Relaxor-like dielectric properties and history dependent effects in a new lead-free $K_{0.5}Na_{0.5}NbO_3$-$SrTiO_3$ ceramic system

V. Bobnar,* B. Malic, M. Hrovat, J. Bernard, J. Holc, and M. Kosec
Jozef Stefan Institute, P.O. Box 3000, SI-1001 Ljubljana, Slovenia

Abstract
A typical relaxor-like dielectric properties such as broad dispersive dielectric maximum, Vogel-Fulcher temperature dependence of the characteristic relaxation frequency, and paraelectric-to-glass crossover in the temperature dependence of the dielectric nonlinearity, have been detected in a newly derived lead-free $K_{0.5}Na_{0.5}NbO_3$-$SrTiO_3$ ceramic system. Relatively large values of the dielectric constant, being almost independent of the frequency in the range of 100 Hz-1 MHz, suggest possible applications based on this environmental friendly system. Furthermore, the history dependent effects, such as aging of the dielectric constant and fatigue of the polarization switching, are much weaker than in some widely used lead-based relaxors.

Keywords: dielectric spectroscopy, relaxor, lead-free ceramics

1. Introduction

Relaxor ferroelectrics exhibit a high dielectric constant and a high strain across a broad temperature range and are therefore very attractive for a variety of applications such as capacitors, sensors, actuators, and integrated electromechanical systems.[1] They are characterized by a broad frequency dispersion in the complex dielectric constant, slowing dynamics, and logarithmic polarization decay.[2] These properties are correlated with the cationic disorder in the same crystallographic site and have predominantly been detected in lead-containing ternary compounds and solid solutions, such as $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) or $(Pb,La)(Zr,Ti)O_3$ (PLZT).[2-6] However, due to the toxicity of lead these compounds represent a possible ecological hazard, which has recently stimulated development of compositionally disordered lead-free solid solutions, exhibiting relaxor-like properties.[7]

Dielectric spectroscopy turned out to be an extremely powerful tool for investigations of relaxor properties.[5,8-9] We have therefore conducted a high-resolution linear as well as nonlinear dielectric measurements of a newly synthesized lead-free ceramic system, derived from $K_{0.5}Na_{0.5}NbO_3$ and $SrTiO_3$ perovskites. A solid solution with a pseudo-cubic structure was obtained for $x = 0.15$-0.25;[10] x denotes the molar ratio of $SrTiO_3$ in $K_{0.5}Na_{0.5}NbO_3$-$SrTiO_3$ (KNN-STO). A typical relaxor-like response has been detected, revealing a compositionally disordered (K, Na, and Sr ions on the A-sites, Nb and Ti ions on the B-sites) perovskite structure. As relatively large values of dielectric constant suggest utilization of KNN-STO, the history dependent effects, playing a major role in most of the applications, were also studied and were found to be much weaker than in some widely used lead-based relaxors.

2. Experimental procedures

KNN-STO ceramic samples were prepared using the solid-state synthesis.[10] The phase composition was determined by X-ray diffraction and a JEOL 5800 scanning electron

*Electronic address: vid.bobnar@ijs.si

microscope was used for the microstructural analysis. Samples having sputtered gold electrodes on both surfaces were used for dielectric measurements. The complex linear dielectric constant $\varepsilon^*(\omega,T)=\varepsilon'-i\varepsilon''$ was measured in the frequency range of 20 Hz-1 MHz by using HP4284A Precision LCR Meter. After heating the samples to 350-450 K, the dielectric response was detected during cooling and subsequent heating runs with the rate of ±0.5 K/min. Similar heating/cooling procedure was used for the third-order nonlinear dielectric response measurements, which were carried out at several frequencies between 1 Hz and 10 kHz by using HP35665A Dynamic Signal Analyzer. Here, the first, ε, and the third, ε_3, harmonic dielectric responses were measured simultaneously, which, in comparison to the separate measurement runs, reduces error in the subsequent computation of the important ratio $a_3=\varepsilon_3/\varepsilon_0^3\varepsilon'^4$. Namely, as it can in fact distinguish between ferroelectric and glass transitions, the temperature dependence of the dielectric nonlinearity a_3 revealed that on cooling in zero electric field relaxors undergo a transition into a glass-like state, rather than into a ferroelectric one.[9]

