Processes of structural disordering and superionic phase transition in the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solution

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Structural disordering and phase transitions in the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions were investigated by Raman spectra. Phase transition from ferroelectric to antiferroelectric phase at t=300÷350°C is clearly seen. In this case the line, corresponding to the stretching modes of oxygen atoms disappears. Thermal disordering of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions structure, introduced by mobile lithium ions, happens gradually. It is facilitated by misorientation and considerable deformation of oxygen octahedra with changing of their symmetry. Static disordering of the structural units in the Nb^{5+} and Ta^{5+} sublattice lowers the point of ferroelectric-antiferroelectric phase transition and can facilitate the transition to the superionic state. However, from the data obtained, it is clear that the phase transition to the superionic state doesn't appear in Raman spectra.

1. Introduction

$Li_xNa_{1-x}Ta_yNb_{1-y}O_3$ ceramic solid solutions have a variety of thermal and concentrational structural phase transitions related to changes in the geometry of the oxygen octahedra, mobility and type of dipole ordering of cations, also the morphotropic regions [1]. These solid solutions are perspective as materials with cross-effects with ferroelectric and semiconducting properties [1, 2]. When x~0.125 at ~400÷460°C $Li_xNa_{1-x}Ta_yNb_{1-y}O_3$ solid solutions possess lithium superionic conductivity [2, 3]. In this case the temperature of the transition and the degree of fuzziness (especially of the transition 'polar-nonpolar' phase) can be changed in wide scope by varying the ordering of structural units in the niobium and tantalum sublattice.

During the phase transition to the superionic state alkali metal sublattice (Li^+ and Na^+) should "melt" when the relative "hardness" of the other sublattices of the structure persists. Normally, phase transition to the superionic state is detected as a sudden jump in the conductivity dependence on temperature with simultaneous essential decrease of the conductivity activation energy [3]. Preferential "melting" of the alkali metal sublattice in the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions can be detected and investigated by Raman spectra. Violation of the correlated vibrational lithium cations motion in the crystal should lead to the significant broadening and decrease of the intensities of lines, corresponding to the vibrations of these cations. When the correlation in the vibration motion of the lithium cations is completely disrupted by the intensive transport of the cations, the phonon Raman spectrum shows a complete blurring of lines to the Rayleigh line. Thus, the lines, do not correspond to the vibrations of the structural units, should remain in the spectrum.

This work is devoted to the investigation of the processes of structural disordering, taking place before the phase transition to the superionic state in the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions, by changes in the phonon Raman spectra, associated with the vibrations of Li^+ and Na^+, Nb^{5+} and Ta^{5+} cations and the oxygen cage of the structure.

2. Experimental

Ceramic $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions were obtained by solid-phase synthesis of the Nb_2O_5:Ta_2O_5:Li_2CO_3:Na_2CO_3 mixture by two-fold annealing and sintering of ceramics at 1100-1300°C. Totally, alkali metal carbonates and niobium and tantalum pentaoxides were taken at molar ratio of 1:1. The more detailed technique is described in [2]. The phase and chemical composition was monitored by X-ray and X-ray diffraction analysis as well as Raman spectra.

For Raman spectra registration the upgraded automated DFS-24 spectrometer, Ramanor U-1000 spectrometer and triple multichannel spectrometer, manufactured at the Institute of Spectroscopy, Academy of Sciences [4] were 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 200 mW. Spectra were registered in the geometry of the "reflection". In the multichannel spectrometer the double premonohromator with dispersion subtraction was used. It suppresses scattered exciting light from the rough ceramic surface and allows detecting Raman spectra from ~35 cm^{-1}. The accuracy of the

frequency, width and intensity measurements was, respectively, ± 1 cm^{-1}, ± 3 cm^{-1} и 5%.

The optical furnace with six double output optical windows made of quartz was manufactured for investigations at different temperatures. The 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.

In order to study the ionic conductivity the dispersion of the complex admittance of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions was investigated. The frequency range was 25– 10^6 Hz and the mode of heating was stepwise.

