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BROADBAND AND INFRARED SPECTROSCOPY OF $Ag_{0.98}Li_{0.02}NbO_3$ CERAMICS

E. Palaimienė [a], J. Macutkevič [b], J. Banys [a], I. Gruszka [c], and A. Kania [c]

[a] *Institute of Applied Electrodynamics and Telecommunications, Vilnius University, Saulėtekio 3, 10257 Vilnius, Lithuania*

[b] *Center for Physical Sciences and Technology, Saulėtekio 3, 10257 Vilnius, Lithuania*

[c] *Institute of Physics, University of Silesia in Katowice, ul. 75 Pułku Piechoty 1, PL-41-500 Chorzów, Poland*

Email: edita.palaimiene@ff.vu.lt

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The dielectric properties of $Ag_{0.98}Li_{0.02}NbO_3$ (ALN2) ceramics were investigated in a broad frequency range (20 Hz – 60 THz). The dielectric spectra of ALN2 ceramics are mainly impacted by electrical conductivity at higher temperatures (above 400 K) and low frequencies (below 100 Hz), ferroelectric domains below ferroelectric phase transition temperature T_c = 330 K and at low frequencies (below 1 MHz), and contribution of the soft ferroelectric mode, the frequency of which is below 50 cm^{-1}. All phononic modes are slightly temperature dependent, thus confirming the influence of Ag, O and Li ions dynamics on the phase transitions. However, the most important contribution to the dynamics of phase transition is made by Nb ions. Ceramics exhibits a huge value of dielectric permittivity and relatively low losses in a microwave frequency range ($\varepsilon' \approx 250$ and $\varepsilon'' \approx 20$ at 10 GHz and room temperature), indicating that it is suitable for various microwave dielectric applications.

Keywords: ceramics, spectroscopy, phonons, ferroelectric

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1. Introduction

Nowadays the leaders in piezoelectric applications are barium titanate ($BaTiO_3$) and lead zirconium titanate (PZT) based materials. They have very attractive piezoelectric and electromechanical properties. However, the general strategy is to eliminate PZT in practical applications due to poisonous lead used in piezoelectric industry. Therefore, it is important to find new materials with optimal piezoelectric features. It is believed that piezoelectric lead-free niobate based materials can be an alternative to already known and used piezoelectric materials [1]. One of such materials is silver niobate ($AgNbO_3$, AN) that has a perovskite structure. Silver niobate is the ferroelectric at room temperature, and its piezo coefficient is d_{33} = 0.24 pC/N, spontaneous polarization is P_s = 0.041 μC/cm^2 (in 11 kV/cm electrical field) and P_s = 52 μC/cm^2 (in 22 kV/cm electric field) [2, 3].

The substitution of Ag by Li ions in mixed $Ag_{1-x}Li_xNbO_3$ (ALN) is a commonly accepted method to improve ferroelectric and piezoelectric properties of ceramics; particularly optimal piezoelectric properties of $Ag_xLi_{1-x}NbO_3$ are observed for x = 0.065, that is close to the morphotropic boundary (MPB) (i.e. for x = 0.05) [4]. The dielectric properties of ALN were investigated mainly at low frequencies (i.e. below 1 MHz) [5–9]. Together with structural and polarization investigations these results show that below the morphotropic phase boundary (i.e. $x \leq 0.05$) the anomaly related to the ferroelectric phase transition shifts to lower temperatures with the increase of Li concentration and becomes more diffused, while the transition between two antiferroelectric phases becomes predominant [5]. Above the MPB (i.e. $x \geq 0.05$) only two transitions are observed, the first one from the paraelectric, of not definitely determined symmetry, to the monoclinic antiferroelectric phase and then to the rhombohedral ferroelectric phase [7, 10]. In the latter concentration region with the increase of Li concentration the anomaly related to ferroelectric phase transition significantly increases and shifts towards higher temperatures, while the antiferroelectric phase transition related anomaly becomes broader. Microwave dielectric properties of ALN ceramics were investigated only in Ref. [11]; however, in this work investigations were performed only in a narrow frequency range and dielectric anomalies related to phase transitions are not clearly expressed. Phonon spectra in ALN were investigated mainly by Raman spectroscopy [8, 9]. However, in work [8] investigations were performed only for $x = 0.04$, while in Ref. [9] only at room temperature. Nevertheless, it is very well known that the main dielectric dispersion in AN and $AgNb_{1-x}Ta_xO_3$ (ATN) is in the terahertz frequency range and it is mainly connected with Nb or Nb/Ta dynamics [11–13]. However, the impact of Ag and O ions dynamics should not be neglected [14–16]. Therefore, the dynamics of phase transitions and electrical conductivity behaviour is rather unknown. These problems become more important after recent investigations of AN by transmission electron microscopy [17] and suggestions of the use of AN based materials in photovoltaic and energy storage applications [18–21].

