Stable dielectric response in lead-free relaxor $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{--SrTiO}_3$ thin films

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$\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{--SrTiO}_3$ (KNN–STO) thin films of different compositions were prepared by the chemical solution deposition method. While structural investigations confirmed the formation of perovskite solid solution in all developed films, dielectric experiments revealed a relaxor broad dispersive maximum in the sample with 15 mol% of STO, exhibiting for a thin film high $\epsilon' \sim 330$ at ~ 210 K. The history-dependent effects of this relaxor sample were compared to those of KNN–STO ceramics and, furthermore, shown to be much weaker than in widely used lead-based ferroelectric and relaxor $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ ceramics: While fatigue endurance results revealed a slight drop in polarization after 3×10^5 switching cycles, the results of aging of the dielectric constant revealed no notable decrease in its values after 10^6 s.

Keywords: Lead-free ceramic thin films; relaxor ferroelectrics; electrical fatigue and aging.

1. Introduction

Relaxor ferroelectrics are very compelling for a variety of electronic applications due to high values of the dielectric constant and a high strain across a broad temperature range.¹ Their characteristic features, a broad frequency dispersion in the complex dielectric constant, slowing dynamics, and logarithmic polarization decay,^{2,3} are correlated with the cationic disorder in the same crystallographic site.^{4,5} Such behavior has been detected in lead-containing ternary compounds and solid solutions, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ (PLZT),² which are currently used in electronic applications, however, due to the toxicity of lead, these substances represent an ecological hazard. Concomitantly, recent research has been directed towards substituting these hazardous substances by safe materials, such as $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{--SrTiO}_3$ (KNN–STO) solid solution.

Over the last decade, structural⁶ and dielectric properties^{6–8} as well as history-dependent effects^{6,7} of KNN–STO ceramics were studied and characterized extensively. In KNN–STO thin films, recent research confirmed solid solubility in solution-derived KNN–STO thin films having thickness ~ 250 nm for the STO contents with $x \leq 0.25$.⁹ In order to further our knowledge and understanding the lead-free KNN–STO system, we performed structural and dielectric investigations, as well as studies of the history-dependent effects, of KNN and KNN–STO thin films.

2. Experimental Procedure

KNN–STO thin films with compositions $x = 0$ (KNN), $x = 0.075$ and $x = 0.15$ (x denotes the molar ratio of STO in KNN–STO) were prepared from stoichiometric solutions,⁹ using potassium acetate (99 + %, Sigma Aldrich), sodium acetate (99.5%, Fluka), strontium nitrate (99.97%, Alfa Aesar), niobium-pentaethoxide (99.99%, Starck), titanium-n-propoxide (99.98%, Alfa Aesar) and 2-methoxyethanol (99.3 + %, Alfa Aesar). The solutions were spin coated onto Pt(111)/TiO₂/SiO₂/Si (AixACCT) substrate and each deposited layer was pyrolyzed at 573 K for 2 min and each third layer was then annealed at 1023 K for 5 min in synthetic air with the heating rate of 10 K/s.⁹ Thin films were characterized by X-ray diffraction (XRD, PANalytical X'pert Pro diffractometer, CuK_{α1} radiation). The data were collected in the 2θ -range from 10° to 65°, with a step of 0.034° and an exposure time of 100 s per step. The phases of KNN and STO were identified using the data in Refs. 10 and 11, respectively, and the microstructures were analyzed by field emission scanning electron microscopy (FE-SEM, Supra 35 VP, Carl Zeiss). The average grain size was determined using linear analysis on the surface micrographs. Fatigue endurance of thin films was measured using aixACCT: TF Analyzer 2000.

Thin films with thickness of (i) 350 nm for $x = 0$ (KNN), (ii) 330 nm for $x = 0.075$, and (iii) 340 nm for $x = 0.15$, and with sputtered upper Cr/Au electrodes (0.4 mm diameter,

RF-magnetron sputtering, 5 Pascal) were used for dielectric measurements. The complex dielectric constant $\varepsilon^*(\nu, T) = \varepsilon' - i\varepsilon''$ was measured by Novocontrol Alpha High Resolution Dielectric Analyzer in a frequency range of 1 Hz–30 kHz and HP4284A Precision LCR Meter in a frequency range of 20 Hz–1 MHz. The real part of the complex ac conductivity $\sigma^* = \sigma' + i\sigma''$ was calculated via $\sigma' = 2\pi\nu\varepsilon_0\varepsilon''$, with ε_0 being the permittivity of free space. The amplitude of the probing ac electric signal was 50 mV. The data were obtained in the temperature range of 100–400 K during cooling runs with temperature change rate of $\Delta T/\Delta t = 0.92$ K/min. The temperature of the samples was stabilized within 10 mK using a lock-in bridge technique with a Pt100 resistor as a thermometer.

