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Crystal structure and orthorhombic–tetragonal phase transition of nanoscale $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$

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Abstract

Lead-free nano $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ powders, with pure perovskite structure and various grain sizes between about 30 and 60 nm, have been successfully synthesized by a novel sol–gel method, in which Nb_2O_5 was used as the Nb source. The refining XRD and Raman spectra were used in combination with TEM to investigate the evolution of lattice structure and phase transformation behavior as a function of grain size. The results demonstrated that the growth process of grains has been divided into two stages, and the distortion of unit cell apparently decreases with decreasing grain size. At around 35 nm, the phase structure of $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ changed from orthorhombic to tetragonal. This phenomenon is related to a grain size-induced structural phase transition. For the well accepted wisdom that niobates get super piezoelectric properties in orthorhombic–tetragonal transition region, our results suggested a critical size for the application of $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ in nano piezoelectric devices.

Keywords: Sol–gel processes; Niobates; Nanocomposites; Grain size; Orthorhombic–tetragonal phase transition

1. Introduction

(Na, K)NbO_3 (NKN) based ceramics have attracted much attention recently as they represent an environmentally friendly alternative to compositions based on heavy metals, such as Pb(Zr,Ti)O_3 (PZT). It is believed that in PZT ceramics, morphotropic phase boundary (MPB), which is nearly vertical in the temperature-composition phase diagram,[1,2] plays a very important role because piezoelectric and dielectric properties show a maximum around the MPB. However, the so-called MPB in NKN based ceramics is very different from that in PZT based ceramics. It is actually an orthorhombic–tetragonal (O–T) polymorphic phase transition (PPT) and shows strong temperature dependence.[3] Generally, the large number of thermodynamically equivalent states near the PPT allows a high degree of alignment of ferroelectric dipoles, which result in a dramatic enhancement in the electrical properties of NKN based ceramic. For the reason that PPT is temperature dependent, many recent studies concern about designing different composites to turn the O–T phase transition from about 200 °C to room temperature.[4,5] Of all the NKN based ceramics, $(Li_{0.06}Na_{0.47}K_{0.47})NbO_3$ (LNKN) is one of the most intensively studied system due to the PPT structure near room temperature. The LNKN ceramics show the large piezoelectric constant d_{33} over 200 pC/N, and are considered as a new generation materials for lead-free piezoelectric devices.[6–8] On the other hand, continuous advances in microelectronics are leading to the miniaturization of piezoelectric components; therefore, the fundamental investigation of properties of nanoscale LNKN become very important due to their potential application in nanoscale devices and a known difference in behavior relative their bulk counterparts. It is well known that the crystal symmetry increases with decreasing grain sizes.[9,10] This phenomenon, which is called "size effect", could cause problems for future miniaturization of piezoelectric components, and size effect on many systems, such as $BaTiO_3$, $(Pb_{0.9}La_{0.1})TiO_3$, and so on, has been intensively studied.[11–13] It is to say, except chemistry composite, grain size could also influence the O–T phase transition of NKN based materials, and which is rarely studied. Therefore, the research of size effect on nanoscale LNKN is one of the

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most important assignments from the scientific and industrial viewpoints.

Sol–gel process has attracted much attention in materials synthesis due to the ease of tuning material composition through the use of molecular precursors. The metal organic complexes mix and react on a molecular-scale favoring a homogeneous product composition.[14–16] Moreover, powders with different grain size could be facilely prepared by the sol–gel process using different calcination temperatures, which favored to the study of size effect of ferroelectric powders. In this study, a newly developed sol–gel route has been used to prepare LNKN nanoscale system. The growth process of nanoscale LNKN and grain size-induced O–T phase transition have been studied, and the mechanism of grain size-induced structural phase transformation has been discussed.

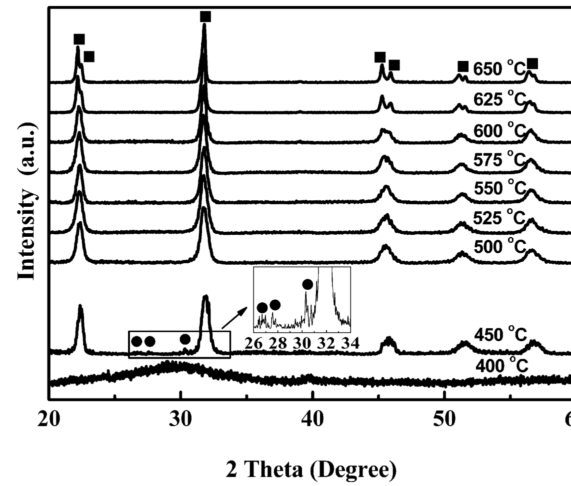

Fig. 1. XRD patterns of LNKN gel powders annealed at various temperatures: ■, perovskite; ●, impurity phases.

