Investigation of the $Li_{0.03}Na_{0.97}Ta_yNb_{1-y}O_3$ Solid Solution Structure and Properties by X-ray Analysis and Raman Spectroscopy

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***Abstract*—The structure of ceramic $Li_{0.03}Na_{0.97}Ta_yNb_{1-y}O_3$ solid solutions and its disorder when changing composition and temperature were investigated by full-profile X-ray analysis and Raman spectroscopy. It was found that at room temperature the structure of the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution is close to that of the $NaNbO_3$ and it corresponds to the $P2_1ma$ space group with four formula units per unit cell. It was shown that the oxygen octahedra in $Li_xNa_{1-x}Ta_{0.1}Nb_{0.9}O_3$ (x = 0, 0.15, 0.03, 0.04, 0.05) solid solutions are slightly distorted and their geometry is identical to that one of the oxygen octahedra in the $NaNbO_3$ structure. By the dependence of the intensity on temperature of the lines in the $Li_{0.03}Na_{0.97}Ta_{0.4}Nb_{0.6}O_3$ solid solution spectrum, corresponding to the Li^+ and Na^+ vibrations in the cuboctahedral cavities of the structure at $T > 322$ °C, strong disorder in the alkali metal sublattice was found. This may indicate a significant abrupt increase of the lithium cations mobility and, therefore, changes of the kinetic and energetic characteristics of the processes of charge ionic transport.**

***Index Terms*—ferroelectricity, solid solutions, perovskite structure, X-ray analysis, Raman spectroscopy, structure study.**

I. Introduction

SOLID solutions $Li_xNa_{1-x}Ta_yNb_{1-y}O_3$ belong to a new class of ferroelectric compounds – ion conductors, where the conductivity is ensured by electrons and mobile Li^+ cations [1], [2]. When studying the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ system of solid solutions with perovskite structure, compounds, characterized at temperatures above 400÷460 °C by sufficiently high lithium conductivity, compared with the conductivity of well-known lithium solid electrolytes ($\sigma \sim 10^{-3} \div 10^{-2}$ $Ohm^{-1}\cdot cm^{-1}$), were found [1]-[8]. In this case, anomalies, specific to the phase transition to the superionic state, in the Raman spectra and by dependencies of conductivity on temperature were observed [2], [5].

In solid solutions, based on sodium niobate ($NaNbO_3$), it is possible to change the ordering of the cation and anion sublattices structural units [1], [2]. Formation of the structure and, consequently, physical characteristics of $Li_xNa_{1-x}Ta_yNb_{1-y}O_3$ solid solutions carry out by changing of the cyboctahedral cavities and octahedral cations ratio [1], [2]. It is important to note that then in the $NaNbO_3$ structure Na^+ (R^+_{Na} = 0.98 Å) is substituted by Li^+ (R^+_{Li} = 0.68 Å) at relatively low lithium concentration ($x \approx 0.03$) the size of the cuboctahedral cavity is larger compared with the lithium cation than for $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions. In this case, lithium cation is relatively “free” within the cuboctahedral cavity [6]-[8] and the transition to the state with high ionic mobility and large values of ionic conductivity may occur at lower temperatures. This temperature also can be lowered by increasing disorder in the niobium and tantalum sublattice during isovalent substitution [1].

In this paper the structural disorder of $Li_{0.03}Na_{0.97}Ta_yNb_{1-y}O_3$ (y = 0.05, 0.4) and $Li_xNa_{1-x}Ta_{0.1}Nb_{0.9}O_3$ (x = 0, 0.15, 0.03, 0.04, 0.05) solid solutions, when changing composition and temperature, was investigated by full profile X-ray analysis and Raman spectroscopy.

II. Experimental Details

Ceramic $Li_xNa_{1-x}Ta_yNb_{1-y}O_3$ solid solutions were obtained by solid phase synthesis of Nb_2O_5 - Ta_2O_5 - Li_2CO_3 - Na_2CO_3 mixture. Alkali metal carbonates and niobium and tantalum oxides were taken in the molar ratio of 1:1. The homogeneity of the components distribution was achieved by double calcination of the blanks with intermediate grinding and mixing of the sinters and ceramic sintering at 1280-1300 °C. Detailed technique of the samples obtaining is described in [1], [2]. Phase composition was monitored by X-ray phase and structural analyzes.

