Effect of Nb cationic substitution on the microstructure and Raman spectra of SrBi$_2$(Ta,Nb)$_2$O$_9$ thin films

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ABSTRACT

Micro-Raman spectroscopy and x-ray diffraction have been used to explore the lattice dynamics of Nb-substituted SrBi$_2$(Ta$_{1-x}$Nb$_x$)$_2$O$_9$ (SBTN) thin crystalline films annealed at low temperature, 700°C. The substitution of Nb at Ta-site leads to the decrease in the SBT lattice parameters, as confirmed by x-ray diffraction data entire the concentration range of Nb varying from 0 to 50 wt. %. The relative intensity of the (115), (006) and (200) X-ray diffraction peaks increases with the increase of the Nb content.

We observed nonmonotonic shift of the Raman band maximum from 810 cm$^{-1}$ (for pure SBT) to 830 cm$^{-1}$ (for SBTN with 20% of Nb) and then back to 810 cm$^{-1}$ with increasing Nb content from 40 to 50 wt. %. We assume that these changes are conditioned by the ferrodistortion occurring in ferroic perovskites, namely by the tilting distortion of (Ta,Nb)O$_6$ octahedra at 20-40 wt. % of Nb. The octahedra tilting can change the coordination environment of the A-cite cation, as well as it lowers the SBTN symmetry below the cubic symmetry. The tilted state at 20-40 wt. % of Nb can explain the nonmonotonic changes of the perovskite phase fraction and remanent polarization with increasing Nb content from 0 to 50 wt.%, in particular their initial increase with Nb content increase up to 20 wt. % followed by a decrease at 30 wt. % of Nb, then increase at 40 wt.% and further decrease for 40 – 50 wt. % of Nb. Hence, the substitution by Nb of Ta-site in SBT has a pronounced impact on the O-Ta-O stretching modes by shifting and splitting the mode frequency at (810 - 830) cm$^{-1}$; however, it does not influence the low frequency Raman modes of SBTN.

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Landau-Devonshire approach is used to explain the experimentally observed nonmonotonic dependence of the ferroelectric perovskite phase fraction and remanent polarization on Nb content in SBTN films, at that the form of the dependence strongly resembles the shift of the Raman band maximum near (810 – 830) cm\(^{-1}\). Thus, the combination of micro-Raman spectroscopy with x-ray diffraction, ferroelectric measurements and phenomenological description allow to establish the influence of Nb doping on the lattice dynamics, microstructure, phase composition and ferroelectric properties of the SBTN thin films.

**Keywords:** ferroelectric, sol-gel method, perovskite structure, crystallization annealing, defects, remanent polarization, SBTN-film, Raman spectroscopy, Landau-Devonshire approach.

### 1. INTRODUCTION

#### 1.1. State of the art

Ferroelectric thin films of Aurivillius compounds, such as layered ferroelectric perovskites strontium bismuth tantalate \(\text{SrBi}_2\text{Ta}_2\text{O}_9\) (SBT) and niobate \(\text{SrBi}_2\text{Nb}_2\text{O}_9\) (SBN) have a relatively high dielectric permittivity, piezoelectric and pyroelectric coefficients, optimal electrooptical properties, and reveal a robust polarization switching \([1, 2, 3]\). These materials, due to their intriguing electronic, ferroelectric and electrophysical properties have been recognized as prominent candidates for applications in non-volatile ferroelectric memories (NvFeRAM) \([4, 5, 6, 7]\) because of their negligible fatigue, low leakage currents, and ability to maintain ferroelectricity in the form of thin films \([8, 9, 10]\).

Recently SBT ferroelectric thin films on Pt electrodes have been extensively investigated for NvFeRAM applications due to their excellent ferroelectric properties. It is well known that the required high post-deposition annealing temperature and low remanent polarization are the two major barriers, which hinder the advanced applications of SBT films. In order to eliminate these two problems, several scientific groups have used various methods, such as forming the solid solutions of \(\text{SrBi}_2(\text{Ta}_x\text{Nb}_{1-x})_2\text{O}_9\) (SBTN) \([11, 12]\), changing the stoichiometry of SBT \([13]\), and controlling the oxygen pressure during the annealing process \([13, 14]\). Also, it needs to take into account that, in the case of undoped SBT, it is still a challenge to obtain a high remanent polarization at low post-deposition annealing temperatures \([15, 16]\). Literature analysis have shown that Nb doping of SBT can reduce the annealing temperature, improve the ferroelectric properties and achieve higher values of remanent polarization and Curie temperature compared to SBT \([11-16]\). Replacing A or B sites in the layered perovskite structure allows effectively improves the dielectric and ferroelectric properties of SBT films. The partial substitution of Ta with Nb in
SBTN systems makes it possible to reduce the annealing temperature, improve the ferroelectric properties, achieve higher remanent polarization and Curie temperature compared to undoped SBT [17]. Since working performances and operating conditions of ferroelectric capacitors for NvFeRAM have a strong relation with the ferroelectric film thickness and post-deposition annealing temperature, one requires to use ferroelectric films not more than (100 - 200) nm thick with relatively high remanent polarization (at least more than 5-10 μC/m²) and low post-deposition annealing temperature (e.g., below 750°C).

In order to reduce the post-deposition annealing temperature, improve the ferroelectric properties and increase the remanent polarization, this work studies $\text{SrBi}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_9$ thin films with different content (from 10 to 50 wt.%) of Ta ions substituted by Nb ions, prepared by sol-gel method. We explore the influence of Ta substitution by Nb on the microstructure and micro-Raman spectrum of sol-gel SBTN thin films annealed at 700°C.

To the best of our knowledge that there are only few works [18], where the Raman scattering technique was used for the investigation of SBTN thin films. Our observations clearly imply that the Raman spectroscopy can be used as a rapid and convenient method for characterization of the layered perovskite SBTN structure, and as a sensitive technique for probing lattice vibrational modes, which can provide unique information for identifying the changes in lattice vibrations, as well as the information about the lattice positions occupied by substitutive Nb ions. In addition, Landau-Devonshire approach is used to explain the experimentally observed nonmonotonic variation of perovskite phase fraction and remanent polarization allowing for the possible appearance of finite size effects related with the nanogranular structure of the polycrystalline SBTN films.

