

Ferroelectric response of $\text{Na}_{0.9}\text{Li}_{0.1}\text{NbO}_3$ at room temperature

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Abstract. Polycrystalline samples of the dielectric, ferroelectric $\text{Na}_{0.9}\text{Li}_{0.1}\text{NbO}_3$ were synthesized by means of solid-state reaction using different ramps of temperature. High purity precursors Nb_2O_5 , Na_2CO_3 and Li_2CO_3 were stoichiometrically mixed and heated at 1373 K for 6 hours in air atmosphere. The $\text{Na}_{0.9}\text{Li}_{0.1}\text{NbO}_3$ samples were characterized by means of diffraction of X-rays using a Panalytical X'Pert Pro diffractometer. The obtained diffractograms were refined by Rietveld procedure using the software Maud. The results show that $\text{Na}_{0.9}\text{Li}_{0.1}\text{NbO}_3$ crystallizes in an orthorhombic structure (space group *Pbma*). The refined diffraction patterns also suggest a possible replacement of the Na ions by Li ions in the parent, ferroelectric NaNbO_3 compound. For electrical characterization of the samples, electrical polarization curves were measured using a Radiant Technologies RT66A test system for ferroelectric materials. The polarization versus applied electrical dependence shows a hysteretic behavior verifying the ferroelectric character of the material. A maxima polarization of $130 \mu\text{C}/\text{m}^2$ is obtained at room temperature.

Keywords: Niobates; Solid state reaction; Perovskites; Polarization; Ferroelectricity.

1. Introduction

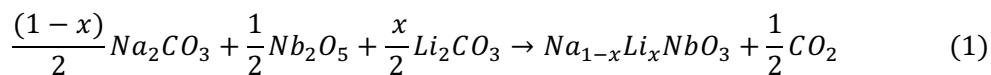
Up to 2003, the most popular piezoelectric material was the PZT ($\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$). Nevertheless, this material was restricted in the European Union because the lead content, which is a dangerous substance for the health and environment [1,2,3]. The discovery of very promising piezoelectric properties in perovskite-type solid solutions of $(\text{K}, \text{Na})(\text{Nb}, \text{Ta})\text{O}_3$ has enabled the development of technologically important lead-free piezoelectric materials and stimulated renewed scientific interest in other members of these solutions, particularly NaNbO_3 (NNO) [4]. A direct mixture of NNO and LiNbO_3 generates the interesting material $\text{Na}_{1-x}\text{Li}_x\text{NbO}_3$ (NLN). NLN is considered as an advanced ferroelectric ceramic for high frequency applications [5,6]. Intensive studies on alkaline niobates-based new dielectric materials have been carried out by many groups around the world in order to obtain suitable materials for high



performance applications. Although NNO is ferroelectric only around 163 K, the NLN system has been found to be ferroelectric at room temperature for doping levels $x \geq 0.02$ [7,8]. On the other hand, recent studies have shown that lithium niobate (LiNbO_3) is a very important material for optical storage, electric wave guides, amplitude modulators, second harmonic generators and acoustic wave transducers applications. The structure and electrical properties of the crystalline LiNbO_3 are different from those of NNO. At room temperature, LiNbO_3 is ferroelectric and NNO anti-ferroelectric with orthorhombic distorted perovskite-type structure. Furthermore, whereas NNO undergo successive phase transitions from low temperatures through high temperatures (10–1500 K), LiNbO_3 remains in the same state until 1523 K [9]. The aim of the present work is basically the study of the effect of doping with Li ions on the electrical properties of the NaNbO_3 compound in bulk at room temperature.