The aim of the work is to investigate phase transition dynamics and electrical properties of $Ag_{0.98}Li_{0.02}NbO_3$ (ALN2) ceramics via broadband dielectric and infrared spectroscopies.

2. Experiment

The $Ag_{0.98}Li_{0.02}NbO_3$ ceramics were prepared by a conventional solid state reaction as described in Ref. [5]. Dielectric measurements were performed in a wide frequency range of 20 Hz – 12 GHz, while IR measurements were performed in a frequency range of 10–2000 cm^{-1}. For this purpose several experimental techniques and apparatuses were used. In the 20 Hz – 1 MHz frequency range an LCR-meter *Hewlett Packard* 4284 was used to measure the capacitance and the loss tangent of samples, and a model of flat dielectric capacitor was used to calculate the complex dielectric permittivity. Measurements of complex transmission and reflection coefficients were performed using an *Agilent* 8714ET network analyzer in the 1 MHz – 1 GHz frequency range. Below 1 GHz measurements were performed in the temperature region 140–500 K. In this case, a multimode capacitor model was used to obtain complex dielectric permittivity. Measurements in the 8–12 GHz frequency range were performed using a scalar network analyzer R2400 produced by *Elmika* company by placing a thin dielectric rod in the centre of a waveguide and monitoring the reflectivity and transmission coefficients. Silver paint was used to make the electrical contact. Infrared reflectivity (IR) spectra were obtained by a *Bruker* V80 spectrometer in the frequency range 10–2000 cm^{-1}. For temperature dependent measurements a *Specac* furnace was used.

3. Results and discussion

Temperature dependences of complex dielectric permittivity for $Ag_{0.98}Li_{0.02}NbO_3$ ceramics at different frequencies are presented in Fig. 1. The dielectric permittivity has the anomaly close to 330 K that is related to the ferroelectric phase transition [8]. The increase of dielectric permittivity above ferroelectric phase transition temperature is related to antiferroelectric phase transition, which is observed at higher temperatures [2, 5]. The contribution of all infrared modes to the dielectric permittivity has the clearly expressed maximum close to the ferroelectric phase transition temperature, indicating that the phonon contribution is less important far from the antiferroelectric phase transition temperature [2, 5]. The maximum position of an imaginary part of complex dielectric permittivity is frequency dependent (in the inset of Fig. 1 there is the reciprocal measurement frequency τ versus the temperature of maximum losses). The values of Arrhenius law fit parameters are $E_A = 0.35\pm0.004$ eV and $\tau_0 = 27.43\pm0.19$ s (where E_A is the activation energy and τ_0 is the pre-exponential

