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Phase transitional behavior of potassium sodium niobate thin films[☆]

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ABSTRACT

Combined X-Ray Diffraction (XRD) and Raman analyses were used to investigate the phase transitions of potassium sodium niobate $(K_{0.5}Na_{0.5})NbO_3$ thin films, prepared from the acetate–alkoxide based precursor solutions with different amounts of alkali acetate excess. Depending on the amount of sodium or potassium excess in the solutions, the microstructures of the about 240 nm thick films on platinized silicon substrates consisted of columnar grains with the width of about 200 nm or of equiaxed grains with the average size of about 50 nm. Raman spectra and XRD patterns provided evidence of both monoclinic to tetragonal ($T_{M–T}$) and tetragonal to cubic ($T_{T–C}$) phase transitions in the films with different microstructures, similar as in the $(K_{0.5}Na_{0.5})NbO_3$ powder. In the films with columnar grains, the Curie temperature was decreased as compared to the value reported for the powder, which was connected to the presence of tensile stresses arising from the thermal expansion mismatch between the substrate and the film, while the $T_{M–T}$ in the films closely corresponded to the powder value which was related to the evolution of a pronounced b-axis orientation. Furthermore, the exact values of the $T_{T–C}$ depended on the chemical composition of the films which was also reflected in different sizes of respective unit cells. In the films with fine grains, the phase transitions had a diffuse character, but they were nevertheless also evidenced by dielectric spectroscopy.

1. Introduction

The requirements for miniaturization of micromechanic and microelectronic components have increased the demand for processing of piezoelectric materials of dimensions in the nanometer range. Downscaling gives rise to new physical phenomena and properties which greatly differ from those of homogeneous bulk materials of the same composition and need to be understood in order to develop ferroelectric and piezoelectric devices [1,2].

Shifts of phase transition temperatures, decreasing and broadening of dielectric permittivity peaks, or disappearence of a polar phase below the critical size (in the range from a few nanometers to a few tens of nanometers) [3,4] have been reported in materials with submicrometer grain sizes, as compared to micron range. Such changes were attributed to the increasing contribution of the grain boundary regions, with different structural properties caused by the surface relaxation, whose volume fractions increase as the grain sizes decrease [4–9].

Frey at al. found that dense $BaTiO_3$ (BT) ceramics with different average grain sizes (from 1700 nm to 70 nm) undergo tetragonal to cubic phase transitions at the same temperature, namely at ~405 K [5]. In contrast, another group reported the temperature shift of T_{max} from 398 K to 363 K in dense BT ceramic, as the average grain size decreased from 1200 nm to 50 nm, respectively [6].

Raman spectroscopy has been found particulary useful for probing the phase transition behaviour of nanostructured materials as in the case of about 50 nm large grain sized dense BT ceramics [10,11]. In addition to the grain size effect, the phase transition behavior in thin films deposited on the substrate may be influenced by compressive or tensile stresses due to clamping with the substrate, thickness and the type of microstructure (columnar/granular) [9,12–17].

$(K_xNa_{1-x})NbO_3$ is considered as a promising class of lead free piezoelectric materials [18] and it is a solid solution of ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$ with the best dielectric and piezoelectric properties near $x = 0.5$. The sequence of phase transitions in $(K_{0.5}Na_{0.5})NbO_3$ or KNN ceramics follows the pattern of many perovskite type ferroelectrics: it goes from the low temperature rhombohedral to monoclinic or orthorhombic phase (assuming a simple perovskite unit cell [19,20]) (further denoted as $T_{R–M}$ or $T_{R–M/O}$), from monoclinic/orthorhombic to tetragonal phase (further denoted as $T_{M–T}$ or $T_{M/O–T}$) and from tetragonal to high-temperature cubic phase (further

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[☆] The article is dedicated to the initiator of this study, Prof. Marija Kosec, who passed away in December 2012.

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denoted as $T_{T\text{–}C}$) at the temperature $T_{R\text{–}M/O}$ ~ 120 K, $T_{M/O\text{–}T}$ ~ 470 K and $T_{T\text{–}C}$ ~ 680 K, respectively [18,20–24].

A combined X-ray powder diffraction and Raman spectroscopy study of KNN powders by microemulsion mediated synthesis demonstrated that coarse particles (>200 nm) had a monoclinic syngony while fine particles (<200 nm) were triclinic at room temperature [25]. Further investigations revealed, that the decrease in symmetry with decresing particle size could originate from the ordering of K^+ and Na^+ cations in the structure [26].

Shibata et al. investigated about 3 μm thick KNN films RF sputtered on platinized silicon substrate [27]. The films consisted of about 100–300 nm large grains. Tensile stresses developed in the film due to the thermal expansion mismatch between the substrate and the film. The temperature dependent dielectric permittivity showed a shoulder at 483 K and a maximum at 633 K and both temperatures of phase transitions were also confirmed by X-Ray Diffraction or XRD.

Lee et al. prepared about 650 nm thick KNN thin films from solutions with 10% excess of alkalis on (111) $Pt/TiO_2/SiO_2/Si$ or Pt/Si substrates. The temperature dependent dielectric permittivity evidenced the orthorhombic to tetragonal and the tetragonal to cubic phase transitions at 468 K and at 597 K, respectively [28].

