Improved Electrical Response in $GdMnO_3$ Doped (K, Na)NbO_3 Piezoelectric Speaker

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Abstract
$[(K_{0.368}Na_{0.432})Li_{0.5}][Nb_{0.86}Sb_{0.04}Ta_{0.1}]O_3$ doped with 0.5 mol% $GdMnO_3$ piezoelectric speakers were obtained, with good frequency sensibility in the range 20 Hz – 20 kHz. The additive used distorts the crystalline structure to a mixture of orthorhombic and tetragonal phases at room temperature. Also the dopants used shift the high temperature phase transitions toward room temperature. Good piezoelectric properties were obtained for doped samples, with an optimum piezoelectric charge constant d_{33} of 127 for $[(K_{0.368}Na_{0.432})Li_{0.5}][Nb_{0.86}Sb_{0.04}Ta_{0.1}]O_3$ - 0.5 mol % $GdMnO_3$, a planar coupling coefficient of 0.39 and a quality factor of 102.

Introduction
The most common piezoelectric ceramics used nowadays for actuators and sensors applications are lead oxide based ferroelectrics, especially $Pb(Zr,Ti)O_3$ (noted as PZT). Their excellent piezoelectric and dielectric properties [1], make suck materials a suitable choice for commercial products. Nevertheless, a major issue of these materials is the toxicity of Pb compounds, relative to the environment and man. As a result of E.U. directives on waste from electrical and electronic equipment (WEEE) and restriction of hazardous substances (RoHS) [2], the latest trends in scientific research are oriented toward "environmental friendly" materials. As a consequence, many lead free piezoelectric materials are nowadays intensively studied: modified $BaTiO_3$ [3], bismuth layer structure ferroelectrics [4], $(Na_{0.5}Bi_{0.5})TiO_3$ [5] and $(K_{0.5}Na_{0.5})NbO_3$ (denoted as KNN) [6, 7]. Presently, the most promising lead-free piezoelectric ceramics are based on potassium sodium niobate modified with different additives, sintering aids or doped with other perovskite structures.
The purpose of this work is to fabricate piezoelectric speakers based on lead free materials. $[(K_{0.368}Na_{0.432})Li_{0.5}][Nb_{0.86}Sb_{0.04}Ta_{0.1}]O_3$ was previously reported with improved piezoelectric properties [8], due to the presence of morphological phase boundaries between orthorhombic and tetragonal crystalline phases at room temperature. $GdMnO_3$ was considered in this work to improve the piezoelectric properties and frequency response of the lead free piezoelectric speaker. The ceramics obtained were characterized using x-ray diffraction (PANalytical X'Pert Pro MPD) and scanning electron microscope (Inspect S Phillips). Dielectric measurements were performed with a programmable RLC-meter TEGAM-3550, ferroelectric hysteresis loop was obtained using a Sawyer-Thomson circuit and an Atten ADS 1152CML digital storage oscilloscope. A complete set of piezoelectric properties were obtained using a network analizer Agilent E5100A. The relative sound pressure generated by the piezoelectric speaker was recorded using Audacity 2.0.5 software.

Experimental
Solid state reaction was used to prepare $(K_{0.5}Na_{0.5})NbO_3$ noted KNN, $[(K_{0.368}Na_{0.432})Li_{0.5}][Nb_{0.86}Sb_{0.04}Ta_{0.1}]O_3$ noted KNLNST, and $[(K_{0.368}Na_{0.432})Li_{0.5}][Nb_{0.86}Sb_{0.04}Ta_{0.1}]O_3$ – 0.5 mol% $GdMnO_3$ noted KNLNST-0.5GM. All the samples were calcined at 880° C with a 5 $deg \cdot min^{-1}$ slope and a five hours dwell time. The

resulting powders were mixed with a 5 mass% PVA binder, cold pressed at 200 MPa into disk samples of 10 mm in diameter and 0.5 mm thickness, respectively into bar shapes of 6 mm in length and 1.8 mm in width/thick, and sintered at 1090°C for 3 hours. Silver electrodes were formed on each side of the disks. The ceramics were polled in silicone oil at room temperature under a direct current electric field of 4 kV/mm for 30 min. The piezoelectric speakers were then constructed from poled disk glue with silver paint to a thin metal plate, serving as a mechanical amplification of the vibrations produced by the piezoceramic.

