and $BaTiO_3$. The $BaTiO_3$ phase was cubic at room temperature. The split peaks merged for 2% and above shows the formation of pseudo-cubic phase. According to SEM micrographs, the composition x=2% shows very porous microstructure and grain size is greater than 1 nm while 4% composition shows dense microstructure and average grain size is less than 1 nm. It is concluded that Heat treatment successfully improved the dielectric properties of the composite powder. The dielectric permittivity of the composite powder was highly increased with increasing concentration of Nb_2O_5 while the dielectric loss slightly increased. It is also concluded that Nb_2O_5 has brought great changes in the dielectric and energy storage properties. High dielectric constant 2200 has been obtained for 4% along with high energy density 1.40, high recoverable energy density 1.10 J/cm^3 and high efficiency of 78.8% is obtained. This material is suitable candidate for power pulsed applications such as food processing, capacitor, weapon, and medical applications due to its excellent energy storage performance, high output power density, high breakdown strength with fast charge and discharge rate and working in a high temperature environment.

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