

Thermophysical Study of Structural Phase Transitions in $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ Solid Solution

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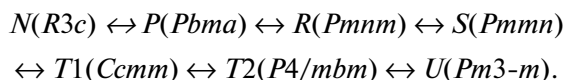
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Abstract—Temperature dependences of specific heat $C_p(T)$ and coefficient of thermal expansion $\alpha(T)$ for $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ sodium–lithium niobate ceramic samples are investigated in the temperature range of 100–800 K. The $C_p(T)$ and $\alpha(T)$ anomalies at $T_3 = 310 \pm 3$ K, $T_2 = 630 \pm 8$ K, and $T_1 = 710 \pm 10$ K are observed, which correspond to the sequence of phase transitions $N \leftrightarrow Q \leftrightarrow S(R) \leftrightarrow T2(S)$. The effect of heat treatment of the samples on the sequence of structural distortions was established. It is demonstrated that annealing of the samples at 603 K leads to splitting of the anomaly corresponding to the phase transition $Q \rightarrow R/S$ in two anomalies. After sample heating to 800 K, the only anomaly is observed in both the $C_p(T)$ and $\alpha(T)$ dependence. Possible mechanisms of the observed phenomena are discussed.

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INTRODUCTION

Sodium niobate NaNbO_3 belongs to a series of unique dielectric crystals. It has become a base for creating promising lead-free functional materials of the piezoelectric, pyroelectric, electro-optical, condenser (including microwave), and relaxor types [1–10]. The difficulties in creating and studying such materials is due to sodium niobate undergoing a record number of different phase transitions characteristic of perovskites. These transitions originate from the rotation of oxygen octahedra or ordered ion displacement. Six distorted phases have been identified so far [1–14]:



The three high-temperature transitions originate from the rotation of octahedral; the next three, from a combination of rotations and the polarization of octahedra, accompanied by the formation of two highly ordered antiferroelectric phases, P and R , and one ferroelectric phase N [2–5]. In addition, even nominally pure NaNbO_3 often contains substantial impurities of the ferroelectric phase $Q(P2_1ma)$ and incommensurate phase [11, 15, 16].

The existence of several competing instabilities makes sodium niobate NaNbO_3 and its solid solutions extremely sensitive to external factors and allows the coexistence of several phases in a wide range of temperatures. On the one hand, the sensitivity to the

external factors is promising for applications; on the other hand, it leads to the properties of materials being strongly dependent on the conditions of their fabrication, their concentration of impurities, and their thermal prehistory, along with pressure and electric fields.

In view of the above, it is important to study the nature of phase states in sodium niobate-based solid solutions and the effect external factors have on them. Despite the great many studies devoted to sodium niobate and its solid solutions, the thermophysical characteristics of NaNbO_3 and $\text{Na}_{0.95}\text{K}_{0.05}\text{NbO}_3$ were thoroughly investigated only recently, in a wide range of temperatures covering all the known phase transitions [6, 7]. The effect of thermal prehistory on the stability of distorted phases remains understudied, despite the available data on the strong effect heat treatment of $\text{Na}_{1-x}\text{Li}_x\text{NbO}_3$ ceramics at 600–700 K has on their properties and phase transition temperatures [17, 18].

The data on phase transitions and the concentration diagram of $\text{Na}_{1-x}\text{Li}_x\text{NbO}_3$ solid solutions in the low-concentration range of $x = 0.00$ – 0.10 were mostly obtained using optical, electrical, and structural techniques and are most contradictory [8–10]. This is because the anomalies in these properties are very weak at many transitions, spread considerably due to sample inhomogeneity, and are not always fixed. In addition, there is a lack of data on structural properties in this range of concentrations. Obtaining information on phase transitions, features of a crystal's structure, and the physical properties of sodium niobate and its

solid solutions for further development of model concepts of the correlation between phenomena of different physical natures is the important problem that must be solved in order to create techniques for fabricating materials with specific controlled properties.