Results and discussion

The X ray diffraction patterns presented in figure 1 of KNN and doped KNN ceramics, shows a perovskite phase structure, with no secondary phases present. The presence of additive change the crystalline structure at room temperature from orthorhombic for KNN, to a mixed orthorhombic-tetragonal for KNLNST and KNLNST-0.5GM, visible from the diffracted angles shift presented in the inset.

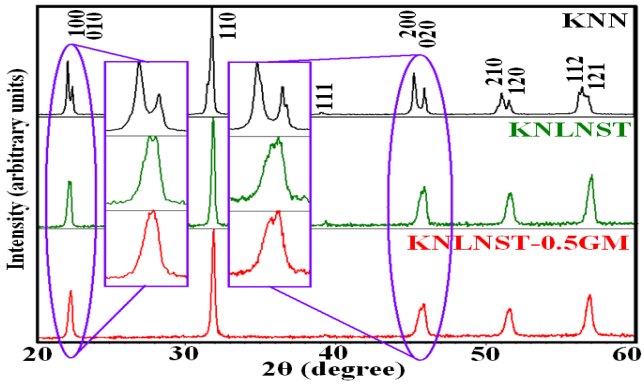

Figure 1. X ray diffractions of the sintered ceramics.

The dielectric constant (figure 2) was measured from room temperature up to 430º C, at 1 kHz. For the reference sample KNN, we can noticed two inflexions of the dielectric constant, corresponding to different phase transitions: from room temperature, where the system crystallize in orthorhombic crystal structure, at 210ºC the system distorts to tetragonal and then to cubic at 410ºC (Curie temperature). Similar behavior was noticed for doped KNN samples, but all the phase transition temperatures are significantly shifted to lower temperatures: 80ºC for orthorhombic - tetragonal and 295ºC for the Curie temperature for KNLNST, respectively 65ºC and 260ºC for KNLNST-0.5GM.

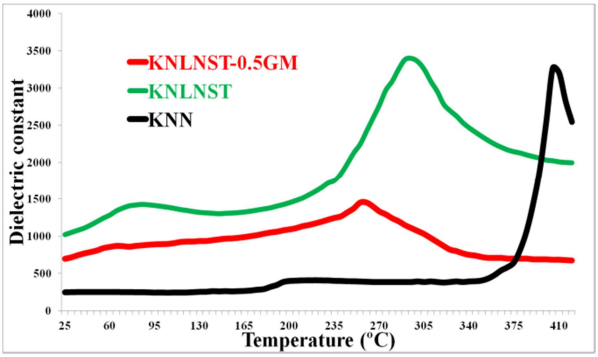

Figure 2. The temperature dependence of the dielectric constant for sintered ceramics.

From the hysteresis loops of the unpoled ceramics (figure 3), we can conclude that all the additives used contribute to a softening of ferroelectric properties. From 13.2 μC/cm^2 for

KNN, the remnant polarization increase up to 13.5 μC/cm^2 for KNLNST, respectively 14.5 μC/cm^2 for KNLNST-0.5GM. The coercive field however drops from 20 kV/cm for KNN, down to 15 kV/cm for KNLNST, respectively 14 kV/cm KNLNST-0.5GM. The observed softening of ferroelectric properties is to be related to a higher freedom of domain walls, due to the presence of dopants, since a lower electrical field is necessary to reduce the remnant field to zero.