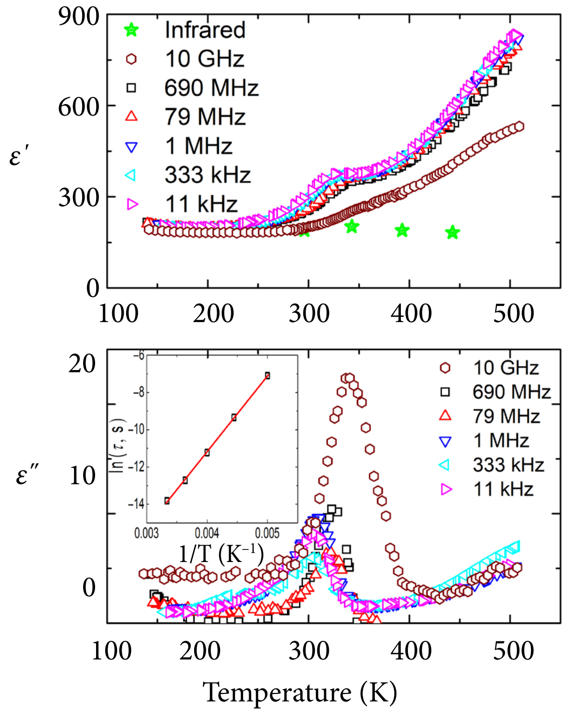

Fig. 1. Temperature dependences of the complex dielectric permittivity for ALN2 ceramics at different frequencies. The inset shows the temperature dependence of relaxation time.

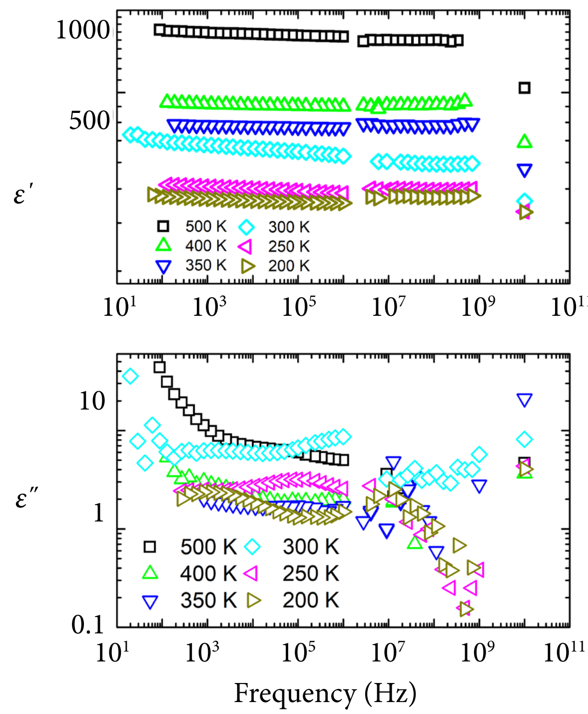

Fig. 2. Frequency dependence of the real ε' and imaginary ε'' parts of complex dielectric permittivity for ALN2 ceramics at different temperatures.

factor). The Arrhenius behaviour of relaxation time is typical of dynamics of ferroelectric domains [22]. The microwave dielectric properties of ALN2 ceramics are substantially better than those previously reported for ALN ceramics [11] and comparable with the best microwave properties of ATN ceramics [23].

Figure 2 shows the frequency dependence of the real and imaginary parts of complex dielectric permittivity of ALN2 ceramics. Three dielectric dispersion parts can be clearly distinguished: a) above 1 MHz, b) in the 100 Hz – 1 MHz range below ferroelectric phase transition temperature (T_c) and c) below 100 Hz and above 400 K. The first one is related to the ferroelectric soft mode that is related to ion dynamics similarly as in pure AN [13–14]. Below 10 GHz frequency only the beginning of this dispersion is observed. The dielectric dispersion in the middle frequency range (100 Hz – 1 MHz) below T_c is related to the dynamics of ferroelectric domains, as was already discussed by analysing the temperature dependence of dielectric losses. The dielectric dispersion below 100 Hz and above 300 K is related to the onset of electrical conductivity.

The IR reflectivity spectra of ALN2 ceramics measured at different temperatures are presented in Fig. 3.