Thermophysical investigations are characterized by high sensitivity and can detect any variations in the energy of a sample, allowing us to study all transitions related to the ferroelastic, ferroelectric, and antiferroelectric transformations. The aim of this work was to investigate the specific heat and thermal expansion of the $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ ceramic samples in the temperature range of 100–800 K.

EXPERIMENTAL

$\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ ceramic samples with a density of 92–95% relative to the theoretical value were prepared according to the standard technique, i.e., solid-state synthesis from a Na_2CO_3 , Li_2CO_3 , and Nb_2O_5 mixture at 800°C with subsequent annealing at 1200°C without pressure. X-ray diffraction analysis revealed no non-perovskite phases.

Thorough investigations of the specific heat in the temperature range of 100–800 K were conducted on a DCM-10Ma differential scanning microcalorimeter in the dynamic regime at a heating and cooling rate of 16 K min^{-1} in a helium atmosphere. The measurements were performed on ceramic samples with masses of $m \sim 200$ mg, packed in an aluminum container. The spread of experimental points relative to the smoothed curve was no more than 1%. The error of determining the integral characteristics (enthalpy and entropy) was ~ 10 –15%.

When analyzing phase transitions, it is especially important to obtain information on the related anomalous specific heat and entropy. Figure 1 therefore shows excess specific heat $\Delta C_p(T)$ obtained as difference $C_p - C_L$ between the total and lattice specific heats. This difference was determined by approximating the $C_p(T)$ data with a smooth polynomial function beyond the region of anomalous specific heat. Upon the first heating of the $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ solid solution, we observed four specific heat anomalies at 500–550, 600, 615–630, and 740–760 K (Fig. 1). Upon cooling, the $\Delta C_p(T)$ dependence contained only one anomaly, at 585–590 K (temperature hysteresis ~ 35 K). It should be noted that the anomaly at 500–550 and 600 K was not always recorded in our experiments. In the next series of heatings, the anomalies at 500–600 K were smoothed and transformed into a shoulder of the main, strongly pronounced anomaly at 626–632 K. The resulting variation in entropy, determined by integrating function $\Delta C_p(T)/T$ was $\Delta S = (4.3 \pm 0.4)$ J mol^{-1} K $^{-1}$. This ΔS value is typical of displacive phase transformations [4, 5]. At the same time, considering the features of sodium niobate NaNbO_3 and

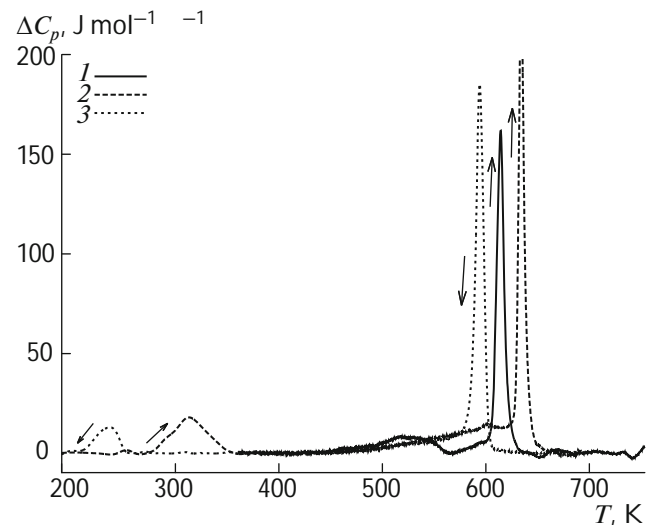


Fig. 1. Temperature dependences of specific heat $\Delta C_p(T)$ for the $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ ceramics upon (1) first and (2) second heating and (3) in the cooling regime.

its solid solutions [7], our results do not exclude the possibility that the phase transitions in $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ are due to the ordering of structural elements.

