Effect of the Na$_2$O–Nb$_2$O$_5$–P$_2$O$_5$ glass additive on the structure, dielectric and energy storage performances of sodium niobate ceramics

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**ABSTRACT**

A phosphate glass Na$_2$O–Nb$_2$O$_5$–P$_2$O$_5$ (NPP) is incorporated into NaNbO$_3$ (NN) ceramics to examine its impact on the density, rearrangement of structural units, dielectric and energy storage features of the elaborated composites. The sodium niobate ceramic (NN) is prepared using the solid state process, whereas, the Na$_2$O–Nb$_2$O$_5$–P$_2$O$_5$ (NPP) glasses are produced using the method of conventional melt quenching. The glass (NPP) is added to the ceramic (NN) according to the composition (100-x) NN-xNPP; (x = 0, 2.5, 5, and 7.5 %wt). The developed composites are denoted as NN-Gx where x represents the content of glass in %wt. The appropriate sintering temperature for the glass-ceramic composites was measured based on the density measurements. It was found that with the addition of glass, their density was decreased and their fritting at lower temperatures was enhanced. The obtained SST for all composites is about 900 °C. After the densification stage, Raman spectroscopy, X-ray Diffraction, Granulo-laser analysis, and scanning electron microscopy are examined to study the structural approach and the morphology of sintered NN-Gx composites. The NN-G5 composite was found to have a fine grain microstructure that was uniform. The dielectric features of the composite revealed that at ambient temperature the NN-G5 had the greatest dielectric constant. The energy storage performance of the composite was investigated from the P-E plots and the parameters of energy storage. Based on the obtained results, it was concluded that incorporating up to 5% wt. of NNP glass in sodium niobate ceramics positively affects their dielectric and energy storage performances.

1. Introduction

Many perovskite structure materials have been used as dielectrical devices to store energy for high-density capacitors. Sodium niobate ceramic NaNbO$_3$ (NN) is considered one of them owing to their exceptionally large permittivity and their weak dielectric loss [1]. The pure NaNbO$_3$ ceramics produced using the conventional solid-state method exhibit the presence of pores between the grains, as NN grain boundaries generally migrate resulting in the growth of grains. The maximum polarization of these ceramics was very high, and the remnant polarization was quite low. Unfortunately, the existence of the defect as pores and grain boundaries in those materials makes their dielectric breakdown strength very limited at about (100 kV/cm) [2].

To reduce the pores and improve the NN ceramics total energy storage, it is necessary that these materials’ dielectric permittivity must be increased while defects must be minimized. Several researchers have thought of improving these properties by adding oxides or glasses to the NN ceramic in order to produce a composite having a high dielectric constant with low dielectric losses and high energy storage density. For instance, the improvement of the energy storage performance of lead-free NaNbO$_3$-based ceramics by adding Bi$_2$O$_3$ is reported [3]. The authors were introduced the Bi$_2$O$_3$ into NaNbO$_3$ in order to increase the energy storage density of the ceramic. It was found about 4.03 J.cm$^{-3}$ with energy efficiency ($\eta$) of 85.4% at 250 kV cm$^{-1}$. It is worth noticing that, the frequency, temperature stability, and fatigue endurance were found excellent also. Similar work on the introduction of Bi$_3^+$ at A-site and Mg$^{2+}$ at B-site of the ceramic NaNbO$_3$ (BMN) was reported. It was found that the composition of 0.85NN-0.15BMN had an energy storage density of 2.7 J.cm$^{-3}$ with a yield of 90% [4]. In order to develop a composite having an excellent dielectric constant and a high dielectric strength, it is worth noticing that, the frequency, temperature stability, and fatigue endurance were found excellent also. Similar work on the introduction of Bi$_3^+$ at A-site and Mg$^{2+}$ at B-site of the ceramic NaNbO$_3$ (BMN) was reported. It was found that the composition of 0.85NN-0.15BMN had an energy storage density of 2.7 J.cm$^{-3}$ with a yield of 90% [4]. In order to develop a composite having an excellent dielectric constant and a high dielectric strength,
Barium titanate ceramic (BaTiO₃) was added to NaNbO₃ ceramic [5]. The results indicated that the microstructure of the sample changed, while the density and the dielectric constant increased. Research on energy storage improvement for NN ceramic by adding glass is still very limited for this work, the glass composition with high niobium content (y/25 mol Nb₂O₅ was calcined at 500 °C). To achieve this objective, we have examined glasses in the ternary system Na₂O–Nb₂O₅–P₂O₅ that contain the identical chemical components as NN. After that, we have investigated their crystalization in the context of heating treatments. Then, using the XRD technique, we focused on identifying chemical compositions that enable the formation of the NaNbO₃ phase in glass-ceramics. We have detected that 25Na₂O–25Nb₂O₅–50P₂O₅ glass reveal the formation of NN embedded in the glass matrix. The effect of this NNP glass on the structural, the dielectric and the energy storage features of NN composites have been the subject of our research.