Solid lines correspond to the experimentally measured spectra and dashed lines are the fits using a commonly used generalized damped oscillator model [24]:

$$\varepsilon^*(\omega) = \varepsilon_\infty \prod_j \frac{\omega_{\mathrm{LO}j}^2 - \omega^2 + \mathrm{i}\omega\gamma_{\mathrm{LO}j}}{\omega_{\mathrm{TO}j}^2 - \omega^2 + \mathrm{i}\omega\gamma_{\mathrm{TO}j}}. \quad (1)$$

Here $\omega_{\mathrm{TO}j}$ and $\omega_{\mathrm{LO}j}$ denote the transverse and longitudinal frequency of the jth phonon, respectively, and $\gamma_{\mathrm{TO}j}$ and $\gamma_{\mathrm{LO}j}$ denote their corresponding damping constants. $\varepsilon^*(\omega)$ is related to the reflectivity $R(\omega)$ by the formula

$$R = \left| \frac{\sqrt{\varepsilon^*} - 1}{\sqrt{\varepsilon^*} + 1} \right|^2. \quad (2)$$

The permittivity ε_∞ resulting from the electronic absorption process was obtained from the frequency-independent reflectivity IR spectra above phonon frequencies (i.e. above 1000 cm^{-1}) and was assumed to be temperature independent. 16 polar modes were distinguished in the IR spectra

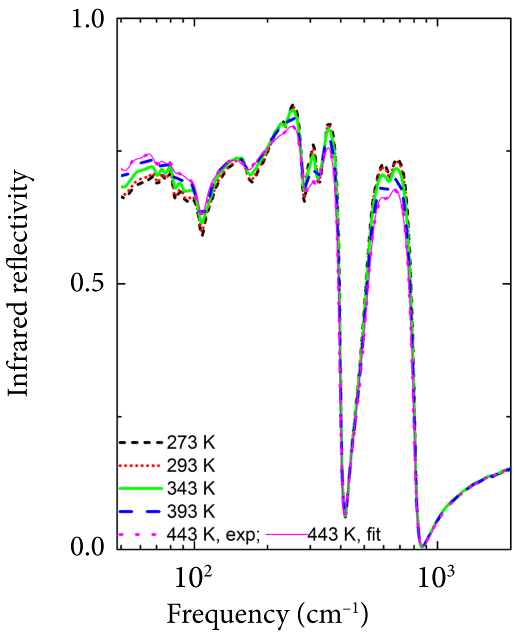

Fig. 3. IR reflectivity spectra of bulk ALN2 ceramics measured at several temperatures. Solid lines correspond to the experimentally measured spectra and dashed lines are the fits using Eqs. (1) and (2).

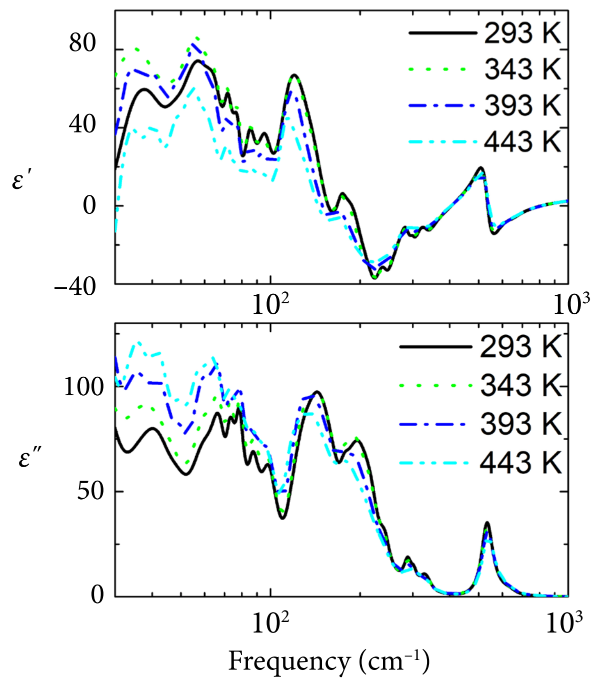

Fig. 5. Frequency spectra of the real (ε″) and imaginary (ε″) parts of the dielectric permittivity obtained from the fits of IR reflectance spectra (Fig. 3) for ALN2 ceramics in the 30–1000 cm^{-1} frequency range.

of ALN2 ceramics in the temperature range 323–450 K (Fig. 4). Taking into account that the crystal symmetry of ALN2 ceramics at room temperature is rombohedral [8], the number of polar modes is in good agreement with the factor group analysis [24]. The dielectric spectra calculated according to the obtained parameters are presented in Fig. 5.

