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FUNCTIONAL MATERIALS

Influence of uniaxial pressure on dielectric properties of (1-x)$Na_{0.5}Bi_{0.5}TiO_3$–$x$$SrTiO_3$ for $x = 0.01$, 0.04, and 0.1 ceramics

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Abstract. The conventional solid-state sintering was applied to synthesized (1-x)$Na_{0.5}Bi_{0.5}TiO_3$–$x$$SrTiO_3$ (x = 0.01, 0.04, and 0.1) ceramics. Dielectric measurements of these ceramics were taken in the temperature range from 20 to 600 °C, in the frequency range from 1 kHz to 2 MHz and under uniaxial pressure ranging from 10 to 1100 bar. The study of the dielectric behaviour showed that the influence of uniaxial pressure on the investigated properties was considerable. The peaks ε_m gradually decreased and shifted towards lower temperatures with an increase of uniaxial pressure for all samples. The first effect developed with an increase of the strontium ion concentration. Experimental results revealed most interesting properties of the material in the context of its potential applications.

Key words: perovskite, ferroelectric materials, dielectric spectroscopy, uniaxial pressure.

1. INTRODUCTION

The development of mainstream technologies in such areas as electronics and teleinformatics has prompted the search for modern materials with the desired features, highlighting a broad field for research in materials engineering and associated disciplines. A wide range of materials used in those applications are ferroelectric materials that exhibit the perovskite structure ABO_3. They are used primarily as actuators, micromechanical systems (MEMS), multilayer capacitors, resonators, filters, transducers, and ferroelectric random access memory (FRAM) [1–3]. The role of solid solutions is far from minor; one of those substances is (1-x)$Na_{0.5}Bi_{0.5}TiO_3$–$x$$SrTiO_3$ (further referred to as (1-x)NBT–xST), which exhibits a wide range of interesting properties.

The base compound, widely reported in the literature on the subject, is bismuth sodium titanate, whose chemical formula is $Na_{0.5}Bi_{0.5}TiO_3$ (hereafter NBT). This compound undergoes two structural phase transitions. At about ~260–300 °C the rhombohedral phase (R3c) is transformed into the tetragonal phase (P4bm). The second phase transition, from the tetragonal to the cubic phase (Pmm), occurs at about ~520–540 °C [4–9]. The rhombohedral and tetragonal phases coexist in a wide range of temperatures [10].

Another basic compound is strontium titanate $SrTiO_3$ (denoted as ST), a paraelectric material containing the cubic phase at room temperature. It undergoes two structural transitions: from the cubic to the tetragonal

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phase at –163 °C and the other at –208 °C, when the structure becomes orthorhombic [11,12]. On the other hand, newer sources (not only the referenced one) claim that only a single phase transition exists: from the cubic to the tetragonal phase at –168 °C (not –163 °C) [13].

The effects of Sr concentration on dielectric, thermal, and Raman spectra of (1-x)NBT–xST ceramics solid solutions for $x = 0.01$–0.1 were investigated in [14–16]. These studies demonstrate that dielectric, thermal, and Raman spectra of (1-x)NBT–xST ceramics depend on the Sr concentration. The presence of Sr ions enhances the dielectric permittivity, causing the permittivity maximum to diffuse and shift towards lower temperatures [15]. Electrical transport in lead-free $(Na_{0.5}Bi_{0.5})_{1-x}Sr_xTiO_3$ ceramics ($x = 0$, 0.01, and 0.02) was examined in [17].

Many sensors, transducers, and actuators are subjected to considerable mechanical preloads [18]. Therefore, it is important to determine the properties of the materials as a function of the applied stress [19]. This study investigates the influence of uniaxial pressure (10–1100 bar) on the temperature and frequency dependence of the dielectric properties of (1-x)NBT–xST ceramics.