The method used allows one to distinguish correctly the contributions of different physical and chemical processes in the measured parameters and to calculate the values of the static conductivity [1-3].

3. Results and discussion

$Li_xNa_{1-x}Ta_yNb_{1-y}O_3$ solid solutions belong to a ferroelectric complex perovskites with $(A'_{1-x}A''_x)(B'_{1-y} B_y'')O_3$ general formula [1, 2] . In the perovskite structure there are the octahedral cavities BO_6 and much larger by size cuboctahedral cavities AO_{12}. Oxygen octahedra as well as polyhedra AO_{12} can be occupied by two types of cations: (B', B'') и (A', A'') [5]. The discrepancy between Li^+ and Na^+ sizes and volume of cuboctahedra AO_{12} in the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions results in significant deformation of the oxygen cage of the ideal perovskite cell, which may manifests itself in the oxygen octahedra BO_6 rotations as a whole and in their deformations when changing the composition of both anionic and cationic sublattices.

In the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ (Na:Li ≈ 7:1) solid solutions cations ordering, oxygen cages deformation and rotation are implemented in such a way as to make from sodium free positions some kind of conduction channels, causing the superionic conductivity at high temperatures [1-3]. The ratio of the Nb^{5+} and Ta^{5+} concentrations determines, in addition, the degree of order of their arrangement in the octahedral cavities and the type of dipole ordering of the crystal structure. Also it is influenced by differences between Nb^{5+} and Ta^{5+} electronic configurations [6]. The $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions with low tantalum content (y≤0.25) is a strong ferroelectric and regardless of the sample's thermal history doesn't show antiferroelectric properties at room temperature, while solid solutions with y≥0.3 could be both ferroelectric and antiferroelctric at room temperature [1, 2].

Phase transition to the superionic state is clearly seen by the conductivity dependence on temperature (Fig. 1) at t=400÷460°C [1, 3]. Phase transition from the disordered antiferroelectric phase to the superionic state is more energetically favorable than the one from the ordered ferroelectric phase [1, 7]. Therefore, phase transition to the superionic state is preceded by diffuse phase transition

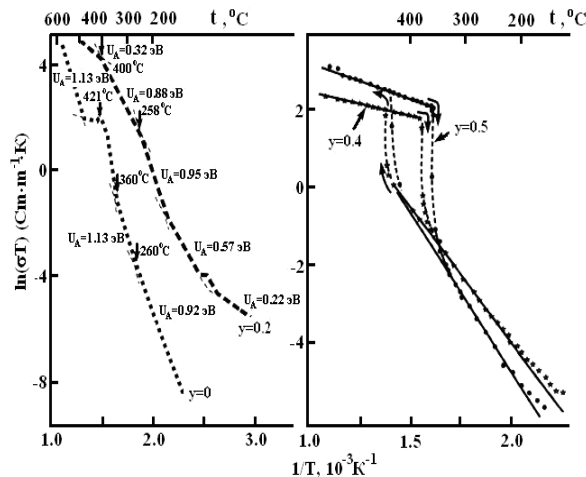ferroelectric – antiferroeletric, occurring for different compositions of solid solutions at 100÷360°C [1, 7].

Fig. 1. The dependence of conductivity on temperature of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions with y =0, 0.2, 0.4, 0.5.