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For Raman spectra registration the Ramanor *U*-1000 spectrometer was used. Argon lasers ILA-120, Spectra Physics (λ_B = 488.0 and 514.5 nm) were applied as a sources of excitation. Power of the exciting radiation does not exceed 100 mW. Spectra were registered in the geometry of the "reflection". The accuracy of the frequency, width and intensity measurements was, respectively, ± 1 cm^{-1}, ± 3 cm^{-1} and 5 %. Spectra treatment was carried out using Bomem Grames and Origin programs.

The optical furnace with six double output optical windows made of quartz was manufactured for investigations at different temperatures. This furnace allows to record spectra in air and inert gas atmosphere and in vacuum. The tablets samples of diameter 10 mm, fixed in a special platinum holder, were placed in the center of the furnace. The temperature adjustment and its stabilization were performed using the temperature controller. The accuracy of thermostatting was ± 1 °C. All measurements were performed in air.

For full-profile X-ray analysis DRON – 6 diffractometer was used (Cu*K*α – radiation). A pyrolytic graphite monochromator was installed in the primary rays. The initial angle of the scattering curve registration was $2\theta_{\min}$ = 3º, the final one was $2\theta_{\max}$ = 145º. In regions of X-ray pattern reflections step of X-ray pattern recording was 0.02°, on the background – 0.2°.Refinement of the ceramics structure was carried out by the Rietveld method using the software packages: «PDWin» and «MRIA» [9]. As the input data, information about structural modifications of the $NaNbO_3$ and $NaTaO_3$ phases known from the literature was used. Cif-files are given in the ICSD database [10], [11]. Refinement was carried out in two stages. In the first stage structural parameters were fixed and profile characteristics were refined. It is worth to note that, by the X-ray analysis data, preferential orientation of the grains in the samples investigated were not detected, as shown by the values of the texture parameters. In the next stage in the number of specific configuration coordinates, isotropic and anisotropic thermal factors and then the ratio of the population of atoms were included. In the final stage, all of the characteristics were refined simultaneously.

III. RESULTS AND DISCUSSION

Fig. 1, a shows the X-ray patterns of $NaNbO_3$ and $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ ceramic samples. It is seen that qualitatively X-ray pattern of the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution is similar to the X-ray pattern of the $NaNbO_3$. After adjustment is was revealed that from all polymorphs of the $NaNbO_3$ ceramic structure of the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution corresponds to the rhombic phase with $P2_1ma$ space group and four formula units per unit cell [12]. Graphically, the results of the refinement are shown in Fig. 1, b.

Table I gives the results of the unit cell periods refinement for the $NaNbO_3$ ceramics compared with data [12] and also clarified values of the structural characteristics for the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution: atomic coordinates (*x*/*a*, *y*/*b* *z*/*c*), ratio of the positions population (*G*1, *G*2), values of isotropic (B_{is}) and anisotropic (B_{ij}) parameters of thermal motion.

The shortest interatomic distances in the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution are given in Table II. The arrangement of atoms in the unit cell, the motives of atoms arrangement in the projection on the coordinate planes and distances O – O and Nb – O in the octahedra NbO_6 and Na – O in the coordination sodium polyhedron are shown in Fig. 2.

Analysis of Tables I and II and Fig. 2 shows that coordinates of atoms and atomic thermal motion parameters of the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution are in agreement with literature data for Na^+ and Li^+ and Ta^{5+} and Nb^{5+} cations in the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solution with the perovskite structure [6], [7], [10]-[12]. Though, they are different: Li^+ content is too high and Ta^{5+} content is too low. At the same time, Li^+ and Ta^{5+} in the structure of the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution substitute randomly Na^+ and Nb^{5+}, respectively.