2. Experimental

Polycrystalline samples of NLN were synthesized by standard solid-state reaction. High purity reactants of Nb_2O_5 , Na_2CO_3 and Li_2CO_3 were stoichiometrically mixed and thoroughly grinded in an agate mortar. The resulting powder was slowly heated up to 1323 K for 2 h at a rate 3°C/min in air atmosphere, and then cooled to room temperature. The total reaction involved in the procedure can be written as [9]



The powders were pressed in form of pellets (6 mm in diameter and thickness ~ 1 mm) using pressures as high as 100 bar. The resulting pellets were slowly heated in air ($\sim 5^\circ \text{C/min}$) up to 1373 K and then sintered there for 6 h. When the process was completed, the samples were cool down to room temperature in the furnace. The crystal structure of the pellets was analyzed by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in a standard θ – 2θ configuration. Crystallographic parameters were obtained through Rietveld refinement using the software Maud. For electrical characterization of the samples, electrical polarization curves were measured using a Radiant polarimeter for ferroelectric materials. A standard bipolar wave with period of 10 ms was applied to cylindrical pellets of 6 mm in diameter and thicknesses of about 1 mm. These pellets were placed between copper electrodes simulating a parallel plate capacitor.

3. Analysis and results

XRD patterns of the polycrystalline $\text{Na}_{1-x}\text{Li}_x\text{NbO}_3$ ($x=0$ and 0.1) samples were recorded at room temperature (Figure 1(a)). The diffraction patterns were simulated by the Rietveld method with the Maud software (crystallographic card 0018684) [10]. The theoretical fit of the XRD data for the doped sample is also presented in Figure 1(b). The results of this procedure indicated that the sintered ceramic samples have an orthorhombic crystal structure (space group *Pbma*) with lattice parameters $a = 5.5655 \text{ \AA}$, $b = 5.5039 \text{ \AA}$ and $c = 15.5131 \text{ \AA}$. These values resulted to be smaller than those reported for the undoped sample [11]. This result suggests a successful replacement of Na ions by Li ions in the structure of the parent compound [12]. Certainly, the XRD peaks of the doped sample ($x=0.1$) are shifted to the right side as compared to those of the NNO compound (see inset of Figure 1(a)). The shift of the peaks to higher angles suggest that the interplane distances decrease. Indeed, the presence of smaller Li ions generates relaxation of the oxygen ions surrounding it, which, in turn, leads to tilting of the oxygen octahedra. Although the XRD patterns show only an additional peaks stemming from impurities, it is known XRD, being a bulk analytical technique, would hardly detect small molar concentrations of

impurities. As a fact of matter, the niobates are pretty difficult to prepare. During the synthesis, the phase NaNb_3O_8 may form easily. Certainly, the peak detected in the XRD spectrum seems to be originated by NaNb_3O_8 (<4%) [13]. Nevertheless, this secondary phase is not ferroelectric at room temperature.

