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Uniaxial stress dependence of the dielectric permittivity of the $Na_{0.5}Bi_{0.5}TiO_3$–$KTaO_3$ system

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ABSTRACT

The dependence of the dielectric permittivity on the uniaxial compressive stress was investigated for the case of $Na_{0.5}Bi_{0.5}TiO_3$–$KTaO_3$ ceramics. Special attention was focused on the reversibility of the permittivity–stress dependence. The results were connected with the transition from the ferroelectric to the relaxor state in the concentration region between 5 and 10 mol% of $KTaO_3$. With this transition, the permittivity–stress dependence changes from non-linear, irreversible and time dependent to linear, instantaneous and reversible. In samples with 10–30 mol% of $KTaO_3$ some minor relaxations were observed, which were suppressed under a small pre-stress. The stress sensitivity was higher at a lower measuring frequency and the reversible change of the permittivity was the highest in the sample with 20 mol% of $KTaO_3$ (the absolute and relative changes of permittivity were 196.5 and 10.3%, respectively, at a pressure change between 8 and 219 MPa). The obtained results are discussed in terms of the macrodomains/microdomains' reorientation under applied pressure and the transition from one to another with a change of the $KTaO_3$ concentration. The use of $Na_{0.5}Bi_{0.5}TiO_3$–$KTaO_3$ ceramics for device applications is described.

1. Introduction

In the field of pressure sensing several methods are used, depending on the frequency of the measured signal. The methods are based on various physical phenomena, such as piezoelectricity, piezoresistivity, and capacitance [1,2]. For high-frequency applications the piezoelectric effect is exploited. The drawbacks of the piezoelectric effect are the depolarization at high temperatures (above, or even below, the temperature of the phase transition) or under high-stress conditions, and its limited capability to be used for static applications. For static and quasi-static applications piezoresistive or capacitive sensors are applied [1] and different techniques were employed to compensate for the nonlinearities and temperature dependences [2]. The stress dependence of the permittivity offers another possible method for measuring the stress or pressure [3]. This, in principle, linear effect has potential applicability in pressure sensing. The practical use of such sensors requires materials with a high permittivity and the associated pressure dependence, a permittivity stable with time and a low temperature coefficient of the permittivity [4]. Relaxors, with their diffuse phase transition, possessing a high permittivity and a small temperature dependence of the permittivity, are good candidates for this type of sensors.

Historically, the effect of uniaxial or hydrostatic pressure on the properties of ferroelectric materials has been extensively studied in the frame of thermodynamics research on the ferroelectric phase transitions [5,6]. However, only a few studies report on the uniaxial stress dependence of the dielectric and other properties of ferroelectric materials [7]. The observed relaxations with time of the measured properties were discussed in terms of domain reorientation under an applied stress. The results, however, do not provide information about the short-term changes in the properties, which is of interest in sensor applications. Later, measurements of the pressure dependence of permittivity, known as the converse electrostrictive effect, were performed in order to determine the electrostrictive coefficients of non-polar materials [8,9], while in polar materials direct electrostriction was applied to measure the electrostrictive coefficients [10,11] due to the additional effect of the coupling between polarization and stress on the converse curve [12]. With the spread of piezoelectric materials to the low-frequency, large-signal-range applications [13], renewed experimental [14,15] and modeling [16] efforts have focused on evaluating and understanding the nonlinear behavior of polar ceramics in the context of domain switching. In these investigations, the stress dependence of the permittivity was also investigated. However, the experiments were performed mostly on poled samples [17,18] and were not concentrated on the

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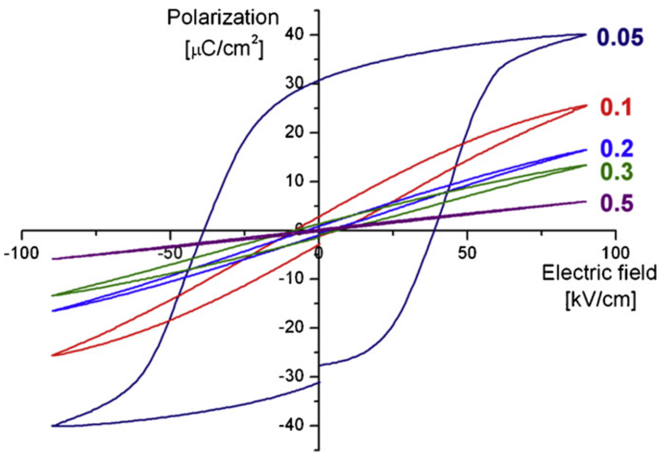

Fig. 1. Polarization–electric-field hystereses loops of samples from the $(1-x)$NBT–xKTa system [26].

permittivity–stress dependence and its potential applicability in sensor technology.

