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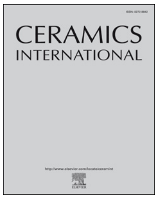

Room temperature multiferroic behavior and magnetoelectric coupling in (K,Na)NbO_3-based ceramics

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ABSTRACT

Polycrystalline $(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}(Nb_{0.95}Sb_{0.05})_{1-x}Fe_xO_3$ ($0 \le x \le 0.030$) ceramics are synthesized by the conventional solid state reaction method. The samples with $0.010 \le x \le 0.030$ are found to possess good ferroelectricity, weak ferromagnetism and large magnetodielectric effect simultaneously at room temperature. Temperature dependence of magnetization and dielectric properties show that there are both magnetic and magnetodielectric anomalies in the vicinity of the ferroelectric rhombohedral-orthorhombic ($T_{\text{R-O}}$) and orthorhombic-tetragonal ($T_{\text{O-T}}$) phase transition temperatures. Furthermore, magnetodielectric effect as large as 16% is observed at 0.9 T near $T_{\text{R-O}}$ when $x = 0.030$. According to these results, a strong spin-lattice coupling is considered to exist in these samples. In the structure transition process, the spin interactions between Fe ions will alter for the severe distortion of the FeO_6 octahedron. Moreover, since there are more possible polarization vectors due to polymorphic phase transition (PPT), the local polarization of FeO_6 will also be greatly affected when the external magnetic field changes the spin interactions.

1. Introduction

Multiferroic materials are of crucial importance in the design of novel functional devices due to the combination of at least two ferroic orders (magnetic, electric, or elastic) and the coupling between ferroelectricity and ferromagnetism [1–6]. Nevertheless, it is still often desirable to utilize single-phase magnetoelectric multiferroic for specific applications and device geometries, such as quantum magnetoelectric effect modulation [4,7].

Large number of complex perovskites are synthesized with general formula A(B′B″)O_3 where B′ and B″ are magnetic (Fe, Ni, Co, Mn, etc.) and non-magnetic (Nb, Ta, W, etc.) transition metal elements, respectively, with a view to obtaining compounds in which magnetic and ferroelectric orders coexist, and even magnetoelectric (ME) coupling presents [8–11]. Pb($Fe_{1/2}Nb_{1/2}$) was discovered as one of the first few ME multiferroic materials, with ferroelectricity in this system caused by the relative displacement between oxygen and Fe/Nb, and the weak ferromagnetism attributed to the super-exchange interactions taking palace via -Fe-O-Nb-O-Fe- pathways originated from local short-range chemical ordering of Fe^{3+} and Nb^{5+} ions in the alternate perovskite cell on the nanoscale [9,12]. Similarly, the ferromagnetic order in double perovskite $La_3Ni_2NbO_9$ and $La_3Co_2SbO_9$ was dominated by the $Co^{2+}(Ni^{2+})$-O-$Sb^{5+}(Nb^{5+})$-O-$Co^{2+}(Ni^{2+})$ super exchange interaction [13].

The above mentioned works reported the realization of weak coupling between ferromagnetism and ferroelectricity under low temperature, which opens up a new way to achieve possible coexistence of ferroelectricity and ferromagnetism with a significant ME coupling at room temperature. Recently, Claridge et al. [5,6] produced a new morphotropic phase boundary (MPB) in single-phase bulk perovskite $(1\text{-}x)BiTi_{(1\text{-}y)/2}Fe_yMg_{(1\text{-}y)/2}O_3–xCaTiO_3$, where $0.075 \le x < 0.175$, $y = 0.25$. In addition to the large switchable polarization afforded by MPB, the x and y can also be adjusted to generate ferromagnetic order and to display strong ME coupling. Although this compound possess lower Néel temperature (~ 340 K) and larger switching field (~ 120 kV cm^{-1}), the strategy of it allow the generation of a range of tunable multiferroic materials. Currently, Li, Sb and/or Ta modified sodium potassium niobate (KNN) has attracted much attention because of its very high Curie temperature (> 600 K), good ferroelectric properties and large piezoelectric response [14]. Its excellent properties are believed to originate from the diffused polymorphic phase transition (PPT) in a wide temperature range resembling the principle characteristics of MPB, which is comparable with lead zirconate titanate (PZT). In the case of $(K_{0.52}Na_{0.48})_{(1\text{-}x)}Li_xNb_{(1\text{-}x)}Sb_xO_3$ (KNLNS) ceramics,