3. Results and Discussion

Figure 1 shows the XRD patterns of KNN and KNN–STO ceramic thin films, which reveal that upon heating the samples to 1023 K all films crystallized in a pure perovskite

Fig. 1. XRD spectra of KNN ($x = 0$) and KNN–STO thin films of different compositions.

phase.⁹ In the case of $x = 0$ (KNN), thin film crystallized with preferential $\{100\}$ orientation. Assuming a simple perovskite unit cell, the asymmetric shape of the $\{h00\}$ diffraction peaks indicate a monoclinic distortion of the unit cell, which is characteristic of KNN.¹⁰ In the cases of $x = 0.075$ and $x = 0.15$, the shapes of the $\{h00\}$ diffraction peaks are symmetric, the peak positions shift to higher 2θ values, and the relative intensities of the diffraction peaks and the degree of preferential orientation decrease upon the increasing values of x , i.e., the STO content.

The results of phase composition of KNN–STO thin films are in concurrence with previous work on the KNN–STO ceramics and thin films,^{6,9,12} which revealed a pseudo-cubic structure of the $x = 0.15$ – 0.25 ceramics⁶ and an increase of the symmetry of the unit cell upon increasing STO content, in the thin films.⁹ Upon increasing STO content, the decrease of the unit cell volume is connected to the incorporation of Sr or Ti on the site of K, Na, or Nb ions in the perovskite lattice^{6,12} and, furthermore, the decrease of the preferential $\{100\}$ orientation is linked to the differences between the average surface charges of the $\{100\}$ planes in both, KNN and STO.⁹

Microstructures of KNN and KNN–STO thin films are depicted in Fig. 2. KNN and KNN–STO thin films with $x = 0.075$ consist of grains of cuboidal shape. The grain size decreased from ~ 80 nm in KNN to ~ 50 nm in KNN–STO thin films with $x = 0.075$, i.e., the grain size decreases upon increasing STO content.⁹ In addition, fracture surface micrographs revealed equiaxed microstructures in all cases (not shown). In the case of KNN–STO thin films with $x = 0.15$ [Fig. 2(c)], small grains with less pronounced cuboidal morphology and a considerable amount of porosity can be seen. These results are in concurrence with results reported in

Fig. 2. Plane view of KNN and KNN–STO thin films of different compositions.

Fig. 3. Temperature dependence of the real part of the complex dielectric constant, ϵ' , measured at several frequencies in KNN (a) and KNN-STO thin films with $x = 0.075$ (b) and $x = 0.15$ (c). The inset to subfigure (c) shows the temperature dependence of the imaginary part of the complex dielectric constant, ϵ'' , of KNN-STO thin film with $x = 0.15$, confirming typical relaxor dielectric behavior depicted in the main frame.

previous work on KNN¹³ and KNN-STO⁹ thin films having thickness of ~ 250 nm.

Figure 3 shows the temperature dependence of the real part of the complex dielectric constant, ϵ' , measured at several frequencies in KNN and KNN-STO ceramic thin films of different compositions. In KNN ($x = 0$), the values of the dielectric constant increase upon increasing temperature due to the approximation of the monoclinic to tetragonal phase transition, which is located at ~ 420 K.¹⁴ Relaxor dielectric behavior was observed in KNN-STO thin films with $x = 0.15$ (see Fig. 3(c)). This was expected due to the pseudo-cubic structure of the material,^{6,7} which was evident from the XRD spectra (see Fig. 1). The KNN-STO solid solution is composed of monoclinic (assuming a simple perovskite unit cell)/orthorhombic ferroelectric KNN¹⁰ and cubic paraelectric

Fig. 4. Frequency dependence of the real part of the complex dielectric constant, ϵ' , and the real part of the complex conductivity, σ' , measured at several temperatures in KNN-STO thin films with $x = 0.075$ (a) and (b) and $x = 0.15$ (c) and (d). Solid lines are a guide for the eye.

STO¹¹ (Kosec *et al.*⁶ found that the $(1-x)$ KNN- x STO, $x = 0.15 - 0.25$ ceramics had a pseudo-cubic structure).