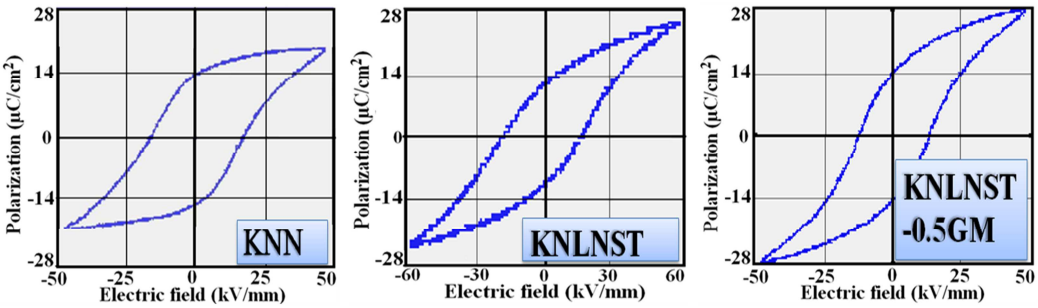

Figure 3. Room temperature hysteresis loops of sintered thin ceramic disks.

After poling of the ceramics at room temperature, in silicon oil under an electric field of 4 kV/mm, the samples were aged for 1 day. Resonance and anti-resonance curves (figure 4) were obtained at room temperature. For a complete determination of piezoelectric coefficients, both radial mode (left) and length mode (right) oscillations were obtained. For the reference sample KNN, poor frequency response was obtained, with badly outlined resonant frequencies and phases shift. An improved and sharper response was obtained for KNLNST and KNLNST-0.5GM ceramics in radial mode. An optimum frequency response was observed for KNLNST-0.5GM in length mode, suggesting improvements of piezoelectric properties.

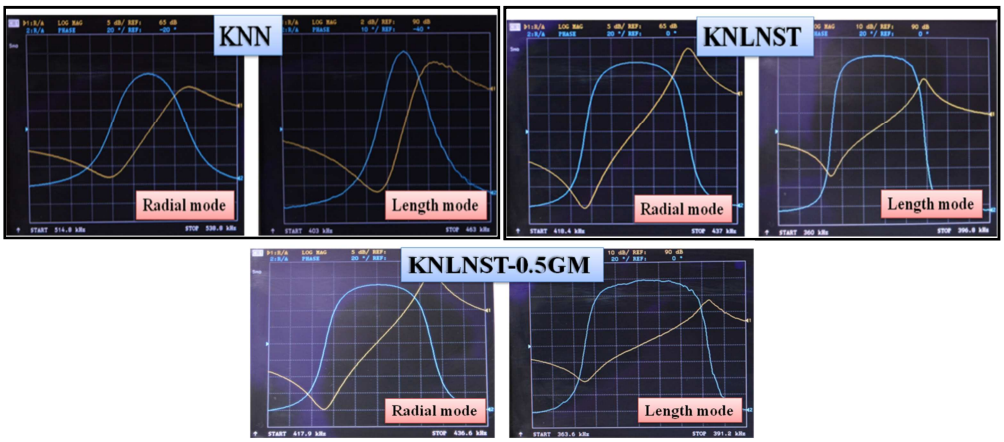

Figure 4. Resonance and anti-resonance curves in radial and length mode.

The frequency response of the piezoelectric speakers, in terms of relative sound pressure, was evaluated in the range 50 Hz- 20000 Hz. The speaker based on KNN (insets in figure 5), responds very well to frequencies up to 180 Hz, and has a moderate response for 180 Hz-2000 Hz, with a rapid decrease in sensitivity for higher frequencies. In the case of the piezoelectric speaker based on KNLNST (figure 5 in the middle), the relative sound pressure recorded show an improved frequency response compared to pure KNN. The speaker maintains a good sensibility to low frequencies (20 Hz -180 Hz) but an increased sensibility is noticed in the frequency range 200 Hz – 4 kHz. At higher frequencies, we notice a similar rapid decrease in sensibility as KNN. For KNLNST-0.5GM, the maximum frequency sensibility is obtained, particularly in the range 600 Hz – 10 kHz. Good piezoelectric

properties were obtained for doped samples (table 1), with an optimum piezoelectric charge constant d_{33} of 127 for KNLNST-0.5GM, planar coupling coefficient of 0.39 and a quality factor of 102.