2. Experimental procedure

NaNbO₃ (NN) (Na: Nb = 50: 50) was made using solid-state reaction process using high purity Na₂CO₃ (Fisher Scientific; ≥99%) and Nb₂O₅ (Fisher Scientific; ≥99.5%). Both raw materials were balanced in suitable proportions, were completely mixed and calcined at different temperatures. The mixtures were then treated for 2 h at 1200 °C. Phosphate glass of composition 50Na₂O–25Nb₂O₅–25P₂O₅ was prepared using the melt-quench technique. It was elaborated from high purity powders of NH₄H₂PO₄, Nb₂O₅, and Na₂CO₃ purchased from Fisher Scientific. The mixture was melted at 1100 °C and then quenched in the air to get the glass. The obtained glass was heated at 300 °C for 2 h to eliminate residual stresses, then crushed to a fine powder in a mortar. In this work, the glass composition with high niobium content (y = 25 mol %) (NNP) was considered according to its dielectric characteristics. In order to obtain the composites, the NNP glass was added to the NN ceramic according to the chemical compositions (100-x) NN-xNNP (x = 0, 2.5, 5, 7.5 mol %) followed by thorough mixing. The (100-x) NN-xNNP mixed powder was calcined at 500 °C for 4h and sintered in an electric furnace at different temperatures for 2 h. The elaborated ceramics were labeled as NN-Gx, where x represents the batched glass concentration (NN-G0, NN-G2.5, NN-G5, and NN-G7.5).

The density of the samples (ρ) was measured by the Archimedes method using water as the immersion liquid. The accuracy of the measurement was 0.02 g.cm⁻³. Raman spectra of the ceramic composites were recorded using DXR2 Raman spectrometer with 633 nm laser excitation. The spectra were acquired in a backscattering geometry in the range of wave numbers from 1400 to 50 cm⁻¹.

3. Results and discussion

3.1. Density measurements

The variation of apparent density with sintering temperature was calculated to determine the appropriate sintering temperature (SST) of the new NN-Gx composites (x = 0, 2.5, 5, 7.5 wt %), which ranged from 800 to 1000 °C as is shown in Figure 1. It may be noted that the values of the density depend on the glass content in the NN ceramic as well as the sintering temperatures. For example at a fixed sintering temperature, it is observed that as the glass ratio in composites is increased, the density values decrease. This may be due to the replacement of a denser NaNbO₃ (p = 4.45 g/cm³) by the glass phase that has a weaker density (p = 2.72 g/cm³) compared to the NaNbO₃ phase. This decrease can also be related to the incorporation of a lighter component NNP glass (132.93 g/mol) in the structure instead of the heavier NaNbO₃ (163.96 g/mol). Figure 1 showed the effect of the sintering temperature on the density. It reveals that the density is also temperature-dependent and exhibits a maximum at 900 °C. The density of the samples sintered at 900 °C is higher than those sintered at 800 °C and 1000 °C. Similar results were reported in borate and silicate-based ceramic composites [8]. This can be demonstrated by the molten state of the added glass that penetrates the pores between the NN grains [9]. In the present work, the suitable sintering temperature (SST) to have a less porous composite with a high density was found to be 900 °C. This result will be confirmed by the SEM micrographs in Figure 4.