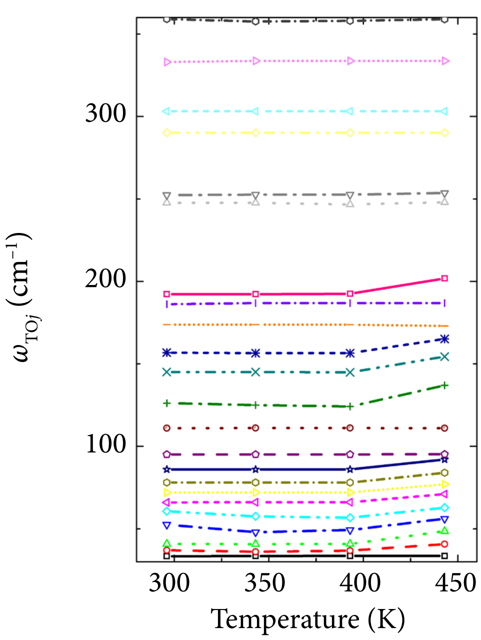

Fig. 4. Temperature dependences of polar phonon frequencies of ALN2 ceramics.

Frequencies of all phonon modes are temperature dependent; however, the most pronounced temperature dependent modes are observed below 50 cm^{-1}. By analogy with pure AN [13–14] these low frequency modes are related with the dynamics of Nb ions. However, dynamics of other ions should not be neglected due to the weak temperature dependence of all other phononic modes (Fig. 4).

4. Conclusions

The dielectric spectra of ALN2 ceramics are mainly impacted by the electrical conductivity at higher temperatures (above 400 K) and low frequencies (below 100 Hz), and the contribution of the soft mode, the frequency of which is below 50 cm^{-1}. Below T_c = 330 K at low frequencies (below 1 MHz), the contribution of ferroelectric domains becomes also important. All phononic modes are slightly temperature dependent, thus confirming the influence of Ag, Li and O ions dynamics on the phase transitions. However, the most important contribution to the dynamics of phase transition is made by Nb ions. Ceramics exhibits a huge value of dielectric permittivity and relatively low losses in the microwave frequency range (ε′ ≈ 250 and ε″ ≈ 20 at

10 GHz and room temperature), indicating that it is suitable for various microwave dielectric applications, similarly as ATN ceramics [23].

References

[1] S. Wada, A. Saito, T. Hoshina, H. Kakemoto, T. Tsurumi, C. Moriyoshi, and Y. Kuroiwa, Silver lithium niobate single crystals and their piezoelectric properties, Ferroelectrics **346**, 64–71 (2007), https://doi.org/10.1080/00150190601180331

[2] A. Kania, K. Roleder, and M. Lukaszewki, The ferroelectric phase in $AgNbO_3$, Ferroelectrics **52**, 265–269 (1984), https://doi.org/10.1080/00150198408209394

[3] D. Fu, M. Endo, H. Taniguchi, T. Tanijama, and M. Itoh, $AgNbO_3$: A lead-free material with large polarization and electromechanical response, Appl. Phys. Lett. **90**, 252907 (2007), https://doi.org/10.1063/1.2751136

[4] D. Fu, M. Endo, H. Tsniguchi, T. Taniyama, S. Koshihara, and M. Itoh, Piezoelectric properties of lithium modified silver niobate perovskite single crystals, Appl. Phys. Lett. **92**, 172905 (2008), https://doi.org/10.1063/1.2918837

[5] A. Kania and S. Miga, Preparation and dielectric properties of $Ag_{1-x}Li_xNbO_3$ (ALN) solid solutions ceramics, Mater. Sci. Eng. B **86**, 128–133 (2001), https://doi.org/10.1016/S0921-5107(01)00666-3

[6] A. Niewiadomski, A. Kania, G.E. Kugel, M. Hafid, and D. Ditko, Raman spectroscopy, dielectric properties and phase transitions of $Ag_{0.96}Li_{0.04}NbO_3$ ceramics, Mater. Res. Bull. **65**, 123–131 (2015), https://doi.org/10.1016/j.materresbull.2015.01.047