It is essential to note that, according to [2], for compositions, enriched in niobium, the conductivity has primarily ionic nature in the region of the ferroelectric phase at ~260÷300°C, well below the temperature of the ferroelectric – antiferroelectric phase transition.
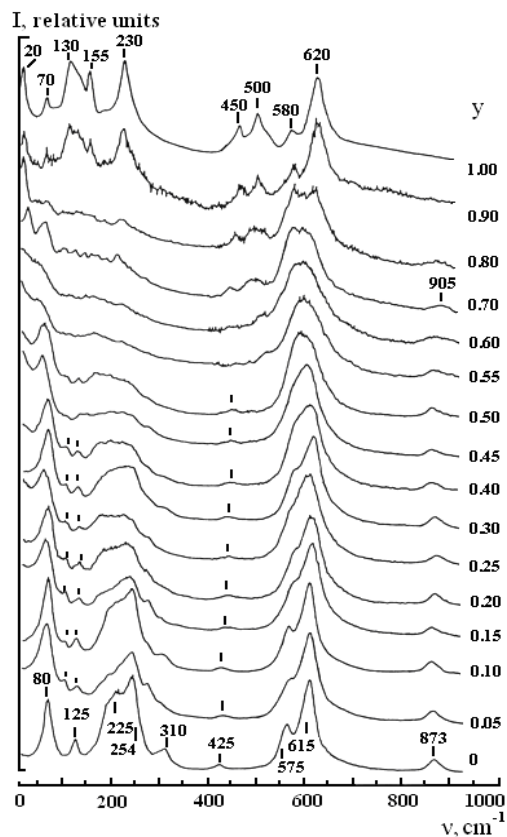

Fig. 2. The concentration changes in the Raman spectra of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions, t=20°C.

For the superionic charge transport in the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions it is necessary to have the geometric opportunity of free movement of mobile Li^+ ions from the cavity into the cavity through a common edges of polyhedra AO_{12} [1]. Thus, the important case that facilitates the phase transition is the presence of a strong compositional disorder both in alkali metal and niobium and tantalum sublattices. In the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions it is possible to vary the static disordering of Nb^{5+} and Ta^{5+} (by changing y) and dipole ordering in the niobium and tantalum sublattices, thereby facilitating the phase transition and changing temperatures of the phase transitions both to the superionic and antiferroelectric states.

Fig. 2 shows the concentration changes in the Raman spectra of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions.

When Nb^{5+} ions are substituted by isovalent Ta^{5+} ions with the same ionic radii ($R_{Nb}=R_{Ta}=0.66$Å) a considerable changes in the phonon Raman spectrum occur: in the region of the oxygen octahedra BO_6 ($B=Nb^{5+},Ta^{5+}$) librations as a whole (80 cm^{-1}); in the region of the Li^+ and Na^+ and Nb^{5+} and Ta^{5+} vibrations in the cuboctahedra AO_{12} and oxygen octahedra BO_6 (100÷350 cm^{-1}); in the region of the oxygen octahedra vibrations (500÷700 cm^{-1}); in the region of the oxygen atoms stretching modes (850÷910 cm^{-1}). The presence of the line, corresponding to the stretching modes (Fig. 2), unambiguously indicates the absence of a symmetry center of the unit cell in the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions and the presence of ferroelectricity [8].

It is worth noting that the lines in the 80, 200÷350, 550÷650 cm^{-1} regions corresponding, respectively, to the oxygen octahedra BO_6 vibrations as a whole, to the Nb^{5+} and Ta^{5+} vibrations in the oxygen octahedra and to the oxygen octahedra vibrations is much stronger than the lines in the 100÷160 and 850÷910 cm^{-1} regions, corresponding, respectively, to the Na^+ and Li^+ vibrations in the cuboctahedral cavities AO_{12} and to the stretching modes of the oxygen atoms along the polar axis (Fig. 2). This indicates a significant change of the polarizability of the unit cell during Nb^{5+} and Ta^{5+} vibrations in the octahedra and vibration of the oxygen cage as a whole than during Na^+ and Li^+ vibrations in the cuboctahedra AO_{12}. It can be seen from Fig. 2, that the oxygen octahedra of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions when y<0.2 are slightly distorted and correspond to the oxygen octahedra of the strong ferroelectric $LiNbO_3$, which are close to the ideal. Raman spectra of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions when y<0.2 in the region of the oxygen octahedra vibrations (550÷650 cm^{-1}), Fig. 2, are almost identical to the $LiNbO_3$ spectrum [2].