Fig. 3 shows Raman spectra of $Li_xNa_{1-x}Ta_{0.1}Nb_{0.9}O_3$ (x=0÷0.05) solid solutions. One can see that in the region of the oxygen octahedra vibrations (500÷700 cm^{-1}) the spectrum is almost identical to the $NaNbO_3$ spectrum (except for the lines widths). It is the confirmation of the X-ray analysis data of the structure of the oxygen octahedra of $Li_xNa_{1-x}Ta_yNb_{1-y}O_3$ (x = 0 – 0.05) solid solutions corresponds to the $NaNbO_3$ oxygen octahedra structure. In the spectra of $Li_xNa_{1-x}Ta_{0.1}Nb_{0.9}O_3$ solid solutions with x = 0÷0.05 in this region there are lines at 570 and 615 cm^{-1} (Fig. 3, a), corresponding to the doubly degenerated and totally symmetrical vibrations of the oxygen octahedra [13]. The same lines are in the spectrum of the $NaNbO_3$ [14]. This is evidence of the identity of point groups symmetry of the octahedral anions NbO_6 in $NaNbO_3$ and $Li_xNa_{1-x}Ta_{0.1}Nb_{0.9}O_3$ (x = 0÷0.05) solid solutions structure. However, in the low-frequency (20-300 cm^{-1}) and high-frequency (850-900 cm^{-1}) regions in the Raman spectra of $Li_xNa_{1-x}Ta_{0.1}Nb_{0.9}O_3$ (x = 0÷0.05) solid solutions there are significant differences for the spectra of different composition.

From Fig. 3, a it is seen that the lines at 20÷300 cm^{-1}, correspond to the totally symmetrical vibrations of the oxygen octahedra as a whole, Nb^{5+} and Ta^{5+} vibrations in the octahedral cavities and Li^+ and Na^+ vibrations in the cyboctahedral cavities of the structure, when increasing lithium content, significantly broaden and become less intensive due to the increase of the structural disorder in cation sublattice. It is worth to note that in the spectrum of the antiferroelectric $NaTa_{0.1}Nb_{0.9}O_3$ (x = 0) solid solution the line at 80 cm^{-1}, corresponding to the libration vibrations of the oxygen octahedra as a whole, is split into two lines, Fig. 3, a. This splitting disappears with further x increasing and with

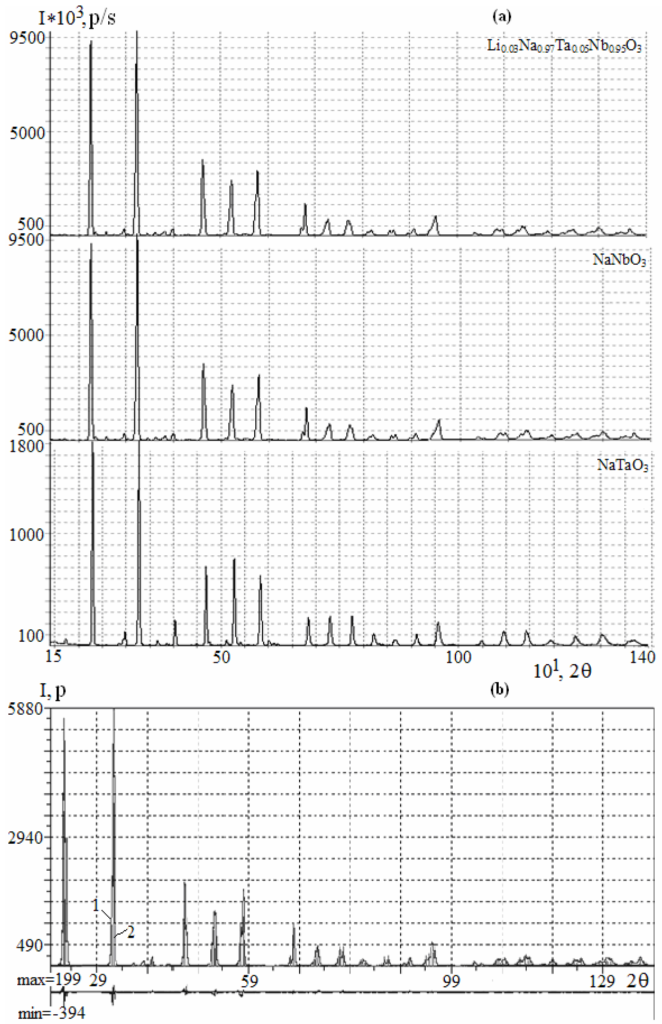

Fig. 1. a) X-ray patterns of solid solutions: $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$, $NaNbO_3$ and $NaTaO_3$; b) Calculated (1) and refined profiles (2) of X-ray patterns of the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution. The subtraction difference curve is shown below.

further transition of the solid solution to the ferroelectric phase with doubling of the unit cell. Splitting of the line at 80 cm^{-1} can be attributed to its two-mode behavior [15] due to the difference in frequencies of libration vibrations of the antiferroelectric phase octahedra with antiparallel direction of dipole moment.

