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The effect of the thickness of a single-crystal $SrTiO_3$ film on its structure and dielectric parameters in the range of $0.3-1.5$ THz

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Single-crystal thin films of strontium titanate ($SrTiO_3$, STO) of various thicknesses (h): 60 nm, 120 nm and 270 nm were grown on $Al_2O_3(001)$ substrates using the RF sputtering method. Using X-ray diffraction analysis, it is shown that all STO films are characterized by a pseudo-cubic cell, and have the same deformation of the unit cell. Using the method of terahertz time-domain spectroscopy, it is shown that in the frequency range $0.3-1.5$ THz, films are characterized by practically no dispersion of the real (ε') and imaginary ε'' parts of the dielectric constant, but as h decreases, there is a significant increase in ε' at comparable ε''.

Keywords: thin films, dielectric characteristics, heteroepitaxy, STO, terahertz time-domain spectroscopy.

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1. Introduction

Ferroelectrics find wide application in modern equipment [1,2], and more and more attention is being paid to nanoscale films. The quality of the film surface, the structure of the interface with the substrate and internal stresses may impact optic, dielectric and ferroelectric properties of the films. The intensively studied materials include solid solutions based on $BiFeO_3$ [3], $Bi_4Ti_3O_{12}$ [4], and quantum ferroelectrics based on STO [5,6]. Active interest in the study of STO film properties for development of terahertz (THz) frequency range devices is confirmed by certain recent papers on non-linear interaction of THz waves with the soft mode [7]. Previously the dielectric properties have already been studied in the terahertz range for various specimens of STO films, differing by thickness, substrate material and growth method [8,9]. Since the unit cell of a bulk STO is cubic, the thin STO film is easily distorted due to the lattice mismatch with the substrate. This substantially influences the position of the soft mode, which in a single crystal is located in the vicinity of 2.62 THz [10]. As a result the dielectric characteristics of the film differ substantially both from the volume specimens and between each other depending on the material and structure of the substrate, and the growth method. This paper is dedicated to the establishment of the patterns of single-crystal STO film thickness influence on their structure and dielectric parameters in the range of $0.3-1.5$ THz at room temperature. The data for such type of the films are not available in the literature.

2. Objects, methods of obtaining and studying specimens

Thin STO films with thicknesses of ~ 60 nm, 120 nm and 270 nm (film growth speed is ~ 6 nm/min) on a single-crystal substrate Al_2O_3 ((001)-cut, polishing — double-sided, thickness — $430\,\mu$m) were prepared by the method of RF cathode sputtering in an oxygen atmosphere in one stage. The target for sputtering was ceramic $SrTiO_3$ (with diameter of 50 mm and thickness of 3 mm). The initial substrate temperature was $\sim 400\,^\circ$C, the pressure of pure oxygen in the chamber was 67 Pa, and the input RF power was — 130 W.

A „RIKOR“ CuK_α-radiation multifunction X-ray diffractometer was used to perform X-ray diffraction analysis (determine the phase composition, structural perfection of the films, unit cell parameters, and orientation relationships between the film and the substrate).

The complex dielectric permittivity (ε^*) of STO films and the substrate $Al_2O_3(001)$ were studied at room temperature in the frequency range of $0.3-1.5$ THz using the method of terahertz time-domain spectroscopy or THz-TDS. The terahertz spectrometer is based on an erbium fiber laser in combination with a second harmonic generation module (Toptica Photonics, Germany), delivering radiation at the

Parameters of lattice cells for STO films/$Al_2O_3(001)$ with thickness of 60, 120 and 270 nm

Thin film	Parameter of el. cell, calculated from $(hhh)_c$, Å	Parameter of el. cell, calculated from $(211)_c$, Å
STO(60 nm)/$Al_2O_3(001)$	3.908	3.914
STO(120 nm)/$Al_2O_3(001)$	3.910	3.913
STO(270 nm)/$Al_2O_3(001)$	3.912	3.913

