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Metastable phases in $H_xLi_{1-x}TaO_3$ waveguide layers and pure $LiTaO_3$

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ABSTRACT The formation of high-temperature phases in low-doped H:LiTaO₃ waveguide layers in Z-cut LiTaO₃ has been observed both by refractive-index and IR-spectra measurements. This permits us to correlate the index jumps to the changes of the OH bonds in the crystal lattice. Reversible phase transitions were detected in the temperature interval $T = 50$–$200\,°C$ over a wide range of hydrogen content including as-grown LiTaO₃. The high-temperature phases are metastable close to room temperature. This was demonstrated by tracing the time evolution of the refractive-index change. It was shown that the high-temperature phases are responsible for the long-term refractive-index instabilities in both H:LiTaO₃ waveguides and virgin LiTaO₃.

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1 Introduction

Lithium tantalate, LiTaO₃ (LT), is a well-known ferroelectric crystal widely used in electro-optics and integrated optics as a substrate material. Proton-exchanged waveguide layers in lithium tantalate (H:LT), with chemical composition $H_xLi_{1-x}TaO_3$, are a promising waveguide medium for electro-optical modulators, integrated lasers, and frequency converters [1, 2] because of the apparent simplicity of their fabrication and the comparatively low temperatures of the reaction, far below the Curie temperature of LT ($\sim 600\,°C$). The applicability of any waveguide system, however, is defined in many respects by the stability of its optical properties, refractive index in particular. At the same time, refractive-index instabilities were occasionally detected in H:LT waveguides [3–7]. In [5] the supposition was made that a possible cause of the index variations with time is the existence of high-temperature phases, similar to the $H_xLi_{1-x}NbO_3$ system [8]. Recently, this hypothesis was confirmed experimentally. The conditions of the high temperature phase formation, the magnitudes of the refractive-index jumps, the relaxation times, and other parameters were determined for highly doped H:LT layers [9–11]. In parallel, a similar study was performed for the $H_xLi_{1-x}NbO_3$

system [10], and it was shown that the evolution of the refractive-index increase Δn_e correlates well with the number and the temperatures of the phase transitions recognized earlier for $H_xLi_{1-x}NbO_3$ powders in the β-phase concentration region [8]. Regrettably, H:LT layers with low hydrogen concentrations, which are most valuable for practical applications, were not investigated. It is reasonable to point out that the phase diagram of $H_xLi_{1-x}TaO_3$ compounds has not been determined up to now. The 'structural phase diagram' of $H_xLi_{1-x}TaO_3$ layers on Z-cut LT, correlating the refractive indices to the crystal cell expansion, has been reported recently [12]. Five phases have been discovered in the layers.

In this report we treat the problem of the sources of the refractive-index instabilities in H:LT layers with low hydrogen content. Following the refractive-index change as a function of the quenching temperature, transitions between equilibrium and high-temperature phases have been observed. In addition, the quenching effect was observed for the first time in the IR-absorption spectra. This is evidence that there is a direct correlation between the variations of Δn_e and the changes of the OH-bond parameters.

2 Experimental techniques

H:LT waveguide layers were formed in Z-cut LT by ion exchange in pure benzoic acid at $T = 240\,°C$. After this, annealings were applied to decrease the hydrogen concentration in the layers to a level which belongs to the range of the desired equilibrium phase. As a criterion of phase assignment, the surface value of the refractive-index increase $\Delta n_e(0)$ was used. The intervals of the refractive-index values, corresponding to the equilibrium phases at room temperature, were taken from [12]. In the following text the notations of the equilibrium phases are kept the same as in [12]. To search for metastable-phase formation the samples were subjected to annealings for 10 min at various temperatures up to $400\,°C$. After this, two cooling regimes were applied: slow (s)-cooling for 2–3 h in the furnace and quick (q)-cooling for 5–7 min (quenching) by taking the samples out of the furnace into room temperature. Waveguide-mode effective indices N_m were measured by the prism-coupling method at a wavelength $\lambda = 0.6328\,\mu m$ with a possible error of ±0.0002. Then, taking the N_m values as a basis, the profiles of Δn_e over the

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waveguide depth were reconstructed with the inverse WKB method [13].