From the Raman spectra it can be also concluded that in the structure of $Li_xNa_{1-x}Ta_{0.1}Nb_{0.9}O_3$ solid solutions octahedral anions NbO_6 when $x = 0$ are centrosymmetrical and when $x \geq 0.015$ they are non-centosymmetrical (ferroelectric solid solution). Non-centrosymmetry of the NbO_6 anions is confirmed by the presence in the spectrum of the line at 871 cm^{-1}, corresponding to the stretching vibrations of the oxygen atoms along the polar axis (Fig. 3, b) and forbidden by selection rules for centrosymmetric octahedra [13].

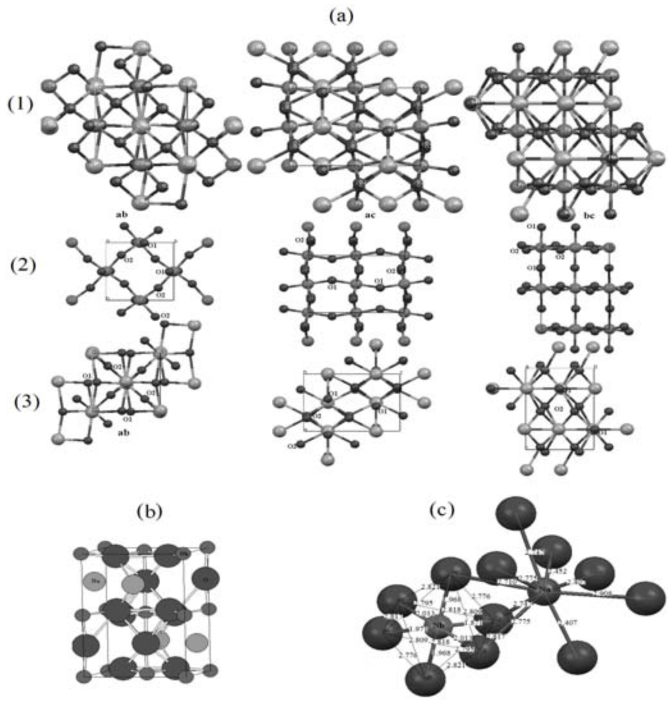

Fig. 2. a) The arrangement of atoms in the unit cell of the $NaNbO_3$ phase (P_{nma} space group); b) The arrangement of atoms in the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution in projections on coordinate planes *ab*, *ac* and *bc*: 1) all the atoms; 2) TaO_6 octahedra; 3) Na–O subsystem; c) Distances O–O and Nb–O in the NbO_6 octahedra and Na–O in the sodium coordination polyhedra.

In [1], [2] it is shown that for $Li_xNa_{1-x}Ta_yNb_{1-y}O_3$ solid solutions it is possible to apply methods of processes of positional ordering of cations consideration, developed for binary solid solutions. It is well known that in binary solid solutions there are special concentration points: $x_i = 0.125$, 0.25, 0.5 and 0.75 [2]. For compositions, corresponding to the special concentration points and their surroundings, there are the effects of short- and long-range order [2]-[5]. Since the degree of ordering determines largely physical properties of the materials, so these compositions of solid solutions may possess abnormal physical properties. In particular, for compositions of ferroelectric $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ ($x_i = 0.12$) solid solutions phase transition to the superionic state is observed [1], [2], [5]. This transition is accompanied by strong disordering ("melting") of the alkali metal sublattice while maintaining the relative "hardness" of the other structure sublattices.

"Melting" of the alkali metal sublattice can be detected by Raman spectra. Violation of the correlated vibration motion of Li^+ cations in the crystal by their intensive hops should lead to preferential, compared with the other lines of the spectrum, significant broadening and decreasing of the lines intensities, corresponding to the vibration of these cations. In the limit, when correlation in the vibration Li^+ cations motion is completely disrupted by intensive cations transport, in the phonon Raman spectrum complete blurring of the corresponding lines to the Rayleigh line should be observed.