central wavelength of 775 nm with a pulse duration of 130 fs, repetition rate of ~ 78 MHz and average power of ~ 100 mW. The THz generator is an interdigital array antenna iPCA-21-05-1000-800-h (Batop GmbH, Germany). Detection of the terahertz field is carried out by the electro-optic sampling method based on the Pockels effect, using a ZnTe(110) with a thickness of 2 mm. The sample under study is placed on the diaphragm in a focal plane between TPX lenses (Tidex, Russia) with a focal length of 100 mm. The detailed description of the installation may be found in [11]. The spectrometer delay line is built on a motorized linear translation stage with feedback M-ILS50HA (Newport, USA), providing for spatial precision of positioning $0.3\,\mu$m, which corresponds to 2 fs in the time domain. It is important to mention this, since the delay of THz-signal caused by passage through the film was more than 18 fs (the value for the thinnest specimen of 60 nm). Besides, the measurements were carried out with the time step of 100 fs, in the range of 60 ps. Four pairwise measurements were made, which were averaged to minimize noise. In the process of the measurement, the reference signal (the etalon) was the spectrum of the substrate $Al_2O_3(001)$. The calculation was carried out using a double-layer model „substrate + film" [12]. The substrate specimen was a fragment of the same wafer that was used to make the substrates for the films. It was preliminarily characterized for the accounting in the numerical model. The film thickness was determined from the sputtering speed of ~ 6 nm/min.

3. Experimental results and discussion

The study of STO/$Al_2O_3(001)$ films of various thickness by X-ray diffraction method found only bright reflexes on the diffraction patterns of all heterostructures, the reflexes being related to the STO films and substrate $Al_2O_3(001)$. No traces of impurity phases were found. Regardless of the STO film thickness, on $\theta - 2\theta$ X-ray pictures in the normal scattering geometry (Figure 1) only reflexes of $(hhh)_c$ family are found (index „c" indicates the reflexes and directions in pseudo-cubic approximation).

This indicates the orientation of axis $[111]_c$ of the films in the direction of the surface normal of the substrate (axis [001] Al_2O_3). All studied films were produced epitaxially on the substrate Al_2O_3, on each of φ-scans of reflexes $(110)_c$ (Figure 2) there are 6 narrow reflexes, the angular positions of which are moved relative to the reflex (104) of the substrate Al_2O_3 on 30°.

In this case the coupling between the STO film and the substrate $Al_2O_3(001)$ in the azimuthal plane happens in the direction $[1{-}10]_c$ and $[-101]_c$. The detected displacement of reflexes $(110)_c$ of the STO films relative to the reflex (104) of the substrate Al_2O_3 corresponds to the misorientation of axis $[1{-}10]_c$ of the STO film relative to the axis [100]Al_2O_3. To determine the distortion of the lattice cell, $\theta{-}2\theta$ X-ray pictures of the $(211)_c$ family reflexes were obtained. The rotation at φ by 60° does not lead to the change in the angular position of the maximum. The angular positions of the reflexes were used to calculate the parameters of the lattice cells (Table), the error is below 0.001 Å.

For the films with thickness of 60 nm and 120 nm you can note minor differences in the lattice cell parameters. This is related to minor distortion in the cubic lattice cell. Since the substrate has hexagonal lattice cell, it is most probable that the lattice cells of the films with the thickness of 60 nm and 120 nm have minor rhombohedral distortion. The STO film with thickness of 270 nm has already a cubic lattice cell with $a = 3.912$ Å, which is only slightly more than the parameter of the volume STO ($a_{\mathrm{bulk}} = 3.905$ Å). I. e. there is a minor extension of the lattice cell (less than 0.2 %). For all STO films/$Al_2O_3(001)$ the low values of vertical and azimuthal misorientation are also specific, which do not exceed 1.9°

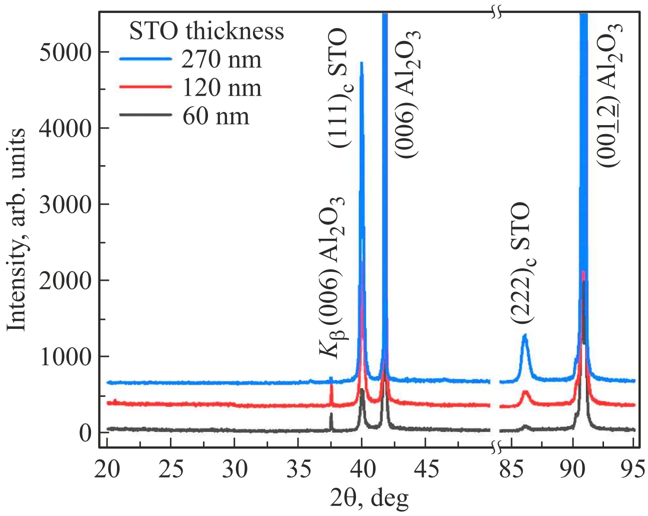

Figure 1. $\theta - 2\theta$ X-ray diffraction patterns of STO films/Al_2O_3 (001) with thickness of 60 nm, 120 nm and 270 nm.

and 3.6°, accordingly. In addition to the low values of axis misorientation, the reflexes corresponding to the STO layer, on all obtained X-ray pictures have a small half-width, which indicates high structural perfection of the STO films.

