Influence of Compressive Stress on Dielectric and Ferroelectric Properties of the (Na$_{0.5}$Bi$_{0.5}$)$_{0.7}$Sr$_{0.3}$TiO$_3$ Ceramics

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Abstract: Good quality lead-free ceramics of (Na$_{0.5}$Bi$_{0.5}$)$_{0.7}$Sr$_{0.3}$TiO$_3$ (NBTS30) have been produced by a solid phase sintering process. The dependence of dielectric and ferroelectric properties on the uniaxial pressure (0-1200 bar) were investigated. A shift and decrease of maximum value of εr, decrease of the thermal hysteresis and coercive field and increase of polarization with increasing pressure were observed. The results were discussed in terms of an elastic changes in inter-ionic distances in a crystal structure and switching nanoregions under the action of pressure. The NBTS30 ceramic is expected to be a new promising candidate for lead-free electronic material.

1. Introduction
At present, the most widely-used piezoelectric materials are PZT-based ceramics due their high performance and excellent piezoelectric properties [1-2]. However, environmental issues call for the use of nonhazardous substances for device fabrication. Therefore, a considerable effort has been devoted to the development of lead-free piezoelectric ceramics with properties comparable to PZT. Research activities have mainly been focused on Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (NBT) and NBT-based materials. The phase of NBT at room temperature is rhombohedral (R3c) [3]. A phase transition to tetragonal phase (P4bm) takes place at about 260°C and to cubic (Pm3m) phase at about 520°C. Besides, there exist two other characteristic temperatures called the depolarization temperature ($T_d$=190°C) and the maximum-permittivity temperature ($T_m$=320°C). At $T_d$, the formation of ferroelectric state occurs (on cooling), which corresponds to a small diffuse bump on electric permittivity profile. SrTiO$_3$ (ST) is a so-called quantum paraelectric, it has a perovskite structure and a cubic symmetry (Pm3m) at room temperature. Below -168°C a transition to a tetragonal phase (14/mcm) is reported [4]. NBT-ST solid solutions show relaxorbehaviour and have been the starting material for the development of many other lead-free materials [5]. However, the properties of these materials are not yet well understood. There are only a few reports on their temperature-dependent dielectric and ferroelectric properties [6-7]. We notice here that in many applications, piezoelectric materials are often subjected to combined mechanical and electrical loading at different temperatures. It is therefore important to determine the dielectric and ferroelectric properties of these materials as function of applied stress and temperature. In this work we concentrate to investigate the influence of uniaxial pressure (applied parallel to ac field) and temperature on the dielectric and ferroelectric properties of (Na$_{0.3}$Bi$_{0.7}$)$_{0.3}$Sr$_{0.3}$TiO$_3$ (NBTS30) ceramics. Such type of investigations have been performed on NBTS30 for the first time.

2. Experimental procedure
Powders of (Na$_{0.3}$Bi$_{0.7}$)$_{0.3}$Sr$_{0.3}$TiO$_3$ were synthesized by solid phase reaction from high purity grade oxides and carbonates: Na$_2$CO$_3$, SrCO$_3$, Bi$_2$O$_3$ and TiO$_2$. The mixture of raw materials was homogenized and milled in an agate ball mill in ethanol for 24 hours, then dried and calcined. Due to
multicomponent composition the two step calcination was chosen: first at – 4 hours at 850°C and then at – 2 hours at 950°C. The calcined powder were reground, cold pressed (100 MPa) and sintered by conventional ceramic technology for 3 hours at the temperature of 1190°C. The obtained ceramics were cream-coloured and translucent. They exhibited very good mechanical properties (see below). Dielectric studies were carried out for silver electrode samples using BM LCR meter in the temperature range of 30-500°C. The compressive stress in the range of 0-1200 bar was applied parallel to the measuring electric field with the use of a lever and a weight.

3. Results and discussion
X-ray powder studies proved that NBTS30 ceramics has single phase of perovskite type with cubic structure (figure 1a). They did not show any evidence of macroscopic distortions in XRD patterns.

