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# Raman spectroscopy, dielectric properties and phase transitions of $Ag_{0.96}Li_{0.04}NbO_3$ ceramics

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ABSTRACT

Silver lithium niobates $Ag_{1-x}Li_xNbO_3$ are promising lead free piezoelectrics. Good quality $Ag_{0.96}Li_{0.04}NbO_3$ ceramics were obtained. Dielectric and DSC studies showed that, in comparison to $AgNbO_3$, temperatures of phase transitions slightly decrease. Dielectric studies pointed to enhancement of polar properties. Remnant polarisations achieves value of 0.6 μC/cm$^2$. Maximum of $\varepsilon(T)$ dependences related to the relaxor-like ferroelectric/ferrielectric $M_1$–$M_2$ transition becomes higher and more frequency dependent. Analysis of Raman spectra showed that two modes at 50 and 194 cm$^{-1}$ exhibit significant softening. Low frequency part of the Raman spectra which involve central peak and soft mode were analysed using two models. CP was assumed as relaxational vibration and described by Debye function. The slope of temperature dependences of relaxational frequency $\gamma_R(T)$ changes at approximately 470 and 330 K, indicating that slowing down process of relaxational vibrations changes in the vicinity of partial freezing of Nb-ion dynamics $T_f$ and further freezing at ferroelectric/ferrielectric phase transition.



## 1. Introduction

Silver niobate-tantalate $AgNb_{1-x}Ta_xO_3$ (ATN) and silver-lithium niobate $Ag_{1-x}Li_xNbO_3$ (ALN) solid solutions, are promising candidates for high-permittivity microwave dielectrics and lead-free piezoelectrics, respectively. $AgNb_{1-x}Ta_xO_3$ ceramics ($x \approx 0.47$) exhibit in the microwave region simultaneously high ($\varepsilon \approx 400$) and temperature stable ($\Delta\varepsilon/\varepsilon = 0$–$0.04$ for $-40$–$60\,^\circ$C) dielectric permittivity and relatively high quality factor ($Q \times f = 860$ GHz), and additionally, at application temperatures a lack of dielectric dispersion for the broad frequency range from 1 kHz up to approximately 100 GHz [1–4]. Dispersion observed in the sub-millimetre region is related to the relaxational mode [1]. Contribution of this mode to dielectric susceptibility is an origin of a broad maximum of the low frequency and microwave $\varepsilon(T)$ dependences in the vicinity of the $M_2$–$M_3$ phase transition [5] and appearance of applicable dielectric properties [6,7]. Spectroscopic studies of ATN samples from the whole concentration range showed that the strength, frequency and temperature range of the relaxational component appearance depend strongly on the Nb/Ta ratio [1,3,8,9]. These results allowed us to connect the relaxational mode with Nb/Ta ion dynamics [1,9] and predict an appearance of structural disorder in the antiferroelectric Nb/Ta ion displacement arrangement [3,10]. These assumptions were recently confirmed experimentally by structural investigations [11,12].

Similarly to $PbZn_{1/3}Nb_{2/3}O_3$–$PbTiO_3$ or $PbMg_{1/3}Nb_{2/3}O_3$–$PbTiO_3$ solid solutions exhibiting "giant piezoelectricity", the structural disorder may also play a crucial role in the appearance of relatively good, as for lead-free materials, piezoelectric properties of $Ag_{1-x}Li_xNbO_3$ solid solutions. Piezoelectric coefficients and electromechanical coupling factors reached values: $d_{31} = 170$ pC/N and $k_{31} = 0.71$ for $Ag_{0.9}Li_{0.1}NbO_3$ single crystals [13] and $d_{33} = 210$ pN/C for $Ag_{0.914}Li_{0.086}NbO_3$ ones [14].

The origin of structural disorder and its influence on polar ordering of the particular phases and nature of phase transitions in silver niobate based materials are also important questions from basic point of view. The disorder phenomenon is most significantly seen in pure silver niobate $AgNbO_3$ (AN).

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Silver niobate undergoes the complex sequence of phase transitions:

$$M_1 \overset{340K}{\rightarrow} M_2 \overset{540K}{\rightarrow} M_3 \overset{626K}{\rightarrow} O_1 \overset{634K}{\rightarrow} O_2 \overset{660K}{\rightarrow} T \overset{852K}{\rightarrow} C$$

where $M_1$, $M_2$, $M_3$ and $O_1$, $O_2$ are phases with orthorhombic symmetry in rhombic and parallel orientation, respectively. T and C denote the tetragonal and cubic phases, respectively [9,10,13–16]. The high temperature $M_3$–$O_1$, $O_2$–T and T–C phase transitions, detectable by diffraction, differential scanning calorimetry DSC and dielectric investigations, are related to oxygen octahedron tiltings [11,12,17–21]. Additionally, the displacements of the Ag and Nb ion appear at $O_2$–T and $M_3$–$O_1$ transitions, respectively [21].