[7] D. Fu, M. Endo, H. Taniguchi, T. Taniyama, M. Itoh, and S. Koshihara, Ferroelectricity of Li-doped silver niobate (Ag, Li)NbO_3, J. Phys. Condens. Matter **23**, 075901 (2011), https://doi.org/10.1088/0953-8984/23/7/075901

[8] A. Newiadomski, D. Kajewski, A. Kania, K. Balin, S. Miga, M. Pawlik, and S. Koperski, Microstructure and characterization of $Ag_{1-x}Li_xNbO_3$ ceramics, Ceram. Int. **42**, 4445–4451 (2016), https://doi.org/10.1016/j.ceramint.2015.11.129

[9] H.U. Khan, I. Sterianou, J. Miao, J. Pokorny, and I.M. Reaney, The effect of Li-substitution on the M-phases of $AgNbO_3$, J. Appl. Phys. **111**, 024107 (2012), https://doi.org/10.1063/1.3677871

[10] Y. Sakabe, T. Takeda, Y. Ogiso, and N. Wada, Ferroelectric properties of (Ag, Li)(Nb, Ta)O_3 ceramics, Jpn. J. Appl. Phys. **42**, 5675 (2001), https://doi.org/10.1143/JJAP.40.5675

[11] V. Porokhonskyy, V. Bovtun, S. Kamba, E. Buixaderas, J. Petzelt, A. Kania, S. Miga, and Y. Yakimenko, Microwave dielectric properties of the $Ag_{1-x}Li_xNbO_3$ ($x = 0 \div 0.06$) ceramics, Ferroelectrics **238**, 137–138 (2000), https://doi.org/10.1080/00150190008008776

[12] A. Kania, K. Roleder, G.E. Kugel, and M.D. Fontana, Raman scattering, central peak and phase transitions in $AgNbO_3$, J. Phys. C **19**, 9 (1986), https://doi.org/10.1088/0022-3719/19/1/007

[13] A.A. Volkov, B.P. Gorshunov, G. Komandin, W. Fortin, G.E. Kugel, A. Kania, and J. Grigas, High-frequency dielectric spectra of $AgTaO_3$-$AgNbO_3$ mixed ceramics, J. Phys. Condens. Matter **7**, 785 (1995), https://doi.org/10.1088/0953-8984/7/4/009

[14] W. Fortin, G.E. Kugel, J. Grigas, and A. Kania, Manifestation of Nb dynamics in Raman, microwave, and infrared spectra of the $AgTaO_3$-$AgNbO_3$ mixed system, J. Appl. Phys. **79**, 4273 (1996), https://doi.org/10.1063/1.361796

[15] A. Ratuszna, J. Pawluk, and A. Kania, Temperature evolution of the crystal structure of $AgNbO_3$, Phase Transit. **76**, 611–620 (2003), https://doi.org/10.1080/0141159021000009007

[16] I. Levin, V. Krayzman, J.C. Woicik, J. Karapetrova, T. Proffen, M.G. Tucker, and I.M. Reaney, Structural changes underlying the diffuse dielectric response in $AgNbO_3$, Phys. Rev. B **79**, 104113 (2009), https://doi.org/10.1103/PhysRevB.79.104113

[17] Y. Tian, J. Li, Q. Hu, L. Jin, K. Yu, J. Li, E.D. Politova, S. Yu, S.Y. Stefanovich, Z. Xu, and X. Wei, Ferroelectric transitions in silver niobate ceramics, J. Mater. Chem. C **7**, 1028–1034 (2019), https://doi.org/10.1039/C8TC05451G

[18] Y. Tian, L. Jin, H.F. Zhang, Z. Xu, X.Y. Wei, E.D. Politova, S.Y. Stefanovich, N.V. Tarakina,

I. Abrahams, and H.X. Yan, High energy density in silver niobate ceramics, J. Mater. Chem. A **4**(44), 17279–17287 (2016), https://doi.org/10.1039/C6TA06353E

[19] X. He, C. Chen, C.B. Li, H.R. Zhen, and Z.G. Yi, Ferroelectric, photoelectric, and photovoltaic performance of silver niobate ceramics, Adv. Funct. Mater. **29**, 1900918 (2019), https://doi.org/10.1002/adfm.201900918

