Phase Diagram and Physical Properties of the Sodium Niobate–Lithium Niobate–Cadmium Niobate Three-Component System


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Abstract—The phase diagram of the (Na,Li,Cd$_{0.5}$)NbO$_3$ ternary system is refined. The electrical properties of solid solutions over a broad range of the component concentrations were studied. The compositions promising for high-temperature transducers were obtained. © 2001 MAIK “Nauka/Interperiodica”.

INTRODUCTION

In this paper, we refine information on the phase transitions and physical properties of the (Na,Li,Cd$_{0.5}$)NbO$_3$ system studied in [1]. The refined phase diagram of this ternary system enabled a more detailed interpretation of its properties. Similar to [1], we considered six cross sections with a content of the $z$ component, Cd$_{0.5}$NbO$_3$, from 5 to 20 mol %. In each of the sections, we synthesized compounds corresponding to the $y$ sections with 1–15 mol % of LiNbO$_3$. Synthesis and sintering conditions were presented in [1].

RESULTS AND DISCUSSION

We studied the phase diagram region adjacent to the NaNbO$_3$ vertex (Fig. 1). Thin lines depict the $y$ and $z$ sections, and thick lines represent interfaces between regions of different symmetry (single-, two-, and three-phase).

The phase diagram of the ternary system is consistent with those of the associated binary systems. In (100–$z$)NaNbO$_3$–$z$Cd$_{0.5}$NbO$_3$ [2], solid solutions (SS) form up to $z = 25$. In the range of $0 < z < 15$, SS have rhombic symmetry. The unit cell parameters are related to the parameters of the perovskite monoclinic cell $a$, $b$, and $\beta$ through the following expressions: $A = 2a \cos \beta / 2$, $B = 4b$, and $C = 2a \sin \beta / 2$ (the $M_4$ phase). At $z \approx 15$, the multiplicity factor for $B$ changes: $B = 2b$ (the $M_2$ phase). In the range of $19 < z \leq 25$, SS have tetragonal symmetry (the $T$ phase); we failed to reveal superstructures here because of the very weak reflections from impurity phases in the X-ray diffraction patterns. The $M_2$ and $T$ phases are separated by the broad region of their coexistence.

In the (100–$y$)NaNbO$_3$–$y$LiNbO$_3$ system [3], as $y$ grows, SS of different symmetry arise in the following sequence: rhombic $M_4$ (0 < $y$ < 3.5) $\rightarrow$ rhombohedral $M_2$ (4 < $y$ < 10.5) $\rightarrow$ rhombohedral $Rh$ (12 < $y$ < 12.5) $\rightarrow$ rhombic $M_2$ (12.5 < $y$ < 14). The monophase regions are separated by regions of phase coexistence. With a further increase in $y$, a broad heterogeneous region is observed where, along with the NaNbO$_3$-based SS, LiNbO$_3$ is present. Accordingly, the area adjacent to the NaNbO$_3$ vertex of the ternary phase diagram is divided into several regions of SS crystallization: broad single-phase $M_2$, $M_4$, and $T$ regions; narrow single-phase $Rh$ and $M_2$ regions; broad two-phase $M_2 + Rh$, $M_2 + T$, and $T + Rh$ regions; narrow two-phase $M_2 + M_4$ and $Rh + M_2$ regions; and a three-phase $M_2 + T + Rh$ region.

We considered the uniform deformation parameter $\delta$ [4] and the electrical parameters of the SS in the $y$ and $z$ sections. The electrical parameters of different ferroelectric SS containing morphotropic regions (MRs) are known [5–7] to exhibit extrema that are located in the vicinity of MRs and correlate with the structure parameters, in particular, with $\delta$.

In this system, sections crossing the greatest number of phases and MRs have been studied most extensively. Among the $z$ sections, such is the cross section $z = 5$. It goes through three phases: $M_4$, $M_2$, and $Rh$; and three MRs: the narrow two-phase MR$_1$ ($M_2 + M_4$), broad three-phase MR$_2$ ($M_2 + T + Rh$), and very narrow two-phase MR$_3$ ($Rh + M_2$) (Figs. 2a, 2b).