3.2. Raman spectroscopy

In order to shed more light on the structural changes in the (1-x) NN-xNNP composites, their Raman spectra have been carried out in the range of wave numbers from 100 to 1400 cm⁻¹ as is shown in Figure 2. Firstly, the NNP glass Raman spectra shows several bands situated in the frequencies of 215–550 cm⁻¹, 635 cm⁻¹, 815 cm⁻¹, 895 cm⁻¹, and 1040 cm⁻¹. The bands in the frequency range of 215–550 cm⁻¹ are associated with the bending vibrations of the phosphate and niobium polyhedrons [10]. The others that appeared at 635 and 815 cm⁻¹ can be attributed to Nb–O vibrational modes in the NbO₆ octahedra. As a matter of fact, the Raman measurement was 0.02 g.cm⁻³. The (P–E) hysteresis loops were measured at room temperature using a ferroelectric tester (RT6000HVA, Radiant Technology, Histersimetro). All the ceramic composites samples were immersed in silicon oil to prevent flashover. https://www.cmrl.fr-definition/aigan%C3%AB.

Figure 1. Bulk density of the (100-x)NN-xNNP ceramics as function of the sintering temperature.
of fact, the band at 635 cm\(^{-1}\) is relative to the Nb–O stretching mode of corner shared octahedral while the one at 815 cm\(^{-1}\) corresponds to Nb–O vibrations in chains like NbO\(_6\) octahedra. The peak positions at 1160 cm\(^{-1}\) and 1040 cm\(^{-1}\) correspond to the symmetric stretching vibration of (PO\(_4\)) in metaphosphate and (PO\(_3\))\(^2\) in pyrophosphate entities, respectively. Thus, the structure of the glass NNP contains niobium in octahedral sites within the phosphate glassy network composed by metaphosphate and pyrophosphate structural units. The niobium ion was shown to adopt an octahedral geometry with oxygen and forms either Nb–O–P and/or Nb–O–Nb linkages.

Secondly, the NN ceramic Raman spectrum displays very similar vibrational modes to those of the previously reported Raman studies on NaNbO\(_3\) ceramics [11]. The bands at 183 cm\(^{-1}\) and 576 cm\(^{-1}\) are attributed to the Na\(^+\) translational modes [12]. As seen in Figure 2, the main signals of NN ceramic are around 874 cm\(^{-1}\), 609 cm\(^{-1}\), 576 cm\(^{-1}\), 434 cm\(^{-1}\), 225-280 cm\(^{-1}\) and 204 cm\(^{-1}\). The bands below 350 cm\(^{-1}\) are attributed to the v5, v6 vibrations, and the ions NbO\(_6\) liberation mode. While the other ones above 350 cm\(^{-1}\) are associated with the v4, v2, v1, and to the combination v5 + v1 vibrations of the NbO\(_6\) group. All the cited vibration modes of NbO\(_6\) octahedron indicate that the perovskite phase NaNbO\(_3\) has been formed [13, 14].

Thirdly, the analysis of the Raman spectra of the composites is made regarding the NNP glass and NN ceramic data. It can be inferred that the orthorhombic structure of the NN phase was well preserved in the composites samples. The addition of NNP glass to NN ceramic with 2.5, 5, and 7.5 wt % did not influence the peak position of the NaNbO\(_3\) phase but it decreases the band’s intensity. It is noticed that the bending mode of the phosphate (PO\(_4\)) tetrahedron appears in the range 344–76 cm\(^{-1}\), and 609 cm\(^{-1}\), where Dp is the average crystallite size, K is the Scherrer constant, \(\lambda\) is the X-ray wavelength (0.15406 nm) and B is the Full Width at Half Maximum of XRD peak. The crystallite size of the pure NN sample was estimated to be 30.37 nm, and it gradually reduced when NNP glass was added, reaching 29.02 nm in NN-G2.5, 27.51 nm in NN-G5, and 28.77 nm in NN-G7.5. The average crystallite size estimates are consistent with the literature [17, 18].

