Energy storage property in lead free gd doped Na$_{1/2}$Bi$_{1/2}$TiO$_3$ ceramics

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A. Lead-free Sodium Bismuth Titanate
B. Ceramics
D. Energy storage

1. Introduction

Energy storage capacitors have attracted, and still do, a great deal of attention, because of the swift increase of enabling technologies that require the development of high efficiency and low cost material to meet the industrial needs [1]. Antiferroelectric materials are very promising candidates for such application, because they have lower remanent polarization and a double hysteresis loops [2]. In fact, in such kind of materials, the high energy density is associated to the reversible electric field-induced antiferroelectric (AFE)-to-ferroelectric (FE) phase transition [2,3]. For instance, only lead-based material are demonstrated to exhibit high power and energy density that can be configured to store, release or interconvert electrical and mechanical energy in a well-controlled manner. Nevertheless, lead is harmful to human health and cause environmental damages.

Nowadays, eco-friendly Pb-free ferroelectric ceramics attract much attention from an environmental perspective. Sodium Bismuth Titanate, (Na$_{1/2}$Bi$_{1/2}$)TiO$_3$ (abbreviated as NBT) is one of the most known candidate for replacing lead-based materials. NBT material presents long range ferroelectric ordering [4] and shows several structural phase transitions within room temperature up to 800 K [5]. However, there are several major issues yet to be solved for the practical device applications of such material to be used for energy storage [5-9]. Those drawbacks are higher dielectric loss, (ii) larger conductivity and (iii) higher coercive field (73 kV cm$^{-1}$). Several approaches have been attempted by different research groups to solve these issues and to enhance its electrical properties [5,6]. Doping with rare earth elements (RE) was one of the possible approaches to resolve the mentioned problems [7,8]. Moreover, in recent years, the NBT based materials systems such BNT-BaTiO$_3$-NaNbO$_3$ [10] or BNT-BaTiO$_3$-LaZrTiO$_3$ [11] have emerged as highly promising lead-free materials for energy storage application [9]. Nevertheless, complexity of such systems makes the preparation and optimization of critical concentration very difficult. In addition, to the thermal instability.

In the present letter, the properties of a simple addition of Gd on NBT properties were examined. Emphasis is placed on observed improved energy storage in Gd-doped NBT ceramic.

2. Experimental procedure

In this paper, we prepared the polycrystalline samples with 2 mol% Gd doped NBT by the solid-state reaction method. Stoichiometric amounts of Na$_2$CO$_3$ (99.8%), Bi$_2$O$_3$ (99.7%), TiO$_2$ (99.99%), and Gd$_2$O$_3$ (99.99%) powders were thoroughly mixed with alcohol in agate mortar for 2 h, then dried, and calcined for 3 h at 800 °C. A little excess amount of Bi$_2$O$_3$ was added to the raw materials to compensate the volatile part of Bi$_2$O$_3$ during high-temperature sintering. The ground powders were pressed into disks of 8 mm in diameter and 1 mm in thickness. The pellets were sintered at 1130 °C for 3 h in air. The density of all samples was analyzed by Archimede’s method. The obtained values were found to be higher than 96%. The phases purities of the samples were checked using X-ray diffraction (XRD) analysis (PanAnalytical X’Pert PRO, CuK$\alpha_1=1.5406$ Å). The grain morphology was analyzed by a scanning electron microscopy (SEM) (Philips XL30). The

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dielectric properties were studied on ceramic discs after deposition of gold electrodes on the circular faces by cathodic sputtering using an impedance analyzer (Agilent 4284A) in the frequency range from 20 Hz to 1 MHz. The ferroelectric hysteresis loops were obtained at different temperatures using a ferroelectric test system (TF Analyzer 2000, aixACCT, together with a voltage amplifier) and a custom made heating stage.

3. Results and discussion

Fig. 1a displays XRD patterns of the calcined NBT and GdNBT samples and reveals a single perovskite phase formation without any trace of secondary phase. The XRD patterns were indexed in the trigonal (rhombohedral) symmetry with R3c space group. It should be noticed that the ionic radius of Bi$^{3+}$ is higher than the ionic radius of Gd$^{3+}$ (1.03 Å and 0.938 Å respectively, in octahedral coordination) [12]. As a result, the GdNBT peaks shift to the larger-angle sides which means the reduction of the lattice parameters and which confirms the introduction of Gadolinium ion into NBT matrix. Fig. 1b shows the grain morphology of the sintered ceramics. For both specimens the grain boundaries are well delineated and no porosity is observed which confirms the result of the density measurements.

Fig. 2 shows the temperature dependence of the relative dielectric permittivity ($\varepsilon'_r$) and dielectric loss tangent (tanδ) for pure NBT and GdNBT ceramics respectively measured at different frequency. It is well known that NBT exhibits at least two dielectric anomalies centered approximately at 500 K (depolarization temperature $T_d$) and 600 K (maximum temperature $T_m$) that are attributed to the ferroelectric–antiferroelectric–ferroelastic/para-electric behavior changes, respectively without any structural phase transition [7,13]. The pure NBT exhibits a high dielectric constant with diffuse phase transition that is in good agreement with many works [14,15]. Fig. 2a shows that pure NBT exhibits also high dielectric losses that release to the high conductivity already known for such material.

