Enhanced energy storage properties of La\(^{3+}\) modified 0.92Bi\(_{0.5}Na_{0.5}\)TiO\(_3\) - 0.06Ba(Zr\(_{0.2}\)Ti\(_{0.8}\))O\(_3\) - 0.02NaNbO\(_3\) ternary ceramic system

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Abstract

The development in field of hybrid vehicles, telecommunication and energy sectors require dielectric materials having high-energy storage density with optimum thermal stability to operate in certain environment. To fulfill such requirement a new set of materials along the ternary solid solutions of 0.92Bi\(_{0.5}Na_{0.5}\)TiO\(_3\) - 0.06Ba(Zr\(_{0.2}\)Ti\(_{0.8}\))O\(_3\) - 0.02NaNbO\(_3\) (NB\(_{1-x}\)L\(_x\)-T-BZT-NN) (x = 0, 0.03, 0.05, 0.07) were fabricated through solid-state mix oxide route. The XRD patterns analysis confirmed a structural phase transformation from rhombohedral to the tetragonal-P4bm phase when x content increased from 0 to 0.07. The SEM study revealed, dense microstructure for all ceramics accompanied by a decrease in the average grain from 1.66 \(\mu\)m to 1.05 \(\mu\)m leading to high densities for these materials with an increase in the x content. The dielectric breakdown field increased from \(~115\) to \(137\) kV cm\(^{-1}\) resulting in an increase in recoverable energy density from \(\sim0.68\) to \(1.14\) J cm\(^{-3}\) with the increase in x content. Furthermore, excellent temperature stability (±15%) in dielectric permittivity was observed in a wide temperature range for each ceramic. In the present study, a recoverable energy density of \(1.14\) J cm\(^{-3}\) along with an efficiency of 70.6% was obtained for the composition of x = 0.07.

1. Introduction

The electronic industry in past few decades has extensively relied on ceramic capacitors and its development [1, 2]. The use of capacitors has increased multifold due to requirement in electromotive, telecommunications, defense, oil explorations, aerospace industries all while operating at in harsh temperature dependent environment. Dielectric behavior of ceramics defines its value and Bi\(_{0.5}Na_{0.5}\)TiO\(_3\) (NBT) is considered as one of the cornerstones [3–8]. Ideally electrical Industries requires the temperature stable capacitors with variation in capapcitance in (±15%). Another important parameter for capacitors is the energy storage capacity which is typically calculated by ferroelectric hysteresis loop (PE-loop) using equation (1) [9].
Here \( W \) is recoverable energy, \( E \) is applied electric field, \( P_1 \) and \( P_{\text{max}} \) are remnant and maximum polarization respectively \([10–12]\). From equation (1), to achieve high energy density the difference between \( P_{\text{max}} - P_1 = \Delta P \) should be maximum. Another way to increase the energy storage density is to increase \( E \) while avoiding electrical breakdown. This is achieved by improving electrical break down strength (BDS) \([13]\). Many Pb-based binary and ternary system compounds \([9, 14–16]\) have been reported to have better dielectric properties than NBT based systems, but lead oxide (PbO) being toxic generally avoided \([16]\).

NBT has gained a lot of attention due to its optimum diffusive phase transition behavior (relaxor behavior) leading to excellent dielectric and ferroelectric properties. At room temperature NBT exhibits rhombohedral (R3c) structure and phase transition occurs from rhombohedral to tetragonal (P4bm) due to variation in composition or temperature \([17, 18]\). Some studies also indicate the presence of both R3c and P4bm phases in unmodified NBT with dominant phase being R3c at room temperature \([14, 19]\). The two phases have different ferroelectric response. In the case of R3c phase long range ferroelectric order has been reported which leads to large \( P \), and reduces \( \Delta P \) giving low energy storage. On other hand, P4bm phase of NBT, \( \Delta P \) value tends to increase leading to a larger energy storage density \([8]\). In order to suppress the R3c phase and enhance the P4bm phase many NBT based solid solutions like \( \text{Bi}_2\text{Na}_{0.5}\text{Ti}_2\text{O}_7-\text{Bi}_{0.5}\text{K}_{0.5}\text{Ti}_2\text{O}_7 \) (NBT-BKT), \( \text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_2\text{O}_7-\text{BaTi}_2\text{O}_7 \) (NBT-BT), \( \text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_2\text{O}_7-\text{K}_0.5\text{Na}_{0.5}\text{NbO}_3 \) (NBT-KNN) have been investigated \([16–20]\). These solid solutions take advantage of two types of dielectric anomalies occurring in permittivity versus temperature \((\varepsilon - T)\) plots. First is depolarization temperature \((T_d)\) and second is curie temperature \((T_m)\). \( T_d \) is associated with an intermediate phase that is formed when polar nano regions (PNR) embedded in ions/paraelectric phases (with different radii and charge) are distributed randomly at A/B-site. In second case \((T_m)\), is where relative permittivity is maximum. There are many views of phase-structure-evolution in \( T_m \) and \( T_d \) region, but majority state that above \( T_d, P_1 \), and coercive field \((E_c)\) decrease \([21, 22]\) leading to larger \( \Delta P \) in NBT based systems. This gives NBT based binary/ternary compounds an advantage in obtaining excellent dielectric and ferroelectric properties.