**1.2. SBTN atomic structure and ferroelectric properties**

The general formula for the Bi containing layer-type compounds is $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$, where A denotes the 12-fold coordinated cation in the perovskite sublattice, B represents the octahedral site, bismuth atoms form the rock-salt type interlayer ($\text{Bi}_2\text{O}_2$) between the perovskite blocks ($\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$), and “n” is the number of octahedral layers within the perovskite sublattice of the structure. For the stoichiometric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (n=2) compound there is one complete perovskite sublattice created by the Ta–O octahedra, in which a 12-fold A cation (in our case Sr$^{2+}$) may reside. The $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ belong to the $\text{ABI}_2\text{B}_2\text{O}_9$ perovskite-like compounds and have a face-centered orthorhombic unit cell, consisting of TaO$_6$ or NbO$_6$ octahedrons, respectively (see **Figure 1**). These materials have a relatively high Curie temperature of the ferroelectric phase transition ($T_C$), around 335°C (for SBT) [19] and around 440°C (for SBN) [20]. In the ordered
perovskite phase at temperatures below $T_C$ the spontaneous polarization vector lies in the plane of these layers.

![Diagram of SBTN structure](image)

**Figure 1.** A simplified fragment of SBTN structure in the centrosymmetric parent phase above $T_C$. The black arrow shows the possible direction of spontaneous polarization in the ordered perovskite phase at temperatures below $T_C$.

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### 2. EXPERIMENTAL DETAILS

#### 2.1. Correlation between SBTN symmetry and active Raman modes

As a first approximation, it is helpful to assign a tetragonal symmetry to the SrBi$_2$Ta$_2$O$_9$ and SrBi$_2$Nb$_2$O$_9$ above the Curie temperature. It corresponds to a I$_{4}mnm$ space group. For this symmetry the following Raman and IR modes should be active [21]:

$$4A_{1g}(R) + 2B_{1g}(R) + 6E_g(R) + 7A_{2u}(IR) + B_{2u}(IR) + 8E_u(IR).$$

At room temperature SBT symmetry is orthorhombic, the space group is $A2_1am$ ($C_{2v}^{12}$), with only slight distortion from tetragonal symmetry. The tetragonal structure is centrosymmetric, so that there is mutual exclusion between infrared and Raman activity. The infrared modes are also Raman active for the orthorhombic structure.

Below the Curie temperature ($T < T_C$), an orthorhombic symmetry is expected in SBT, so that each $E_g$ mode splits into $B_{2g} + B_{3g}$ modes. The splitting at room temperature in these two components must be consistent with the orthorhombic distortion [22, 23].

SBT has an orthorhombic crystal structure with the $A2_1am$ space group in the ferroelectric phase, which becomes tetragonal in the paraelectric phase with the I4/mmm space group for the temperatures $T$ above 335°C. The inclusion of any cations substituting Sr, Bi or Ta leads to the change in the SBT crystal structure and symmetry depending on the valence and ionic radii of the cations. Nb cation has a smaller ionic radius than Ta, and its location at the Ta-site changes the ionic bond length inside the layered SBT unit cell. Given the mass of Nb and Ta, it is expected...
that a smaller mass of Nb can shift the vibrational modes to higher frequencies. Because the mass of Nb ion is less than Ta ion, the effective mass of the SBT unit cell becomes smaller after the Ta substitution with Nb, and the effective mass of SBTN cell decreases proportionally to the amount of Nb ions.

2.2. Materials and methods

The starting product for sol-gel preparation and subsequent formation of the SrBi$_2$(Ta$_x$Nb$_{1-x}$)$_2$O$_9$ layer was 0/01 mol/l solution of inorganic metal salts (tantalum, niobium and rare earth chlorides, bismuth and strontium nitrates in toluene). Deposition of SBTN films on Pt/TiO$_2$/SiO$_2$/Si substrate was performed by spin-coating of stable solution at the substrate rotation frequency from 800 to 1500 rot/min during 2 to 5 seconds. The adhesion of Pt to conventional dielectrics, such as SiO$_2$, is poor and TiO$_2$ provides an excellent adhesion layer between Pt and SiO$_2$, preventing the formation of platinum silicide. The organic solvent was removed by multi-stage drying under temperature increase from 80 to 350°C for 6 min. The required thickness of SBT and SBTN films (~100-120 nm) was obtained by layer-on-layer deposition of 2-3 sol-gel layers with heat treatment of each layer at a temperature 700°C. Perovskite SBTN structure was formed during a crystallization post-deposition annealing at 700°C for one hour.

The crystallographic orientation of the films was analyzed by x-ray diffraction (XRD) in the glancing-angle detector scan mode. Raman spectra have been measured using a InVia micro-Raman spectrometer (Renishaw) equipped with a confocal DM2500 Leica optical microscope, a thermoelectrically cooled CCD as a detector and a laser operating at a wavelength $\lambda = 633$ nm excitation from the He–Ne laser.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. X-ray and microstructure of SBTN films
Crystallite orientation and phase formation in the SBT and SBTN films were determined by XRD. From the structural point of view, SBT belongs to the bismuth layered perovskite family with the lattice parameters $a = 5.531$ Å, $b = 5.534$ Å, $c = 25.984$ Å in the orthorhombic structure [24]. The highly anisotropic structure of SBT ($c >> a, b$) results to the strong dependence of its ferroelectric properties on the crystallographic orientation of the film. It has been reported that the ferroelectric properties of SBT thin films in the $a – b$ plane are much stronger than those along the $c$ axis. This is because the continuous perovskite structure exists in the $a – b$ plane only. Therefore, preparation of SBT thin films with (200) preferential orientation is highly desirable.
Figure 2 shows the XRD patterns of SBT and SBTN thin films substituted with Nb content \(x = 10, 20, 30, 40\) and 50 wt.%. As it can be seen from the figure, SBT film annealed at 700 °C is a mixture of the layered orthorhombic perovskite and fluorite phases. It is known that the fluorite phase initially forms at lower temperatures and then transforms either into a bismuth-layered structure, or into a pyrochlore phase \(\text{SrBi}_x\text{Ta}_2\text{O}_9\) \((x<1.2)\) after the thermal treatment at 750°C.

It can be seen from Figure 3 that the intensity of \((115)\) peak increases with the increase of Nb content \(x\) in the SBTN film, indicating the grain growth. In addition, the intensity of \((200)\) peak also increases with the increase of Nb concentration in the film. These results suggest that the structure of SBT thin films can be controlled by the Nb-substitution process. The SBTN films are polycrystalline with a dominant orientation of crystallites along \((115)\) direction; they show the presence of \((200)\) peak responsible for ferroelectric properties. In addition, the peak at the angle \(2\theta = 29.4^\circ\) corresponds to a secondary phase and appears at the higher 20 component of the \((115)\) peak. This peak has been attributed to the distortion of the perovskite unit cell [16], while authors [25, 26] identified it as the non-ferroelectric pyrochlore phase; and the formation of this peak suppresses growth of the ferroelectric \((115)\) peak, which in turn affects the remanent polarization of the SBTN film. This secondary phase is a Bi-deficient pyrochlore phase, which is formed as a result of Bi diffusion into the Pt layer and/extracting of Bi by Pt in the Pt layer. In our case we also observed the decreasing of the ferroelectric \((115)\) peak for SBTN thin films substituted with 40 and 50 wt.% of Nb. Also, the broadening of \((115)\) peak profile is observed for SBTN thin films after Nb-doping more than 20 wt.% due to the increase of the peak intensity at the angle \(2\theta = 28.5^\circ\) for films substituted by 30% and 40 wt.% of Nb, and due to the increase of the peak at the angle \(2\theta = 29.4^\circ\) for films substituted by 40 and 50 wt.% of Nb.