Several changes were affected the dielectric behavior with the incorporation of Gadolinium ion into the NBT matrix (Fig. 2b):

(i) The frequency dispersion at $T_m$ vanished; as the dispersion detected in pure NBT could arise from the presence of oxygen vacancies created by the volatility of Bi during sintering [7], the substitution of Bi$^{3+}$ with Gd$^{3+}$ decreases the concentration of Bi vacancies according to the following equation (using Vink–Kroger notation), and suppresses the frequency dispersion of $T_m$:

$$\text{Gd}_2\text{O}_3 + 2\text{V}_{\text{Bi}}^\text{a} + 6\text{h}^\text{a} \rightarrow 2\text{Gd}_{\text{Bi}} + \frac{3}{2}\text{O}_2$$

(ii) The permittivity peak becomes larger probably as a result of increasing the A-site disorder, and shifted to higher temperature together with a large decrease in the value of $\varepsilon_{\text{max}}$ [16]. The same behavior was observed in NBT-doped erbium [17].

(iii) The depolarization temperature ($T_d$) centered at approximately 500 K for pure NBT becomes more pronounced for NBT-
doped Gd and shifts to lower temperature (centered around 400 K). It suggested that the temperature corresponding to this dielectric anomaly is related to the relief of structural distortion [18].

(iv) The dielectric losses observed for NBT (Fig. 2a) decreases significantly with the introduction of Gd ion which can be interpreted as a decrease in the conductivity of pure NBT and which was one the drawbacks of this material.

Hysteresis loops (P–E) were measured over a range of temperatures from room temperature up to 413 K. The results for selected temperatures are shown in Fig. 3. At room temperature, P–E curve exhibits a typical ferroelectric (FE) character. With further increasing temperature over 373 K, the E and P values decrease dramatically. As the temperature increases a double pinched P–E hysteresis loop was observed for T ≥ 373 K. Probably, at this temperature the FE order tends to disappear and the "Antiferroelectric-like (AFE)" order tends to appear. Unfortunately, there is no structural evidence supported such behavior [19]. Further, the recent advanced TEM investigation reported by Dorcet et al.[20] did not give any sound information supporting anti-polar domains existence. It worth mentioning that the literature examination reveals the observation of pinched hysteresis loops in several BNT-based materials under different temperature conditions that depend on the composition [21,22]. Furthermore, different mechanisms are proposed to explain it [23–26]. For example, Viola et al.[25] reported that for the pinched hysteresis observed under temperature conditions, the application of an electric field produces a transformation from an ergodic relaxor state to a metastable ferroelectric ordered, accompanied with a return back to the original ergodic relaxor state while removing electrical field. In addition, Tai et al. [19] suggested, on studying NBT-based systems, that the octahedral tilting governed the temperature-dependent ferroelectric domain morphology, thus the electrical and electromechanical properties.

As fat of that, anti-ferroelectric (AFE) materials have a higher energy-storage density (W) and better dielectric properties rather than ferroelectric (FE) materials [27]. Therefore, and basing on the ferroelectric properties it was fundamental to study this property. The energy-storage density W is obtained by integrating the area between the polarization axis and the discharge curve of the unipolar P–E hysteresis loops, using the flowing equation [28]:

\[W = \int_{P_r}^{P_{max}} E dP\]

E is the applied electric field. The maximum of polarization \(P_{max}\) and remnant polarization \(P_r\) are obtained from the discharge curve of the unipolar P–E hysteresis loops. The mentioned equation suggests that high energy storage density can be obtained by huge difference between \(P_{max}\) and \(P_r\) [29]. The results of the energy storage dependence temperature are summarized in the Table 1.

As expected, the W values were increased as the increase of the temperature (see table) and reached the value of \(W=0.85 \text{ J cm}^{-3}\) at 413 K. Zhao et al. [30] reported that the energy storage ceramics with more “slanted” and “slender” P–E loops would possess higher energy storage density than that of “square” ones which is in good agreement with our results.

It is worth noting that, there are many future application require high-energy density capacitors at operating temperatures of 200°C and above such as filtering, voltage smoothing, coupling, de-coupling, dc-blocking, power conditioning, snubbing, electromagnetic interference (EMI) suppression, and commutation (typically used in resonant converters) in power electronic circuits [3], the results obtained in this work could lay the basis for the development of lead free materials to meet this urgent needs.

4. Conclusion

In summary, NBT and GdNBT ceramics were obtained using solid state reaction method. The XRD analyses confirm the incorporation of Gadolinium ion into the NBT matrix. This insertion was found to improve the dielectric properties with the observation of a significant decrease of the conductivity, which was one, the drawbacks of pure NBT materials. Further, GdNBT ceramic was found to exhibit a double pinched P–E hysteresis loop with high energy storage density at 413 K, which can be considered as a promising candidate for a large variety of application.

References


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