3. Results and discussion

Figure 1 shows a broad dispersive dielectric maximum in the temperature dependence of ε' in KNN-STO samples of different compositions. Contrary to ferroelectrics, relaxors do not undergo a symmetry-breaking transition into a long-range ordered state on cooling in zero electric field, but rather only polar nanoregions persist down to the lowest temperatures. The dispersive maximum in ε' therefore does not denote a phase transition, but is the result of the fact that ε' at a certain temperature, that depends on the experimental time, scale starts to deviate from its static value.[5,11] This deviation occurs when, due to the rapidly increasing polydispersivity of the relaxation spectrum on cooling, the longest relaxation times exceed the experimental frequency window. As the temperature of the dielectric maximum clearly decreases on increasing $SrTiO_3$ content, one can deduce that relaxation times of polar nanoregions are becoming shorter, i.e. polar nanoregions in KNN-STO are, due to a higher compositional disorder, smaller on higher $SrTiO_3$ content. The inset to Fig. 1 shows that ε' is almost independent of the frequency in the range of 100 Hz-1 MHz.

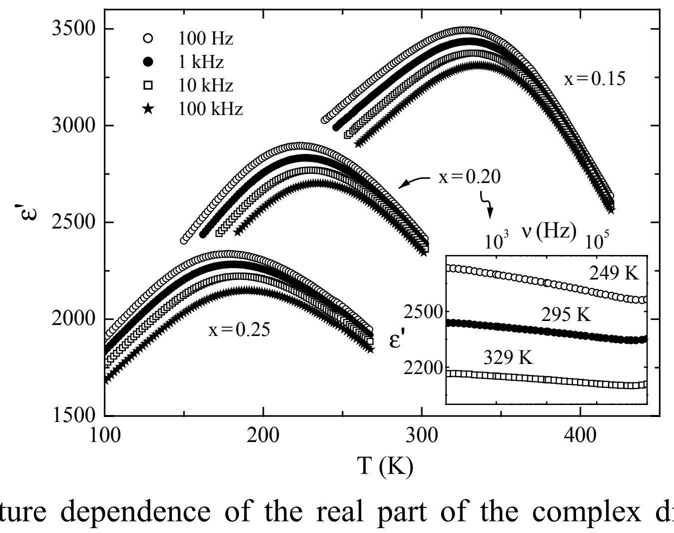

Figure 1: Temperature dependence of the real part of the complex dielectric constant, ε', measured at several frequencies in KNN-STO samples of different compositions. The inset shows that ε' is almost independent of the frequency in the range of 100 Hz-1 MHz.

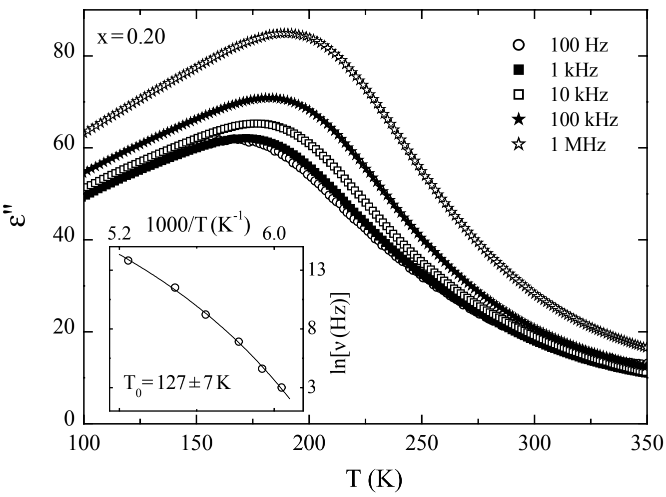

Figure 2: Temperature dependence of the imaginary part of the complex dielectric constant, ε'', measured at several frequencies in KNN-STO sample with x = 0.20. The inset shows that the characteristic relaxation frequency follows the Vogel-Fulcher law.

