IMPROVED QUALITY FACTOR IN (K,Na)NbO$_3$ BASED UNVIRONMENT FRIENDLY PIEZOCERAMICS

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Abstract

Perovskite crystalline structures of (1-x)(K$_{0,5}$Na$_{0,5}$)NbO$_3$ – xGdMnO$_3$ (KNN – xGM) were obtained by solid state reaction. The phase purity was confirmed by X-ray diffraction. The homogeneity of the samples was studied by S.E.M investigations. From hysteresis loops we can observe that the ferroelectric quality depends on the concentration of the dopants. Good piezoelectric properties, along with an excellent quality factor were observed for the doped samples.

Introduction

Ferroelectric ceramics are known for their widespread applications like capacitors, piezoelectric actuators, sensors and transducers etc [1, 2, 3]. The development of lead-free piezoelectric ceramics as substitutes for Pb(Zr, Ti)O$_3$ is recent [4], due to the high toxicity of lead based materials. Ferroelectric materials such KNN ((K$_{0,5}$Na$_{0,5}$)NbO$_3$) are investigated for their excellent electric properties and also for their non-toxic behavior.

Current studies on KNN materials are focusing on the improvement of material proprieties. Material improvement can be accomplished by chemical substitution [5], alteration of phase transitions [6] or structural material alterations [7]. In this paper we are considering the use of GdMnO$_3$ doping, on improving ferroelectric and piezoelectric proprieties of KNN.

Experimental

(K$_{0,5}$Na$_{0,5}$)NbO$_3$ – xGdMnO$_3$, where x= 0 mol%, 0,25mol%, 0,75mol%, 1 mol%, 1,5 mol% and 2,5 mol% were obtained by solid state method in air, starting from K$_2$CO$_3$ (99%; Scharlau, Sentmenat, Spain), Na$_2$CO$_3$ (99%; Scharlau), Nb$_2$O$_5$ (99%, Merck, Darmstadt, Spain), Gd$_2$O$_3$ (99%; Fluka, Buchs, Switzerland) and Mn$_2$O$_3$ (99%, Sigma-Aldrich, St. Louis, USA). The powders were calcined at 880ºC for 5h. After mixing with 5 mass% polyvinyl alcohol binder solution, samples with different geometries (accordingly to the dimensional requirement of each measurement) were cold-pressed at 200Mpa. The sintering was performed at 1090ºC for 3h. The crystalline structure of the sintered samples was examined by long time x-ray diffraction using a PanAnalytical X'Pert Pro MPD diffractometer. The bulk density was measured using the Archimedes method. The microstructure of the sintered samples was investigated using scanning electron microscope model Inspector S Phillips (FEI, Netherlands). Silver electrodes were deposited onto the samples using Emitech K975X thermal evaporator (Ashford, UK). The hysteresis loop of each composition was obtained at 100Hz using a Sawyer-Thomson capacitive voltage divider, coupled with an Atten ADS 1152CML digital storage oscilloscope (Helmond, Netherlands). For the piezoelectric measurements, the samples were polled at 120 - 190ºC in a silicon oil bath, under a direct current electric field of 4 kV/mm, for 10 min.

Results and discussion

The X-ray diffraction patterns presented in figure 1 confirmed that all obtained samples of KNN ceramics are indexed as perovskite with an orthorhombic crystalline structure. We

observe from the x-ray diffraction that the presences of the signals from some secondary phases are getting more visible as the doping percent increases.
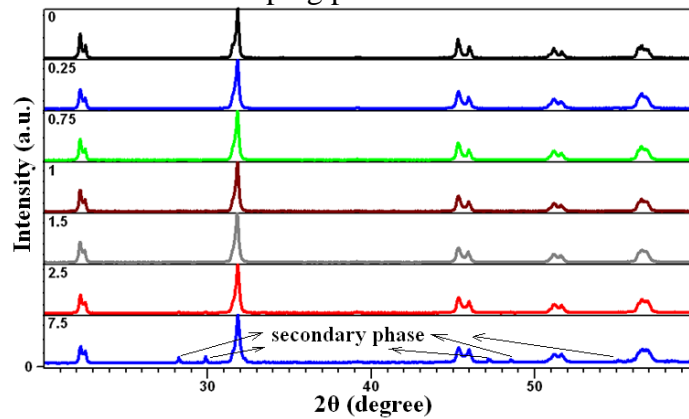
**Figure 1.** X-ray diffraction patterns of KNN material obtained