The effect of NaNbO\( _3 \) (NN) in NBT-BT-NN based ceramics has previously been studied \([14, 19]\) the findings revealed a temperature stable system having optimum dielectric properties. Furthermore, increasing amount of NN leads to reduction in the R3c phase hence and a relaxor behavior in energy storage density of 0.71 \( \text{J cm}^{-3} \). Moreover, addition of NN causes a shift towards the relaxor phase \([13]\). NBT modified with \( \text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3 \) (BZT) also gives a similar result with enhanced \( \varepsilon_i \) and \( T_m \). That is due to incorporation of Zr and Ti-ions at B-site in NBT-BZT system. The disordering created by Zr substitution has an effect on phase transition diffusivity and \( T_m \) \([23–35]\). Aksel et al \([26]\) have reported modification NBT with \( \text{La}^{3+} \) also reduces \( T_d \) which could also be beneficial in achieving good energy storage properties. In this study \( \text{0.92Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.06\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3 \) O3-0.02NaNbO\( _3 \) ternary solid solution modified with \( \text{La}^{3+} \) at A-site was investigated to obtain a high-temperature stable composition with optimum dielectric and ferroelectric properties. The effects of various concentrations of \( \text{La}^{3+} \) substitution on phase, microstructure, dielectric and ferroelectric properties for the \( \text{0.92Bi}_{0.5(1-x)}\text{La}_{x}\text{Na}_{0.5}\text{TiO}_3-0.06\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.02\text{NaNbO}_3 \) \((0.00 \leq x \leq 0.07)\) are discussed in detail.

2. Experimental

2.1. Materials and methods

All compositions in \( \text{0.92Bi}_{0.5(1-x)}\text{La}_{x}\text{Na}_{0.5}\text{TiO}_3-0.06\text{Ba(Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.02\text{NaNbO}_3 \) \((0.00 \leq x \leq 0.07)\) series were fabricated via solid-state sintering process using reagent grade \( \text{Bi}_2\text{O}_3 \) (99.99%), \( \text{La}_2\text{O}_3 \) (99.99%), \( \text{Nb}_2\text{O}_5 \) (99.99%), \( \text{Ti}_2\text{O}_3 \) (99.99%), \( \text{Na}_2\text{CO}_3 \) (99.9%), \( \text{BaCO}_3 \) (99.50%), and \( \text{ZrO}_2 \) (99.50%). The reagents were weighed in stoichiometric ratios followed by ball milling for 24 h in 2-propanol using \( \text{ZrO}_2 \) balls as grinding media. The obtained slurries were air-dried using a hot air oven at 100 °C and sieved using size 300 mesh. Calcination of the milled powders was carried out at 800 °C for 2 h with a ramp rate of 5 °C min\(^{-1}\) followed by remilling and sieving. Pallets of 12 mm diameter of the calcined powders were made using steel die and manual hydraulic pellet press operated at 100 MPa pressure. The green body pellets were sintered without binder at 1175 °C in air for 2 h with a ramp rate of 5 °C min\(^{-1}\).