### 3.4. Microstructure analysis

It is well known that the microstructural features play an important role in the functional characteristics of the Ferro-ceramics and, therefore, their morphology and distribution can be used to plan new strategies in designing new composite materials with improved functional properties. From this perspective, the relationships between microstructure are studied here using the SEM micrograph, as shown in Figure 4. Figure 4 (a) relative to the pure NN phase showed a dense and intergranular porous microstructure with a large grain size. Most of the grains have an angular appearance with plane interfaces. Smaller grains were also observed in NN ceramic. The addition of NNP glass to the NN ceramic affects its microstructure as shown in Figure 4 (b-d). With the increase in the glass content, it is observed that grain size and pore size decreased from the NN-G2.5 to NN-G5. The incorporation of 2.5 wt % of NNP glass

![Figure 2. Raman spectra of the NNP glass, the ceramic NN and the composites (100-x)NN-xNNP.](Image)

![Figure 3. XRD patterns of the (100-x)NN-xNNP composites.](Image)
as shown in Figure 4 (b) leads to a reduction of the space between the grains and consequently to a partial decrease of the pores. The vitreous phase is generally located at the NN ceramic grain boundaries [8]. A similar glass effect is reported in the literature by the addition of a silicate glass to BaTiO3 ceramic [19]. The NN-G5 composite has a uniform and denser microstructure as shown in Figure 4 (c) which can be explained by the homogeneity and the almost complete disappearance of the pores. The formation of this kind of microstructure could be due to the low melting temperature of the glass NNP which leads to the densification of the composite by the liquid phase sintering process [20]. Supplementary addition of glass up to 7.5 wt % as seen in Figure 4 (d) shows a decrease in density and the appearance of cracks and voids. This result is in agreement with the reported literature data on the sintering lithium niobate ceramics with glass additions [21]. From the obtained results, it can be concluded that incorporating 5 wt% of NNP glass has a dual effect on the NN ceramics microstructure. On the one hand, the grain size of the NN phase is considerably reduced; on the other hand, the pore size has decreased. This would have a positive impact on NN-Gx composites’ dielectric properties.

Figure 4. SEM micrographs of the polished surface of the composites (100-x) NN-xNNP; (a) NN- G0, (b) NN-G2.5, (c) NN- G5 and (d) NN- G7.5.

Summarizing, the average grain size of the composites decreases with increasing NNP glass content (Figure 5) and then increases on a further increase of the glass content, specifically, for the highest NNP glass content (NN-G7.5). Two interesting results stand out from the study of the evolution of the GSD (Figure 5); at first, the NN-G0 and NN-G2.5 composites have a multimodal distribution of particle size, where bigger particle the particles are enclosed by small ones, such as; at second, if the NNP glass content rises, the GSD shifts toward a unimodal distribution. As a result, it is reasonable to conclude that adding glass to the device results in a more uniform particle distribution with much small particle size.

3.5. Dielectric properties

The dielectric properties, εr and tan δ, as a function of frequency from 100Hz to 1 MHz at room temperature of the NN-Gx composites sintered at 900 °C are represented in Figure 6(a-b). Many polarization mechanisms can occur in dielectrics such as electronic, ionic, dipole orientation, migration, and space charge. The polarization of the orientation and the polarization of a migration/space charge are frequency-dependent; and generally diminish at higher frequencies. It is well known that the orientation polarization depends on temperature and decreases owing to thermal agitation. The migration polarization is also temperature-dependent but increases with increasing temperature. Generally, in a dielectric, the permittivity is due to the rotation of ions around their negative sites and to short-range dipole transport. From the analysis of Figure 6 (a-b), it can be seen that the dielectric parameters increase rapidly with the decreasing frequency while they reach small independent frequency values at higher frequencies. The low-frequency region is linked to many factors that can influence the dielectric properties such as defects, fluctuation in composition, migration of charge carriers, space charge, and sample-electrode polarizations [22]. The accumulation of charge carriers in the composite-electrode interface does not allow the further transfer of charge carriers through the NN-Gx composites. In the high-frequency region, the effect of the periodic reversal electric field