2. EXPERIMENTAL

The samples of ceramic composites (1-x)NBT–xST ($x = 0.01$, 0.04, and 0.1) were prepared by a solid-state reaction, by the same route as that reported in [20] for NBT. The obtained ceramic composites were cream-coloured and translucent; their relative density was above 96–97% of the theoretical density. Ceramic composites have very good mechanical properties [14–16]. The samples used in measurements were 1.25 mm × 1.0 mm × 0.2 mm in size. Prior to measurements, the samples were duly prepared and silver electrodes were applied. The uniaxial pressure in the range of 10–1100 bar was applied parallel to the electric field with the use of a lever and a weight. Dielectric properties were measured with a Gwistek Precision LCR Meter 8110G device. Measurements were taken in the frequency range from 1 to 2 MHz and at temperatures from 20 to 600 °C with a constant rate of temperature change (4 °C/min). Prior to measurements, the samples were heated up to 600 °C and kept at this temperature for 120 min.

3. RESULTS AND DISCUSSION

Figure 1 (a, b, and c) shows the temperature/pressure dependence of dielectric permittivity $\varepsilon(T)$ (at heating). For all samples, thermal hysteresis was observed during heating and cooling (inserts in Fig. 1). Some interesting behaviours were registered as the pressure increased: (1) decrease of thermal hysteresis; (2) gradual decrease of ε_m; (3) maximum temperature T_m shifting towards lower temperatures. This effect is enhanced as the ST concentration increases. The shift of T_m and the change of the ε_m value under the applied uniaxial pressure were ~3 °C/kbar and 250/kbar for $x = 0.01$ (Fig. 1a) to 35°C/kbar and 750/kbar for $x = 0.1$ (Fig 1c), respectively.

Similar patterns were obtained when studying the dielectric loss factor (Fig. 2, a, b, and c). To complete the characteristics of the (1-x)NBT–xST ($x = 0.01$, 0.04, 0.1) ceramics, the shifts of the pressure dependence of $T^x_m – T^{10}_m$ and the change of $\varepsilon^x_m – \varepsilon^{10}_m$ were calculated during the cooling and heating process (Fig. 3). It is readily seen that $\varepsilon^x_m(p)$ dependence exhibits two different ranges (two different slopes): at 10–300/350 bar and 300/350–1100 bar. The ε_m changes are irregular: at first it increases with pressure up to 300–350 bar and then decreases almost linearly. The calculated values are $\partial\varepsilon_m/\partial p = -1.3 \pm 0.5$/kbar, -0.8 ± 0.5/kbar, -1.5 ± 0.5/kbar (heating), and $\partial\varepsilon_m/\partial p = -1.9 \pm 0.5$/kbar, -1.3 ± 0.5/kbar, -2.2 ± 0.5/kbar (cooling) for $x = 0.01$, 0.04, and 0.1, respectively. Thus 0.96NBT–0.04ST ceramic is characterized by a consistently low value of $\partial\varepsilon_m/\partial p$ both during heating and cooling. In all doped ceramics, the difference ($\varepsilon^x_m – \varepsilon^{10}_m$) is shifted to lower values with increasing ST contents. The $T_m(p)$ plot also reveals two sections similar to the $\varepsilon_m(p)$. The following values were obtained: $\partial T_m/\partial p = -2.4 \pm 0.5$ °C/kbar, -2.0 ± 0.5 °C/kbar, -2.1 ± 0.5 °C/kbar (cooling), and $\partial T_m/\partial p = -1.6 \pm 0.1$ °C/kbar, -1.3 ± 0.5° C/kbar, -0.7 ± 0.5 °C/kbar (heating) for $x = 0.01$, 0.04, and 0.1 ceramics, respectively.

Our results implicate the threshold pressure $p_{threshold} \approx 300$–350 bar, interpreted as the existence of an internal clamping pressure, which has to be balanced by the external pressure higher than $p_{threshold}$. This clamping pressure can appear at the domain walls, grain boundaries, or at the local imperfections (e.g. dislocations), where point defects accumulate as a result of mechanical stress [21–23].

Although NBT–ST ferroelectrics are also weak ferroelastics, certain interconnections between ferroelectric and ferroelastic properties will still persist. The mechanical load used in the experiments is sufficient to induce the domain walls movement and also domain switching in the investigated samples. The mechanical load reduces the non-180 domain density in the direction parallel to the applied stress and increases their density in the perpendicular direction. The decrease in permittivity under the applied pressure can be attributed to the constraining of domain walls, which effectively reduces their mobility.