Figure 3 presents the measured dielectric constants for the sapphire substrate in the terahertz spectrum.

For (001)-cut, these values correspond to an ordinary wave, i.e., polarization of the THz wave is orthogonal to the c-axis of the sapphire, and agree well with the literature data. Dispersion ε' in the range of 0.3–2.5 THz was approximated by the Sellmeier's equation:

$$\varepsilon' = 9.398 - \frac{4.83\nu^2}{\nu^2 - 13.25^2},$$

where ν is frequency in THz.

Parameter 13.25 THz in the denominator is fixed during approximation and complies with the frequency of the

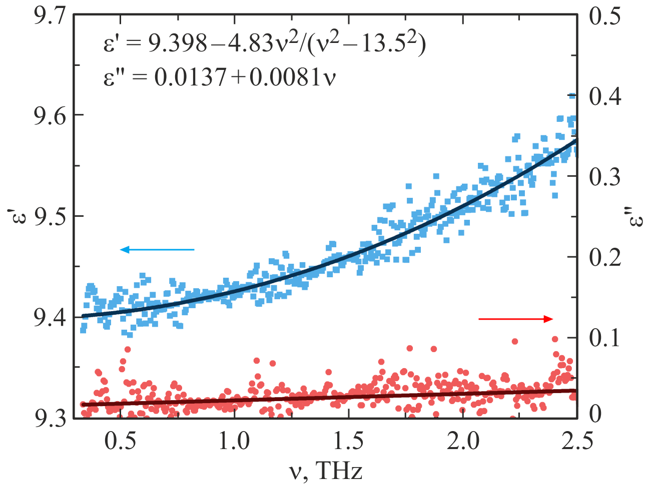

Figure 3. Complex dielectric permittivity of sapphire substrate. Blue — actual part; red — imaginary part. Symbols — experimental data; solid — approximation.

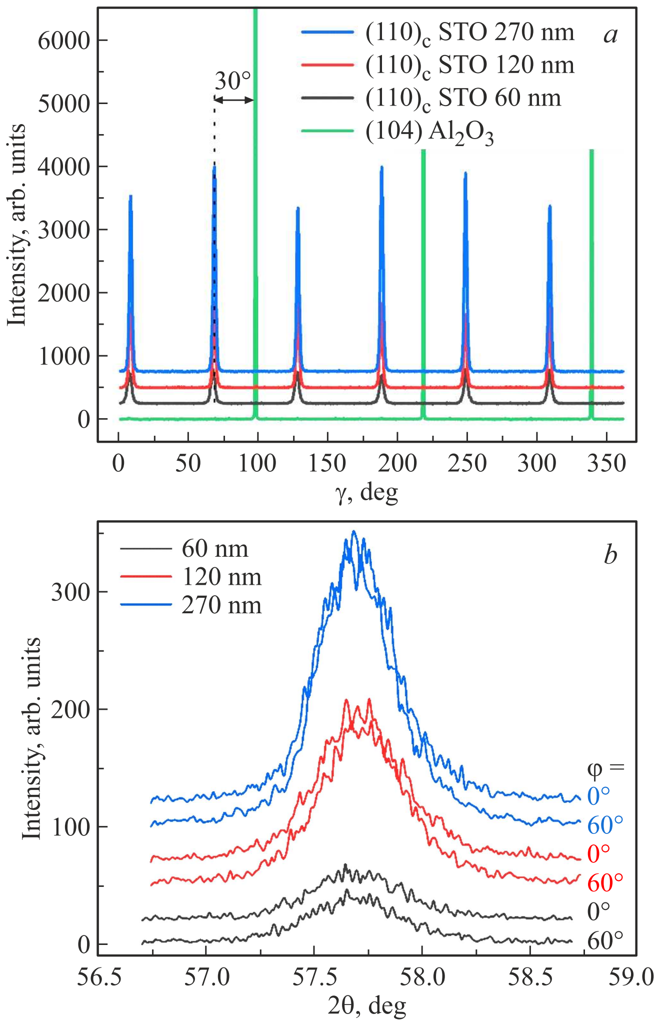

Figure 2. a) X-ray pictures of φ-scans of reflex $(110)_c$ of STO layer and (104) substrate Al_2O_3 for STO/Al_2O_3 (001) with thickness of 60, 120 and 270 nm. b) $\theta - 2\theta$ X-ray pictures of reflex $(211)_c$ with rotation by φ at 60° for STO films/Al_2O_3 (001) with thickness of 60, 120 and 270 nm.