The IR-absorption spectra were recorded with a Perkin-Elmer 1430 spectrometer in the frequency range 3000–4000 cm^{-1} with a resolution of 1 cm^{-1}. The measurements were taken in air at room temperature. The light fell perpendicular to the sample face, i.e. we recorded the absorption due to OH bonds oriented in the plane perpendicular to the Z-axis, for Z-cut samples, and oriented both in and out of that plane, for Y-cut samples.

The LT substrate birefringence was measured with an LEF-801 'Microscan' ellipsometer (home-made, ISP) at $\lambda = 0.6328$ μm in transmittance configuration. A wide laser beam (1 mm) was used to average the index fluctuations over the illuminated area. The parameter $\Delta = 2\pi d(n_e - n_o)/\lambda$, where d is the sample thickness and n_e and n_o are the extraordinary and ordinary refractive indices, respectively, was measured. Considering the influence of the beam-positioning irreproducibility, the absolute accuracy of the measurement was estimated to be $\delta\Delta = \pm 0.1°$. This gives an error of 1×10^{-5} in the birefringence variation, possible temperature variations having been taken into account.

3 Results and discussion

3.1 *H:LT waveguide layers*

The dependences of $\Delta n_e(0)$ on the quenching temperature T in low-protonated LT layers are shown in Fig. 1. It is evident that at $T = 100–200$ °C a high-temperature phase with an increased value of $\Delta n_e(0)$ is formed. For all the samples the transition is totally reversible – the initial surface index level and profile can be restored by applying s-cooling after annealing at the highest temperature used in the quenching experiment. Therefore, the refractive index profile modifications caused by diffusion are negligible, the hydrogen concentration profile is not changed during the heating procedures, and in the phase diagram we move only along the temperature axis. An empirical rule can be deduced that the refractive-index jump induced by the transition is nearly 30% of the $\Delta n_e(0)$ level of the $H_xLi_{1-x}TaO_3$ equilibrium phase under room-temperature conditions. As one might expect, the magnitude of the index jump decreases on decreasing the hydrogen concentration in the layer, and in the α'-phase [12] the sensitivity of the prism-coupling method is not high enough to measure solidly the index variations. The curve with initial value $\Delta n_e = 0.004$ shows a two-step transition. This value of $\Delta n_e(0)$ exactly corresponds to that of the upper boundary of the α'-phase [12]. It seems that the layer is a combination of two equilibrium phases, α'- and residual α-phases. In such a case, the two-step curve is a result of two superimposed transitions to the related high-temperature phases with slightly shifted transition temperatures.

In Fig. 2 a diagram, in which the $H_xLi_{1-x}TaO_3$ phases in Z-cut layers are correlated to the index increase, is demonstrated. The index-increase values, corresponding to the boundaries of the equilibrium phases, were taken from [12]. The temperature intervals of the transitions from equilibrium to high-temperature phases, including those found in the present study, are sketched by vertical segments. So, the existence of high-temperature phases is detected over a wide

range of hydrogen concentrations, including the α'-phase which is a solid solution of H in LT. These high-temperature phases are metastable at room temperature and the variation of the refractive index is induced by the continuous transition to the corresponding equilibrium phase. The temperatures at which the high temperature phase formation begins are relatively low, 60–100 °C in all the cases, and are in the range of the usual operating temperatures of high-frequency electro-optical modulators [14]. Therefore, initiation of the process is possible by technological heat treatments or due to fluctuations of the device working temperature.

The stability of the high-temperature α-phase at nearly room temperatures was tested experimentally. To do this an α-phase layer was quenched from 300 °C and the variation of $\Delta n_e(0)$ with time was traced. The results are presented