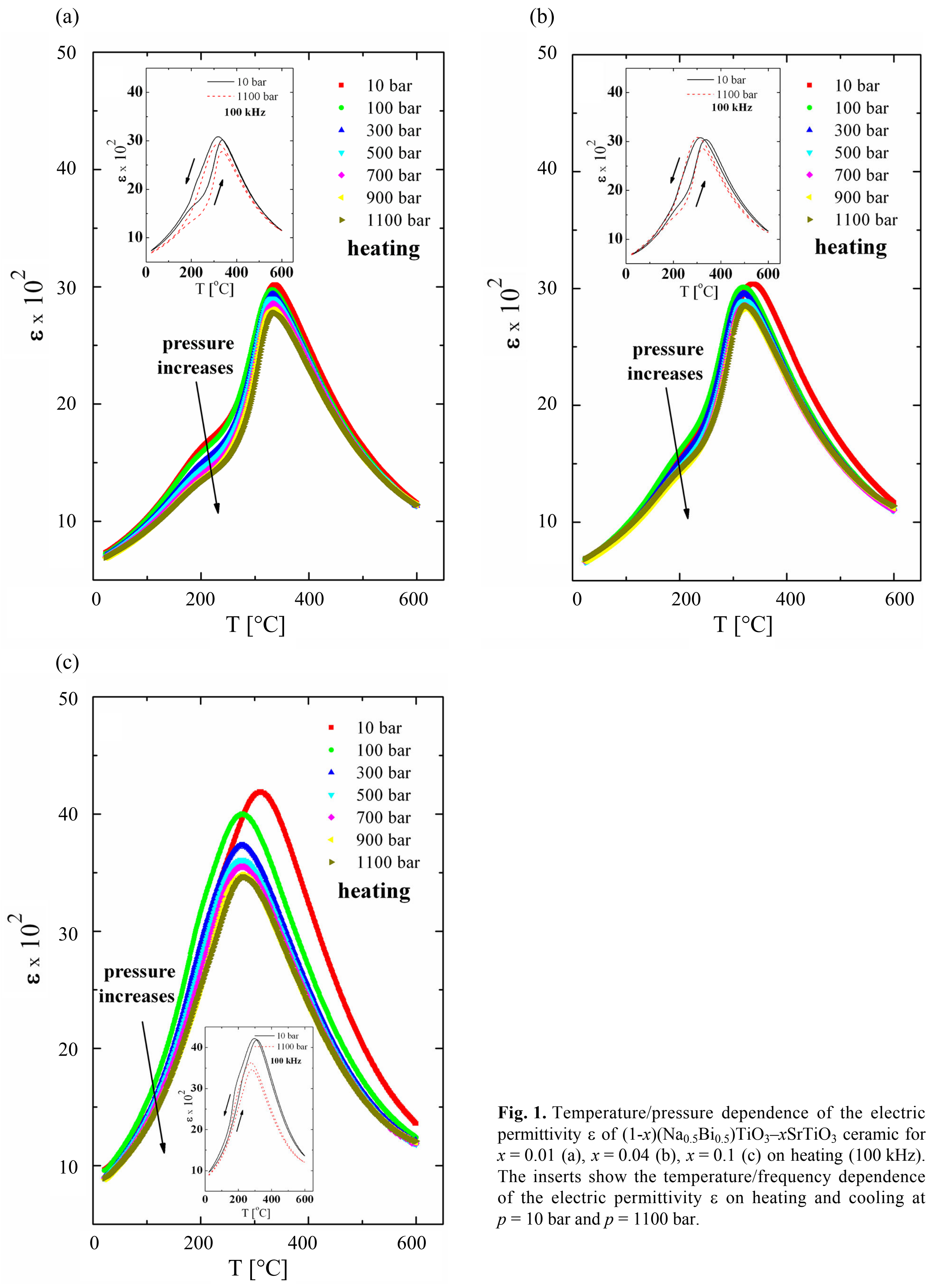
