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Exploring different sintering atmospheres to reduce nonlinear response of modified KNN piezoceramics

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Abstract

Dense lead-free $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ piezoelectric ceramics are prepared by the conventional mixed oxide method. The effect of different sintering conditions (synthetic air, O_2 and Ar) on some structural, dielectric and piezoelectric properties is studied. A long sintering time (16 h) promotes the formation of a secondary phase, which is assigned to $K_3LiNb_6O_{17}$, tetragonal tungsten-bronze. High values of longitudinal piezoelectric constant are obtained when ceramics are sintered under Ar or O_2 for low dwell time (2 h). However, the nonlinear response turns out to be significantly dependent on the sintering atmosphere. Results are discussed taking into account the formation of complex defects capable of pinning domain wall when oxygen vacancies are created by sintering. Thus, sintering in an inert atmosphere appears to be a good way of reducing nonlinear response in KNN-based piezoceramics.

Keywords: Dielectric properties; Piezoelectric properties; Niobates; Perovskites; Lead-free piezoceramics

1. Introduction

Excellent piezoelectric and electromechanical properties are obtained in a series of lead-based ferroelectric ceramics, especially $Pb(Zr,Ti)O_3$ (PZT). Since the electromechanical properties of PZT are attributed to the morphotropic phase boundary (MPB),[1] strong emphasis is laid on investigating systems containing MPBs. It is believed that the existence of thermodynamically equivalent phases permits almost a continuous rotation of the polarization vector under the external electric field, which enhances dielectric, piezoelectric and electromechanical responses.[2,3] However, environmental issues may ultimately require the replacement of these lead-based materials in electronic components.[4,5] Therefore, extensive studies on MPB lead-free materials have been undertaken.[6–8]

Over the last few years, much attention has been focused on $(K,Na)NbO_3$ (KNN) based ceramics because of their good electromechanical properties and high Curie temperature for compositions close to MPB.[9–14] Exceptionally high piezoelectric properties (~416 pC/N) in the system $(K,Na)NbO_3$–$LiTaO_3$–$LiSbO_3$, prepared by a complex processing method, were reported by Saito et al.[9] Unfortunately, it is difficult to obtain samples with such characteristics by a technological and economically available process, although good piezoelectric properties have been reported for samples obtained by the conventional ceramic route. In particular, the composition $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ (KNL–NTS) exhibits interesting properties, e.g. longitudinal piezoelectric coefficient and Curie temperature over 260 pC/N and 250 °C, respectively, which probably make it the most workable lead-free piezoelectric system known to date.[12] Nevertheless, some of its properties are not suitable for all purposes. The dielectric and mechanical losses are similar to those reported for a typical soft PZT ceramic at room temperature.[12] In addition, KNL–NTS response shows a noticeable nonlinear behavior (i.e. properties dependent on the applied electric field and/or mechanical stress), which is due mainly to extrinsic effects.[15] As a consequence, research fields are opening up with the aim of obtaining new KNN-based materials capable of replacing hard PZT in power devices.

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Compositional modification by doping is a very active research line for obtaining lower dielectric losses and a higher mechanical quality factor. Good results are expected by means of hardener substitutions, such as those that occur in other perovskites,[16] although some structural and electrical aspects remain controversial as regards the role of dopants in the KNN system. It has recently been shown that Cu-doped KNN-modified compounds may exhibit typical characteristics of "hard" behavior.[17–21] A high mechanical quality factor and low dielectric losses have been reported in all these materials. However, a low piezoelectric response ($d_{33} < 100\,\text{pC/N}$) is also a feature common to all of them that limits their commercial use. Furthermore, nonlinear response of those "hard" compositions has yet to be explored. Taking into account that KNN-based materials are very processing sensitive,[22] new sintering routes and processing conditions should be explored in order to take a step toward better "hard" materials.

The addition of hardener ions to a perovskite compound (e.g. Cu^{2+} ions replace Nb^{5+} ions in Cu-doped KNN) leads to the creation of oxygen vacancies, forming the so-called complex defects.[23] These defects operate as pinning centers by hampering the motion of the domain walls. This domain wall pinning effect is responsible for the reduction in dielectric losses and the stabilization of properties (i.e. nonlinear response reduction) in ferroelectrics.[24] Thus, it is interesting to explore different ways to create oxygen vacancies in KNN systems. It is well known that the sintering atmosphere may determine the appearance of oxygen vacancies in perovskite systems. As a consequence, the sintering atmosphere may influence KNL–NTS properties by reducing the nonlinear response, for example. Changes in the sintering atmosphere affect the structure of perovskite compounds, as has been verified in KNN systems.[25] Consequently, in this work the effect of sintering conditions on the structural and nonlinear dielectric properties of KNL–NTS ceramics is studied.