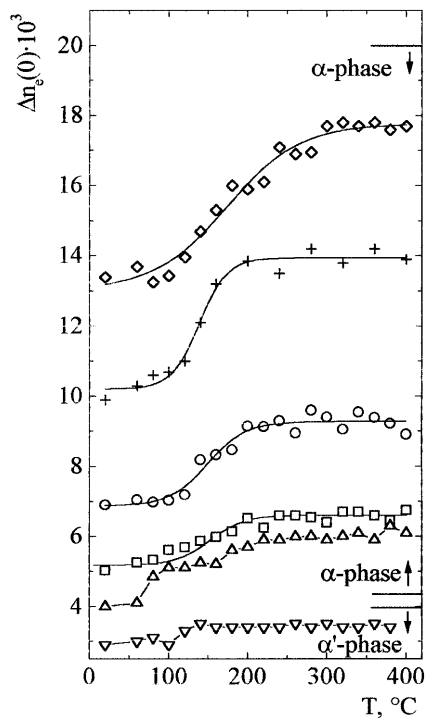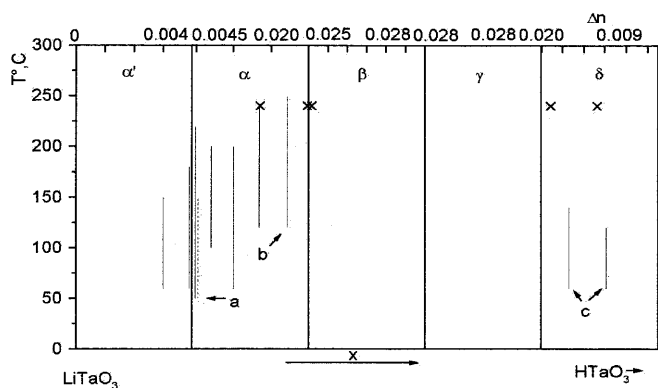**FIGURE 1** Surface refractive-index increase vs quenching temperature in low-doped H:LT waveguides

FIGURE 2 Temperature intervals (*vertical segments*) of the transitions from equilibrium phases at $T = 20$ °C to high-temperature phases in $H_xLi_{1-x}TaO_3$ layers. Data from literature: a [5]; b [9]; c [11]. *Marks* '×' mean only the existence of a transition has been detected [7]

in Fig. 3. The reduction of $\Delta n_e(0)$ can be well described by a monotonic function without any periodic bulges as those observed in [3]. It is seen that at room temperature the relaxation of the high-temperature phase is very slow and the index jump created by the quenching procedure decreases only to half of its value after two months of storing. Earlier, a similar relaxation time was measured for an α-phase layer with a higher equilibrium value of $\Delta n_e(0) = 0.0166$ [11]. So, the high-temperature α-phase exhibits a long relaxation time over a wide range of hydrogen concentrations. For comparison, complete relaxation of the high-temperature states in $H_xLi_{1-x}NbO_3$ (H:LN) layers takes as little as 300 h of storing at $T = 20\,°C$ [10]. For H:LT layers, the transition in equilibrium state can be greatly accelerated if the sample is stored at higher (up to $100\,°C$) temperature. At such temperature the relaxation process can be completed in one day. So, a special heat treatment at a temperature slightly below $100\,°C$ followed by s-cooling could be used as a final stage in a device-fabrication process in order to stabilize the index value in H:LT waveguides.

It can be supposed that index variations, induced by quenching, are correlated to a transformation of the OH bonds in the crystal lattice. The influence of the q-cooling on the IR-absorption spectra of a Z-cut waveguide is shown in Fig. 4. The sample had $\Delta n_e(0) = 0.008$ after s-cooling and we assume it to be in the α-phase. It is seen that after quenching the OH band is $\sim 2\,cm^{-1}$ shifted to lower frequencies, keeping its intensity the same. After a long enough low-temperature treatment and s-cooling, it returns to its initial position. Thus, the quenching effect leads to changes in both the refractive-index values and the structure of the OH-absorption band.

It is worth testing the refractive-index stability in H:LT waveguides produced with s-cooling. In this case the presence of equilibrium phases only should be supposed. Two waveguides with very different hydrogen contents, assigned to δ- and α-phases, were subjected to annealing at $400\,°C$, followed by s-cooling. The refractive-index dependences on time for these samples are shown in Fig. 5. There is no in-
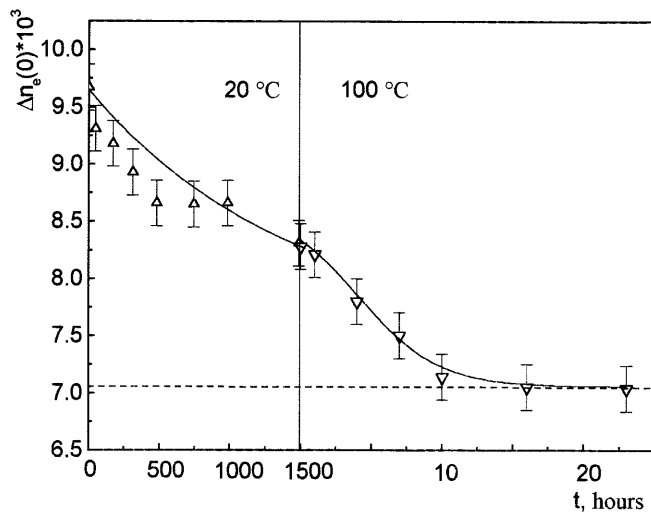