On the contrary, the low temperature $M_1$–$M_2$ and $M_2$–$M_3$ transitions are hardly detectable by diffraction or thermal methods. They are observed as diffuse maxima of $\varepsilon$(T) dependences. The average symmetry of all M phases determined by diffraction experiments is orthorhombic with the Pbcm space group and $\sqrt{2}a_c \times \sqrt{2}a_c \times 4a_c$ unit cell ($a_c$ – lattice parameter of pseudo-perovskite unit cell), and antiferroelectric array of the Nb and Ag ion displacements [11,21,22]. Combined X-ray, neutron and electron diffraction and extended x-ray absorption fine structure (EXAFS) distinguished between average symmetry determined from diffraction methods and local symmetry deduced from the diffuse scattering patterns (TEM) and EXAFS profiles. This study pointed also to very weak structural modifications connected with phase transitions between M phases [11,12]. Evolution of the Nb ion dynamics is related to changes of the local symmetry. In the O phases the Nb ions are randomly displaced along eight $(111)_C$ directions which gives on average the ideal positions. Below the $M_3$–$O_1$ phase transition the Nb ions become partially ordered with two average anti-parallel displacements along $[110]_C$ direction. Locally they still occupy these eight positions but two of them are preferred. With decreasing temperature occupancy probabilities for the remaining six sites decrease and vanish below the freezing temperature $T_f$ = 448 K [11]. Below $T_f$ long range order of $[11l]_c$ $(0 \leq l \leq 1)$ Nb ion displacement into anti-polar array appears. However, two site disorder is still remained, i.e., these displacements are ordered in Nb chains along the orthorhombic c axis while disordered in chains perpendicular to this axis. It means that the $M_2$ and $M_3$ phases are disordered antiferroelectric ones. The freezing of Nb ion dynamics was confirmed by nonlinear dielectric studies [23]. The Ag ion displacements create also an

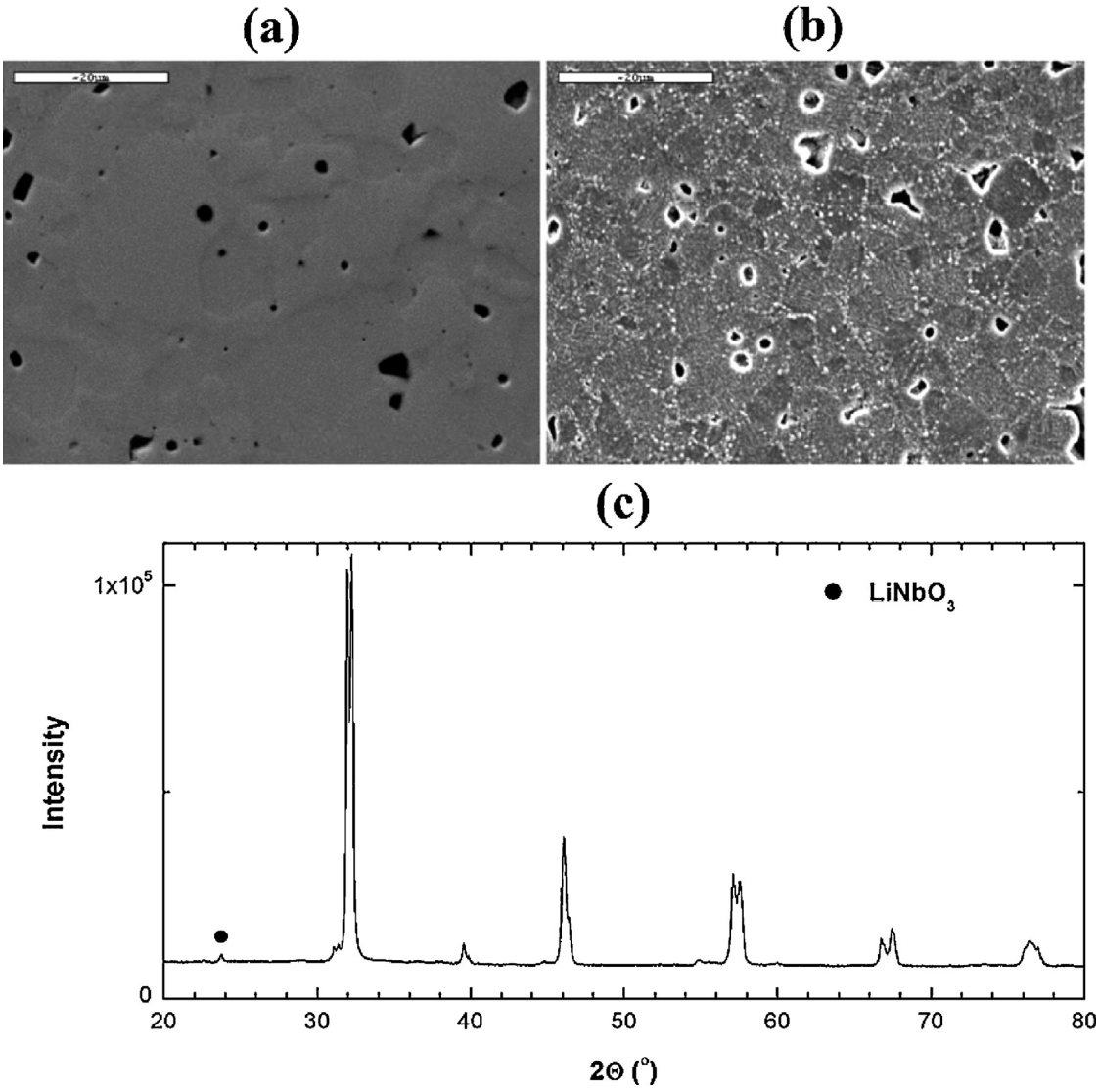


**Fig. 1.** SEM micrographs of $Ag_{0.96}Li_{0.04}NbO_3$ ceramics. (a) Images of the polished surface (backscattered electrons), (b) images of polished and then thermally etched surface (secondary electrons), and (c) the X-ray patterns of $Ag_{0.96}Li_{0.04}NbO_3$ ceramics (Cu Kα radiation). Disks mark $LiNbO_3$ phase.