Thermal expansion was studied on a NETZSCH DIL-402C dilatometer in the dynamic regime at a rate of temperature variation of 2–5 K min^{-1} in the temperature range of 100–800 K. The measurements were performed in a helium flux. Fused quartz etalons were used to calibrate the measuring system and allow for its thermal expansion. As in our specific heat investigations, in the first series of thermal expansion measurements, along with $\alpha(T)$ anomalies at ~ 310 and ~ 630 K and a small anomaly at ~ 720 K, we observed anomalies in the range of 500–600 K that were not reproduced in the next series of measurements after exposing the samples to high temperatures. The temperatures of the anomalies changed somewhat from one series to another: $T_3 = 310 \pm 3$ K, $T_2 = 630 \pm 8$ K, and $T_1 = 710 \pm 10$ K (Fig. 2). The temperature of the main anomaly upon cooling was highly stable in all series of measurements: 589 ± 2 K. As in our specific heat study, the temperature hysteresis was found to be substantial: $\delta T_2 \approx 35$ K (Fig. 2).

Annealing the sample at 750 K for an hour resulted in no appreciable displacement of the specific heat and thermal expansion anomalies at T_2 . However, annealing at 603 K for the same amount of time resulted in the anomaly splitting into two anomalies at $T_2'' = 619$ K and $T_2' = 636$ K (Figs. 3 and 4). Upon cooling the sample heated to 750 K, and upon repeated heating, the only specific heat maxima were observed at $T_{2\downarrow} = 590$ K and $T_{2\uparrow} = 630$ K, respectively. As can be seen in Fig. 4, which shows the measured specific heat and thermal expansion, increasing the

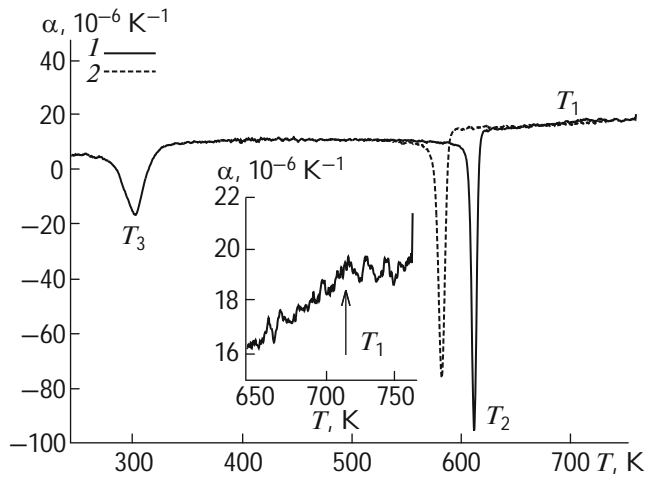


Fig. 2. Temperature dependences of thermal expansion coefficient $\alpha(T)$ for the $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ ceramics upon (1) heating and (2) cooling.

time of annealing broadened the range of temperatures between the split anomalies. Upon cooling, we always observed one anomaly in the specific heat and thermal expansion at a temperature of $T_{2\downarrow} = 590 \pm 2$ K, regardless of the annealing temperature and time.

Note too that the resulting variations in enthalpy (ΔH) and deformation ($\Delta L/L$) related to the split anomalies remained invariable within the accuracy of determination upon multiple annealings and thermo-cycling.

Annealing at other temperatures (590, 606, 608, 610, 615, and 750 K) and approaching from the side of both high and low temperatures caused neither significant changes in the specific heat and thermal expansion behavior nor splitting of the anomaly at 630 K. Note that similar results were reported in [17], where the electrical properties of $\text{Na}_{1-x}\text{Li}_x\text{NbO}_3$ ceramics were investigated.

Thus, only annealing in a narrow range of temperatures below transition temperature $T_{2\uparrow}$ upon heating, but above transition temperature $T_{2\downarrow}$ upon cooling, and only when approaching the annealing temperature from the region of stability of the high-temperature phase $T > T_2$, led to splitting of the specific heat and thermal expansion anomalies.