![Figure 1](image1.png)

**Figure 1.** XRD pattern (a) and SEM micrographs (b) of the NBTS30 ceramic (magn. 5000x).

Figure 1(b) shows the SEM micrographs of the NBTS30 ceramics. The ceramic are well sintered. The polyhedral grains and grain boundaries accompanied with the occurrence of small pores are observed. The average grain size of the grains is ca. 5 µm. The EDS analysis confirmed the high purity and the expected quantitative composition of the sample. The samples were characterized by the bulk density which exceeds 95% of the theoretical density, unit cell parameter \( a = 3.904 \pm 0.02 \) Å, a spontaneous polarization \( P_s = 21 \mu \text{C/cm}^2 \), a coercive field \( E_c = 30 \text{kV/cm} \); piezoelectric coefficient \( d_{33} = 446 \) pm/V; elastic constants: Young modulus \( E = 148.41 \pm 3 \text{ GPa} \), shear modulus \( G = 58.77 \pm 0.1 \text{ GPa} \) and Poisson’s ratio \( \nu = 0.263 \pm 0.006 \) (all parameters are at room temperature).

![Figure 2](image2.png)

**Figure 2.** Temperature/frequency dependence of \( \varepsilon \) (a) and hysteresis loops (b) of NBT and NBTS30 ceramics. Hysteresis loop of NBTS30 at \( p = 200 \) bar is also show.
In general, after Sr doping to NBT (figure 2) the dielectric and ferroelectric properties are enhanced: electric permittivity ($\varepsilon$) increases, their maximum ($\varepsilon_m$) is more diffuse and is shifted to lower temperature; $\varepsilon_m$ decreases and is shifted to higher temperature as the frequency increases, similar to relaxor ferroelectrics; polarization and coercive field increases and decreases, respectively. Figure 3(a) shows Raman spectra for NBT, ST and NBTS30 ceramics. No modes are Raman active in the cubic phase and seven ones are predicted for tetragonal phase of ST [8]. ST displays two broad bands at about 100-200, 200-400, 450-650, and 750-900 cm$^{-1}$ exist. These broad bands can be assigned to second-order Raman scattering [8]. On the other hand, the modes of NBT (R3c phase) are mainly at about 100-200, 200-400, 450-650, and 750-900 cm$^{-1}$. The low-frequency one is associated with Na-O vibrations, the second one with Ti-O vibrations, whereas the higher frequency bands can be assigned to vibrations of the TiO$_6$octahedra [9]. The high-frequency range above 700 cm$^{-1}$ can be caused by the vibrations resulting from the shift of oxygen [10] and also correlated to present of oxygen vacancies. Raman spectra of NBTS30 show shifting and broadening for most of the bands. Moreover, a new mode is visible shown as a shoulder at the right side of the low-frequency mode (~138 cm$^{-1}$, indicated by arrow) and is evident of a structural change associated with A-site symmetry change. The mode in second region (~256 cm$^{-1}$) appear as two overlapping modes. Another additional mode appeared as a shoulder at the lower side of 450-650 cm$^{-1}$ mode (indicated by arrow). In spite of the cubic symmetry (figure 1a), the existence of first-order Raman scattering indicates that the phase change. The mode in second region (~256 cm$^{-1}$) can be caused by the vibrations resulting from the shift of oxygen [10] and also correlated to present of oxygen vacancies. Raman spectra of NBTS30 show shifting and broadening for most of the bands. Moreover, a new mode is visible shown as a shoulder at the right side of the low-frequency mode (~138 cm$^{-1}$, indicated by arrow) and is evident of a structural change associated with A-site symmetry change. The mode in second region (~256 cm$^{-1}$) appear as two overlapping modes. Another additional mode appeared as a shoulder at the lower side of 450-650 cm$^{-1}$ mode (indicated by arrow). In spite of the cubic symmetry (figure 1a), the existence of first-order Raman scattering indicates that the phase has a considerable local departure from the macroscopic cubic structure. Indeed, the appearance of additional modes in Raman spectra indicate that the rhombohedral phase of NBT change to a cubic phase through an intermediate noncubic phase or both phases may be coexist (e.g. small rhombohedral islands in cubic matrix-polar nanoregions in nonpolar matrix).