Taking into account that the peaks \((115)\) \((2\theta = 29^\circ)\) and \((200)\) \((2\theta = 32.4^\circ)\) correspond to the ferroelectric phase of SBT [27], it can be assumed that the maximal fraction of the perovskite phase in SBTN films corresponds to \((10 – 20)\) wt. % of Nb (see Figures 2 and 3).
Figure 2. XRD patterns of SBT and SBTN films with various Nb content (in wt.%).

Figure 3. XRD patterns of SBT and SBTN films with different Nb contents: (a) in the region of the multiphase peaks near the angle $2\theta = 29^\circ$; and (b) in the region near the angle $2\theta = 32-33^\circ$. 

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Figure 4. AFM images of the SBT and SBTN films surface: a – SBT film; SBTN films with Nb content: b – 10, c – 20, d – 30, e – 40, f – 50 wt. %.

It is seen from the AFM images in Figure 4, that the average grain size increases with increasing Nb concentration above 30 wt. % and reaches (100 – 120) nm. The size of crystallites in the latter case is 23 nm. It can be seen from Figures 4b and 4c that the SBTN film consists of fine-grained spherical structures with the average grain size about (83–86) nm for (10 – 20) wt. % of Nb (see Figures 4b and 4c). We assign these spherical grains to the ferroelectric (115) phase. The formation of rod-like grains can be observed in SBTN film when the percent of Ta ions substituted by Nb ions is 50 wt. % (see Figure 4f).

Unlikely the rod-shaped grains contribute to the ferroelectric (115) peak, since, as it can be seen from Figure 2, its XRD intensity decreases when the percent of Ta ions substituted by Nb ions is (40-50) wt. %. We suggest that the rod-like grains correspond to the bismuth-deficient pyrochlore phase with the XRD maximum at the angle 20 = 29.4°, which intensity increases for the SBTN film doped with 40 and 50 wt.% of Nb (see Figure 3a).

3.2. Raman spectroscopy of SrBi$_2$(Ta$_{1-x}$Nb$_x$)$_2$O$_9$ thin films

Below we analyze Raman spectra of SrBi$_2$(Ta$_{1-x}$Nb$_x$)$_2$O$_9$ thin films with different percent of Ta ions substituted by Nb ions (from 10 to 50 wt.%), annealed at 700 °C. The obtained Raman spectra indicate that the studied films are polycrystalline (see Figure 5). Other studies reported that the Raman spectrum of a SBT ceramics exhibits intense bands with maxima at approximately
163, 210, 600, and 805 cm\(^{-1}\); other bands at 319, 356, and 455 cm\(^{-1}\) corresponded to weak features [28, 29]. Our results are in overall agreement with these studies, but we register the pronounced Raman bands at approximately 161, 204, 316, 590, and 810 cm\(^{-1}\) in the SBT and SBTN films (see Figure 5).

![Raman spectra of SrBi\(_2\)(Ta\(_{1-x}\)Nb\(_{1-x}\))\(_2\)O\(_9\) films annealed at 700°C and doped with different wt. % of Nb (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5).](image)

**Figure 5.** Raman spectra of SrBi\(_2\)(Ta\(_{1-x}\)Nb\(_{1-x}\))\(_2\)O\(_9\) films annealed at 700°C and doped with different wt. % of Nb (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5).

The band at 161 cm\(^{-1}\) is associated with the lattice vibrations of the Ta\(^{5+}\) ions at the B-site, namely it corresponds to the TO mode A\(_{1g}\) [30]. The shift of the A\(_{1g}\) mode to higher or lower wavenumbers is related with the grain growth. The nondegenerate A\(_{1g}\) mode vibrate in the plane perpendicular to the c-axis, and its shift to higher frequency occurs because the Ta\(^{5+}\) ions are replaced by the lower mass Nb\(^{5+}\) ions (Ta\(^{5+}\): \(\approx 181\) amu, 0.68 Å; Nb\(^{5+}\): \(\approx 93\) amu, 0.66 Å).

Relatively small shifts of this mode are observed in SBTN films, only some slight nonmonotonic shifts of this band to higher frequency were observed for (10-50) wt. % of Nb, as shown in Figure 6. The nonmonotonic variation of the frequency shift of the band at 161 cm\(^{-1}\) can be related with the transition from the symmetric (Ta-O-Ta) to asymmetric (Ta-O-Nb) bonding with different binding strength under the partial substitution of Ta\(^{5+}\) ions with Nb\(^{5+}\) ions with concentration (10 - 30) wt.%; or to the symmetric (Nb-O-Nb) bonding in the oxygen octahedra under Nb\(^{5+}\) ions substitution with concentration (40 - 50) wt. %.
The TO mode at 204 cm\(^{-1}\) is related to the vibration of the A-site ion, in our case Sr\(^{2+}\). The position of this mode does not change significantly with the addition of Nb (see Figure 5). This indicates that Nb does not incorporate into A-site and has only an indirect effect on the site by changing the configuration of the bonds of oxygens during replacing Ta\(^{5+}\) by Nb\(^{5+}\) cations at the B-site. Note, that the intensities ratio, \(I_{161}/I_{204}\), of the bands at 161 cm\(^{-1}\) and 204 cm\(^{-1}\) reveals a non-monotonic behavior with the increase of Nb content \(x\). The minimum of this ratio is observed for SBTN films substituted by Nb 50 wt.\% due to the strong increase of the intensity of the band near 204 cm\(^{-1}\), which could be assigned to SrO-group vibration.

The band observed at about 76 cm\(^{-1}\) refers to the \(E_g\) mode, where the Bi-O atoms in Bi\(_2\)O\(_2\) layers vibrate out of phase [31]. Since the band with maximum at 76 cm\(^{-1}\) does not reveal any frequency shifts (see Figure 6), except for a slight broadening appearing with the increase of Nb content, we can conclude that Nb\(^{5+}\) does not replace Bi\(^{3+}\) in Bi\(_2\)O\(_2\) layers and has only an indirect effect consisting in the changing of the bismuth-oxide layers configuration.