FIGURE 4   OH-absorption spectra of a H:LT layer: a initial α-phase; b after quenching from $T = 300\,°C$; c after annealing at $T = 100\,°C$ for 15 h and s-cooling

FIGURE 5   Surface refractive-index increase vs. time at $T = 65\,°C$ in H:LT waveguides, formed with s-cooling. *Point 'a'* shows the restoration of the initial state

FIGURE 3   Relaxation of the refractive index in an α-phase H:LT waveguide after quenching from $T = 300\,°C$. *Dotted-dashed line* marks the $\Delta n(0)$ level of the equilibrium phase at room temperature
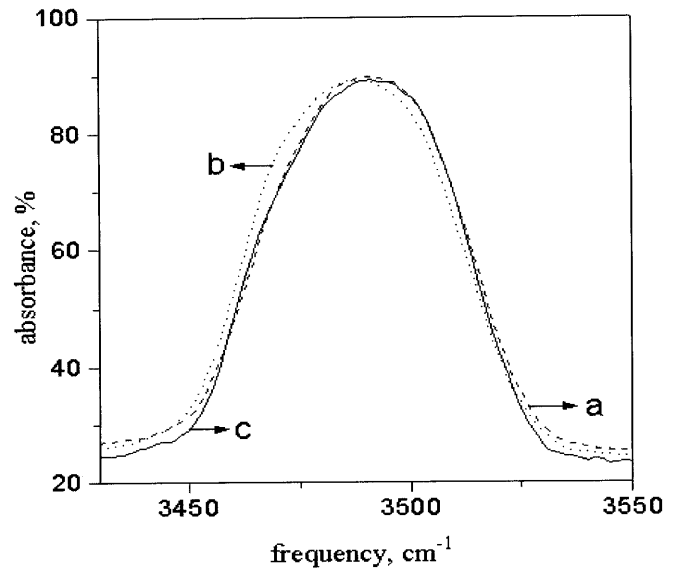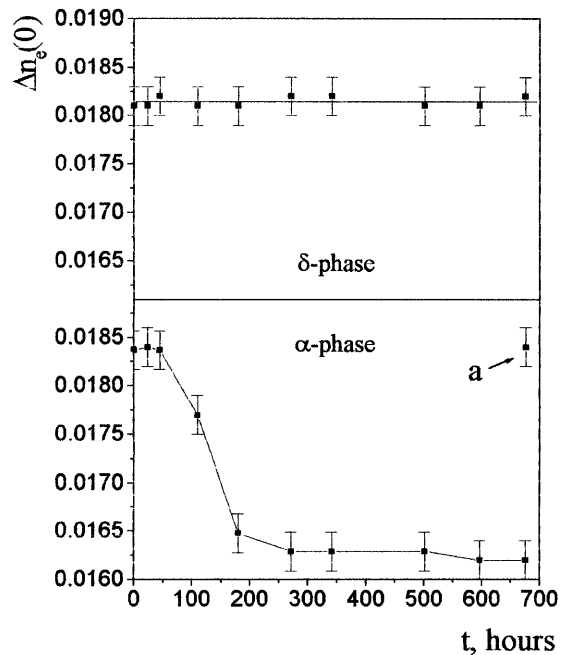
dex variation in the δ-phase layer. On the contrary, a strong index variation was detected in the α-phase layer. It is interesting that in the latter case the period of time can be divided into two intervals of index stability: less than 50 h and more than 200 h. So, this is a curve of different type compared to the one that was observed earlier for the relaxation process of the metastable α-phase (Fig. 3). Further, after next heating to $400\,°C$ and s-cooling, the high level of the refractive index and the profile shape were restored. This guarantees the absence of noticeable hydrogen diffusion during the long-time relaxation. To understand this strange behavior, it is reasonable to point out that the equilibrium value of $\Delta n_e(0)$ of this layer is
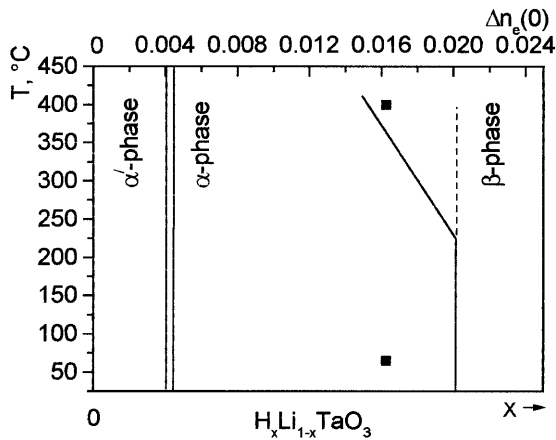
FIGURE 6 Supposed structure of the boundary between α- and β-phases in $H_x Li_{1-x} TaO_3$ layers

