PHASE TRANSITIONS IN LEAD FREE PIEZOELECTRIC MATERIALS

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Abstract

$(K_{0,5}Na_{0,5})NbO_3$ doped with 1 mol% $SmBO_3$ (where B= Al, Co, Cr, Fe, Mn) ceramics were obtained through solid state method in air. The refinement of the unit cell reveals a shift from orthorhombic to tetragonal crystalline structure at room temperature, for KNN-$SmMnO_3$, KNN-$SmFeO_3$ and KNN-$SmCrO_3$. The variation of the dielectric constant at different frequencies shows an increase of almost one order of magnitude for KNN-$SmCoO_3$ and KNN-$SmMnO_3$, compared to the reference KNN.

Introduction

A major impediment of the currently widely used piezoelectric ceramic, namely $Pb(Zr,Ti)O_3$, is the high toxicity of Pb compounds [1, 2]. Hence, the latest trends in research are oriented toward ‘‘environmentally friendly’’ piezoelectric materials, such as $(K, Na)NbO_3$.

$(Na_xK_{1-x})NbO_3$ is a solid solution of orthorhombic ferroelectric $KNbO_3$ and anti-ferroelectric orthorhombic $NaNbO_3$ [3]. A morphologic phase boundary at 50% $KNbO_3$, or $(K_{0.5}Na_{0.5})NbO_3$ (noted KNN), was observed to enhanced piezoelectric and ferroelectric properties [4]. At room temperature, KNN is a ferroelectric perovskite, with orthorhombic crystalline structure. As previous authors pointed out [5], the improvement of the piezoelectric properties can be achieved by the shifting of orthorhombic to tetragonal polymorphic phase transitions (PPT) to room temperature, or preparation of improved composition closed to an morphologic phase boundary (MPB) through chemical additions or doping.

The purpose of this work is to investigate the crystallographic phase transitions that may occur during doping with Samarium based perovskite, at a morphologic phase boundary of 50% $KNbO_3$. Also, the dielectric behavior of the piezoelectric ceramics will be evaluated in terms of frequencies.

Experimental

$(K_{0,5}Na_{0,5})NbO_3$ (noted KNN) and $(K_{0,5}Na_{0,5})NbO_3$ doped with 1 mol% $SmBO_3$ (where B= Al, Co, Cr, Fe, Mn) (noted KNN-$SmBO_3$) ceramics were obtained using the solid state method in air. The starting materials were K_2CO_3 (99%; Scharlau, Sentmenat, Spain), Na_2CO_3 (99%; Scharlau), Nb_2O_5 (99%, Merck, Darmstadt, Spain), Gd_2O_3 (99%; Fluka, Buchs, Switzerland). $SmBO_3$ powders were prepared in air at 1100ºC using the following reagents: Mn_2O_3 (), $AlN_3O_9•9H_2O$ (99%, Fluka, Buchs, Switzerland), $Co(NO_3)_2•6H_2O$ (99%; Scharlau),$Co(NO_3)_3•9H_2O$ (99%; Scharlau),$Co(NO_3)_3•9H_2O$ (99%, Fluka, Buchs, Switzerland). KNN-$SmBO_3$ were calcined at 850ºC for 6h, with a heating rate of 5 º/min. After calcinations and x-ray purity check, the powders obtained were grinded and mixed with a 5 mass% polyvinyl alcohol binder solution. Disk samples of 6 mm in diameter and approximately 1 mm thick were cold pressed at 200Mpa. The disks were sintered at 1050ºC for 6h. After grinding, the crystalline structure of the sintered samples was examined by x-ray

diffraction using a PanAnalytical X'Pert Pro MPD diffractometer. The refinement of the unit cell was performed using Treor algorithm in X'Pert HighScore Plus software. The variation of the dielectric constant at different frequencies was obtained using an Impedance/LRC meter TEGAM model 3550 (Geneva, OH, USA).