In addition, for a thin film, high values of dielectric constant $\epsilon' \sim 330$ were detected. In the case of KNN-STO thin films with $x = 0.075$, Fig. 3(b), dielectric behavior with shoulder-shaped curves was detected. Here, the dielectric behavior shows no significant increase or decrease upon increasing temperature from 200 K towards room temperature. Such dielectric behavior is more pronounced in Fig. 4, which depicts the frequency dependence of the real part of the complex dielectric constant, ϵ' , and the real part of the complex conductivity, σ' , measured at several temperatures in KNN-STO thin films with $x = 0.075$ and $x = 0.15$, and has been reported in KNN-STO compositions with $0.08 \leq x \leq 0.10$.⁸ Furthermore, in both, KNN-STO ceramics and thin films, for $x \geq 0.10$, a change in the dielectric response from ferroelectric to relaxor was reported,^{6,9,8} which is consistent with the relaxor response detected in KNN-STO thin film with $x = 0.15$. A possible reason for the difference in the plateau values of the dielectric constant between KNN-STO thin film with $x = 0.075$ and $x = 0.15$ lies in the positions of main dielectric constant peaks. In the case of $x = 0.15$, the main ϵ' peak was detected around 200 K. In the case of KNN-STO with $x = 0.075$, the main ϵ' peak is proposed to be above 400 K by Kupec and Malič⁹ in addition, similar dielectric behavior was detected in KNN-STO ceramics.^{6,8}

Figure 5 depicts the fatigue endurance, i.e., normalized maximal polarization as a function of the switching cycles, measured in the KNN-STO thin film with $x = 0.15$. These results are compared to those detected in the ferroelectric 8/65/35 PLZT ceramics¹⁵ and in the relaxor KNN-STO ceramics with $x = 0.15$ ⁷; results for PLZT thin films

Fig. 5. Normalized maximal polarization in KNN-STO thin films with $x = 0.15$ as a function of switching cycles, compared to data obtained in ferroelectric PLZT ceramics (from Ref. 15) and KNN-STO ceramics with $x = 0.15$ (from Ref. 7). The inset shows a relaxor-like hysteresis loop of KNN-STO thin film with $x = 0.15$, which remained almost unchanged over 10^6 switching cycles although some leakage through the sample occurred.

are not shown here as significant fatigue occurs only above 10^8 switching cycles.^{17,18} The inset of Fig. 5 shows a relaxor-like hysteresis loop of KNN-STO thin film with $x = 0.15$, which remained almost unchanged over 10^6 switching cycles although some leakage through the sample occurred. In KNN-STO thin films, the values of $P_{\max}/P_{\max}(t=0)$, measured with the AC electric field having amplitude of 60 kV/cm and frequency of 1 kHz, drop only slightly after 3×10^5 switching cycles, which imparts an important quality of the thin films as several applications are based on the application of ac field. It should also be stressed, that the fatigue in lead-free KNN-STO is almost negligible most likely due to much lower concentration of defects. It has been proposed that the suppression of the switchable polarization is a result of the domain-wall pinning process caused by entrapment of defects, mainly oxygen and lead vacancies^{19–22}. In lead-based ceramic systems, the latter result from the volatilization of PbO during the synthesis, which already begins at temperatures as low as 800 K. Although alkaline perovskites may exhibit high leakage, which is attributed to the alkali deficiency,^{23,24} the studied KNN-STO system seems to be very stable.

A similar mechanism, the freezing of polar nanoregions due to the pinning on diffusing point defects, has been suggested for the so-called aging process, detected in relaxor lead-based ceramics.²⁵ Figure 6 shows aging of the dielectric constant obtained in KNN thin films and KNN-STO thin films with $x = 0.15$ in comparison with data obtained in the relaxor KNN-STO ceramics with $x = 0.20$,⁷ and in the relaxor 9/65/35 PLZT ceramics.¹⁶ In all systems, data were taken at temperatures near the dispersive dielectric maximum. Similar to ceramics, the values of ϵ' do not change

Fig. 6. Normalized real part of the complex dielectric constant in KNN thin films and KNN-STO thin films with $x = 0.15$ as a function of the waiting time, compared to data obtained in relaxor PLZT ceramics (from Ref. 16) and KNN-STO ceramics with $x = 0.20$ (from Ref. 7). Solid lines are a guide for the eye.

significantly with time in KNN-STO thin film. In KNN thin films, ϵ' decreases almost 5% at 20 Hz, while it decreases only slightly at 1 MHz after 3 h.

4. Conclusion

Structural and dielectric properties, as well as history-dependent effects were studied in lead-free KNN and KNN-STO thin films of different compositions. In KNN-STO thin films with $x = 0.15$, which exhibit a typical relaxor broad dispersive dielectric maximum, (i) $\epsilon' \sim 330$ at the dispersive dielectric maximum at ~ 210 K was measured, (ii) fatigue endurance results revealed only a slight drop in $P_{\max}/P_{\max}(t=0)$ after 3×10^5 switching cycles, and (iii) the results of aging of the dielectric constant revealed no notable decrease in the values of ϵ' . In addition, a decrease of ϵ' to 5% was detected at low frequencies in KNN ceramic thin films after 3 h. The history-dependent effects in these lead-free thin films are therefore found to be much weaker than in some widely used lead-based ferroelectric and relaxor ceramic systems.

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