near the boundary between the α- and β-phases. So, we suggest the following explanation of the effect. It seems that the topology of the α-β boundary is more complex than a simple vertical line along the temperature axis (Fig. 6). It can be supposed that at this hydrogen concentration and at $T = 400\,°C$ the layer has a β-phase structure. During the s-cooling for 3 h the transition to the α-phase was not fully completed and additional treatment for 200 h at 65 °C was necessary to finish the process. Correspondingly, the refractive-index level, measured after the long-time treatment at $T = 65\,°C$, is the true index level of the equilibrium α-phase. Formation of the $β_1$-phase extending into the lower concentration region after an increase in the exchange temperature was reported recently for H:LN layers [15]. Thus, the complex topology of the interphase boundaries is a new source of possible long-term refractive-index instabilities in H:LT and H:LN waveguides.

3.2 Virgin LT substrates

It is well known that the waveguide-mode confinement is governed by the difference between the refractive indices of the doped layer and the substrate. Typically, the so-called 'pure' LT contains a certain quantity of hydrogen atoms, incorporated into the lattice during the high-temperature crystal growth. The hydrogen presence can be routinely detected by IR spectroscopy [16–18]. Thus, the virgin LT should be classified as a solid solution of hydrogen in lithium tantalate or, in other words, as a low-doped α'-phase of the $H_x Li_{1-x} TaO_3$ compounds. So, it is reasonable to test the dependence of the crystal properties of virgin LT substrates on quenching. The phase diagram of the Li_2O-Ta_2O_5 system is known only roughly [19]. Nevertheless, it should be emphasized that there was no low-temperature transition in the $LiTaO_3$ phase field detected by X-ray analysis. Also, to our best knowledge, there are no reports in the literature on the instabilities of virgin LT crystal properties at nearly room temperatures.

The IR-absorption spectra of two samples of Z- and Y-cut virgin LT were recorded; first, before any heat treatment and then after quenching from $T = 300\,°C$ (Fig. 7). The temperature from which the samples were quenched was estimated (see Fig. 1) to be high enough, completing the supposed tran-

sition into the high-temperature state. It is seen from the figure that for both cuts measured, after quenching the position of the OH band is shifted to lower frequencies by 8 cm^{-1}. To test the reversibility of the variations both samples were annealed at $T = 60\,°C$ for 36 h with slow cooling. After this procedure the spectra exhibit only ~ 1 cm^{-1} and ~ 0 cm^{-1} shifts to higher frequencies of the OH-band maximum position for Z- and Y-cuts respectively. Full restoration of the initial spectra was achieved by three months relaxation at $T = 65 \pm 5$ °C. So, the formation–relaxation process of a high-temperature phase is obvious.