A certain contribution to the increase of the Li^+ cations mobility may introduce a static (rigid) disorder of the isovalent cations in the Nb^{5+} and Ta^{5+} sublattice. Temperature changes in the low-frequency Raman spectra of the $Li_{0.03}Na_{0.97}Ta_{0.4}Nb_{0.6}O_3$ solid solution, characterized

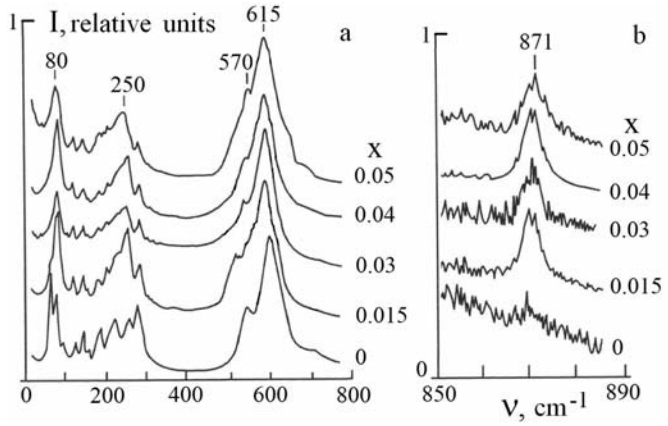

Fig. 3. Raman spectra of $Li_yNa_{1-x}Ta_{0.1}Nb_{0.9}O_3$ (x = 0÷0.05), t = 20 °C solid solutions: a) the region of the cations vibrations in octahedral and cubocrahedral cavities of the structure (0÷400 cm^{-1}) and the region of the oxygen cage vibrations (500÷800 cm^{-1}); b) enlarged scale of the region of the stretching modes Nb(Ta)-O-Nb(Ta) (850÷900 cm^{-1}).

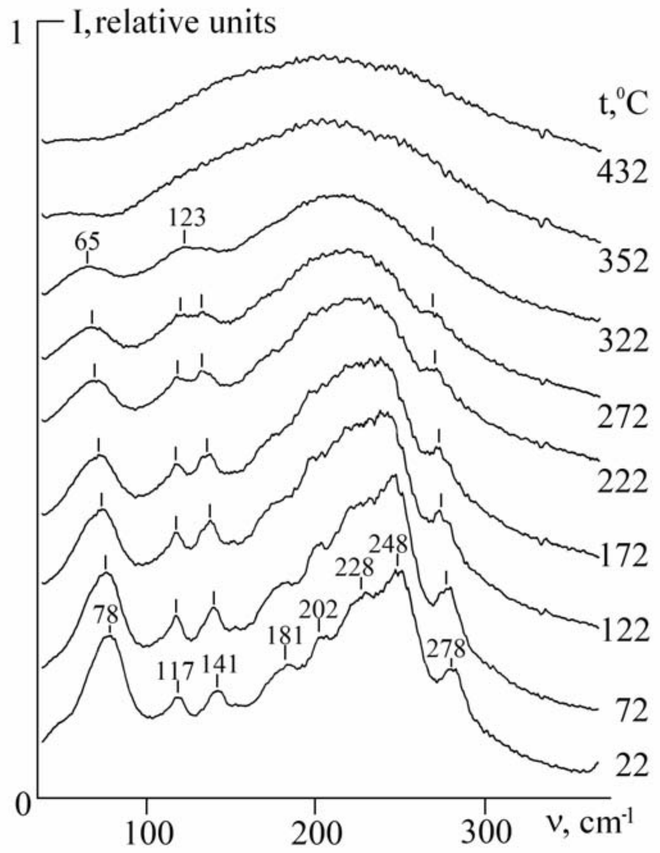

Fig. 4. Temperature changes in the Raman spectra of the ceramic $Li_{0.03}Na_{0.97}Ta_{0.4}Nb_{0.6}O_3$ solid solution. The region of the oxygen octahedra BO_6 librations as a whole, and translational vibrations of cations in the octahedral and cuboctahedral cavities of the structure.