2. Experimental

Nb_2O_5 (99.9%), KOH (97%), Li_2CO_3 (97%), Na_2CO_3 (99.8%), K_2CO_3 (99%), acetic acid (CH_3COOH, 99.5%), oxalic acid ($(COOH)_2\cdot 2H_2O$, 99.5%), citric acid ($C_6H_8O_7\cdot H_2O$, 99.5%), HNO_3 (65.0–68.0%), and $NH_3\cdot H_2O$ (25.0–28.0%) were used as raw materials. The LNKN gels were synthesized by a novel sol–gel method,[17] in which Nb_2O_5 was changed into a water-soluble species through the chemical chelation as the Nb source. In order to obtain nano powders with different grain sizes, the calcination temperatures of gels were precisely controlled from 400 to 650 °C.

The crystal phase of the powders was determined using X-ray diffractometry (XRD; Model D8 Advance, Bruker AXS, Karlsruhe, Germany) in θ–2θ mode with graphite monochromatized Cu Kα radiation ($\lambda = 0.154178$ nm). The scan step was 0.005° and the scan speed was 0.3 s/step in the ranges of 20°–60°. The average grain size was calculated from the full width at half maximum (FWHM) of the diffraction lines by using Topas 2P software according to Scherrer's relation[18]:

$$d = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where d is the grain diameter, λ the X-ray wavelength, θ the diffraction angle, B the FWHM of the diffraction peak, and K the Scherrer constant. In addition, the microstrain of the particles was also refined by using Topas 2P software. To reduce errors, all diffraction peaks between 20° and 60° were used to calculate the average grain size and microstrain. The powder morphology was observed by a transmission electron microscopy (TEM; Model JEM-2000 F, JEOL, Tokyo, Japan). Raman scattering spectra of powders were recorded at room temperature from a Raman spectrometer (Model T64000, Jobin-Yvon, Paris, France) under backscattering geometry. Excitation was taken as the 488 nm line of Ar^+ laser with 50 mW output power.

3. Results and discussion

It has been reported in many papers, that the observed O–T PPT seem to be inherited from the $KNbO_3$ system.[3,19,20] The effect of $LiNbO_3$ doping shifts the phase transition temperatures without altering the order of polymorphic transitions.[21] So, like $KNbO_3$ powders, the size effect on nanoscale LNKN powders would show a phase transition rather than a relative contents change of *orthorhombic and tetragonal* phase.

The crystallization process of the LNKN gels annealed at various temperatures was monitored, as shown in Fig. 1. The powders calcinated below 400 °C exhibit the typical amorphous pattern, showing a broad peak around 30°. When the annealing temperature reaches 450 °C, the characteristic diffraction peaks of LNKN crystals begin to appear. However, there still exist some impurity phases, as marked with "●". With further increasing temperature to 500 °C and above, only pure LNKN perovskite phase can be observed and there was no evidence of second phase.

It is well known that both the small grain size and microstrain can cause the distinct broadening of diffraction lines. According to this, based on Eq. (1), the average grain size of LNKN powder with different annealing temperature was refined using Topas 2P software, and the results and errors are shown in Fig. 2. The inset in Fig. 2 shows the variation of microstrain with dif-

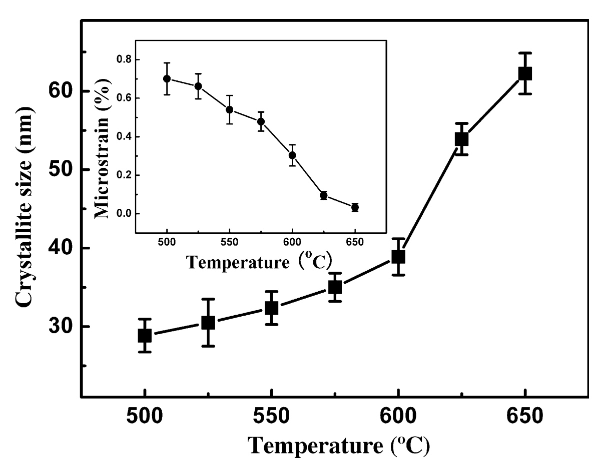

Fig. 2. Variation of the grain size with the annealing temperature. Inset: variation of the microstrain with the annealing temperature.