Now it is reasonable to consider the source of the OH-band shift observed earlier due to quenching in the α-phase waveguide layer. Indeed, the band shown in Fig. 4 is a superposition of two components, the first from proton-doped layers on the upper and lower surfaces of the sample and the second from virgin LT bulk. The intensity of the latter component is ~ 25 times lower and the magnitude of the frequency shift of the maximum position due to quenching is nearly ten times higher than those of the integrated signal. In principle, the combination of the relations permits the hypothesis that the shifts shown in Fig. 4 are governed by the substrate-component variations. But in this case the OH-band relaxation characteristics for quenched virgin LT and the sample with α-phase layers should be the same. Contrary to that the available experimental data reveal a noticeably higher stability of the high-temperature state of virgin LT. So, it seems that the shifts
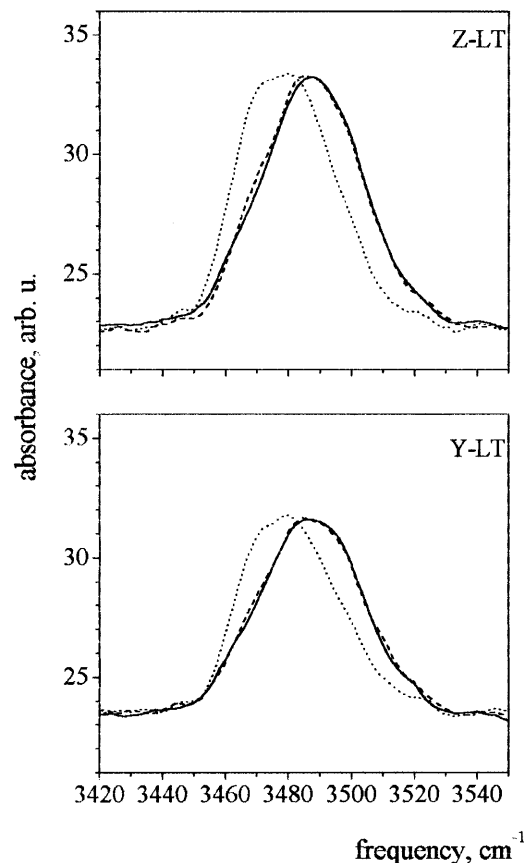

FIGURE 7 OH-absorption spectra of virgin $LiTaO_3$: *solid* – initial state; *dotted* – induced by quenching from $T = 300\,°C$; *dashed* – after 3 months relaxation at $T = 65\,°C$

Sample	Δ, degree before quenching	Δ, degree after quenching	$\delta(n_e - n_o)$
S1	20.6	151.4	0.00013
S2	74.5	248.9	0.00018

TABLE 1   Virgin LT substrate parameters before and after quenching

in the OH-band position demonstrated in Fig. 4 should be related, at least dominantly, to the formation–relaxation cycle of the high-temperature α-phase layers on the sample surfaces.

Our attempts to measure the related variations in the refractive indices by the prism-coupling method were not successful because the indices variations on quenching, if any, are lower than the sensitivity of the technique. That is why, in order to detect the expected small effect, the ellipsometric method was applied. Two X-cut samples of virgin LT (cut from the same bulk crystal) with $d = 1.73$ mm were analyzed. The samples have different prehistories: S1 was initially annealed in air at 800 °C for 9 h and at 1100 °C for 21 h, followed by s-cooling and S2 was not subjected to any heat treatment. Both S1 and S2 were heated to 200 °C and then quenched. Their characteristics, before and after the quenching, are presented in Table 1. The birefringence variation $\delta(n_e - n_o)$ was evaluated from the variation of Δ on quenching, supposing the sample thickness to be constant. One can see that the jump in the birefringence due to quenching is higher for S2. It could be supposed that in S1 the smaller magnitude of $\delta(n_e - n_o)$ is because of the lower hydrogen content reduced slightly by the initial heat treatments. So, the existence of a high-temperature phase was detected even in virgin LT. The birefringence jump, due to such a transition, is relatively small but should be taken into account when precise adjustment of the refractive indices is necessary.

4   Summary

The index variation with time in H:LT layers is related to the process of relaxation of a high-temperature phase, frozen by quick cooling to room temperature. Three possible sources of refractive-index instabilities in hydrogen-doped LT layers have been revealed experimentally: high temperature phase formation; complex structure of the boundary between $H_xLi_{1-x}TaO_3$ phases; and substrate-indices variation on quenching. The former two sources are dominant in magnitude. To avoid these effects either a very slow cooling should be applied after any heat treatment or a special annealing procedure at $T = 100$ °C for ~ 20 h followed by s-cooling (~ 10 h) to room temperature should be carried out.

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