transverse optic phonon for α-Al_2O_3 $\sim 442\,\mathrm{cm}^{-1}$. For simplicity $\varepsilon''(\nu)$ may be approximated with linear dependence $\varepsilon'' = 0.0137 + 0.0081\nu$. With account of the approximated values for the substrate, the characteristics of the produced STO films are calculated (Figure 4). The data for the real part (Figure 4, a), have higher validity, because they are determined by the phase or time delay of the THz-signals, which is noticeable in the unprocessed time signals of the spectrometer. Due to the artifacts caused by the diffraction of long waves on the aperture diaphragm 4 mm, the values below 0.3 THz are not given in the spectra. Higher dispersion in the proximity of frequencies 1.1–1.2 THz and 1.6–1.7 THz and above is due to considerable absorption by water molecules in the atmosphere. The measurement path was not dried or purged with dry nitrogen during the measurement.

Figure 4, a demonstrates the decrease of ε' with the film thickness increase. Besides, its frequency dependence does not demonstrate a noticeable dispersion within the limits of the measurement error. For specimens 120 and 60 nm ε'' decreases below zero (Figure 4, b), i.e. it actually turned out to be immeasurable. This means that the level of THz-radiation attenuation in the film is less than the amplitude of noise and drift of the spectrometer signal. To compare with the other papers, we assume that values ε'' do not exceed 50 in the range below 1 THz for all specimens. Previously the properties of the STO films on sapphire substrates were studied in the far IR- or THz-ranges in three papers [9,13,14]. In paper by Fedorov et al. the properties of the STO film with thickness of 275 nm, applied by laser ablation method on substrate Al_2O_3 with r-cut were studied [13]. The properties were calculated after processing of the substrate transmission spectra with and without the film obtained on the Fourier transform spectrometer. Besides, the authors guess about

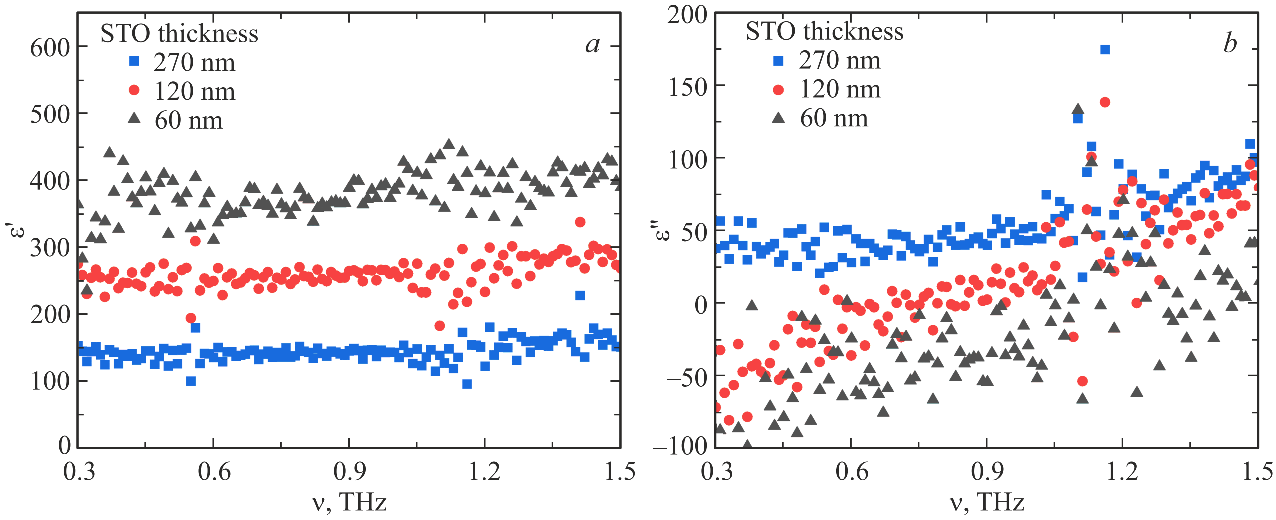

Figure 4. Real (a) and imaginary (b) parts of the complex dielectric permittivity of STO films on sapphire substrate.