Results and discussion

Figure 1 shows the x-ray diffraction patterns of the obtained $SmBO_3$ (B= Al, Co, Cr, Fe, Mn) powders. All compositions obtained posses an orthorhombic crystalline structure at room temperature.

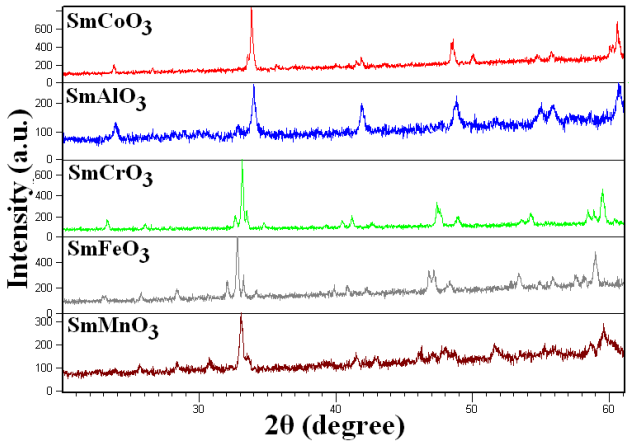
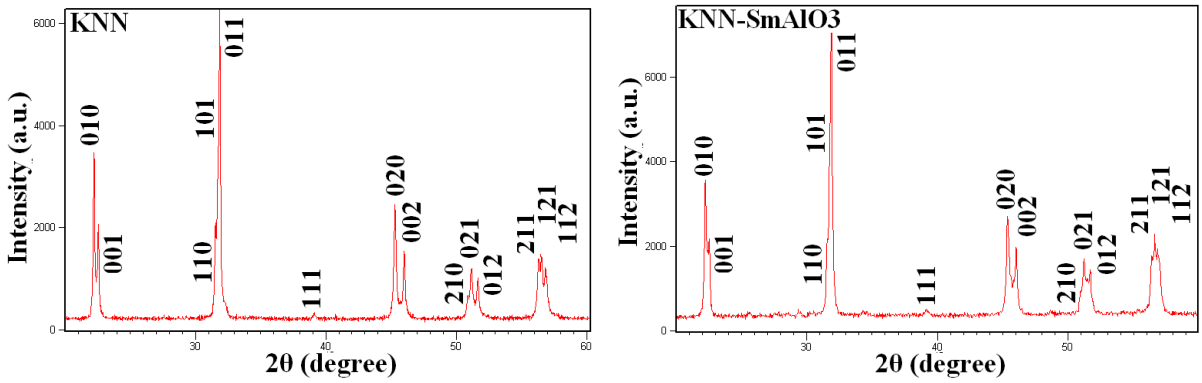


Figure 1. X-ray diffraction patterns of $SmBO_3$ (B= Al, Co, Cr, Fe, Mn) ceramics.

Figure 2 shows the X-ray diffraction pattern of the reference sample $(K_{0.5}Na_{0.5})NbO_3$, along with the X-ray diffractions patterns of KNN-$SmBO_3$ ceramic powders. The reference sample was indexed as pure perovskite using the JCPDS-ICDD file number 01-071-2171. The refinement of the unit cell revealed an orthorhombic crystalline structure (space group P2mm(25)) at room temperature, easily identified from the difference in peak intensity of the crystallographic plane splitting at [010]-[001], respectively [020]-[002]. Similar diffractions patterns were observed for KNN-$SmAlO_3$ and $SmCoO_3$. However, for the rest of the combination differences in the above mentioned crystallographic reflections were observed. The explanations of such observations are intimately related to the alteration of the unit cell parameters, as we can see below.