[20] Z.N. Yan, D. Zhang, X.F. Zhou, H. Qi, H. Luo, and K.C. Zhou, Silver niobate based lead-free ceramics with high energy storage density, J. Mater. Chem. A **7**, 10702–10711 (2019), https://doi.org/10.1039/C9TA00995G

[21] Z. Liu, T. Lu, J.M. Ye, G.S. Wang, X.L. Dang, E. Whithers, and Y. Liu, Antiferroelectrics for energy storage applications: a review, Adv. Mater. Technol. **3**, 10800111 (2018), https://doi.org/10.1002/admt.201800111

[22] D. Damjanovic, Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics, Rep. Prog. Phys. **61**, 1267 (1998), https://doi.org/10.1088/0034-4885/61/9/002

[23] M. Valant and D. Suvorov, New-high permittivity $AgNb_{1-x}Ta_xO_3$ microwave ceramics: Part II, dielectric characteristics, J. Am. Ceram. Soc. **82**, 88 (1999), https://doi.org/10.1111/j.1151-2916.1999.tb01727.x

[24] S. Kamba, D. Nuzhnyy, S. Veljko, V. Bovtun, J. Petzelt, Y.L. Wang, N. Setter, J. Levoska, M. Tyunina, J. Macutkevic, and J. Banys, Dielectric relaxation and polar phonon softening in relaxor ferroelectric $PbMg_{1/3}Ta_{2/3}O_3$, J. Appl. Phys. **102**, 074106 (2007), https://doi.org/10.1063/1.2784972

PLAČIAJUOSTĖ $Ag_{0,98}$ $Li_{0,02}NbO_3$ KERAMIKŲ DIELEKTRINĖ IR INFRARAUDONOJI SPEKTROSKOPIJA

E. Palaimienė [a], J. Macutkevič [b], J. Banys [a], I. Gruszka [c], A. Kania [c]

[a] *Vilniaus universiteto Taikomosios elektrodinamikos ir telekomunikacijų institutas, Vilnius, Lietuva*

[b] *Fizinių ir technologijos mokslų centras, Vilnius, Lietuva*

[c] *Katovicų Silezijos universiteto Fizikos institutas, Chožuvas, Lenkija*

Santrauka

Bešvinė pjezoelektrinė niobato sistemos medžiaga galėtų būti alternatyva jau žinomoms ir naudojamoms pjezoelektrinėms medžiagoms. Viena iš tokių feroelektrinių medžiagų yra perovskito struktūros sidabro niobatas $AgNbO_3$ (AN). Sidabro niobato keramika yra feroelektrikas kambario temperatūroje. Tyrimais nustatyta, kad didinant ličio koncentraciją sidabro niobato junginyje feroelektrinio fazinio virsmo temperatūra taip pat didėja. Šiame darbe publikuojami $Ag_{0,98}Li_{0,02}NbO_3$ (ALN2) dielektrinių ir IR tyrimų rezultatai. Tyrimai atlikti plačiajuostės dielektrinės ir IR spektroskopijų metodais 20 Hz – 60 THz dažnių diapazone esant 140–500 K temperatūrai. ALN2 keramikos dielektriniams spektrams daugiausia įtakos turi elektrinis laidumas (aukštesnei temperatūrai (per 400 K) ir žemiems dažniams (žemiau 100 Hz)), feroelektriniai domenai (žemiau T_c = 330 K, esant žemiems dažniams (žemiau 1 MHz)) ir minkštos feroelektrinės modos, kurios dažnis yra mažesnis nei 50 cm^{-1}, įtaka. Ag ir O jonų dinamika turi įtakos faziniams virsmams, tai lemia fononines modas, kurios šiek tiek priklauso nuo temperatūros. Svarbiausią indėlį į fazinių virsmų dinamiką turi Nb jonai. ALN keramika turi didžiulę dielektrinės skvarbos vertę ir santykinai mažus nuostolius mikrobangų dažnių diapazone ($\varepsilon' \approx 250$ ir $\varepsilon'' \approx 20$ esant 10 GHz ir kambario temperatūrai).