2.2. Characterization techniques

The phase(s) analysis of the sintered samples of each composition was carried out at room temperature using x-ray diffractometer (Pan Analytical XPert\(^3\), Netherlands). For microstructure analysis samples of each composition were polished and thermally etched at a 1050 °C for 30 min followed by Au-coating in a sputtering machine. The microstructure was examined via a scanning electron microscope (JEOL, Japan, and JSM5910) equipped with an energy dispersive x-ray spectroscopy (EDX) (Oxford instruments, U.K.-INCA200). For
dielectric property measurements, both surfaces of each composition pellets were first well-polished and then silver paste was applied on both sides for electrode purpose followed by heat treatment at 500 °C for 15 min. Precision LCR meter (E4980A, Agilent, USA) coupled with custom-designed furnace and computerized data logger were used to collect temperature-dependent dielectric properties. The hysteresis loop data were collected using a ferroelectric tester system (RT66A, Radiant Technologies, USA).

3. Results and discussion

3.1. Phase analysis

Crystal structure of NB$_{1-x}$La$_x$-BZT-NN for (0.00 ≤ $x$ ≤ 0.07) sintered at 1175 °C/2 h were analyzed using x-ray diffraction (XRD) figure 1(a). The result suggests a pure perovskite solid solution was obtained with no secondary phase. Figure 1(b) shows an enlarge view of three different anomalies. First of peak (110) at 2θ ~ 32.5°, indicating a clear peak shift towards a smaller value. Solid-state crystal chemistry dictates that ions replacement is only possible if they have the same valency, coordination number, and approximately the same ionic radii. From Shannon’s ionic radii charts, the effective ionic radii of Bi$^{3+}$ _R12_ = 1.30 Å (R = Radii, 12 = coordination number) and La$^{3+}$ _R12_ = 1.36 Å. therefore, it is most likely that La$^{3+}$ replaces Ba$^{3+}$ at A-site which are in agreement with previous studies [28, 29]. The replacement of relatively larger ion causes an increase in d-spacing and hence a decrease in 2θ as both are inversely related (equation (2)).

$$2d = \frac{n\lambda}{\sin \theta}$$

(2)

The second anomaly in figure 1(b) at 2θ ~ 40°, is marked by peaks (003) and (021) for $x$ = 0.00 indicating the presence of rhombohedral (R3c) phase which upon increasing the x-content converges to form a single peak marked by (111). This convergence coupled with the third anomaly of dual peaks (002) and (200) at 2θ ~ 46.5° indicates the presence of the tetragonal (P4bm) phase [17, 30, 31] which is backed by improved PE-loop data. The presence of both R3c and P4bm phases at $x$ = 0.00 is in agreement with previous studies [14, 19]. The transformed tetragonal (P4bm) phase matches with ICDD card # 01-070-4760.

3.2. Surface morphology

Figures 2(a)–(d) shows secondary electron SEM images of NB$_{1-x}$La$_x$-BZT-NN; (0.00 ≤ $x$ ≤ 0.07) ceramics with grain size distribution charts. The relative density versus average grain size is given in figure 2(e) for all samples. The relative density was calculated using the already defined method [17]. All samples reflect homogenous morphology with distinct grain boundaries and good densification. EDX results were also found to be in accordance with stoichiometric data for overall samples showing mainly NBT elements. The average grain size values are given in figure 2(e); were calculated using ImageJ software. It is evident that as the value of $x$ increases relative density increases from 91.2% to 97.8% and the grain size decreases accordingly from 1.66 μm to 1.05 μm, implying that the addition of La$^{3+}$ restricts the grain growth. The reduction in grain size could be...
attributed to the Solute drag mechanism which states that the difference in radii of host and impurity atoms causes the reduction in grain growth expressed by equation (3). (lattice strain energy-ΔG_{strain})

\[
\Delta G_{\text{strain}} = 4\pi N_A M \left( \frac{r_o}{2} \left( r_d - r_o \right)^2 + \frac{1}{3} \left( r_d - r_o \right)^3 \right)
\]

where \( r_o \) represents the optimal radius of the lattice site, \( r_d \) is the ionic radius of dopant, \( N_A \) is Avogadro’s number, and \( M \) is Young’s modulus. From XRD data it is clear that La^{3+} R_{12} = 1.36 Å > Bi^{3+} R_{12} = 1.30 Å. Thus, the increasing content of La^{3+} can hinder the grain boundary mobility and disrupt the grain size growth. This behavior has also been reported previously. The increased density (less porosity) and reduced grain size data mentioned in figure 2(e) also suggest a larger dielectric breakdown strength (BDS) given by equation (4)

\[
\text{Grainsize} \propto \frac{1}{\sqrt{\text{BDS}}}
\]