When y→0.5 the distortion of the oxygen octahedra BO_6 increases markedly, resulting in significant broadening of the corresponding lines in the 550÷650 cm^{-1} region of the Raman spectrum, Fig. 2. In this case the structural deformation of the whole oxygen cage is the most markedly seen when y≥0.6 (after concentrational phase transition) by the appearance of a new lines in the 450÷500 cm^{-1} region (Fig. 2). This deformation is determined by the effects of short-range and long-range order in the niobium and tantalum sublattices and by the inequality of Nb-O and Ta-O bonds.

When y≈0.9 the phase transition from ferroelectric to antiferroelectric occurs and it is manifested in the disappearance of the 873 и 905 cm^{-1} lines, corresponding to the stretching modes of the oxygen atoms (Nb(Ta)-O-Nb(Ta)) along the polar axis, Fig. 2. This vibration is active in the noncentrosymmetric ferroelectric phase and is forbidden in centrosymmetric antiferroelectric phase, according to the selection rules [8]. By Raman data in the antiferroelectric phase oxygen octahedra are significantly distorted compared with octahedra in the ferroelectric phase, as evidenced by the high intensity of 450, 500 cm^{-1} lines which are absent in the spectrum of the ferroelectric phase, Fig. 2. It must be noted that, when y→0.5, the disappearance of the 100÷160 cm^{-1} lines, corresponding to Na^+ and Li^+ vibrations in polyhedra AO_{12} is not observed (Fig. 2).

When y≈0.5 and the degree of long – range order in the Nb^{5+} and Ta^{5+} sublattice is close to zero [1-2], there are some frequency gaps (Fig. 3) and the appearance of new lines in the Raman spectrum (Fig. 2).
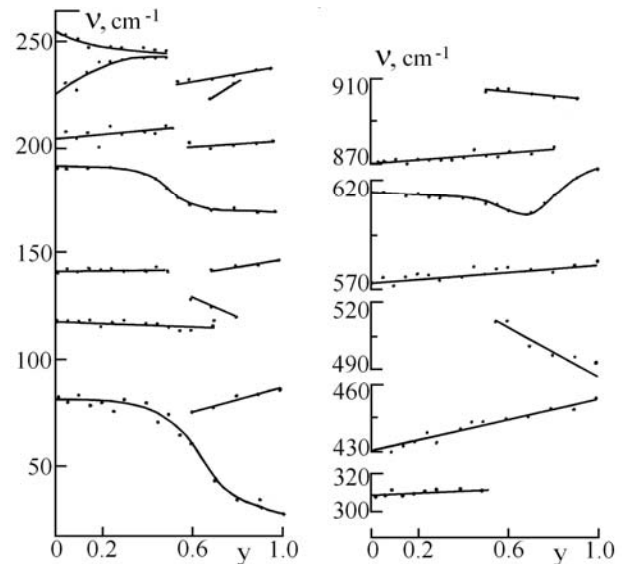

Fig. 3. The concentrational frequency changes in the Raman spectra of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions, t=20°C

This indicates the presence of the concentrational phase transition with radical reorganization of the whole crystal structure, associated both with a change in the order of Nb^{5+} and Ta^{5+} arrangement in the oxygen octahedra and with a considerable distortion and change of the symmetry of the oxygen octahedra. It is worth noting that this phase transition, according to the Raman data, occurs not at y=0.5, but at y≈0.55÷0.60, which is caused by inequality of Nb-O и Ta-O bonds. In this case, when y→0.55÷0.60, the line at 80 cm^{-1}, corresponding to the librations of oxygen octahedra as a whole, gradually broadens and blurs to the Rayleigh line, moreover, its intensity decreases. This indicates a significant violation of the correlation in the octahedra librations, apparently, due to disorientation of the octahedra. After the concentrational phase transition, taking place when y≈0.55÷0.60, with an

increase of Ta^{5+} concentration the frequency of this line decreases considerably and when $y \approx 0.7$ it splits into two lines, Fig. 2. Disorientation of the oxygen octahedra as a whole and its deformation occurs in the Raman spectrum by the appearance of new lines in the $450 \div 500$ cm^{-1} region (Fig. 2) and will undoubtedly increase geometrical possibilities for Li^+ transport at high temperatures.