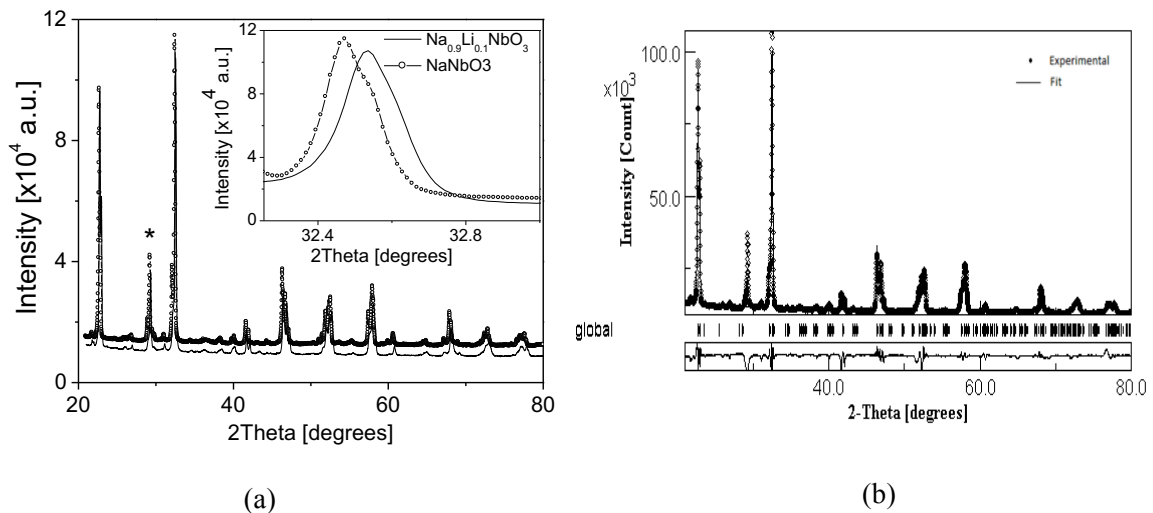


Figure 1. (a) X-ray powder diffraction patterns of polycrystalline $\text{Na}_{1-x}\text{Li}_x\text{NbO}_3$ ($x=0$ and 0.1) samples synthesized by standard solid state reaction. Inset: XRD diffractograms plotted on an enlarged scale around the main peaks. Here, the symbol (*) represents the secondary phase denoted by NaNb_3O_8 (b) Rietveld refinement for the sample with $x=0.1$.

Measurements of polarization as a function of the applied electric field (Figure 2) on undoped and Li-doped samples evidence a hysteretic feature, which is the characteristic of the ferroelectric materials. The ferroelectric behavior of the materials are clearly observed at different voltages. Although the values of the electrical polarization of $\text{Na}_{0.9}\text{Li}_{0.1}\text{NbO}_3$ are certainly too small for technical applications, the results suggest that enhancement of the electrical properties of NNO is possible upon Li doping.

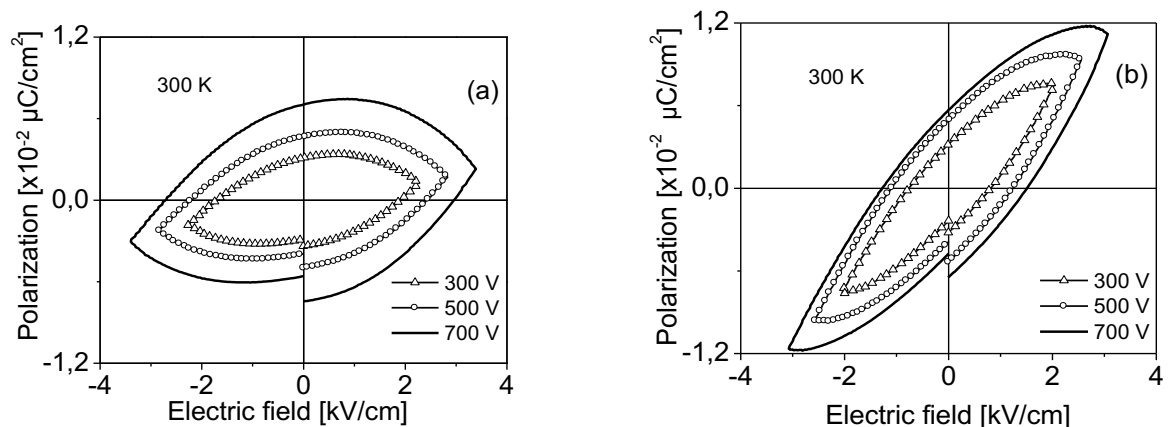


Figure 2. (a) Polarization as a function of the electric field for NaNbO_3 and (b) $\text{Na}_{0.9}\text{Li}_{0.1}\text{NbO}_3$ at various voltages.

Conclusions

Polycrystalline $\text{Na}_{0.9}\text{Li}_{0.1}\text{NbO}_3$ samples were successfully synthesized by standard solid-state reaction. This synthesis method allows to this material with orthorhombic structure. The replacement of the Na ions by Li ions was verified by XRD measurements. Low concentration of impurities was also confirmed by this technique. Electric polarization measurements at room temperature showed ferroelectric behavior of the compound. The results are encouraging in the sense that $\text{Na}_{0.9}\text{Li}_{0.1}\text{NbO}_3$ could represent a new class of ferroelectric materials working at room temperature.

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