Concomitantly to ε', $\varepsilon''(T)$, shown in Fig. 2 for the x = 0.20 sample, also exhibits a broad frequency dispersion. The inset to Fig. 2 shows another typical relaxor behavior – the characteristic relaxation frequency, determined from peaks in $\varepsilon''(T)$, follows the Vogel-Fulcher law $\nu = \nu_0 \exp[-U/k(T-T_0)]$ with the Vogel-Fulcher temperature $T_0 = 127 \pm 7$ K.

Figure 3 shows the temperature dependence of the dielectric nonlinearity a_3. Similar to lead-based inorganic[9] and polymer-based organic relaxors,[11] a_3 undergoes a crossover from decreasing paraelectric-like to increasing glass-like temperature dependence on cooling. Such a behavior confirms the absence of the long-range order and a relaxor-like structure of KNN-STO solid solution. For a comparison, a_3 in a classical lead-based relaxor PMN[9] is shown in the inset to Fig. 3.

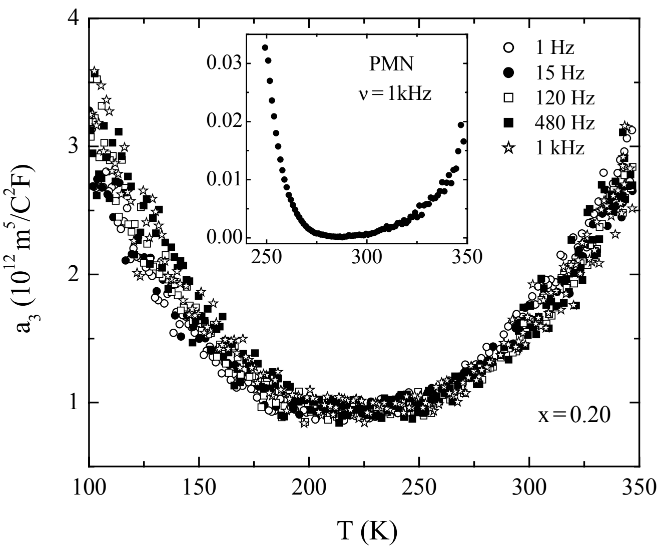

Figure 3: Paraelectric-to-glass crossover in the temperature dependence of the dielectric nonlinearity a_3 in KNN-STO ceramics with x = 0.20. The inset shows identical temperature dependence of a_3 in a lead-based relaxor system PMN.[9]

Figure 4 shows the remanent polarization as a function of the switching cycles, measured in the KNN-STO sample with x = 0.15. This composition has the highest values of ε' around the room temperature (cf. Fig. 1) and is therefore the most promising for applications. The inset to Fig. 4 shows a typical relaxor-like slim hysteresis loop of this sample, which remained unchanged over 10^6 switching cycles. Results in the main frame are compared to those detected in the ferroelectric 8/65/35 PLZT ceramics.[12] We are aware that, due to the absence of the long-range order and consequently a low value of the remanent polarization, relaxor systems are not very suitable for applications based on the polarization switching, e.g. ferroelectric memories. However, it has clearly been shown[12] that fatigue of the switchable polarization is accompanied by decreasing of dielectric and piezoelectric constants. We can therefore conclude that relatively large values of dielectric constant as well as strain values in KNN-STO remain almost unchanged over at least 10^6 switching cycles, thus demonstrating an important quality of the material, as many applications are based on the application of the ac electric field.