![Graph](image)

**Figure 6.** Compositional dependence of the band with center position about 162 cm\(^{-1}\) (left scale, black squares) and the band with center position about 76 cm\(^{-1}\) (right scale, blue triangles) from different wt.\% of Nb (\(x = 0, 0.1, 0.2, 0.3, 0.4\) and 0.5).

The bands in the range (200-300) cm\(^{-1}\) can be associated with the O-Ta-O bending and tilting modes [32], which are likely to be of B\(_{2g}\)+B\(_{3g}\) origin due to the degeneracy lifting of the \(E_g\) mode. The band around 600 cm\(^{-1}\) can be related with the rigid sublattice mode associated with the Ta-O2...
or Nb-O2 motions. These modes share their oxygen atom with another Ta or Nb atom, respectively. Modes above 300 cm\(^{-1}\) and 590 cm\(^{-1}\) bands are the rigid sublattice modes, in which all shifts of anions (O) and cations (Sr, Bi, Ta or Nb) are equal and opposite [23 - 25].

The main significant changes in the Raman spectra of SrBi\(_2\)(Ta\(_{1-x}\)Nb\(_{1-x}\))\(_2\)O\(_9\) films with different x (from 0 to 0.5) are observed for the band with the maximum around 820 cm\(^{-1}\), which is sensitive to the SBTN crystallization degree and corresponds to the stretching mode of (Ta,Nb)O\(_6\) octahedra, as it can be observed from Figure 5. In the case of pure SBT, the octahedral mode (also known as the breathing mode arising due to volume vibrations) has a frequency of ~810 cm\(^{-1}\); it expands and shifts to the higher wavelengths when Ta ions replaced by Nb ions [11]. A similar blue shift was observed for all Nb concentrations in Figure 5.

In the SBTN films the Raman bands consists of the stretching mode vibrations in SBT (\(\approx 813\) cm\(^{-1}\)) and SBN (\(\approx 838\) cm\(^{-1}\)) thin films [23], which are shifted from 810 to 838 cm\(^{-1}\) under the Nb substitution of Ta. These frequency variations seem to be associated not only with Nb substitution of Ta in the central B ion in the perovskite BO\(_6\) octahedra, but also with the number of defects (atoms in non-equilibrium positions, impurities, incomplete solid-state reaction, etc.) existing in the film [33 34]. The bands at approximately 600 cm\(^{-1}\) and 810 cm\(^{-1}\) can be attributed to the internal vibration of the (Ta,Nb)O\(_6\) octahedron. However, the oxygen ions contributing to the two bands are different. The band at 600 cm\(^{-1}\) can be attributed to the vibration of the oxygen ion (O\(_2\)) at the apex of the TaO\(_6\) octahedron. The band at about 810 cm\(^{-1}\) can be attributed to the vibration of oxygen ions (O\(_4\), O\(_3\)) in the (Ta,Nb)O\(_6\) octahedra (see Figure 8). This prominent feature corresponds to the stretching mode (A\(_{1g}\) symmetry), and is associated with the symmetric stretching vibrations of the TaO\(_6\) and NbO\(_6\) octahedrons [13, 25]. The Raman band around 161 cm\(^{-1}\) is assigned to the A\(_{1g}\) bending mode, involving motions of Bi\(^{3+}\) ions perpendicular to the layers.

For better understanding of this mode nature in SBT and SBTN films, we perform the deconvolution of Raman band with maximum at about 810 cm\(^{-1}\) (for SBT) and about 826 cm\(^{-1}\) (for SBTN) using the Gaussian fit. Appeared that the band at 810 cm\(^{-1}\) for undoped SBT films decomposes into a single maximum, which corresponds to TaO\(_6\) mode. An example of deconvolutions of the Raman bands at about 810 cm\(^{-1}\) and at about 826 cm\(^{-1}\) with and without Nb doping are shown in Figure 7. The Raman band at about 826 cm\(^{-1}\) decomposes into two maxima, at ~(809-813) cm\(^{-1}\) and at ~(830 - 837) cm\(^{-1}\), which correspond to TaO\(_6\) and NbO\(_6\) modes, respectively.
Figure 7. Deconvolution of the Raman bands with peak maximum around 810-830 cm\(^{-1}\) into Gaussian components for SrBi\(_2\)(Ta\(_{1-x}\)Nb\(_x\))\(_2\)O\(_9\) films annealed at 700°C. Six plots correspond to x=0, 0.1, 0.2, 0.3, 0.4 and 0.5 (see legends). Black solid curves are experimental Raman spectra, dashed red curves are fit, green and blue curves are the components corresponding to the TaO\(_6\) and NbO\(_6\) tilting modes, respectively.
Assignment of the dependence of the Nb-O-Nb/Ta-O-Ta ratio on Nb concentration obtained from the deconvolution of the Raman band with maxima at about (810-830) cm\(^{-1}\) is shown in Figure 8. It is seen from the figure that the FWHM of this mode changes by about 50%.

**Figure 8.** Assignment of the dependence of the Nb-O-Nb/Ta-O-Ta ratio obtained from the deconvolution of the Raman band with maxima at about (810-830) cm\(^{-1}\) (left scale, red circles), its halfwidth (FWHM) (left scale, black squares), and the position of the fitting center of the band (right scale, blue triangles), depending on the Nb concentration in SBTN films.

The increase in the Raman linewidth usually has two origins. One is an increase in the anharmonic effect due to, e.g., a phase transition shortening the phonon lifetime. The other is a distribution of the mode frequency due to some structural disorder. When we consider the symmetric distribution without a change in the mode frequency, the latter explanation seems to be more probable. Nb additives at the B-site are expected to induce a structural disorder in the environment of the octahedra due to the charge imbalance and to the differences in the mass and the ionic radius.

Most important is that we observed a nonmonotonic shift of the Raman band maximum from 810 cm\(^{-1}\) (for SBT) to 830 cm\(^{-1}\) (for SBTN with 20 wt. % of Nb) and then back to 810 cm\(^{-1}\) with increasing Nb content from 30 to 50 wt. %. We assume that these changes are conditioned by the ferro-distortion occurring in perovskites, namely by the tilting distortion of (Ta,Nb)O\(_6\).
octahedra (Figure 9). The octahedra tilting can change the coordination environment of the A-cite cation, as well as it lowers the SBTN symmetry below the cubic symmetry. To resume, the substitution of Nb at Ta-site of SBT has a pronounced influence on the O-Ta-O stretching modes by shifting and splitting the mode frequency at (810 - 830) cm$^{-1}$.