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the sample with $x \sim 0.05$ shows more possible polarization orientations and improves piezoelectric properties at room temperature by forming a PPT [15]. Meanwhile, the introduction of slight Fe (~ 0.3%) at B site can effectively increase its piezoelectric properties and electric fatigue behavior, but its magnetic property is hardly considered [16]. In this work, $(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}(Nb_{0.95}Sb_{0.05})_{1-x}Fe_xO_3$ (KNLNSF) ceramics are fabricated by introducing Fe on B site (Nb-site) of KNLNS, and the coexistence of ferroelectricity and weak ferromagnetism at room temperature is realized. Additionally, the magnetoelectric coupling is also observed.

2. Material and methods

A series of polycrystalline $(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}(Nb_{0.95}Sb_{0.05})_{1-x}Fe_xO_3$ ($0 \leq x \leq 0.035$, abbreviated as KNLNSF) ceramics were synthesized by the conventional solid state reaction method with the raw materials of high purity Na_2CO_3 (99%), Li_2CO_3 (99.99%), K_2CO_3 (99%), Nb_2O_5 (99.99%), Sb_2O_3 (99.5%) and Fe_2O_3 (99.99%). Appropriate percentage mixtures of these starting reagents were mixed thoroughly in alcohol using agate ball for 24 h. The ground and well mixed powders were preheated at 850 °C for 6 h, then again milled for 24 h, pressed into pellets of 20 mm diameter and 1.3 mm thickness. Sintering was carried out at 1040–1080 °C for 3 h for all the compositions. Platinum electrodes were sputtered on both sides of the samples for electrical measurements.

Ceramic phase assemblage was examined by X-ray powder diffraction (XRD, D8, Bruker, Germany) with Cu Kα radiation. Scanning electron microscopy (SEM, Quanta200, FEI, Holland) and Raman scattering spectra (T64000, Jobin Yvon, France) were used for analyzing the microstructure of the samples. The ferroelectric hysteresis loops were measured using a TF2000 standard ferroelectric test unit (TF-2000, aix-ACCT, Aachen, Germany). Weak-field dielectric responses were measured with a computer controlled precision LCR Impedance Analyzer (4294A, Agilent Santa Clara, CA). The magnetic properties were characterized using a quantum design superconducting quantum interference device (SQUID, MPMS XL, Quantum Design, USA).

3. Results and discussion

Fig. 1a shows the SEM surface morphologies for KNLNSF ($0 \leq x \leq 0.035$) ceramics. No obvious variation of grain size was observed for all samples. Room temperature (RT) XRD patterns (Fig. 1b) reveal that the samples with $x \leq 0.030$ exhibit a pure perovskite structure. In general, the phase structure of KNN-based ceramics can be quantified by assessing the relative intensities of (002) and (200) peaks (Fig. 1c) [17,18]. For the orthorhombic phase, this ratio (I_{002}/I_{200}) is about 2:1, while it is reciprocal for a tetragonal phase. With x increases from 0 to 0.020, the ceramics experience a tetragonal perovskite structure ($x = 0$), a coexistent state of tetragonal and orthorhombic phases ($x = 0.010$), and a dominated orthorhombic phase ($x = 0.020$), which is accompanied by the diffraction peaks moving to higher angles and the characteristic orthorhombic splitting (002, 200, 020) becoming more and more clear [15,19]. The Rietveld refinement of the powder X-ray diffraction data for $x = 0.010$ confirmed the coexistent of two-phases (Fig. S1). With further increasing Fe content, the structure remains at orthorhombic, however, the peak position changes slightly. Compared with the sample of $x = 0.020$, the diffraction peaks shift towards lower angles as x increases from 0.020 to 0.030 due to the larger radius of Fe^{3+} (0.645 Å) and Fe^{2+} (0.780 Å) than that of Nb^{5+} (0.640 Å) and Sb^{5+} (0.600 Å). While this tendency is alleviated when $x = 0.035$, indicating that excess Fe ions are segregated into the $LiFe_5O_8$ second phase and the actual substitution of Fe at Nb-site does not increase further. Thus in the discussions hereafter, we will not refer to $x = 0.035$ samples anymore.