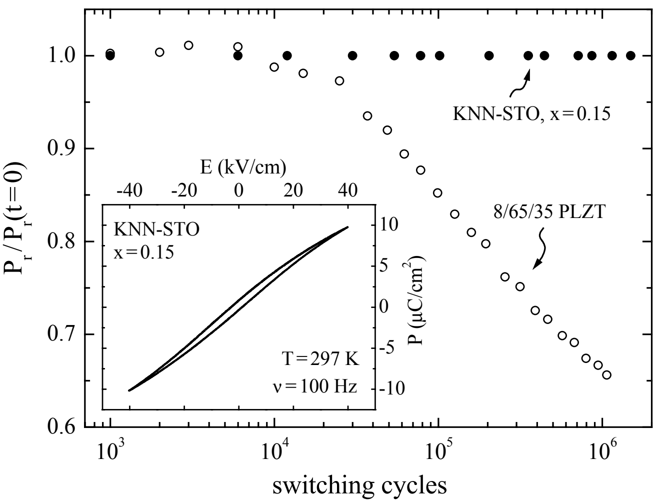

Figure 4: Normalized remanent polarization in KNN-STO sample with x = 0.15 as a function of switching cycles, compared to data obtained in the ferroelectric PLZT ceramics.[12] The inset shows a relaxor-like slim hysteresis loop in KNN-STO (x = 0.15), remaining unchanged over 10^6 switching cycles.

It has been proposed, on the basis of different experimental results, that suppression of the switchable polarization is a result of the domain wall pinning process caused by entrapment of defects, mainly oxygen and lead vacancies.[13-16] Models that involve oxygen vacancy migration have strongly been supported by fatigue measurements in atmospheres of varying oxygen concentration.[15] Lead and oxygen vacancies in lead-based ceramic systems result from the volatilization of PbO during the synthesis, which already begins at temperatures as low as 550°C. Therefore, fatigue in PbO-free KNN-STO is almost negligible most probably due to the much lower concentration of defects.

Similar mechanism, 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.[17] Namely, even without an ac electric field applied, values of dielectric constant decrease in time. Figure 5 shows aging of the dielectric constant in the relaxor 9/65/35 PLZT ceramics[5] and results obtained in KNN-STO system. In both systems data were taken at

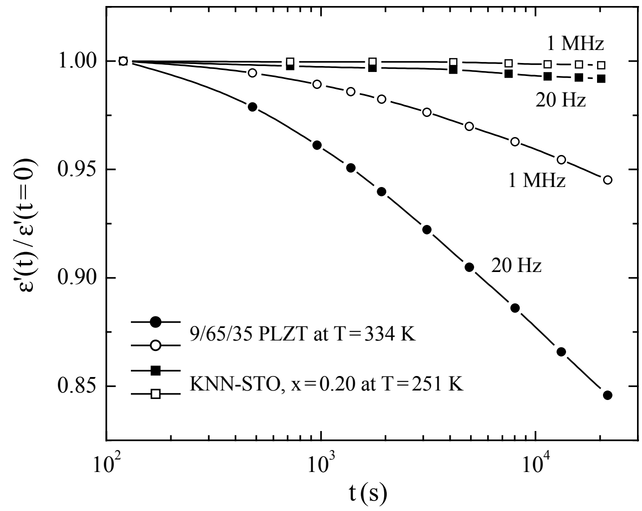

Figure 5: Normalized real part of the complex dielectric constant in KNN-STO ceramics with x = 0.20 as a function of waiting time, compared to data obtained in the relaxor PLZT ceramics.[5]

temperatures near the dispersive dielectric maximum. While in PLZT ceramics ε' decreases for almost 15 % in the first three hours after the annealing, in KNN-STO ε' does not change in time. It should be stressed out that not only possible applications, but also basic experimental research can strongly be influenced by the history dependent effects – decreasing of linear and nonlinear dielectric constants during experiments alter the obtained results and can bend our conclusions on dynamic processes occurring in the system under investigation.

4. Summary

A typical relaxor-like linear as well as nonlinear dielectric response has been detected in a newly derived lead-free $K_{0.5}Na_{0.5}NbO_3$-$SrTiO_3$ ceramic system, thus confirming that a compositionally disordered perovskite solid solution has been formed. The facts that relatively large values of the dielectric constant are almost independent of the frequency and that history dependent effects play only a minor role in comparison to some widely used lead-based relaxors, suggest possible applications based on this environmental friendly system.

Acknowledgment

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