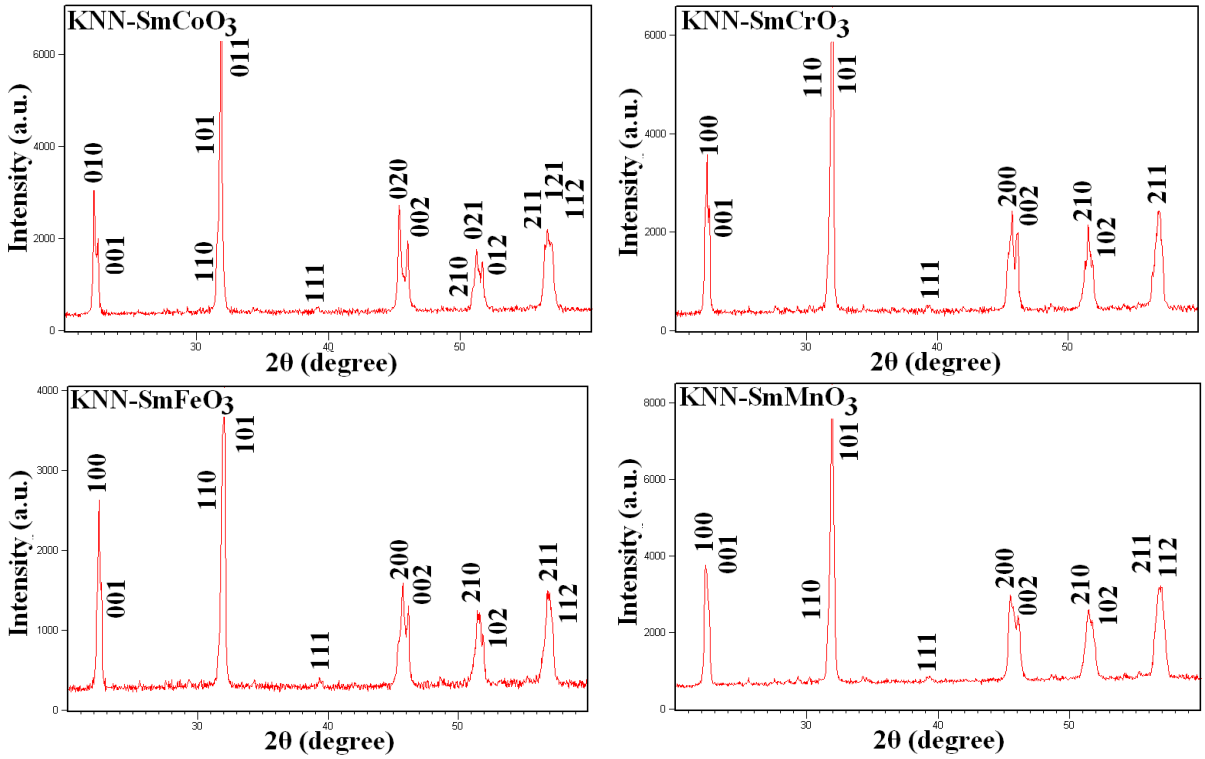


Figure 2. X-Ray diffractions of KNN, respectively KNN-$SmBO_3$ (B= Al, Co, Cr, Fe, Mn) sintered piezoelectric ceramics.

The results of the unit cell refinement are presented in figure 3. As a general observation, all dopants used decrease the values of a and b, and slightly alters the value of c. As a direct consequence, the unit cell volume decrease for all compositions studied, compared to the reference sample KNN. The refinement of the unit cell also revealed a shift from orthorhombic P2mm(25) crystalline structure for KNN-$SmAlO_3$ and KNN-$SmCoO_3$, to tetragonal P4mm(99) for the rest of the compositions, where a=b≠c.