by high static disorder in the Nb^{5+} and Ta^{5+}sublattice, are shown in Fig. 4. From the figure, it is seen that with the temperature increasing the lines in the spectra broaden significantly, decrease in intensity and blur to the Rayleigh line. In this case, preferential disappearance of the line at 78 cm^{-1}, corresponding to the oxygen octahedra vibrations as a whole, and also the lines in the region 100÷160 cm^{-1}, corresponding to the Li^+ and Na^+ vibrations, are seen. Such a behavior of the lines corresponds to the "melting" of the alkali metal sublattice and may point to a state with a high superionic conductivity at temperatures above ~ 320 °C (Fig. 4). It is worth to note, that blurring of the lines, corresponding to the Li^+ and Na^+ cations vibrations in the AO_{12} cuboctahedra, to the Rayleigh line for the $Li_{0.03}Na_{0.97}Ta_{0.4}Nb_{0.6}O_3$ solid solution is observed at lower temperatures than for the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ system, investigated in [5].

Apparently, for the $Li_{0.03}Na_{0.97}Ta_{0.5}Nb_{0.5}O_3$ solid solution, where maximum degree of disorder in the Nb^{5+} and Ta^{5+} sublattice is observed, the state with high Li^+ and Na^+ mobility and high ionic conductivity will occur at even lower temperatures. However, it is impossible to monitor spectrum of the $Li_{0.03}Na_{0.97}Ta_{0.5}Nb_{0.5}O_3$ solid solution transformation with temperature increasing due to a very strong blurring in the spectrum as a result of static disorder of the structural units in the Nb^{5+} and Ta^{5+} sublattice at room temperature [1], [5].

Thus, by Raman spectra, "melting" of the alkali metal sublattice in $Li_{0.03}Na_{0.97}Ta_yNb_{1-y}O_3$ solid solutions was observed, which indicates the existence of the state with the high mobility of the alkali metal cations and with ionic conductivity.

IV. CONCLUSION

The structure of ceramic $Li_{0.03}Na_{0.97}Ta_yNb_{1-y}O_3$ solid solutions and its disordering when changing the composition and temperature was investigated by full-profile X-ray analysis and Raman spectroscopy. It was shown, that the structure of the solid solutions is close to the $NaNbO_3$ structure and characterized by $P2_1ma$ space group with four formula units per unit cell. In general, the atomic coordinates and parameters of the atomic thermal motion in the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution are consistent with the literature data for Na^+ and Li^+ и Ta^{5+} and Nb^{5+} in $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions with perovskite structure. But, nevertheless, they are different: lithium content is too high and tantalum content is too low. In this case, Li^+ and Ta^{5+} cations in the structure of the $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ solid solution randomly substitute Na^+ and Nb^{5+}cations in their positions, respectively. It is confirmed by Raman spectra, that oxygen octahedra geometry in the structure of $Li_xNa_{1-x}Ta_{0.1}Nb_{0.9}O_3$ (x = 0÷0.05) solid solutions is identical to that one in the structure of the $NaNbO_3$, and it is established that solid solutions with $x \geq 0.015$ are ferroelectrics. By the dependence of the intensity of the lines in the Raman spectrum on temperature, corresponding to the Li^+ and Na^+ vibrations in the cuboctahedral cavities of the structure of the $Li_{0.03}Na_{0.97}Ta_{0.4}Nb_{0.6}O_3$ solid solution at the temperature over 322 °C, "melting" of the alkali metal sublattice was observed, and this may indicate the existence of the state with the high mobility of the alkali metal cations and with ionic conductivity.

TABLE I. PERIODS AND VOLUMES OF THE UNIT CELLS OF THE $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ SOLID SOLUTION AND $NaNbO_3$ CERAMICS. REFINED STRUCTURAL CHARACTERISTICS OF THE $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ SOLID SOLUTION AND $NaNbO_3$ CERAMICS. THE *R*-FACTORS $R_{WP}(\%) = 8.02$, $R_P(\%) = 5.67$, $R_E(\%) = 9.08$, $GOFF = 0.88$.