![Raman spectra of NBT, ST and NBTS30 ceramics](image)

**Figure 3.** Raman spectra of NBT, ST and NBTS30 ceramics (a) and temperature/pressure dependence of $\varepsilon$ of NBTS30 ceramic (b). The insert a and b in figure 3(b) show temperature/frequency dependence of $\varepsilon$ of NBTS30 ceramic at $p=0$ and 1200 bar, respectively. Insert c show temperature dependence of $\varepsilon$ of NBTS30 ceramic on heating/cooling at $p=0$ and 1200 bar.

The temperature/pressure dependence of $\varepsilon$ shown in figure 3(b) reveal five main features with increasing pressure: (1) the $\varepsilon(T)$ maximum ($\varepsilon_m$) seems to be gradually less diffuse for pressure up to 900 bar and then becomes more diffuse, (2) the temperature of $\varepsilon_m$ first shifts towards lower temperatures of approximately -70°C/kbar (up to pressure about 200 bar), and then increases of approximately +13°C/kbar, (3) the dielectric dispersion slightly increases above $T_m$ (insert a and b in figure 3(b)), (4) $\varepsilon_m$ first increases (up to pressure about 200 bar, $\partial\varepsilon_m/\partial p=+3920\pm20$ kbar), and then...
decreases ($\frac{\partial \varepsilon_m}{\partial p} = -988 \pm 20 / \text{kbar}$), the thermal hysteresis decreases (inserts $c$ in figure 3(b)). Thus, dielectric measurements of NBTS30 ceramic under uniaxial pressure show the occurrence of the threshold pressure $p_{\text{thresh}} \approx 200 \text{ bar}$. It has been found that character of $c$ changes below $p_{\text{thresh}}$ is different to that above this pressure. This effect can be attributed to a manifestation of the clamping pressure, which can be overcome by external pressure higher than $p_{\text{thresh}}$. This clamping pressure may appear at the interphase boundaries or local imperfections like dislocations, where point defects hoard during ageing and consequently accumulate mechanical stress.

In general, the changes in the properties of materials under compressive stress in the present experiments can arise from (1) an elastic change of distances between ions in the crystal structure, (2) a change in nanoregions structure, and from (3) creating/annihilating of defects [11]. The first effect can lead to the mainly decrease of dipole moments, causing the decrease of their contribution to dielectric response. In NBTS30 electric and elastic nanoregions coincide, they can be reoriented both by electric field and uniaxial pressure. The mechanical load (0-1200 bars) was large enough to induce nanoregions orientation. In present experiments, the uniaxial pressure reduces the number of nanoregions oriented in the direction of applied and thus leads to a decrease in the nanoregions ordering. The hysteresis loops area is found to decrease with increasing the stress applied parallel to the electric field direction (decrease of polarization is observed, figure 2(b)), confirming this suggestion. The hysteresis loop area represents the unit-volume polarization dissipation energy of a ferroelectric material subjected to one full cycle of electric field loading. Polarization dissipation energy is related directly to the amount of domain participating in the switching process during an electric field loading cycle. A decrease in the polarization dissipation energy with increasing compressive stress indicates that less and less nanoregions are remained (they are oriented by the stress in an opposite direction) and cannot be reoriented by the electric field, i.e. they cannot participate in the polarization reversal. As a consequence, the polarization become lower with increasing stress. The coercive field seems to be decreases under pressure (figure 2(b)). The decrease in permittivity is likely from the constraining of the interphase walls under stress, resulting in a decrease of interphase walls mobility.

4. Conclusions
Good quality lead-free ceramics of (Na$_{0.5}$Bi$_{0.5}$)$_0.7$Sr$_0.3$TiO$_3$ (NBTS30) have been produced by a solid phase sintering process. The present investigations show that Sr-doping to NBT enhanced their dielectric and ferroelectric properties. The uniaxial pressure strongly affects their dielectric and ferroelectric properties shown by change of electric permittivity maximum, a shift in $T_m$, a decrease of thermal hysteresis, coercive field and of polarization. The obtained data were discussed basing on the strength of the elastic change in distances between ions in the crystal structure and nanoregions ordering under the influence of pressure. It is obvious that NBTS30 ceramics are promising materials for high-frequency transducer and actuator applications.

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