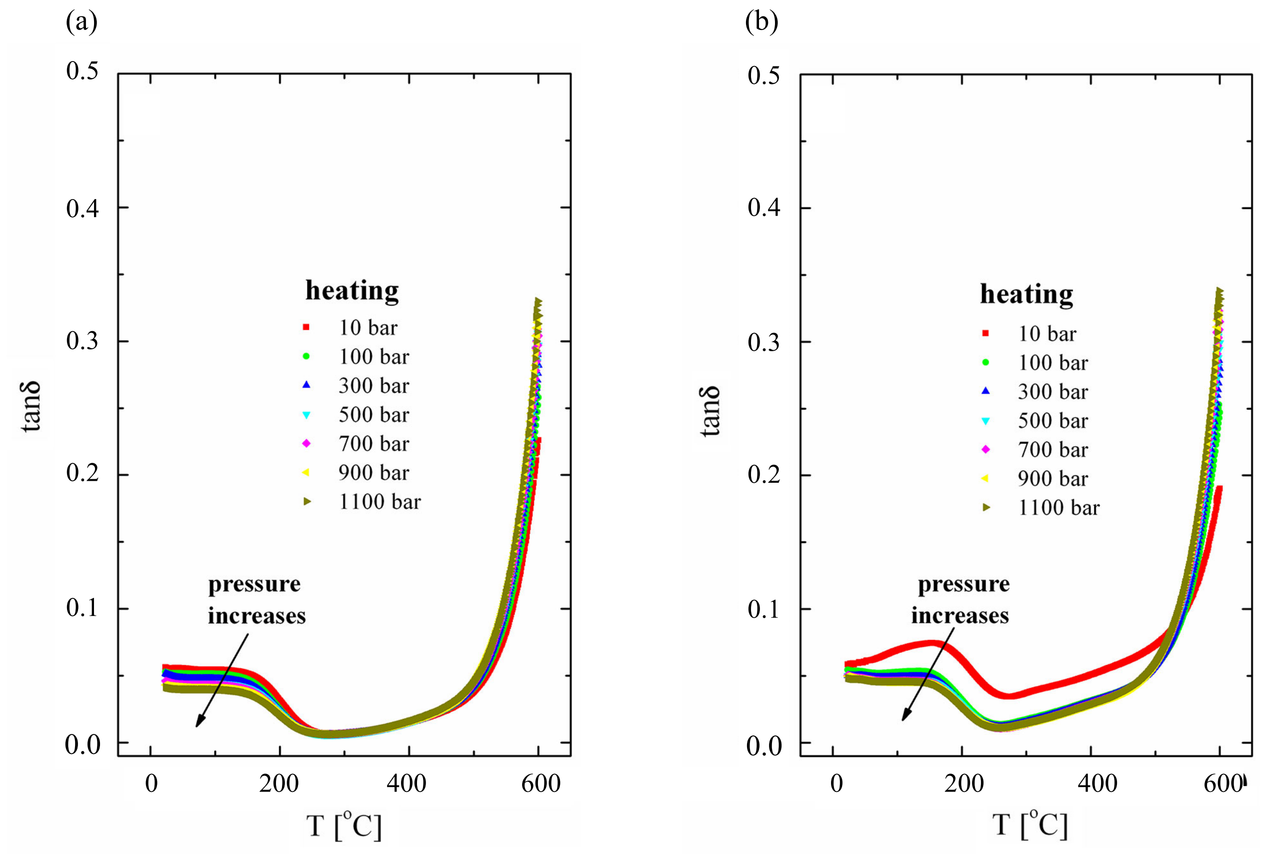