Figure 2 presents the variation of bulk density for the sintered samples. Compared to the reference sample KNN with a relative density of of 4.21 g/cm^3, as the doping percent increases, the density also increases almost linearly. Starting from a value of 4.28 g/cm^3 for KNN-0,25GM, the bulk density increases up to 4.4 g/cm^3 for KNN-2.5GM.
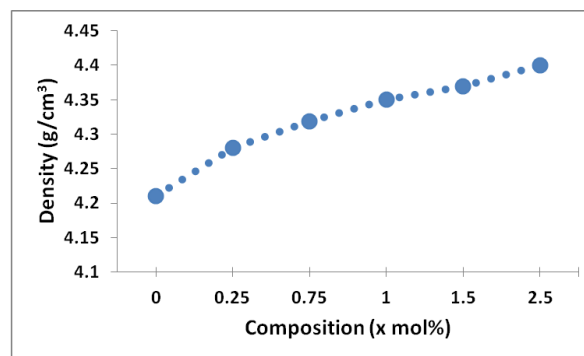

Figure 2. Variation of bulk density

The microstructure of KNN–xGM ceramics sintered at 1090ºC is shown in figure 2. As we can observe, GdMnO$_3$ inhibit the grain growth. From around 3 μm for KNN, the crystallite size decreases to around 1 μm for KNN-2.5GM. The grain morphology changed from smooth cubical grains for KNN-0GM, to round cornered grains for KNN-2,5GM.

The dielectric properties of KNN-xGM relative to the temperature, are presented in figure 4. Two distinctive inflexions can be noticed in the figure, associated with two phase transition temperatures. At around 200ºC a ferroelectric orthorombic to tetragonal phase transition is present, and also at around 400ºC a paraelectric tetragonal to cubic phase transition exists. The variation of the real part of the dielectric constant confirm that at room temperature the ceramic crystalise in orthorombic symetry. The addition of GdMnO$_3$ do not produce any significant alteration of the transition temperatures and assures a good dielectric loss, with a value below 0,5 at room temperature.
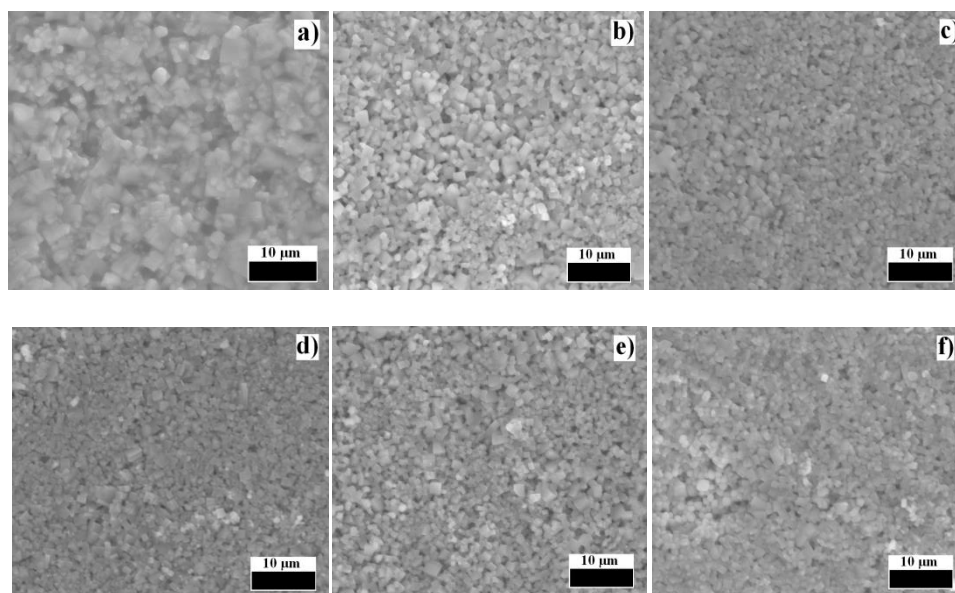
Figure 3. Surface morphology of (a) KNN – 0GM. (b) KNN – 0,25GM , (c) KNN-0,75GM, (d) KNN- 1GM, (e) KNN- 1,5 GM, (f) KNN – 2,5 GM sintered ceramics.
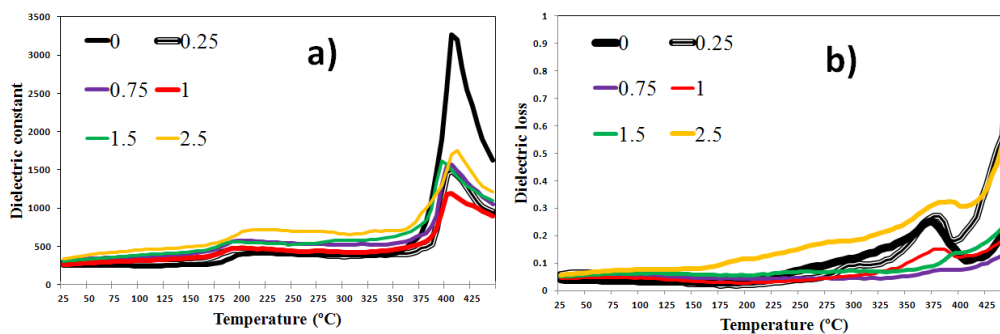
Figure 4. Temperature dependence of the dielectric constant (a) and dielectric loss (b) for thin disks of doped KNN ceramics.
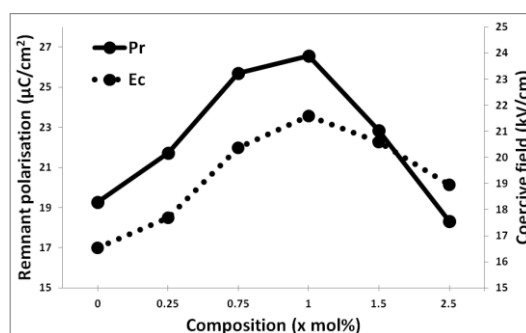
Figure 5. Remnant polarization and coercive field of KNN-xGM ceramics.