Fig. 4, a, b, c shows the temperature changes in the Raman spectrum of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions with y=0, 0.2 and 0.4.
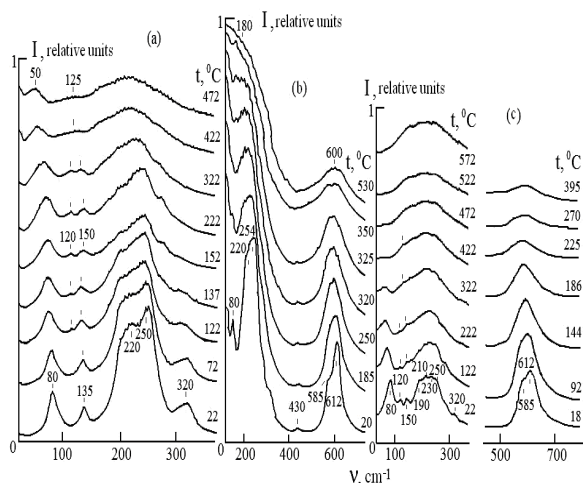

Fig. 4. Raman spectra of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions at different temperatures: (a) - $Li_{0.12}Na_{0.88}NbO_3$; (b) - $Li_{0.12}Na_{0.88}Ta_{0.2}Nb_{0.8}O_3$; (c) -$Li_{0.12}Na_{0.88}Ta_{0.4}Nb_{0.6}O_3$

It is evident that disordering of the structure with the temperature increasing appears gradually in the spectrum. Thus, Raman lines considerably broaden and the entire spectrum, with the temperature increasing, gradually blurs to the Rayleigh line. In this case the differences in the temperature behavior of the different parts of the spectrum for the ceramics of different composition are observed. In the spectrum of the $Li_{0.12}Na_{0.88}NbO_3$ solid solutions (Fig. 4, a) there is a preservation of the line at 80 cm^{-1} corresponding to the librations of the oxygen octahedra as a whole over the entire temperature range ($20 \div 472$ ^oC). The line at $100 \div 160$ cm^{-1} corresponding to the Li^+ and Na^+ vibrations is also preserved. At the same time, for the $Li_{0.12}Na_{0.88}Ta_{0.2}Nb_{0.8}O_3$ and $Li_{0.12}Na_{0.88}Ta_{0.4}Nb_{0.6}O_3$ solid solutions, characterized by the stronger disorder in the Nb^{5+} and Ta^{5+} sublattice, the line at 80 cm^{-1} is blurred to the Rayleigh line at 250 and 422^oC, respectively (Fig. 4, b, c). Thus, the line corresponding to the stretching modes of the oxygen atoms is present in the spectrum of the investigated solid solutions up to the point of the phase transition to the centrosymmetric antiferroelectric phase. In the antiferroelctric phase this line is absent.

4. Conclusions

From the experimental data obtained it is seen that phase transition from ferroelectric to antiferroelectric state occurs for the investigated solid solutions at $300 \div 350$ ^oC.

Thus, the line of the stretching modes of the oxygen atoms, active in the noncentrosymmetric phase and forbidden by the selection rules in the centrosymmetric antiferroelectric phase, disappears during this phase transition. The thermal disordering of the $Li_{0.12}Na_{0.88}Ta_yNb_{1-y}O_3$ solid solutions structure introduced by mobile lithium atoms occurs gradually; it is relatively homogeneous and can reach certain equilibrium with respect to the other degrees of freedom of the system. The increase in the translational mobility of the light lithium ions is facilitated by the oxygen octahedra BO_6 disorientation and their considerable deformation which changes radically the octahedra symmetry. Static disordering of the structural units in the Nb^{5+} and Ta^{5+} sublattice, taking place when the composition of the solid solution is changed, and the inequality of Nb-O and Ta-O bonds lower the point of the phase transition from ferroelectric to antiferroelectric and can facilitate the transition to the superionic state. However, the data obtained show that the phase transition to the superionic state is not manifested in the Raman spectra.

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