2. Experimental

$(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$ compound was prepared by a conventional ceramic processing route. Na_2CO_3 (99.5%), Li_2CO_3 (99.5%), K_2CO_3 (99%), Nb_2O_5 (99.9%), Ta_2O_5 (99%) and Sb_2O_5 (99.995%) were used as starting raw materials. The method for optimizing the particle size distribution of the raw materials has been described elsewhere.[26] The powders were attrition-milled using ZrO_2 balls in ethanol medium for 3 h, dried, calcined at 700 °C for 2 h, attrition-milled again and pressed at 200 MPa into 10-mm diameter and 0.7-mm thick disks. The pellets were sintered at 1125 °C at different atmospheres: synthetic air (80% N_2, 20% O_2), oxygen or argon. Sintering was performed at two different times, 2 h or 16 h, in order to maximize the effect of sintering atmosphere on the KNL–NTS microstructure.

Crystalline symmetry was determined by X-ray powder diffraction analysis using a PANalytical X'Pert PRO MPD system with Cu Kα radiation and an X'Celerator detector equipped with a focusing primary Ge(1 1 1) monochromator. Lattice parameters were refined by global simulation of the full diagram using *Fullprof* program. Microstructure was evaluated by scanning electron microscopy (SEM) with a JEOL JSM-840 instrument. For electrical characterization, the pellets were coated with silver paint on their upper and lower surfaces. The impedance spectroscopy technique was used to obtain the permittivity of the studied materials as a function of temperature and frequency. Admittance values were measured using an impedance analyzer (HP 4192A) in the frequency range 100 Hz–1 MHz. A closed-loop cold-finger cryogenic system and a programmable furnace were used to examine the temperature dependence of permittivity from −250 °C to room temperature (RT) and from RT to 600 °C, respectively. The permittivity dependence with a sub-switching ac electric field was measured at 1 kHz and at RT, by means of a capacitance comparator bridge specially designed for this type of measurement. *P–E* hysteresis loops were determined by an RT 6000 HVS hysteresis meter (Radiant Technologies Inc.) at RT. The poling process was carried out in a silicone oil bath at 25 °C under a dc electric field of 40 kV/cm during 30 min. After that, the longitudinal piezoelectric coefficient was measured using a piezo-d_{33} meter (YE2730A, APC International) at RT.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of ceramics samples as a function of the sintering time and atmosphere. Single-phase perovskite is revealed in samples sintered under O_2 or Ar for 2 h, whereas a secondary phase of $K_3LiNb_6O_{17}$ (PDF#36-0533) with tetragonal tungsten-bronze (TTB) structure begins to appear in samples sintered under synthetic air for 2 h (Fig. 1a). In a previous study involving Li- and Ta-modified $(K,Na)NbO_3$ piezoceramics, the occurrence of this secondary phase was attributed to the volatilization and segregation of the alkali elements during the thermal treatment.[27] Oxidizing and inert atmospheres seem to inhibit the formation of the TTB phase, maybe due to the high formation energy of the Nb vacancies in KNN systems.[28] On increasing the sintering time, the TTB phase becomes more significant regardless of the atmosphere used, as shown in Fig. 1b. This demonstrates therefore that the TTB phase formation is strongly influenced by both the sintering atmosphere and sintering time.

In general, the formation of a solid solution involving $(Na,K)NbO_3$–$LiTaO_3$–$LiSbO_3$ is quite difficult to obtain due to the structural differences between $KNbO_3$ and $NaNbO_3$ with a perovskite structure and $LiTaO_3$ with a pseudo-ilmenite structure. Consequently, the solubility of $LiTaO_3$ into KNN is generally low.[29] A careful examination of the X-ray diffraction patterns reveals a tetragonal structure with *P*4*mm* point group for all samples. The enlarged XRD patterns of the ceramics in the range of 2θ from 44° to 47° clearly show the splitting of the tetragonal (0 0 2) and (2 0 0) diffraction peaks with an intensity ratio of the two characteristic peaks $I_{(0\,0\,2)}/I_{(2\,0\,0)}$ close to 0.50, associated with a tetragonal structure.[30] Lattice parameters, obtained by the Rietveld method using Fullprof program, are shown in Table 1. As reported recently, the best piezoelectric properties in KNL–NTS piezoceramics are obtained for tetragonal symmetry, and therefore a linear correlation exists between