Figure 5. Particle size distributions of the composites (100-x) NN-xNNP.
occurs and provokes the decrease of the polarization issued from the space charge accumulation and causes a drop in the dielectric parameters. The dielectric constant of the pure ceramic NN is nearly 230.4 with losses up to 0.21 at 1MHz. Unfortunately, it is worth noticing that even this permittivity value is high, the pure ceramic NN had a low breakdown strength because of the existence of defects as pores and grain boundaries [2]. The addition of glass NNP had a significant role in improving the dielectric properties of NN-Gx composites at high frequencies. For example, the addition of 2.5 wt % and 5 wt % of NNP glass leads to an observable increase in the permittivity up to 406 and a decrease in losses down to 0.01. But the extra addition of glass 7.5 wt % negatively influenced the permittivity. The composite dielectric properties are related to their composition. The greater dielectric results are observed for NN-G5 composite. It had a good permittivity constant with low dielectric losses. This is because NN-G5 composite was distinguished by a dense microstructure because of the decrease in pores as shown in Figure 4. The diminishing dielectric constant for NN-G7.5 composite can be explained by the existence of the glassy phase excess and the formation of the secondary non-dielectric phase (NaPO3) as illustrated in Figure 3.

3.6. Energy storage performance

In general, for dielectric materials, the energy storage properties are described by three parameters calculated using the Eqs. (2), (3), and (4) [23]:

$$W_{rec} = \int_{P_{max}}^{P_{r}} E dP$$  \hspace{1cm} (2)
\[ W_{\text{loss}} = \int_0^{P_{\text{max}}} E dP - W_{\text{rec}} \]  

(3)

\[ \eta = \frac{W_{\text{rec}}}{W_{\text{rec}} + W_{\text{loss}}} \times 100 \]  

(4)

Where \( E \), \( P_{\text{max}} \), \( P_r \) stands for the electric field, maximum polarization, and remnant polarization, respectively. \( W_{\text{rec}} \) is the energy density that can be recovered, it equal to the integral area between the polarization axis and the discharge curve in the \( P-E \) hysteresis loop. \( W_{\text{loss}} \) is the energy loss density which is the area of the \( P-E \) loop. The parameter \( \eta \) is the energy efficiency is defined as the ratio of the energy density released to the energy density stored, see Figure 8 (a). The calculated parameters of the \( P-E \) loops composites, \( W_{\text{rec}}, W_{\text{loss}}, \) and \( \eta \), are summarized in Table 2.

Unfortunately, since the amplitude of the voltage in this system is small, the highest electric field that can be applied to the materials is 40 kV cm\(^{-1} \) at room temperature. This means that the composites’ estimated energy density is significantly smaller than their actual density. The energy storage density is also underestimated since the hysteresis loop is tested at the high frequency of 5 kHz, which partially excludes the Maxwell Wagner-Sillars polarization measured at low frequencies. Many high-frequency applications, especially in electronics, benefit from the energy measured in these experimental conditions.

The \( P-E \) hysteresis loops of the composites (100-x)NN-xNNP are plotted in Figure 8 (a). Because of the limitation of the measuring device voltage amplitude, the composites hysteresis loops exhibit a lossy behavior due to the leakage current occurring in the samples. The source of this leakage current is due to defects that caused a hopping phenomenon [24]. From Figure 8 (a), it can be clearly seen that the pure NN displays a large remnant polarization of 0.03 μC/cm\(^2 \) and a \( P_{\text{max}} \) of 1.31 μC/cm\(^2 \). Depending on the glass content added to the composite, the values of these two parameters differ as well as the shape of the loops \( P-E \). From Figure 8 (a), it can be observed that with increasing NNP glass content to 5 wt %, the loops of the composite NN-G2.5 and NN-G5 become much slimmer than that of pure NN. By increasing the glass content up to 7.5 wt % the loop of NN-G7.5 composite becomes larger again.