the complexity of the processing related to the birefringence occurring in the substrate, which they remove using spectral algorithms of filtration. In the paper the estimated value ε' for the STO film is ~ 120 in the proximity of 1 THz at room temperature. Despite the nuances of calculations and processing, these results agree well with our case for the film with thickness of 270 nm and also demonstrate weak dispersion in the range below 1.5 THz. At room temperature ε'' also takes the values below 50.

The group from the Czech Republic and Germany studied the specimens of the STO films produced by chemical vapor deposition method (thickness 290 nm, orientation $\langle 111 \rangle$) and from the solution (thicknesses 360 and 720 nm, polycrystalline) onto the sapphire substrate with c-cut [9]. The studies were carried out using the IR Fourier transform spectrometer and backward-wave oscillators. The film with the thickness of 290 nm, having practically perfect crystalline orientation $\langle 111 \rangle$ orthogonally to the substrate surface, has $\varepsilon' \approx 300$. For polycrystalline specimens $\varepsilon' \approx 180$. This is related to the fact that the estimated position of the soft mode for the first specimen is located in the proximity of 2.4 THz at room temperature, and for two other ones — in the proximity of 3.3 THz. Despite the fact that ε' is more than in our case, the curves in the range of < 1.5 THz similarly demonstrate weak dispersion. Our results are closer the values of ε'' samples produced by the method of chemical deposition from a solution. For the film prepared by the chemical vapor deposition method (290 nm), $\varepsilon'' > 100$ at frequencies of more than 1 THz. This agrees with the lower frequency position of the soft mode for this specimen.

In a paper by the group of Peter Kužel, the change in the dielectric characteristics in the range of 0.2–2 THz in the STO films depending on the applied voltage was studied [14]. The films with a thickness of 313 nm are prepared on the CeO sublayer on the substrate from r-cut of the sapphire using the laser deposition method. A planar capasitor cell is formed on the surface of the specimens by sputtering of the interdigital structure of the electrodes. The paper shows the change in the dielectric constants of the film to 10 % in the low-frequency spectrum when voltage is applied at around 100 kV/cm to the structure. Complex dielectric permittivity of the films in the paper differs substantially from our case: $\varepsilon' \approx 330$, $\varepsilon'' \approx 270$ for the frequency in the proximity of 1 THz. The authors of the paper claim that the approximation of the obtained data by the oscillator model provides the position of the soft mode in the proximity of 2.7 THz (90 cm^{-1}). However, the expressed abnormal dispersion for ε', and higher value ε'' compared to the single-crystal specimen may indicate strong broadening of its contour.

It also makes sense to compare our results with the single-crystal specimens of STO. Matsumoto group et al. showed that the soft mode for the single crystal was located in the proximity of 2.62 THz [10]. Spectra ε^* measured using the THz-ellipsometry are approximated well with the parameters extracted from the measurements of the IR-reflection on the Fourier transform spectrometer. In their case $\varepsilon \approx 300$ in the low-frequency area, however, ε'' drops to unmeasurable values below 1 THz. This may potentially correspond to the specimen of our film with thickness of ~ 120 nm.

The review of the above papers confirms the idea that the dielectric properties of the STO films in the THz range differ substantially and depend on many factors. They may include the method of production, the substrate orientation and the thickness. Therefore, we do not do the comparison to the publications, which present the data for the other substrates. However, the comparison to the results of other authors for the films on the sapphire substrates makes it possible to suggest the following for our specimens. Absence of dispersion ε' in the range below 1.5 THz, and a small value ε'' indicates high-frequency displacement of the soft mode with the growth of the sputtered film thickness. Probably, the mode frequency lies above the value of 2.62 THz, specific for a single crystal. Besides, its width complies with the high-quality specimens of the STO films. This may be confirmed in the future by the studies on the terahertz spectrometers with the spectral range of more than 3.5 THz or IR Fourier transform spectrometers. Additional information may also be provided by the temperature measurements.