![Diagram of structural changes and tilting distortion of (Ta,Nb)O$_6$ octahedra.](image)

**Figure 9.** Structural changes and tilting distortion of (Ta,Nb)O$_6$ octahedra.

Dependence of the remanent polarization and the perovskite phase fraction on the Nb content in SBTN thin films is shown in Figure 10. The form of the nonmonotonic changes of the perovskite phase fraction and remanent polarization with increasing Nb content from 0 to 50 wt. % (in particular their initial increase with Nb content increase from 0 to 20 wt. % followed by a decrease at 30 wt.% of Nb, increase at 40 wt.%, and further decrease for 40 – 50 wt. % of Nb) strongly resembles the nonmonotonic shift of the Raman band maximum from 810 to 830 cm$^{-1}$ (compare with Figure 8). The oxygen octahedra tilting can explain the nonmonotonic changes of the perovskite phase fraction and remanent polarization with increasing Nb. To describe quantitatively the experimentally observed nonmonotonic dependence of the ferroelectric perovskite phase fraction and remanent polarization on Nb content in SBTN films, we use Landau-Devonshire approach in the next subsection.
Figure 10. Dependence of the remanent polarization (left scale, black squares) and the perovskite phase fraction (right scale, blue triangles) on the Nb content in wt.% in SBTN thin films.

3.3. Landau-Devonshire approach for the description of the perovskite phase fraction and polar properties of SBTN

The finite size effect on phase transitions in SrBi$_2$Ta$_2$O$_9$ nanoparticles have been investigated by in situ Raman scattering by Yu et al [35], and by thermal analysis and Raman spectroscopy by Ke et al [36]. The finite size and Nb substitution effects impact the phase diagrams, polar and dielectric properties of the SBTN nanogranular films [37, 38]. These effects can be described using the phenomenological Landau-Devonshire approach, taking into account the effect of Nb substitution on the structural ferrodistortion of SBTN and the charge state of this (nominally isovalent) dopant.

The addition of Nb increases the Curie temperature $T_C$, and thus improves the ferroelectric properties. It is reasonable to assume that at low concentrations of Nb the dependence $T_C(x)$ decomposes into a series of Nb content $x$, $T_C(x) = T_C(1 + \sum_{i=1}^{n} a_i x^i)$, where $a_i$ are unknown decomposition coefficients. However, with a further increase in $x$, the tilting and disorder in the
system of oxygen octahedrons increases, because Nb and Ta have different force matrices. The
degree of disorder is the maximum for x = 50 %, and with further increase, we gradually move to
the ferroelectric SBN. The effect of variable valence is also not excluded, although it is unlikely
to play a key role. The increase in disorder and tilting affect the magnitude of spontaneous
polarization due to nonlinear interaction with the structural subsystem and the correlation of the
structural and polar order parameters. We assume that the nonlinearity also decomposes into a
series of x (because it is at least an even interaction), \( \beta(x) = \beta_t (1 + \sum_{i=1}^{n} b_i x^i) \), where \( b_i \) are
unknown decomposition coefficients. In this simplest model we have the following x-dependent
coefficients in the SBTN Landau-Devonshire free energy:

\[
F = \frac{a'(T,x)}{2} p^2 + \frac{\beta(x)}{4} p^4 + \frac{\gamma}{6} p^6 - PE
\]

(1)

Here \( P \) is the polarization, \( E \) is the electric field, and \( \alpha, \beta, \gamma \) are the coefficients of expansion into
\( P \)-series. Due to the finite size effect related with the films nanogranular structure, the “effective”
coefficient \( \alpha(T,x) \) can depend on the average sizes of the grains, which are modeled by
nanoellipsoids with semi-axes \( R \) and \( L \) [38]:

\[
\alpha^*(T,x) = \alpha(T,x) + \frac{n_d}{\varepsilon_0(\varepsilon_b n_d + \varepsilon_e (1-n_d)+n_d(R/L))} \quad \alpha(T,x) = \alpha_t [T - T_c(x)].
\]

(2a)

Here \( \varepsilon_b \) and \( \varepsilon_e \) are the dielectric permittivity of ferroelectric background [39] and external media
respectively, \( n_d = \frac{1-\xi^2}{\xi^3} \left( \ln \frac{1+\xi}{1-\xi} - \xi \right) \) is the depolarization factor, \( \xi = \sqrt{1 - (R/L)^2} \) is the
eccentricity ratio of ellipsoid with a shorter semi-axes \( R \) and longer semi-axis \( L \) [40]; and \( D \) is the
ellipsoid semi-axis (\( R \) or \( L \)) in the direction of spontaneous polarization \( P \).

The dielectric stiffness \( \alpha(T,x) \) and the nonlinearity \( \beta(x) \) can be written as follows:

\[
\alpha(T,x) = \alpha_t \left( T - T_c \left( 1 + \sum_{i=1}^{n} a_i x^i \right) \right), \quad \beta(x) = \beta_t \left( 1 + \sum_{i=1}^{n} b_i x^i \right).
\]

(2b)

Where \( T \) is the absolute temperature, \( T_c \) is the Curie temperature, the coefficients \( \alpha_t \) and \( \beta_t \) are
positive. Coefficient \( \gamma \geq 0 \), and the \( \gamma \)-term can be neglected for the case of the second order phase
transitions, and then the spontaneous polarization and coercive field are equal to:

\[
P_s(T,x) = \sqrt{\frac{\alpha(T,x)}{\beta(x)}}, \quad E_c(T,x) = -\frac{2}{3} \frac{\alpha(T,x)}{\beta(x)} \sqrt{\frac{-\alpha(T,x)}{3\beta(x)}}.
\]

(3a)

Knowing \( P_s(T,x) \) and \( E_c(T,x) \) from the experiment, we can determine the coefficients of Landau-
Devonshire expansion \( \alpha(T,x) \) and \( \beta(x) \):

\[
\alpha(T,x) = -\frac{3\sqrt{3} E_c(T,x)}{2 P_s(T,x)}, \quad \beta(x) = -\frac{\alpha(T,x)}{P_s^2(T,x)} \equiv \frac{3\sqrt{3} E_c(T,x)}{2 P_s^2(T,x)}
\]

(3b)

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Since $T_C \approx (314 - 426) ^\circ C$ for SBT and $T_C \approx (414 - 494) ^\circ C$ for SBN [41], the Curie-Weiss constant $C_{CW}$ can be determined from the value of the linear dielectric constant of SBT at room temperature, for which the formula $\frac{1}{2\varepsilon_0 \alpha \varepsilon_0 (T_C - T)}$ and its value (180-200) for a bulk homogeneous SBT and SBN, respectively. We obtain the value $C_{CW} = (2 - 0,55) \cdot 10^5$ K. The dependences of the Landau expansion coefficients $\alpha(T, x)$ and $\beta(x)$ on the Nb concentration can be adjusted by means of polynomial functions by fitting the experimental values of spontaneous polarization and coercive field.