Fig. 1. Temperature/pressure dependence of the electric permittivity ε of (1-x)($Na_{0.5}Bi_{0.5}$)TiO_3–$x$$SrTiO_3$ ceramic for $x = 0.01$ (a), $x = 0.04$ (b), $x = 0.1$ (c) on heating (100 kHz). The inserts show the temperature/frequency dependence of the electric permittivity ε on heating and cooling at $p = 10$ bar and $p = 1100$ bar.



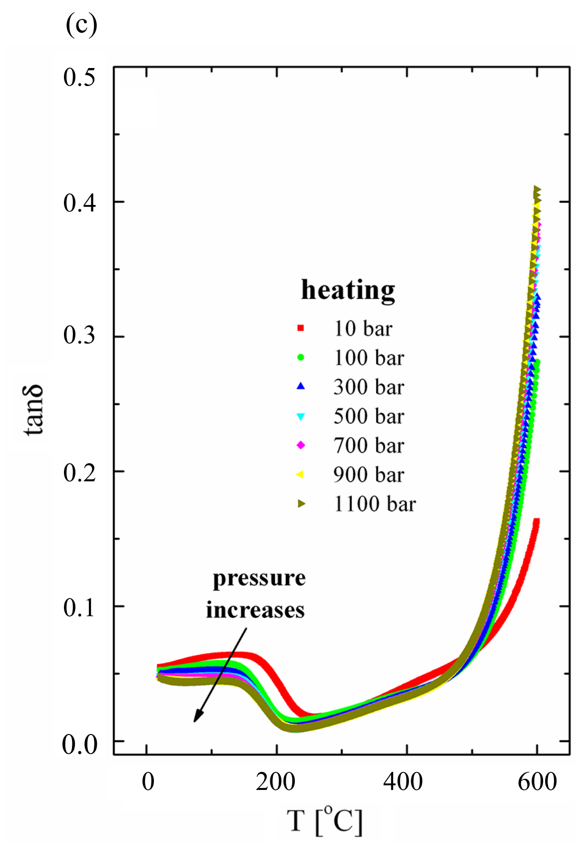


Fig. 2. Temperature/pressure dependence of the loss factor tanδ of (1-x)($Na_{0.5}Bi_{0.5}$)TiO_3–$x$$SrTiO_3$ ceramic for x = 0.01 (a), x = 0.04 (b), and x = 0.1 (c) on heating (100 kHz).