The first author to present the converse electrostrictive effect as a way to sense pressure was Uchino [3], who concentrated on studying high-permittivity ceramic materials [3,11]. The results on the uniaxial stress dependence of $Pb(Mn_{1/3}Nb_{2/3})O_3$-based materials above the diffuse permittivity maximum showed a reversible decrease in the dielectric permittivity, which is in accordance with the converse electrostrictive law. However, the possible relaxations were not investigated in these studies. The uniaxial stress dependence of the permittivity of ceramic materials in different phases was later studied by Steiner et al. [4]. The investigation showed relaxation phenomena in ferroelectrics as well as in relaxors below the permittivity maximum, while the response in paraelectrics and relaxors above the permittivity maximum was instantaneous and reversible. Moreover, a study of the stress–permittivity relationship in $BaTiO_3$ [19] revealed a strong influence of the grain size and measuring frequency on the shape of the curve. According to the complex behavior of the permittivity under pressure, a study of the pressure dependence of the permittivity should be precisely conducted. Recently, the use of a stress-dependent dielectric material in combination with an inductive (L) [20] or resistive (C) [21] component to form an LC or RC oscillator and measure the stress from the shift of the oscillators' resonant frequency was proposed. In the former case, the LC resonator was placed inside an external loop antenna to achieve passive wireless telemetry.

In the described literature, the majority of the investigated materials are lead-based, while only a few studies were focused on lead-free materials [22,23]. Recently, we reported on the axial pressure dependence of dielectric properties in the $Na_{0.5}Bi_{0.5}TiO_3$–$NaTaO_3$ (NBT–NTa) system [24]. A detailed analysis of the history, time and temperature dependence of the stress–permittivity relation revealed irreversible changes and relaxations in samples from the whole solid-solution region, including compositions in the paraelectric state. Such behavior was explained by the ferroelastic properties of the samples. The investigation also disproved the linear and reversible stress–permittivity relation in pure $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), as reported previously [25]. It was shown that the history and temperature conditioning of the domain-structured samples has a decisive influence on the stress–permittivity curve.

In this contribution we focused on the related $Na_{0.5}Bi_{0.5}TiO_3$–$KTaO_3$ (NBT–KTa) system, which exhibits typical relaxor properties in the major part of the solid-solution region (Fig. 1) [26]. A more in-depth investigation of the permittivity response to the applied uniaxial stress is reported, with an evaluation of the composition, time and frequency dependence. Additional experiments were performed to test the reversibility of the response.

2. Experimental

Samples with various $KTaO_3$ (KTa) concentrations (5, 10, 20, 30, 50, and 70 mol%) were prepared by a solid-state reaction method. Details of the synthesis conditions and the characterization are given elsewhere [26]. Corresponding amounts of reagent-grade Na_2CO_3 (Alfa Aesar, Karlsruhe, Germany, 99.997%), K_2CO_3 (Alfa Aesar, 99.997%), Bi_2O_3 (Alfa Aesar, 99.975%), TiO_2 (Alfa Aesar, 99.8%), and Ta_2O_5 (Alfa Aesar, 99.993%) were weighed and mixed thoroughly in an agate mortar under ethanol. Prior to weighing, the Na_2CO_3 and K_2CO_3 powders were dried to remove any water content, cooled to room temperature in a silica-gel-filled desiccator and then weighed in air quickly. The mixed powders were dried, uniaxially pressed into pellets and annealed in air several times (750, 850, 950, and twice at 1100 °C for 10 h) with intermediate cooling and grinding or milling in a planetary mill at 200 rpm for 1 h using 3-mm yttria-stabilized zirconia balls and ethanol media. The annealed samples were then cold isostatically pressed and sintered at 1150 °C for 5 h. Multiple annealings were required for a good homogenization of the matrix phase; nevertheless, a small content of secondary phases was observed from the microstructures [26].

The uniaxial stress (i.e., the axial pressure) dependence of the dielectric properties was measured using a mechanical lever press and the procedure as previously reported [24]. The maximum pressure applied to a disk-shaped sample with a 5-mm diameter was approximately 220 MPa, with 10 measuring points across the measured stress range. The stress applied to the sample by the lever arm alone is termed the pre-stress, and its value was around 8 MPa. Gold was sputtered on the parallel surfaces to serve as the electrode. At least three samples of each composition were tested. The dielectric measurements were performed at frequencies from 1 kHz to 1 MHz with a 1-V amplitude, using a HP 4284A LCR meter (Agilent Technologies, Santa Clara, CA). A long integration time was used to obtain a good signal-to-noise ratio. A stepwise increase of the static pressure (approximately 20 MPa per step) in 1-min intervals was used in the experiments. The dielectric properties were measured 1 min after the increase of the pressure, just before the next increase. The compression test consisted of two successive stress cycles (i.e., a stepwise stress increase and a single-step stress release and a second stepwise stress increase) and a time interval under a constant maximum pressure (>200 MPa), followed by a stress release. After the first stress cycle the pressure was reduced to the pre-stress value (~8 MPa), while at the end of the test the pressure was completely removed (Fig. 2a).

3. Results and discussion

The results of the uniaxial stress dependence of the permittivity of a virgin sample with 5 mol% of KTa measured at a frequency of 1 MHz are shown in Fig. 2b. In the first stress cycle, the permittivity decreases with increasing axial pressure. The decrease is not linear and no saturation can be observed up to the highest applied pressure (212 MPa). The relative change in the permittivity at 200 MPa is approximately 11%, which is almost four times higher compared to pure NBT (3%) [24].

Similar to the case in NBT, significant differences between the first and second stress cycles were observed. After the first stress cycle, the permittivity settles at around 95% of the starting value, thus giving an irreversible change of more than 5%. In the second stress increase the permittivity linearly decreases and the permittivity value at the maximum pressure (−12.1%) is lower compared