The experimental data from Table 1 were used to fit the experimental results. The results of fitting $P_S(T, x)$ and $E_C(T, x)$ using polynomial functions of the 4-th order and Eqs.(3a) are shown in Figures 11a and 11b, respectively. Figures 11c and 11d show the dependences of the Landau free energy coefficients $\alpha(T, x)$ and $\beta(x)$ on the Nb concentration (as a percentage), calculated from equations (3b) for SBTN at room temperature. As follows from Figure 11a, SBTN films with Nb content of 10 and 20 wt. % have the highest spontaneous polarization [42].

**Table 1.** Dependence of polar characteristics of SBT and SBTN on Nb content [42].

| Parameters                                | SBT | SBTN (in wt. % of Nb) |
|-------------------------------------------|-----|-----------------------|
| Content of Nb, wt. %                     | 0   | 10                    |
| Perovskite phase, %                       | 65  | 86                    |
| Spontaneous polarization, C/m²            | 0.0268 | 0.079                  |
| Coercive field, kV/m                      | 50  | 90                    |
| Bulk dielectric susceptibility at 293 K, dimensionless | 180 - 200 | 180 - 200              |
Figure 11. Dependences of the spontaneous polarization (a), coercive field (b), Landau expansion coefficients $\alpha(T, x)$ (c) and $\beta(x)$ (d) on Nb content, calculated from Eqs.(3) for SBTN films at different Nb content (in wt.%) at room temperature. The symbols in graphs (a) and (b) are the experimental results [42].

As follows from Figure 12a, SBTN film with 10 and 20 wt. % of Nb is as close as possible to the perovskite structure and the surface of the film has a finer grain structure (average grain size about 83-86 nm). An increase above 20 wt. % in the Nb concentration leads to a decrease in the fraction of the perovskite phase, as is evidenced by the expansion of the XRD line (115) and a decrease in its intensity at the angle $2\theta \sim 28.9$ deg shown in Figure 2. The change in the fraction of the perovskite phase with the introduction of the Nb ions into the $\text{Sr}_y\text{Bi}_{2+x}\text{Ta}_2\text{O}_9$ matrix can be explained by the change in the parameters of the crystal lattice, its bond strength and rigidity, and
the surface energy of the material. The appearance of the crystal structure anisotropy leads to a decrease in the perovskite phase fraction in the SBTN film, with an increase above 20 wt.% in the Nb content. An increase to 50 wt. % of Nb in the SBTN film leads to the formation of cylindrical grains with an average size of $R = (105 \pm 3) \text{ nm}$, $L = (200 \pm 3) \text{ nm}$, which leads to the deterioration of the ferroelectric properties ($P_s = 2.1 \mu \text{C/cm}^2$, see Figure 11a). The average grain size increases with the increase of Nb concentration above 30 wt. % and it is about (100-120) nm (the crystallite size in this case is 23 nm). The SEM and AFM images shown in Figures 12b and 12c, demonstrate the formation of elongated quasi-ellipsoidal grains for 50 wt. % of Nb.

Figure 12. (a) Dependence of the perovskite phase fraction (in %) on the Nb content (in wt. %), calculated from equations (3a) for SBTN. (b) SEM-images of SBT and SBTN films: a – SBT-film; SBTN films with Nb content: b – 10, c – 20, d – 30, e – 40, and f – 50 wt.%. (c) AFM-images of the SBT and SBTN films surface: a – SBT film; SBTN films with content of Nb: b – 10, c – 20, d – 30, e – 40, f – 50 wt.%. Symbols in the part (a), SEM and AFM images in the part (b) and (c) are experimental results [42].

It is reasonable to assume that $P_s(T, x)$ is proportional to the fraction of the perovskite phase, and this is confirmed by comparing the shape of solid curves in Figures 11a and 12a. This comparison is an additional basis for the applicability of equations (3) to the analysis of experimental results in order to determine the previously unknown dependences of the Landau free energy coefficients $\alpha(T, x)$ and $\beta(x)$ on the Nb content. Hence, the comparison of theoretical
results with experimental ones, shown in Figures 11 and 12, reveals a linear correlation between the spontaneous polarization of nanogranular SBTN films and the perovskite phase fraction in them. This is an additional basis for the applicability of the Landau-Devonshire approach to the analysis of experimental results in order to determine the previously unknown dependences of the Landau expansion coefficients on the concentration of substitutes and dopants. To resume, the Landau-Devonshire approach describes the experimentally observed nonmonotonic dependence of the ferroelectric perovskite phase fraction and remanent polarization on Nb concentration. Important that the form of the nonmonotonic dependences shown in Figures 11a and 12a strongly resembles the dependence of the shift of the Raman band maximum from 810 cm\(^{-1}\) to 830 cm\(^{-1}\) shown in Figure 8.

4. CONCLUSION

In summary, polycrystalline SBT and SBTN thin films substituted with 10, 20, 30, 40 and 50\% wt. of Nb were prepared by sol-gel method and annealed at relatively low temperature, 700\(^\circ\)C. The relative intensity of (115) and (200) peaks in XRD spectrum depends strongly on the Nb content. Micro-Raman spectroscopy was used to study the lattice vibrational modes, and to explore the internal structure, polycrystalline nature, and crystallization behavior of the SBTN thin films with Nb ions at Ta-sites.

The vibration mode at 810 cm\(^{-1}\) observed in the case of the undoped SBT sample, is also known as the octahedral stretching mode (or breathing mode). The mode shows a significant shift to higher frequencies (up to 830 cm\(^{-1}\)) and broadening upon substitution of Ta\(^{5+}\) ions with Nb\(^{5+}\) ions up to 40 \% wt of Nb. The effect is explained by the presence of vibrations of both types, Ta-O-Ta and Nb-O-Nb, in the structure. The substitution of Nb at Ta-site shows a significant splitting of O-Ta-O octahedral stretching mode. Unexpectedly, we observed a nonmonotonic shift of the Raman band maximum from 810 cm\(^{-1}\) (for pure SBT) to 830 cm\(^{-1}\) (for SBTN with 20\% of Nb) and then back to 810 cm\(^{-1}\) with increasing Nb content from 40 to 50 wt. \%. We assume that these changes are conditioned by the ferrodistortion occurring in ferroic perovskites, namely by the tilting distortion of (Ta,Nb)O\(_6\) octahedra happened at 20-40 wt. \% of Nb. The octahedra tilting can change the coordination environment of the A-cite cation, as well as it lowers the SBTN symmetry below the cubic symmetry. The tilted state at 20-40 wt. \% of Nb can explain the nonmonotonic changes of the perovskite phase fraction and remanent polarization with increasing Nb content from 0 to 50 wt.\%, in particular their initial increase with Nb content increase up to 20 wt. \% followed by a decrease at 30 wt. \% of Nb, then increase at 40 wt.\% and further decrease for 40 – 50 wt.\% of Nb.
The nonmonotonic variation of the frequency shift of the Raman band at 161 cm$^{-1}$ is related with the transition from symmetric (Ta-O-Ta) to the asymmetric (Ta-O-Nb) bonding with different binding strength under the partial substitution of Ta$^{5+}$ ions with Nb$^{5+}$ ions with concentration 10-30 wt.%, or symmetric (Nb-O-Nb) bonding in the oxygen octahedrons under Nb$^{5+}$ ions substitution with concentration 40 wt. % and more. This behavior was explained in terms of smaller ionic radii of Nb than Ta at B-site.