The ferroelectric properties were evaluated in terms of remnant polarization and coercive field variations presented in figure 5. All values were derived from hysteresis loops obtained with a Sawyer-Thomson capacitive voltage divider. At room temperature, for the reference sample values of $19.28 \mu C/cm^2$ and 16,53 kV/cm were measured for remnant polarization, respectively coercive field. As GM percent increases, both values increases up to $26,56 \mu C/cm^2$, respectively 21,58 kV/cm for KNN-1GM. Beyond this composition, the ferroelectric properties degrade, with a drop in both values down to $18.31 \mu C/cm^2$, respectively 18,95 kV/cm.

In figure 6, the variations of the main piezoelectric properties are presented across the compositions studied. All values presents similar trends to the variation of remnant polarization and coercive field, hence we can conclude there is a optimum composition of KNN-xGM, where all ferroelectric and piezoelectric properties are maximum: KNN-1GM. Starting with values of d_{33}= 89,2 pC/N, k_{33}= 0,475, Q_m= 407.07 and k_p= 0,347 for the reference sample KNN, the values increases to d_{33}= 97,1 pC/N, k_{33}= 0,482, Q_m= 1180 and k_p= 0,426. Beyond this composition, all value degrade significantly down to d_{33}= 83 pC/N, k_{33}= 0,433, Q_m= 592.07 and k_p= 0,37. The results show that $GdMnO_3$ addition contribute in a small extent to the charge constant and coupling factor growth, but to a large extent to the increase of the mechanical quality factor Q_m.
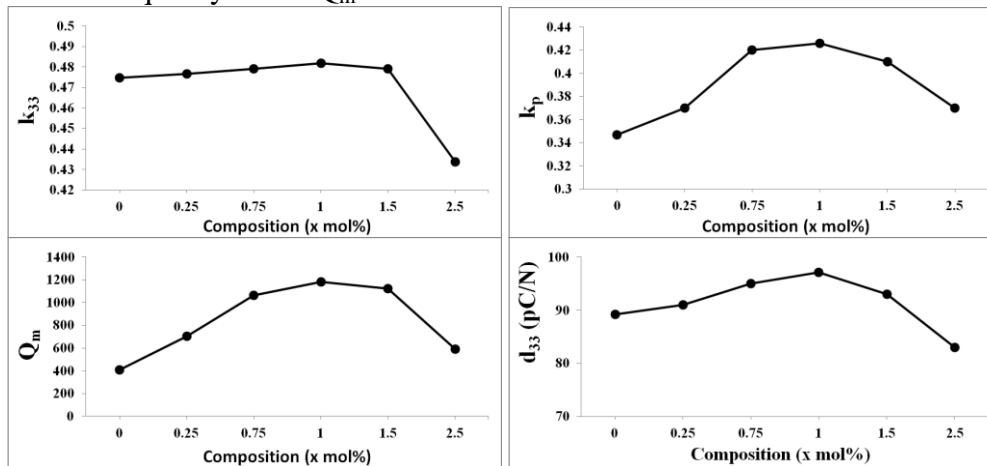

Figure 6. Piezoelectric properties of KNN-xGM ceramics.

Conclusion

$(1-x)(K_{0,5}Na_{0,5})NbO_3$ – $xGdMnO_3$ceramics were obtained by solid state reaction with orthorhombic perovskite crystalline structure at room temperature. The addition of $GdMnO_3$ decreases the grain size and increases the bulk density. While maintaining good dielectric loss values, the addition of $GdMnO_3$ do not produce any significant shift in the transition temperature. Also, $GdMnO_3$ addition improves in small measure the values of k_{33}, k_p, respectively d_{33}, and significantly increases the mechanical quality factor.

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