Sample	ICSD	*a*, [Å]	*b*,[Å]	*c*, [Å]	*V*, [Å^3]
ceramics		5.5741(5)	7.7585(1)	5.5097(5)	238.3(1)
$NaNbO_3$	247313	5.571(1)	7.766(1)	5.514(5)	238.55
$NaNbO_3$	247314	5.571(1)	7.766(1)	5.513(5)	238.51
$NaNbO_3$	247315	5.569(1)	7.764(1)	5.512(5)	238.32

	El1	El2	*G*1	*G*2	*x*/*a*	*y*/*b*	*z*/*c*	B_{is}, [Å^2]
ceramics	Nb^{+5}	Ta^{+5}	0.98(1)	0.02	0.0000	0.0000	0.0000	0.29(1)
	Na^{+1}	Li^{+1}	0.91(1)	0.09	0.4936(10)	0.2500	0.0039(9)	1.31(1)
	O^{-2}		1.00		0.5115(13)	0.2500	0.5593(5)	1.44(1)
	O^{-2}		1.00		0.2185(4)	0.0313(3)	0.2877(3)	2.87(2)
$NaNbO_3$ 247313	Nb^{+5}		1.00		0.0000	0.0000	0.0000	
	Na^{+1}		1.00		0.4793(9)	0.2500	0.0025(7)	
	O_1^{-2}		1.00		0.5091(5)	0.2500	0.5600(3)	
	O_2^{-2}		1.00		0.2172(2)	0.0301(1)	0.2838(2)	
$NaNbO_3$ 247314	Nb^{+5}		1.00		0.0000	0.0000	0.0000	0.25(3)
	Na^{+1}		1.00		0.4958(8)	0.2500	0.0026(7)	1.10(4)
	O_1^{-2}		1.00		0.5111(4)	0.2500	0.5619(3)	0.45(3)
	O_2^{-2}		1.00		0.2158(2)	0.0308(1)	0.2817(2)	1.15(3)
$NaNbO_3$ 247315	Nb^{+5}		1.00		0.0000	0.0000	0.0000	0.73(1)
	Na^{+1}		1.00		0.4867(6)	0.2500	0.0004(6)	1.08(2)
	O_1^{-2}		1.00		0.5212(8)	0.2500	0.5633(6)	0.93(3)
	O_2^{-2}		1.00		0.2144(3)	0.0313(3)	0.2844(4)	0.86(3)

	El1	El2	*B*11, [Å^2]	*B*22, [Å^2]	*B*33, [Å^2]	*B*12, [Å^2]	*B*13, [Å$^{2]}$	*B*23, [Å^2]
ceramics	Nb^{+5}	Ta^{+5}	0.60(2)	0.23(2)	0.03(1)	0.06(1)	0.23(2)	0.268
	Na^{+1}	Li^{+1}	2.47(4)	0.52(5)	0.94(3)	0.000	-1.31(1)	0.000
	O^{-2}		4.35(2)	0.10(1)	-0.13(1)	0.000	0.50(1)	0.000
	O^{-2}		2.35(1)	7.22(2)	-0.97(1)	1.36(1)	1.47(1)	0.34(4)
$NaNbO_3$ 247313	Nb^{+5}		0.71(4)	0.31(5)	0.38(5)	0.0	0.0	0.0
	Na^{+1}		2.32(1)	0.80(1)	1.67(1)	0.0	0.0	0.0
	O_1^{-2}		2.05(1)	-0.09(1)	0.77(1)	0.0	0.0	0.0
	O_2^{-2}		2.15(1)	0.73(1)	1.726	0.0	0.0	0.0

TABLE II. THE SHORTEST INTERATOMIC DISTANCES IN THE $Li_{0.03}Na_{0.97}Ta_{0.05}Nb_{0.95}O_3$ SOLID SOLUTION. *N* – THE NUMBER OF IDENTICAL DISTANCES IN THE COORDINATION POLYHEDRA.

atom 1	atom 2	*r*, [Å]	*N*	atom 1	atom 2	*r*, [Å]	*N*
Nb	O_2	2.013(1)	2	Na	O2	2.775(3)	2
Nb	O_1	1.968(1)	2	Na	O2	2.407(3)	2
Nb	O_2	1.971(1)	2	Na	O2	2.747(3)	2
Nb	Nb	3.919(1)		Na	O1	2.908(5)	1
Nb	Nb	3.879(1)		Na	O1	2.710(3)	1
Na	Na	3.880(1)		Na	O1	2.452(4)	1
Na	Na	3.949(6)					
Na	Na	3.889(6)					

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