The Raman band at about 76 cm$^{-1}$ refers to the E$_g$ mode, where the Bi-O groups in Bi$_2$O$_2$ layers in the same plane vibrate out of phase. The band maximum shows the almost absence of any frequency shift with the increasing of Nb content. Hence, we concluded that Nb$^{5+}$ does not replace Bi$^{+3}$ in Bi$_2$O$_2$ layers and has only indirect influence consisting in changing the configuration of the bismuth-oxide layers. Since Nb is pentavalent and has been embedded in an octahedral lattice, the low-frequency modes do not undergo significant changes.

It has been shown experimentally, that the changes of the perovskite phase fraction and remanent polarization values, which appear with Nb content increase from 0 to 50 wt.% in SBTN thin films, are the same as the nonmonotonic dependences of both factors, the Raman band maximum shift from 810 cm$^{-1}$ to (833-837) cm$^{-1}$, and its halfwidth, on the concentration of Nb. Performed theoretical analysis shows the correlations between the structural phase changes and Raman bands shift. In particular, Landau-Devonshire approach describes the experimentally observed nonmonotonic dependence of the ferroelectric perovskite phase fraction and remanent polarization on Nb content. The form of the nonmonotonic dependence strongly resembles the nonmonotonic shift of Raman band maximum from 810 cm$^{-1}$ to 830 cm$^{-1}$ appearing with Nb content increase.

Thus, the combination of the micro-Raman spectroscopy with x-ray diffraction, ferroelectric measurements and Landau-Devonshire theoretical approach allows to establish the role of Nb doping and to reveal the physical origin of strong correlations between the lattice dynamics, microstructure, phase composition and ferroelectric properties of the SBTN thin films annealed at relatively low temperature.

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Authors' contribution. O.M.F., A.D.Y., T.V.T., O.P.B. conducted experiments and wrote the experimental part of the work. L.W., A.V.S and V.V.S. prepared samples. A.N.M. performed calculations and wrote the theoretical part of the work. All authors worked on the results discussion and manuscript improvement.

References

1. Y. Shimakawa, and Y. Kubo, Y. Nakagawa, T. Kamiyama, and H. Asano, F. Izumi. Crystal structures and ferroelectric properties of SrBi2Ta2O9 and Sr0.8Bi2.2Ta2O9. Appl. Phys. Lett. 74, 1904 (1999).
2. G. Senthil Murugan, and K. B. R. Varma. Journal of Electroceramics 8, 37-48 (2002).
3. A. Moure, and L. Pardo. Journal of Electroceramics 15, 243-250 (2005).
4. R. E. Jones Jr, Peter Zurcher, B. Jiang, J. Z. Witowski, Y. T. Lii, P. Chu, D. J. Taylor, and S. J. Gillespie. Integrated Ferroelectrics 12, 23-31 (1996).
5. J. F. Scott and C. A. Paz de Araujo, Science 246, 1400 (1989).
6. C.A. Paz de Araujo, J.D. Cuchiaro, L.D. Mcmillan, M.C. Scott, J.F. Scott, Nature 374, 627 (1995).
7. Y. Noguchi, A. Kitamura, L.C. Woo, M. Miyayama, K. Oikawa, T. Kamiyama, J. Appl. Phys. 94, 6749 (2003).
8. Y. Yan, M. M. Al-Jassim, Z. Xu, X. Lu, D. Viehland, M. Payne, and S. J. Pennycook. Applied Physics Letters 75, 1961-1963 (1999).
9. V.V. Sidsky, A.V. Semchenko, A.G. Rybakov, V.V. Kolos, A.S. Turtsevich, A.N. Asadchyi, W. Strek. Journal of Rare Earths. 32, 277–281 (2014).
10. Y. Wu, M. J. Forbess, S. Seraji, Steven J. Limmer, T. P. Chou, G. Cao. Materials Science and Engineering, B86, 70–78 (2001).
11. Chen, T.C. Impedance spectroscopy of SrBi2Ta2O9 and SrBi2 Nb2O9 ceramics correlation with fatigue behavior / T.C. Chen, C.L. Thio,S.B. Desu // J. Mater. Res. – 1997. – Vol. 12. –P. 2628–2637
12. S. B. Desu, P. C. Joshi, X. Zhang, and S. O. Ryu, Appl. Phys. Lett. 71, 1041 (1997).
13. T. Atsuki, N. Soyama, T. Yonezawa, and K. Ogi, Jpn. J. Appl. Phys., Part 1 34, 5096 (1995).
14. Y. Ito, M. Ushikubo, S. Yokoyama, H. Matsunaga, T. Atsuki, T. Yonezawa, and K. Ogi, Jpn. J. Appl. Phys., Part 1 35, 4925 (1996).
15. G. D. Hu, I. H. Wilson, J. B. Xu, W. Y. Cheung, S. P. Wong, and H. K. Wong. Structure control and characterization of SrBi2Ta2O9 thin films by a modified annealing method. Applied Physics Letters 74, 1221 (1999); doi: 10.1063/1.123505.
16. S. B. Desu and D. P. Vijay, Mater. Sci. Eng., B 32, 75 (1995).
17 Miura, K. Difference in the Electronic Structure of SrBi2Ta2O9 and SrBi2 Nb2O9 / K. Miura, M. Tanaka // Jpn. J. Appl. Phys. – 1998. – Vol. 37.P. 606–607.
Raman Spectroscopic Fingerprint of Ferroelectric SrBi2Ta2O9 Thin Films: A Rapid Distinction Method for Fluorite and Pyrochlore Phases, Jpn. J. Appl. Phys. Vol. 40 (2001) pp. L 891–L 893, Part 2, No. 8B, 15 August 2001.