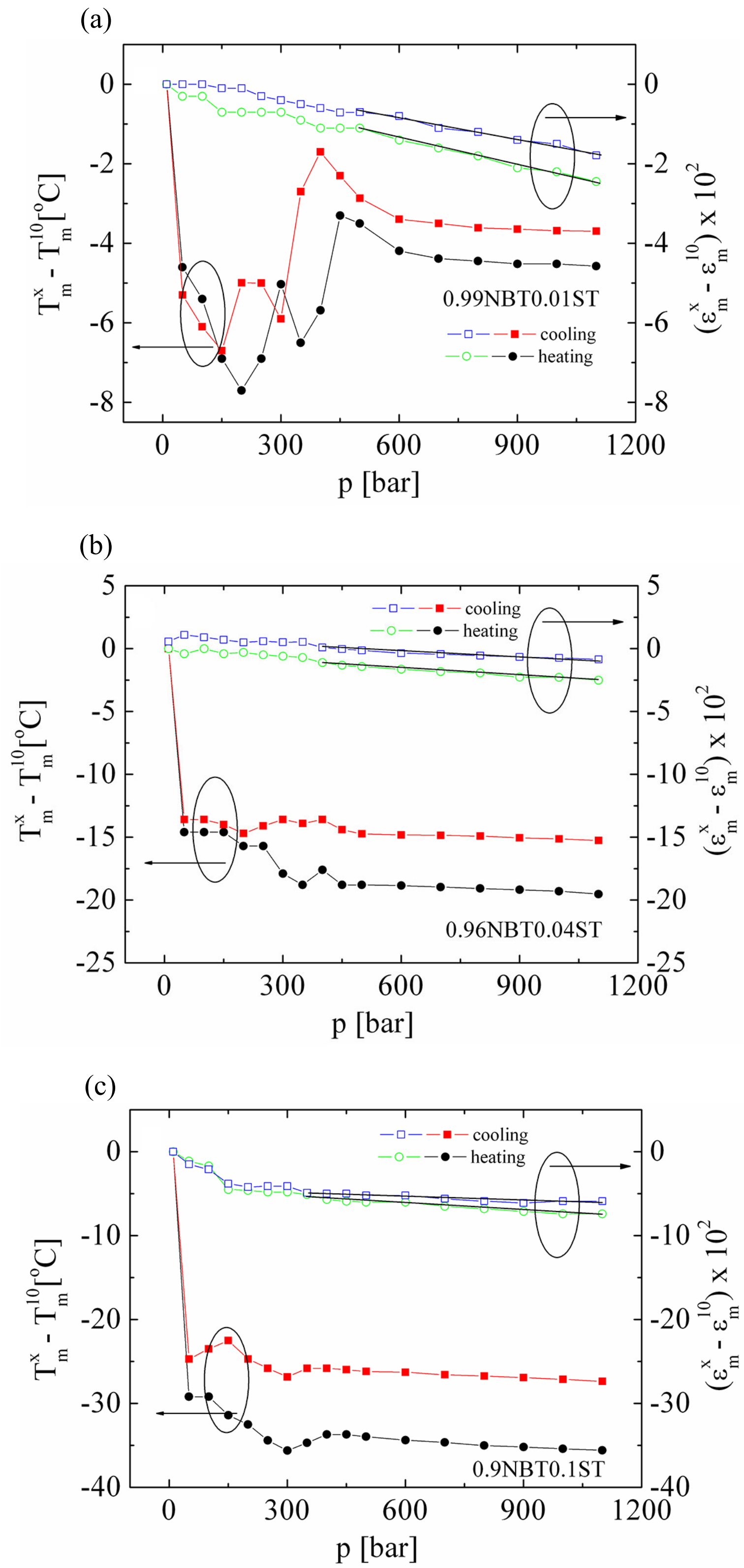


Fig. 3. Shift of the transition temperature and change of maximal value of electric permittivity as a function of pressure for (1-x)NBT–xST for $x = 0.01$ (a), $x = 0.04$ (b), and $x = 0.1$ (c) ceramics in heating and cooling. T^x_m and T^{10}_m are the transition temperature at pressure X_i and 10 bar, respectively; ε^x_m and ε^{10}_m are the maximal value of electric permittivity at pressure X_i and 10 bar, respectively.

4. CONCLUSION

The (1-x)NBT–xST, x = 0.01, 0.04, and 0.1, ceramics were fabricated by the conventional solid-phase synthesis method and their electric properties under uniaxial pressure were investigated. Dielectric spectroscopy was employed to evaluate the dielectric permittivity ε and loss factor tanδ at varying temperature/pressure. The values $\partial\varepsilon_m/\partial T$, $\partial T_m/\partial T$, and $\partial\varepsilon_m/\partial p$, $\partial T_m/\partial p$ were calculated for different ST contents. The threshold pressure $p_{threshold} \approx$ 300–350 bar can be reliably inferred from the dielectric behaviour under uniaxial pressure.

Under the applied uniaxial pressure, the value of the ε_m decreases and shifts towards the lower temperature range. The width of thermal hysteresis decreases with the increasing uniaxial pressure, which can be indicative of stress reduction in the examined samples as the force applied to them increases. This effect can be attributed to the domain walls transformation and pressure-induced switching of domains. The ability to change the dielectric properties of NBT–ST under uniaxial pressure could be effectively used in a wide range of applications.

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Rõhu mõju (1-x)$Na_{0,5}Bi_{0,5}TiO_3$–$x$$SrTiO_3$ (x = 0,01, 0,04, 0,1) keraamika dielektrilistele omadustele

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Uuriti rõhu mõju (1-x)$Na_{0,5}Bi_{0,5}TiO_3$–$x$$SrTiO_3$ (x = 0,01, 0,04 ja 0,1) keraamika dielektrilistele omadustele. Uurimisobjektid sünteesiti tavapärase tahkefaasilise paagutamisega. Dielektriliste omaduste mõõtmised tehti temperatuurivahemikus 20–600 °C, sagedusvahemikus 1–2 MHz ja ühesuunalise rõhu vahemikus 10–1100 baari. Uuringud näitavad, et rõhu mõju uuritavatele omadustele on märkimisväärne. Rõhu kasvades dielektrilise läbitavuse maksimumid vähenevad järk-järgult ja liiguvad madalamate temperatuuride suunas kõigi proovide puhul. Efekt kasvab koos strontsiumioonide kontsentratsiooni suurenemisega. Efekti seostatakse domeenide seina ümberkujundamise ja rõhust põhjustatud domeenide vahetumisega.

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