We report the phase transitional behavior of about 240 nm thick solution-derived KNN thin films. In order to compensate the expected alkali losses, the films were prepared from solutions with different amounts of sodium or potassium acetate excess. After heating at 750 °C, the films, prepared from the solutions with 10 mole % or 5 mole % alkali excess consisted of columnar or fine, equiaxed grains, respectively. The energy dispersive X-ray spectroscopy or EDXS revealed that the chemical composition of the former films remained very close to the solution composition, and with the increased (Na + K)/Nb ratios (1.07 in both cases). In contrast, the films, prepared from the solutions with 5 mole % sodium or potassium excess, were both K-depleted, and had (Na + K)/Nb ratios very close to the stoichiometric value [29]. The films were studied by XRD, Raman spectroscopy and also by dielectric spectroscopy.

2. Experimental details

We deposited KNN thin films on Pt/Si substrates from the acetate-alkoxide based precursor solutions with 5 or 10 mole % of Na- or K-acetate in excess and these are further denoted as 5K-, 5Na-, 10K-, and 10Na-KNN films. The about 240 nm thick films were processed by repeated spin coating and pyrolysis at 300 °C, 2 min, followed by final annealing at 750 °C in synthetic air, for 5 minutes. The films were annealed in the rapid thermal annealing furnace (LPT, TM100-BT) with the heating rate of 12.5 K/s. The processing details are reported elsewhere [29].

Fig. 1 presents the XRD patterns of KNN thin films, obtained by X-ray powder diffractometer (PANalyticalX`Pert PRO MPD, Cu-$K_{\alpha1}$ radiation) in the 2Θ region from 10° to 37°. After annealing, the films crystallized in a pure perovskite phase with preferential {100} orientation. Splitting of the {h00} diffraction peaks at about ~22° 2Θ in the films, prepared from the 10 mole % alkali excess solutions indicated the monoclinic distortion of the unit cell. The asymmetric shape of the peaks in the 5K- and 5Na-KNN films indicated a decreased symmetry of the unit cell. The size of the crystalites, as determined by the Williamson-Hall plot, was about 50 nm in these films, while it was about 100 nm in the films prepared from the solutions with 10 mole % alkali excess [29].

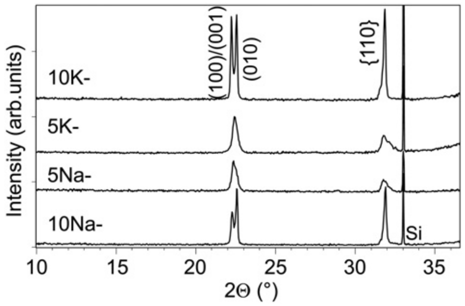

Fig. 1. XRD patterns of the films from solutions with different alkali excess solutions at room temperature. After [29].

Fig. 2 shows the surface microstructures of the films as obtained by scanning electron microscopy (FE-SEM: Jeol 7600f). The 10K- and 10Na-KNN films consisted of about 200 nm large grains, while the grains were much smaller (about 50 nm) in both films prepared from solutions with 5 mole % alkali excess.

The phase composition of the thin films was followed using a two axis X-Ray diffractometer in Bragg-Brentano geometry with the Cu-K_β radiation in the temperature range between 300 K and 750 K. The Cu-K_β radiation was chosen instead of the $CuK_{\alpha1}$ one because the intensity of the Bragg peaks is three times stronger (due to a more selective monochromator for $CuK_{\alpha1}$), allowing a more reasonable acquisition time for the temperature dependent measurements. The 2Θ angle ranges from 21° to 24° and from 31° to 33° were selected in order to follow the behavior of {100} and {110} family peaks. The 2Θ position, integral intensity and full width at half maximum (FWHM) of the XRD peaks at various temperatures were determined using the profile fitting software Labspec and the interplanar distances (d) of the unit cell were determined using the Bragg's law.

Raman measurements were performed using a LABRAM spectrometer in backscattering geometry with the 632.8 nm excitation line from a He-Ne laser focused to a spot of 2 μm diameter. We checked that the laser power did not produce significant heating or damage of the sample. The measurements were performed between 100 K and 700 K using a Linkam cell.

For dielectric characterization of the thin films with 5 mole % alkali excess, Cr/Au top electrodes were applied through a shadow mask by sputtering. The diameter of the electrodes was 0.4 mm. The temperature and frequency dependent dielectric properties of the films were measured upon heating from 300 K to 700 K and from 5 kHz to 100 kHz, in vacuum (HP 4284A LCR Meter) in a high temperature stage (MMR, K-20).

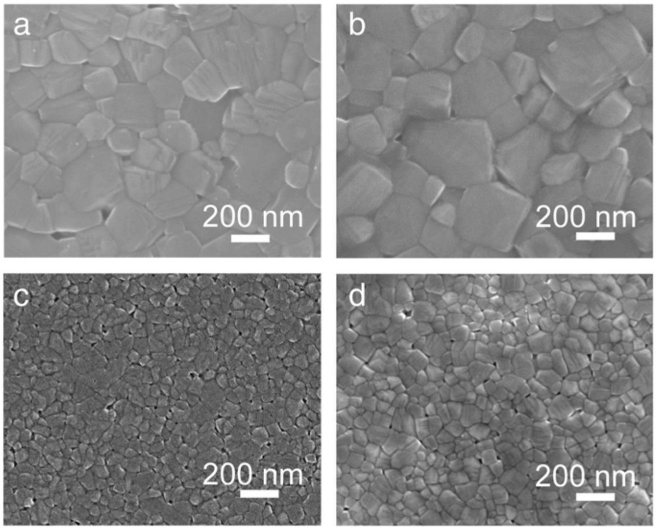

Fig. 2. Surface microstructures of the (a) 10K-, (b) 10Na-, (c) 5K- and (d) 5Na-KNN thin films. After [29].