Figure 2a presents the concentration dependences of $\delta$, the relative permittivities $\varepsilon/\varepsilon_0$ and $\varepsilon_{53}^T/\varepsilon_0$, the electro-
mechanical coupling coefficient $K_p$, and the piezoelectric parameters $d_{31}$ and $g_{31}$. Figure 2b shows these dependences for the dielectric loss tangent $\tan \delta$, the mechanical $Q$ factor $Q_M$, the sound velocity $V_{R}$, and Young’s modulus $Y_{11}$. It is evident from Fig. 2a that the permittivities, as well as $K_p$ and $d_{31}$, exhibit two maxima: the higher maxima approach the center of the three-phase MR$_2$, and the lower ones are located at the right edge of the narrow MR$_1$. The positions of the latter maxima with respect to the MR$_1$ cannot be considered accurate, since the measurement step was rather large, 2 mol %, whereas the MR$_1$ width is about 1 mol %. Note also that all of the above-mentioned parameters have minima within the MR$_2$ phase.

The maxima of the piezoelectric parameter $g_{31}$, which is known to be proportional to the residual polarization $P_r$, are shifted to the left of both MRs toward the $M_2$ and $M_4$ phases (in the $M_4$ phase, this maximum is incomplete due to a lack of appropriate samples). Such positions of the $g_{31}$ maxima are typical of ferroelectric systems [5, 6].

The above dependences of the electrical parameters correlate with the run of $\delta$, which has a minimum in both MRs and peaks in the $M_2$ phase.

It is worth noting that the higher maximum of $\varepsilon_{33}^T/\varepsilon_0$ in Fig. 2a is not beyond the right edge of the broad MR$_3$, which is common [5, 6], but lies within it. The same situation was observed for several cross sections of the (Na,Li,Pb$_{0.5}$)NbO$_3$ system [7]. This fact was attributed [7], in particular, to the coexistence of the $M$ and $Rh$ phases, resulting in a considerable increase in the number $N$ of possible directions of the spontaneous polarization ($N = 8(Rh) + 12(M) = 20$) compared with that in the monophase regions. (In PZT-based systems [5, 6], this number is considerably smaller, $N = 8(Rh) + 6(T) = 14$, and virtually does not affect the position of the $\varepsilon_{33}^T/\varepsilon_0$ maximum.) In the three-phase MR$_2$, $N$ is still greater, $N = 8(Rh) + 12(M) + 6(T) = 26$, which markedly increases the orientation part of the permittivity inside the MR and affects the position of $\varepsilon_{33}^T/\varepsilon_0$ and $\varepsilon_{33}^T/\varepsilon_0$ peaks. This in turn influences the maxima of $K_p$ and $d_{31}$, which are much less affected by $g_{31}$ (in addition, the $g_{31}$ values are small in this system). The same is also observed in the narrow MR$_1$, where $N = 12(M_2) + 12(M_4) = 24$ and the maximum of $\varepsilon_{33}^T/\varepsilon_0$ has a greater effect on $K_p$ and $d_{31}$ than that of $g_{31}$.

The concentration dependences of $\tan \delta$, $Q_M$, $V_{R}$, and $Y_{11}$ (Fig. 2b) can be explained in terms of SS ferroelectric elasticity, which characterizes the domain stability to external actions [5]. According to [5], with a growth of the ferroelectric elasticity, $\delta$, $Q_M$, $V_{R}$, and $Y_{11}$ increase, while $\varepsilon_{33}^T/\varepsilon_0$ and $\tan \delta$ decrease. That is the reason why the maxima and minima of $\varepsilon_{33}^T/\varepsilon_0$ and $\tan \delta$ are close to each other (Fig. 2b), whereas the max-