19. E. Ching-Prado, W. Pérez, A. Reynés-Figueroa, R. S. Katiyar, D. Ravichandran & A. S. Bhalla (1999) Raman study of SrBi2Ta2O9 thin films, Ferroelectrics Letters Section, 25:3-4, 97-102, DOI: 10.1080/07315179908204589.

20. D. P. Volanti, L. S. Cavalcante, E. C. Paris, A. Z. Simoes, D. Keyson, V. M. Longo, A. T. de Figueiredo, E. Longo, and J. A. Varela, F. S. de Vicente, A. C. Hernandez, Photoluminescent behavior of SrBi2Nb2O9 powders explained by means of $\beta$-Bi$_2$O$_3$ phase, Applied Physics Letter, 90, 261913 (2007).

21. P. R. Graves, G. Hua, S. Myhra, and J. G. Thompson, J. Solid State Chem., 114, 112 (1995).

22. S. Kojima, R. Imaizumi, S. Hamazaki, and M. Takashige, Jpn. J. Appl. Phys., 33, 5559 (1994).

23. W. Perez, R. R. Das, P. S. Dobal, Y. I. Yuyuk, P. Bhattacharya, R. S. Katiyar, Effect of Cation Substitution on Raman spectra of SrBi2Ta2O9 ceramics and thin Films, Mat. Res. Soc. Symp. Proc. Vol784, (2004)

24. A. D. Rae, J. G. Thompson, and R. L. Withers, “Structure Refinement of Commensurately Modulated Bismuth Strontium Tantalate, Bi$_2$SrTa$_2$O$_9$”. Acta Crystallogr., Sect. B: Struct. Sci., B48, 418–428 (1992); http://dx.doi.org/10.1107/S0108768192001654.

25. S. T. Tay, C. H. A. Huan, A. T. S. Wee, R. Lui, W. C. Goh, C. K. Ong, and G. S. Chen, Substrate temperature studies of SrBi$_2$(Ta$_{1-x}$Nb$_x$)$_2$O$_9$ grown by pulsed laser ablation deposition/ Journal of Vacuum Science Science&Technology A20, 125 (2002).

26. Ai-Dong Li, Di Wu, Hui-Qin Ling, Tao Yu, Zhi-Guo Liu, Nai-Ben Ming, Role of interfacial diffusion in SrBi2Ta2O9 thin-film capacitors, Microelectronic Engineering, 66, 654-661, 2003.

27. R. Dinu, M. Dinescu, J. D. Pedarnig, R. A. Gunasekaran, D. Bäuerle, S. Bauer-Gogonea, S. Bauer, “Film structure and ferroelectric properties of in situ grown SrBi$_2$Ta$_2$O$_9$ films ”. Appl. Phys. A, 69, 55–61 (1999); DOI 10.1007/s003399900056/

28. Ortega N, Bhattacharya P and Katiyar R S 2006 Mater. Sci. Eng. B 130 36.

29. Moret M P, Zallen R, Newnham R E, Joshi P C and Desu S B 1998 Phys. Rev. B 57 5715.

30. Guo Zhen Liu, et al. Raman scattering study of La-doped SrBi$_2$Nb$_2$O$_9$ ceramics. Journal of Physics D: Applied Physics, 2007, 40.24: 7817.

31. Kojima, Seiji. "Optical mode softening of ferroelectric and related bismuth layer-structured oxides." Journal of Physics: Condensed Matter 10.20 (1998): L327.

32. K. Miura, “Electronic and structural properties of ferroelectric SrBi$_2$Ti$_2$O$_8$, SrBi$_2$Nb$_2$O$_8$ and PbBi$_2$Nb$_2$O$_8”, Journal of the Korean Physical Society, 42, S1244-S1247 (2003).

33. Noguchi Y., Miwa I., Goshima Y. & Miyayama M., “Defect control for large remanent polarization in bismuth titanate ferroelectrics, doping effect of higher-valent cations”, Jpn. J. Appl. Phys., 39, L1259-L1262 (2000).

34. Noguchi Y., Miyayama M., Oikawa K., Kamiyama T., Osada M. & Kakiyama M., “Defect engineering for control of polarization properties in SrBi$_2$Ta$_2$O$_9$”, Jpn. J. Appl. Phys., 41, 7062-7075 (2002).
35. T. Yu, Z. X. Shen, W. S. Toh, J. M. Xue, and J. Wang. Size effect on the ferroelectric phase transition in SrBi$_2$Ta$_2$O$_9$ nanoparticles. J. Appl. Phys., 94, 618, (2003).

36. H. Ke, D. C. Jia, W. Wang, Y. Zhou. Ferroelectric phase transition investigated by thermal analysis and Raman scattering in SrBi$_2$Ta$_2$O$_9$ nanoparticles. Solid State Phenomena Vols. 121-123, pp 843-846 (2007).

37. N.V. Morozovsky, A.V. Semchenko, V.V. Sidsky, V.V. Kolos, A.S. Turtsevich, E.A. Eliseev, and A.N. Morozovska. Effect of annealing on the charge-voltage characteristics of SrBi$_2$(Ta,Nb)$_2$O$_9$ films. Physica B: Condensed Matter, 464, Pages 1–81 (2015).

38. E.A. Eliseev, A.V. Semchenko, Y.M. Fomichov, M. D. Glinchuk, V.V. Sidsky, V.V. Kolos, Yu.M. Pleskachevsky, M.V. Silbin, N.V. Morozovsky, A.N. Morozovska. Surface and finite size effects impact on the phase diagrams, polar and dielectric properties of (Sr,Bi)Ta$_2$O$_9$ ferroelectric nanoparticles. J. Appl. Phys. 119, 204104 (2016).

39. A. K. Tagantsev and G. Gerra. J. Appl. Phys. 100, 051607 (2006).

40. L.D. Landau, E.M. Lifshitz, L. P. Pitaevskii. Electrodynamics of Continuous Media, (Second Edition, Butterworth-Heinemann, Oxford, 1984).

41. J. A. Cho, S. E. Park, T. K. Song, M. H. Kim, H. S. Lee, S. S. Kim. Dielectric and Piezoelectric Properties of Nonstoichiometric SrBi$_2$Ta$_2$O$_9$ and SrBi$_2$Nb$_2$O$_9$ Ceramics. Journal of Electroceramics, 13(1-3), 515–518 (2004); doi:10.1007/s10832-004-5150-7.

42. V. V. Sidsky, A. V. Semchenko, V. V. Kolos, A. N. Petlitsky, V. A. Solodukha, N. S. Kovalchuk. Influence of processing conditions on the structure and ferroelectric properties of SBTN films obtained by the sol-gel method. Problems of physics, mathematics and technology, no. 1 (30), 2017 17-21.