3.3. Frequency and temperature dependent dielectric properties

Temperature-dependent dielectric behavior for NB_{1-x}La_T-BZT-NN; (0.00 ≤ x ≤ 0.07) ceramics at different frequencies (1 kHz, 10 kHz, 100 kHz, 250 kHz, and 1 MHz) are shown in figures 3(a)–(d). There are three distinct anomalies marked \( T_d, T_s, \) and \( T_m \) respectively. \( T_d \) generally corresponds to depolarization temperature, a point where ferroelectric relaxor phase transition occurs and it can be seen that as x-content increases \( T_d \)
shifts towards lower temperature, which is consistent with past studies [28]. The second anomaly appears at $T_s$ (saturation temperature) with broad characteristics frequency dispersions and is considered a ferroelectric relaxor property [34] which might indicate a transition from rhombohedral ($R3c$) phase to tetragonal ($P4bm$) phase as has been previously reported [35, 36].

There have been studies that suggest that if $T_s$ is dependent on frequencies which is true in this case then it can also be an indication of polarization of polar nano regions (PNR) [37]. The third and final anomaly marked $T_m$ corresponds to maximum temperature also called Curie temperature at which $\varepsilon_r$ reaches a maximum value and represents a transition between non-polar and paraelectric state [38]. Studies suggest that relatively broad peaks at $T_m$ correspond to diffusive phase transition which means that either A- or B-site are being occupied by two or more cations which are true for NBT [39, 40]. The random distribution of Na$^{+}$, Bi$^{3+}$, and La$^{3+}$ ion at A-site in NB$_{1-x}$La$_x$T-BZT-NN ceramic might be the cause of diffusive phase transition near $T_m$.

It is generally reported that $\varepsilon_r$ of dielectric materials strongly depends on frequency. Lower frequencies lead to high $\varepsilon_r$ and vice versa. The permittivity of each composition decreases with increasing frequency from 1 kHz to 1 MHz because at high frequencies the dipoles of respective polarization do not follow the frequency leading to low polarization and hence low $\varepsilon_r$. The Curie temperature $\varepsilon_r$ at 1 kHz for operational range with ±5%, ±10%, and ±15% deviation, and (f) The temperature dependence of $\Delta\varepsilon_r$ – stability range for composition NB$_{1-x}$La$_x$T-BZT-NN ceramic.

Figure 3. (a)–(d) Represents the relative permittivity ($\varepsilon_r$) and dielectric loss ($\tan\delta$) as a function of temperature with values of $T_p$, $T_s$ and $T_m$ for NB$_{1-x}$La$_x$T-BZT-NN ($0.00 \leq x \leq 0.07$), (e) $\Delta\varepsilon_r/\varepsilon_{150^\circ C}$ @ 1 kHz for operational range with ±5%, ±10%, and ±15% deviation, and (f) The temperature dependence of $\Delta\varepsilon_r$ – stability range for composition NB$_{1-x}$La$_x$T-BZT-NN ceramic.
reported that dielectric loss strongly depends on frequency and temperature. Dielectric loss normally increases rapidly above $T_m$ \[\text{[16, 41]}\]. In this case $\tan \delta < 0.05$ up to $\sim 350 ^\circ C$ for all the samples.

### 3.4. Ferroelectric and energy storage properties

The thermal stability of capacitance or dielectric constant with varying temperature of $\text{NB}_1-x\text{L}_x\text{T}-\text{BZT-NN}$ ($0.00 \leq x \leq 0.07$) composition at 1 kHz is given in figures 3(e), (f) calculated via equation (5).

$$\Delta \varepsilon_r = \frac{\varepsilon_r - \varepsilon_{150 ^\circ C}}{\varepsilon_{150 ^\circ C}}$$

Figure 4. Plot of $\ln(1/\varepsilon_r - 1/\varepsilon_{150 ^\circ C})$ as a function of $\ln(T-T_m)$ for $\text{NB}_{1-x}\text{L}_x\text{T}-\text{BZT-NN}$ ceramics ($0.00 \leq x \leq 0.07$) @ 1 kHz, the solid line indicates fitted results using modified Curie–Weiss law.