The composition dependencies of the energy density (\( W_{\text{rec}} \)) and the energy loss (\( W_{\text{loss}} \)) of the composites are plotted in Figure 8 (b). It is seen that with increasing glass content up to 5 mol%, the \( W_{\text{rec}} \) increase while the \( W_{\text{loss}} \) decrease. The NN-G5 composite exhibits the higher recoverable energy density (\( W_{\text{rec}} \)) value of 68.4 mJ/cm\(^3 \) and the lower energy loss (\( W_{\text{loss}} \)) value of 12.2 mJ/cm\(^3 \) which yields an energy efficiency (\( \eta \)) value.

\[ \begin{array}{|c|c|c|c|c|}
\hline
\text{sample} & \text{T (\degree \text{C})} & \varepsilon_r & \text{Tan} \delta \\
\hline
\text{NN-G0} & 30 & 230.49 & 0.14 & \\
 & 300 & 246.19 & 0.21 & \\
\text{NN-G2.5} & 30 & 233.68 & 0.01 & \\
 & 300 & 399.27 & 0.13 & \\
\text{NN-G5.0} & 30 & 406.44 & 0.01 & \\
 & 300 & 487.00 & 0.12 & \\
\text{NN-G7.5} & 30 & 183.47 & 0.01 & \\
 & 300 & 377.48 & 0.21 & \\
\hline
\end{array} \]

Figure 8. Energy storage performance of the (100-x) NN-x NNP composites: (a). \( P-E \) hysteresis loops of the composites as a function of the glass content at the electric field of 40 kV/cm, (b). The \( W_{\text{rec}} \) and \( W_{\text{loss}} \) evolution as a function of the incorporate glass content in the ceramic NN, (c). Energy efficiency (\( \eta \)) of the (100-x) NN-xNNP composites.
as high as ~ 84.8% at room temperature as shown in Figure 8 (c). With the further addition of NNP up to 7.5 mol% (NN-7.5), one can note that the recoverable energy density, energy loss, and the energy efficiency of the composite NN-7.5 decrease to 23.7 mJ/cm³, 54.3 mJ/cm³, and 30.3% respectively but still higher than the pure ceramic NN.

The addition of the NNP glass to NN ceramic can affect the energy storage performance for the (100-x)NN-xNNP composites. The enhancement of the NN-G2.5 and NN-G5 composites’ energy density is explainable by considering the microstructure and SEM image (Figure 4), which indicated a reduction in grain size and a decrease in the amount of pores. This leads to a reduction in the trapping of free charge through the grain boundary and the pore that controls ferroelectric polarization. Furthermore, as the glass’s content is increased, the polarization hysteresis loop is affected, lowering the value of the remnant and saturation polarization at the same time, resulting in a decrease in the energy storage density. Moreover, the addition of more glass can also damage the core-shell structure during the sintering process resulting in grain growth and secondary phase formation. For that, it is necessary to control the glass content added to a pure ceramic by controlling the composition in order to enhanced the composites energy storage performance.

4. Conclusion

The Na2O–Nb2O5–P2O5 glass was added to the pure NaNbO3 (NN) ceramic, it has positively affected the fretting temperature, microstructure, dielectric, and energy storage features of the NN ceramic. The obtained results revealed that the control of the ceramic microstructure is regulated by the amount of the introduced NNP glass. Specifically, it is found that the NN-G5 composite exhibited a high increase in permittivity and low dielectric losses, less than 0.01, and also a high improvement of the recoverable energy density reached 68.4 mJ/cm³ with an efficiency energy of 84.8%. This behavior is due to the diminution of the porosity and defects existing in the NN ceramic as well as the reduction of the grain size which caused a synergistic effect with the NNP glass network to improve the dielectric properties of the composites. Regarding the actual results, one can conclude that the phosphate NNP glass is suitable to perform NN-based glass-ceramics which exhibits enhanced energy storage performance. The optimum content of the NN glass in the composites was found 5%. Therefore, it can be concluded that NN-G5 glass-ceramic composite is an attractive dielectric candidate for energy storage capacitor ceramics.

Declarations

Author contribution statement

S. Benyounoussy: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
L. Bih: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.
F. Munoz: Contributed reagents, materials, analysis tools, or data; Wrote the paper.
F. Rubio-Marcos: Analyzed and interpreted the data; Wrote the paper.
A. El Bouari: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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