RESULTS AND DISCUSSION

To interpret the observed specific heat and thermal expansion anomalies and relate them to structural variations in a sample, let us consider the main data obtained by different means and the $x-T$ phase diagrams of the $\text{Na}_{1-x}\text{Li}_x\text{NbO}_3$ system built in [8, 9] on the basis of these data. The phase diagrams presented in these studies differed considerably for crystals and ceramics prepared via conventional annealing and hot

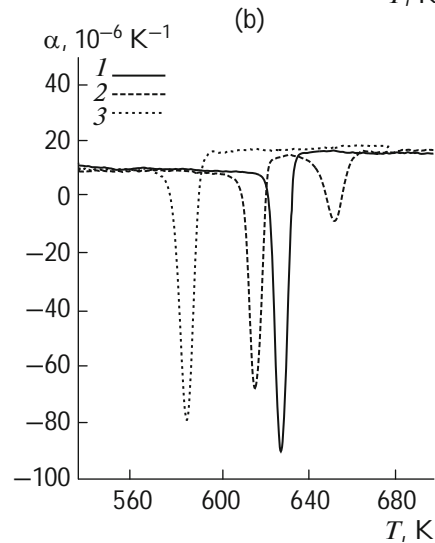
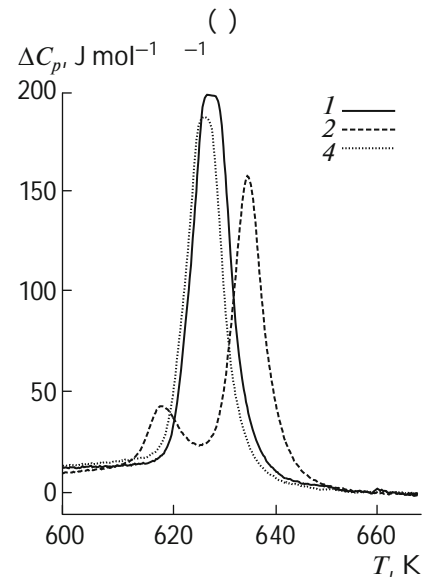


Fig. 3. Effect of annealing at 603 K for time t on (a) specific heat ($t = 1$ h) and (b) thermal expansion ($t = 3$ h) of the $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ ceramics. (1) Heating before annealing, (2) heating after annealing, (3) cooling, and (4) second heating after annealing and subsequent heating to 750 K.

pressing, especially at low Li concentrations. Due to structural inhomogeneity, the phase transition temperatures changed strongly and could even be missing from samples with the nominally identical concentrations.

The authors of [8–10] concluded that with an increase in the Li concentration, the Q phase contained in pure sodium niobate stabilizes and coexists with the P phase in the concentration range of $x < 3\%$. At high Li concentrations, the samples become homogeneous ferroelectrics with the structure typical of the Q phase. The diagrams obtained in [8, 9] are to a large extent similar. In [8], however, transition $Q \leftrightarrow S$ to the paraelectric phase was assumed to occur, while in [9],

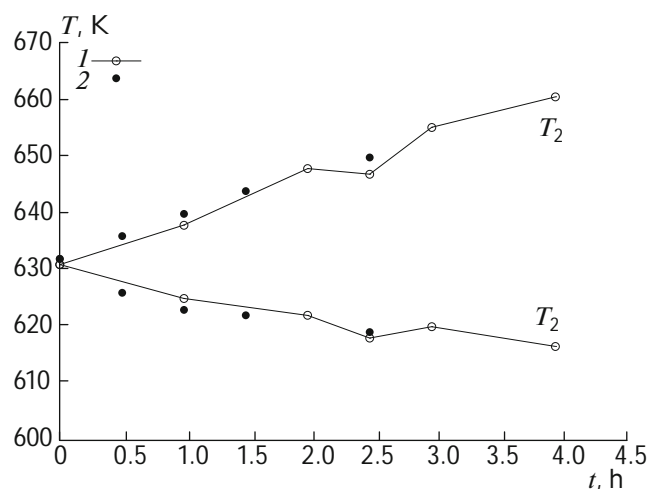


Fig. 4. Effect of the time of annealing at 603 K on phase transition temperatures T_1' and T_2'' for the $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ ceramics, determined from the data on (1) thermal expansion and (2) specific heat.