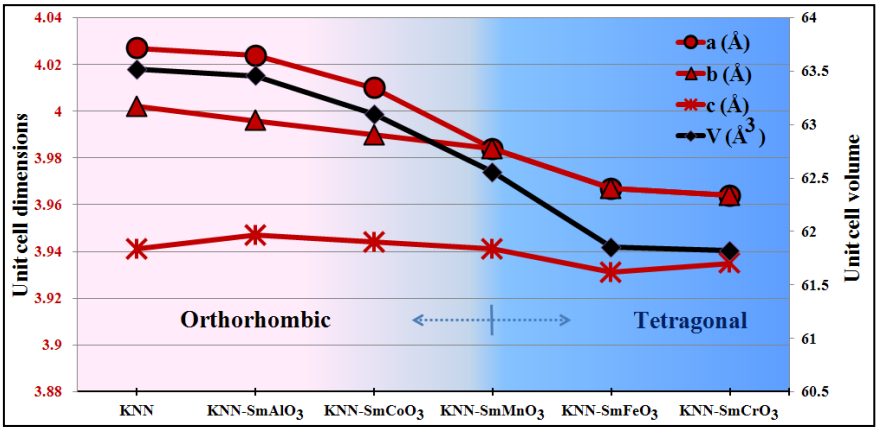


Figure 3. Unit cell dimensions of KNN and KNN-$SmBO_3$ (B= Al, Co, Cr, Fe, Mn) ceramics.

The dielectric constant of the studied materials was measured at six different frequencies and is presented in figure 4. Starting from a low dielectric constant at room temperature, of 213 (100 Hz) for the reference sample KNN, all composition studied improve

the real part of the electric permittivity significantly. At low frequency, the dielectric constant is higher, but as the frequency increases, all ceramics are affected by the dielectric relaxation, where epsilon tends to decrease. An outstanding increase of the dielectric constant was achieved for KNN-$SmCoO_3$ (1067 at 100 Hz) and KNN-$SmMnO_3$ (1115 at 100 Hz). Since the dielectric constant is intimately related to the charge that can be stored in a piezoelectric capacitor, significant improvements of the piezoelectric materials are expected for these materials.

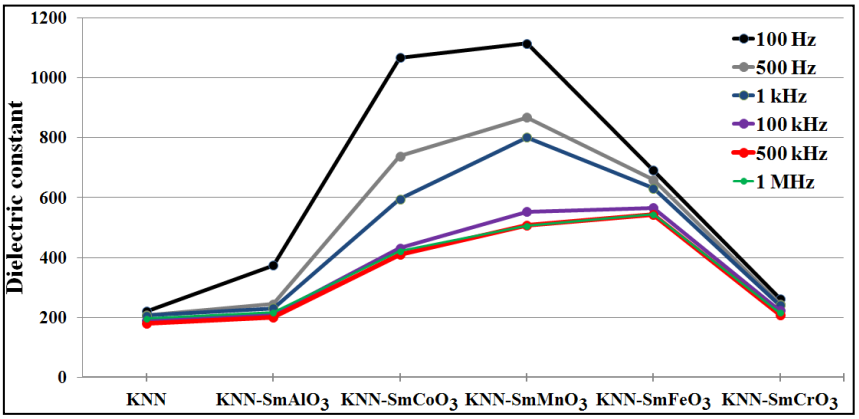


Figure 4. Variations of the dielectric constant at different frequencies for KNN and KNN-$SmBO_3$ (B= Al, Co, Cr, Fe, Mn) ceramics.

Conclusion

KNN and KNN-$SmBO_3$ (B= Al, Co, Cr, Fe, Mn) ceramics were successfully obtained by solid state method. The crystalline structure remain orthorhombic P2mm(25) for KNN-$SmAlO_3$ and KNN-$SmCoO_3$, and is shifted to tetragonal P4mm(99) for KNN-$SmMnO_3$, KNN-$SmFeO_3$ and KNN-$SmCrO_3$. For all compositions studied the unit cell volume decrease compared to the reference KNN. The variation of the dielectric constant at different frequencies revealed a significant increase of almost one order of magnitude for KNN-$SmCoO_3$ and KNN-$SmMnO_3$, suggesting these materials as candidates for improved lead-free piezoelectric application.

Acknowledgements

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