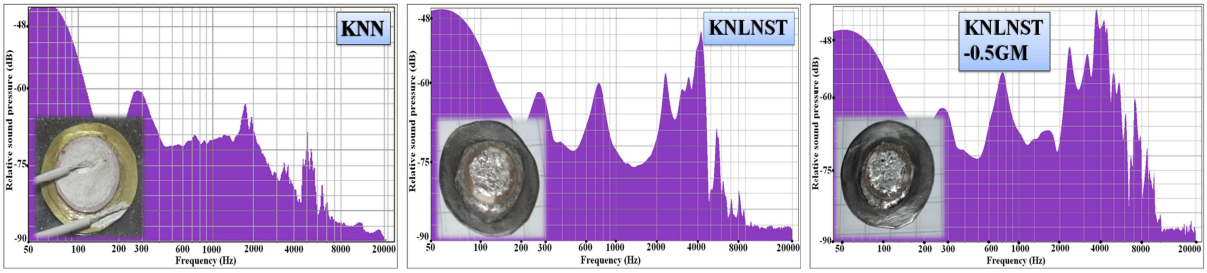

Figure 4. Relative sound pressure response of KNN based speakers, and insets illustrating the piezoelectric speaker disks.

Table 1. Piezoelectric properties of sintered ceramic.

Properties	KNN	KNLNST	KNLNST-0.5GM
Q	407	158	102
k_{31}	0.19	0.21	0.17
k_p	0.35	0.38	0.39
S^E_{11}[10^{-12} m^2/N]	7.4	5.9	10.1
S^E_{12} [10^{-12} m^2/N]	2.5	2.4	4.1
S^D_{11} [10^{-12} m^2/N]	6.76	5.68	9.83
d_{31} [10^{-12} C/N]	28.8	41.7	45.9
g_{31} [10^{-3} Vm/N]	9.4	5.7	7.1
k_{33}	0.38	0.42	0.42
d_{33} [10^{-12} C/N]	82	93	127
g_{33} [10^{-3} Vm/N]	17.3	14.6	10.1
S^D_{33} [10^{-12} m^2/N]	9.4	20	11.1
S^E_{33} [10^{-12} m^2/N]	10.5	21.1	13.1

Conclusion

We have successfully obtained $(K_{0.5}Na_{0.5})NbO_3$, $[(K_{0.368}Na_{0.432})Li_{0.5}]$ $[Nb_{0.86}Sb_{0.04}Ta_{0.1}]O_3$, $[(K_{0.368}Na_{0.432})Li_{0.5}]$ $[Nb_{0.86}Sb_{0.04}Ta_{0.1}]O_3$ – 0.5 mol% $GdMnO_3$ piezoelectric speakers. At room temperature Li, Sb and Ta distorts the crystalline structure from orthorhombic to a mixed orthorhombic-tetragonal, while GdMnO3 maintain such distortion. The remnant polarization increase from 13.2 µC/cm2 for KNN, to 14.5 µC/cm2 for KNLNST-0.5GM. Compared to the reference sample KNN, the presence of additive decrease the coercive field, suggesting a softening of ferroelectric properties. Also the additives decrease the temperature of all phase transitions. Good piezoelectric properties were obtained for doped samples, with an optimum piezoelectric charge constant d_{33} of 127 for KNLNST-0.5GM, planar coupling coefficient of 0.39 and a quality factor of 102. The piezoelectric speaker based on $[(K_{0.368}Na_{0.432})Li_{0.5}][Nb_{0.86}Sb_{0.04}Ta_{0.1}]O_3$ – 0.5 mol% $GdMnO_3$ has the best frequency response in the range 20 Hz -20 kHz. The high relative sound pressures recorded suggest that this composition can be successfully used for practical applications.

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