4. Conclusion

Using the RF cathode sputtering method, single-crystal thin STO films were grown with three thicknesses: 60, 120, and 270 nm, which are characterized by a cubic cell and have the same deformation of the lattice cell. Using the method of terahertz time-domain spectroscopy, it was shown that in the frequency range $0.3-1.5$ THz the films are characterized by the absence of the noticeable dispersion of ε' and relatively low values of ε''. As the film thickness increases, substantial drop of ε' occurs while the value of ε'' stays lower than 50 for frequencies below 1 THz. This may be related to the shift of the soft mode to a higher frequency area with the film thickness growth. Dielectric properties for the STO film with the thickness of 270 nm correspond to the high-quality specimens of close thicknesses, grown on the substrates from the single-crystal sapphire by other scientific groups. To sum up, note that the method of RF cathode sputtering makes it possible to obtain the films of strontium titanate of high quality with thickness from dozens to hundreds of nanometers. This confirms the potential of their use in the integral devices of terahertz frequency range.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] L.W. Martin, A.M. Rappe. Nat. Rev. Mater., **2**, 16087 (2016). DOI: 10.1038/natrevmats.2016.87

[2] K. Yao, S. Chen, S.C. Lai, Y.M. Yousry. Adv. Sci., **9**, 2103842 (2022). DOI: 10.1002/advs.202103842

[3] M. Botea, C. Chirila, G.A. Boni, I. Pasuk, L. Trupina, I. Pintilie, L.M. Hrib, B. Nicu, L. Pintilie. Electronic Materials, **3**, *2*, 173 (2022). DOI: 10.3390/electronicmat3020015

[4] A.S. Anokhin, S.V. Biryukov, Yu.I. Golovko, V.M. Mukhortov. Nauka Yuga Rossii, **14**, *1*, 29 (2018). (in Russian). DOI: 10.23885/2500-0640-2018-14-1-29-34

[5] J. Petzelt, T. Ostapchuk, S. Kamba, I. Rychetsky, M. Savinov, A. Volkov, B. Gorshunov, A. Pronin, S. Hoffmann, R. Waser, J. Lindner. Ferroelectrics, **239**, *1*, 117 (2000). DOI: 10.1080/00150190008213313

[6] V.A. Gritsenko, D.R. Islamov. *Fizika dielektricheskikh plenok: mekhanizmy transporta zaryada i fizicheskie osnovy priborov pamyati* (Parallel', Novosibirsk, 6). (in Russian).

[7] M. Kozina, M. Fechner, P. Marsik, T. van Driel, J.M. Glownia, C. Bernhard, M. Radovic, D. Zhu, S. Bonetti, U. Staub, M.C. Hoffmann. Nat. Phys. **15**, 387 (2019). DOI: 10.1038/s41567-018-0408-1

[8] R. Kinjo, I. Kawayama, H. Murakami, M. Tonouchi. *Advances in Materials Physics and Chemistry*, **3**, 58 (2013). DOI: 10.4236/ampc.2013.31009

[9] T. Ostapchuk, J. Petzelt, V. Zelezny, A. Pashkin, J. Pokorny, I. Drbohlav, R. Kužel, D. Rafaja, B.P. Gorshunov, M. Dressel, Ch. Ohly, S. Hoffmann-Eifert, R. Waser. Phys. Rev. B, **66**, 235406 (2002). DOI: 10.1103/PhysRevB.66.235406

[10] Naoki Matsumoto, Takashi Fujii, Keisuke Kageyama, Hiroshi Takagi, Takeshi Nagashima, Masanori Hangyo. Jpn. J. Appl. Phys, **48**, 09KC11 (2009). DOI: 10.1143/JJAP.48.09KC11

[11] A. Rybak, V. Antsygin, A. Mamrashev, N. Nikolaev. *Crystals*, **11**, *2*, 125 (2021). DOI: 10.3390/cryst11020125

[12] V. Antsygin, A. Mamrashev. Avtometriya. **53**, *6*, 92–96 (2017). (in Russian).

[13] I. Fedorov, V. Železn, J. Petzelt, V. Trepakov, M. Jelínek, V. Trtík, M. Čerňansk, V. Studni. Ferroelectrics, **413**, 208 (1998). DOI: 10.1080/00150199808014890.

[14] P. Kužel, F. Kadlec, H. Němec, R. Ott, E. Hollmann, N. Klein. Appl. Phys. Lett., **88**, 102901 (2006). DOI: 10.1063/1.2183370

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