transition $Q \leftrightarrow R$ to the antiferroelectric phase was assumed to occur. The choice of the S phase in [8] was based on data from dilatometric measurements, and the statement that the main structural distortions should correspond to the transition to the ferroelectric Q phase from the paraelectric S phase, rather than from the antiferroelectric R phase. In our measurements, as in the structural study in [11], it was established that the change in volume upon transition $Q \leftrightarrow R$ in pure NaNbO_3 is substantial ($\delta V/V = -2.5 \times 10^{-3}$ [6]) and comparable to $\delta V/V = -2.3 \times 10^{-3}$ in $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ at 630 K. We should therefore not exclude the possibility of transition $Q \leftrightarrow R$ with symmetry variation occurring in this composition at 630 K.

The temperatures of specific heat and thermal expansion anomalies in $\text{Na}_{0.95}\text{Li}_{0.05}\text{NbO}_3$ found upon the first heating do not agree with the presented phase diagrams, due possibly to the inhomogeneity of the investigated samples. Anomalies are observed that are typical of both compositions with high Li contents and pure sodium niobate. After multiple heatings to 800 K and heat treatments, only the main anomalies at T_3 , T_2 , and T_1 were observed in the behavior of the specific heat and thermal expansion. These correspond to transitions $N \leftrightarrow Q \leftrightarrow S \leftrightarrow T_2$ [9] and $N \leftrightarrow Q \leftrightarrow R \leftrightarrow S$ [8] characteristic of compositions with $x > 0.05$. After an annealing cycle, the investigated sample apparently homogenizes.

Of course, the reason for the splitting of anomalies in the thermal properties at 630 K cannot be established based only on the investigations conducted in this study. We can only propose several possible mechanisms.

We should note the results from thermodynamic analyses of the phase transitions in NaNbO_3 [12, 13] in the temperature region where the energies of many ferroelectric and antiferroelectric phases are similar. Lithium additions reduce the energy of the Q phase with respect to the energy of the P phase and phase transition $R \leftrightarrow Q$ in the compositions with high lithium contents. Upon annealing a sample in the area of the phase transition hysteresis, a mixture of phases can form, and the transition can split upon the next heating.

Another possible reason is sample imperfection. In the $\text{Na}_{1-x}\text{Li}_x\text{NbO}_3$ composition, the dependence of the reduced crystal lattice parameter on the Li concentration in the range of $x < 0.06$ deviates substantially from the linear dependence typical (according to Vegard's rule) of substitutional solid solutions. It was assumed in [14–16] that the compounds form with a sodium deficiency of ~1–2%, leading to the emergence of a block structure and shear planes. The authors of [14–16] concluded that as the Li concentration rises, the Q phase contained in pure sodium niobate stabilizes and coexists with the P phase in the concentration range of $x < 3\%$. At high Li concentrations, the samples become homogeneous ferroelectrics with the structure typical of the Q phase.

We may assume that during the synthesis of the solid solutions, small Li cations first occupy vacant positions in the lattice, including tetrahedral cavities in the block structure. Only when all the vacant positions are occupied (at $x > 0.05$ – 0.07) do lithium ions start substituting for sodium ions. Annealing a sample at 603 K can result in lithium redistribution. In this case, conditions (e.g., stresses or local electric fields in the shear planes) can change, which alters the sequence of phase transitions as in, e.g., epitaxial ferroelectric fields.

CONCLUSIONS

Clarification of the observed phenomena requires further thorough investigations of the local structure, local electric fields and stresses, and their effect on the sequence of structural transformations in $\text{Na}_{1-x}\text{Li}_x\text{NbO}_3$ solid solutions with low lithium concentrations.

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