Figure 5. (a)–(d) P-E loop for $\text{NB}_{1-x}\text{L}_x\text{T}-\text{BZT-NN}$ for $x = 0.00, 0.03, 0.05$ and $0.07$ ceramic. Of all the composition $x = 0.07$ show highest thermal stability, followed by $x = 0.03$. To further analyze the dielectric behavior and to confirm the diffusive phase transition (DPT) modified Curie Weiss law defined by equation (6)
is applied [42–44].

\[
\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)}{\varepsilon}; \quad T > T_m
\]  

Where \(\varepsilon\) and \(\varepsilon_m\) are dielectric constant values at temperature \(T\) and \(T_m\) respectively, \(C\) is Curie constant and \(\gamma\) is phase transformation diffusivity coefficient, whose value varies between 1 and 2. When the value of \(\gamma = 1\) then the material has ferroelectric nature if greater than 1, then the material is a relaxor ferroelectric [13]. Figure 4 shows the evaluated \(\gamma\) value graph plotted between \(\ln(1/\varepsilon - 1/\varepsilon_m)\) and \(\ln(T - T_m)\). For all specimens \(\gamma\) value calculated after linear fitting at frequency of 1 kHz are given for \(x = 0.00, 0.03, 0.05\) and 0.07 are 1.68, 1.74, 1.81, and 1.96 respectively suggesting that DPT behavior enhanced with increasing \(x\)-content [45–47].

Figures 5(a)–(d) shows P-E loop of NB\(_{1-x}\)L\(_x\)-T-BZT-NN for (0.00 \(\leq x \leq 0.07\)) ceramic at room temperature. Figures 6(a), (b) gives the polarization and electric field values. It can be seen from the figures that with increasing \(x\)-content \(P_r\) first increases then starts to decrease with its lowest value of 2.57 \(\mu\text{C cm}^{-2}\) @ \(x = 0.07\). \(P_{\text{max}}\) on the other hand increases follows a zig-zag movement of increase-decrease-increase with values of 14.1, 19.14, 15.0 and 22.47 \(\mu\text{C cm}^{-2}\) for \(x = 0.00, 0.03, 0.05\) and 0.07 respectively. It is also evident that \(\Delta P\) is maximum for \(x = 0.07\). The coercive field \(E_c\) decreases gradually but the increase for \(x = 0.07\) on other hand \(E_{\text{max}}\) increase gradually with increasing \(x\)-content. The behavior depicted in figure 6(a) can be attributed to the grain size and density of the samples. From table 1 it can be seen that BDS also follows the zig-zag movement of increase-decrease-increase this can be explained by equation (2) in which grain size is inversely related to BDS or \(E_{\text{max}}\).
Figure 6(b) shows the total energy $W_t$, recoverable energy $W_{rec}$ and energy loss $W_{loss}$ for 
NB$_x$LaxTiO$_3$-BZT-NN for (0.00 ≤ $x$ ≤ 0.07) ceramics calculated from the PE-loops using equation (1). 
The efficiency of ceramic samples is 76.7, 61.5, 60.3, and 70.6% respectively with maximum recoverable energy being 
1.14 J cm$^{-3}$ @ 70.6% efficiency for $x = 0.07$. From this data it’s clear that the introduction of La content 
4. Conclusion

0.92Bi$_{0.5}$(Li$_{1-x}$La$_x$)$_{0.5}$Na$_{0.3}$TiO$_3$—0.06Ba(Zr$_{0.2}$Ti$_{0.8}$)$_3$O$_3$—0.02NaNbO$_3$ (0.00 ≤ $x$ ≤ 0.07) lead free relaxor ferroelectric ceramics have been prepared using the conventional solid-state technique. The XRD results show that La$^{3+}$ has completely diffused into the lattice forming a homogenous solid solution. The substitution of La$^{3+}$ decreased the average grain size. The introduction of La$^{3+}$ causes structural ordering and the evolution of PNRs. This behavior enhances the energy storage properties. In the present work, an efficiency of 70.6% with recoverable energy of 1.14 J cm$^{-3}$, and storage energy density of 1.63 J cm$^{-3}$ are obtained for $x = 0.07$ demonstrating that the electroceramics can have protential application in high-performance temperature stable energy storage application.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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