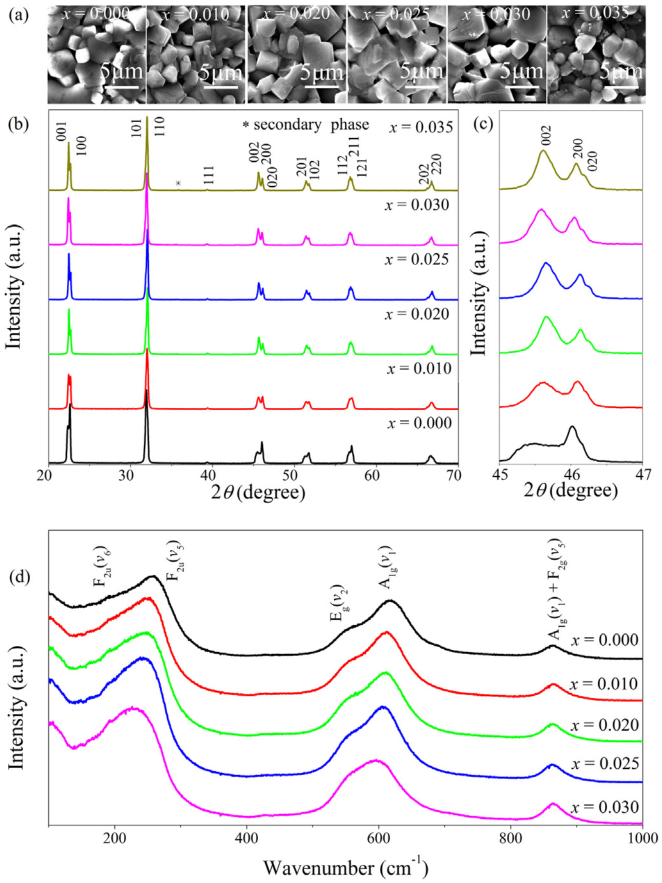

Fig. 1. (a) SEM surface photographs of KNLNSF ceramics. (b) XRD patterns of the ceramics with different Fe contents. * denotes $LiFe_5O_8$ second phase. (c) The enlarged (002) and (200) peaks. (d) Raman scattering spectra of KNLNSF ceramics.

Raman scattering is known to be very sensitive to nonuniform distortions of the crystal lattice in short-range ordering, and can be used to further examine the influences of the Fe content on the KNLNSF ($0 \leq x \leq 0.030$) lattice. According to the literatures [20,21], Raman spectrum in Fig. 1d can be decomposed into five vibrational modes: $A_{1g}(\nu_1)$ (~ 615 cm^{-1}) and $E_g(\nu_2)$ (~ 555 cm^{-1}) are associated with O–Nb–O bond stretching modes, while $F_{2u}(\nu_6)$ (~ 200 cm^{-1}), $F_{2g}(\nu_5)$ (~ 260 cm^{-1}) and $A_{1g}(\nu_1) + F_{2g}(\nu_5)$ (~ 860 cm^{-1}) are related to O-Nb-O bending modes. These peaks can all be attributed to the internal modes of the NbO_6 octahedron, but no vibrational mode born of Fe oxide. With x increasing from 0 to 0.030, both ν_5 and ν_1 slightly shift to lower wave numbers. Since the substitution of larger Fe ions for B-sites may give rise to the distortion of the crystal lattice, which contains the variation of both the O-Nb-O angles and the distance between Nb^{5+}/Sb^{5+} and its coordinated oxygens, the force constant and the binding strength of [BO_6] would be weaker.

Polarization versus electrical field (*P-E*) hysteresis loops of KNLNSF ($0 \leq x \leq 0.030$) ceramics, measured at room temperature under an applied electric field of 50 kV cm^{-1} and 100 Hz, are presented in Fig. 2a, and the inset gives the corresponding remnant polarization $2P_r$ and coercive field E_c. All the samples exhibit typical *P-E* loops and good ferroelectricity. Compared with the $x = 0$ sample ($2P_r \sim 66.4$ μC cm^{-2}, $E_c \sim 14.9$ kV cm^{-1}), the $x = 0.010$ sample exhibits a slightly smaller $2P_r$ (~ 65.1 μC cm^{-2}) and E_c (~ 14.1 kV cm^{-1}). As the Fe content goes on increasing, the remnant polarization and coercive field decrease greatly, which, on one hand, is possibly due to the decrease of off-center shift in [BO_6] octahedron caused by the partial occupation of Fe ions at the Nb-sites [22], and might be related to the transform from the coexistence of tetragonal and orthorhombic phase to the single