High-temperature phases with increased refractive index in $H_xLi_{1-x}TaO_3$ waveguide layers

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Abstract: *Optical properties and relaxation kinetics of high-temperature $H_xLi_{1-x}TaO_3$ phases have been investigated in proton exchanged waveguide layers. Temperature intervals and refractive index of high-temperature phases have been evaluated for concentration intervals of α', α and δ-phases of $H_xLi_{1-x}TaO_3$ solid solutions. The decay of high-temperature phase in δ-phase $H_xLi_{1-x}TaO_3$ has been traced and life times of metastable states are estimated at T=20°C and 100°C. The nature of metastable states in $H_xLi_{1-x}TaO_3$ and $H_xLi_{1-x}NbO_3$ has been discussed.*

Introduction

Lithium tantalate (LT) is a well-known ferroelectric crystal widely used in integrated optics as a substrate material. One of the basic methods used for optical waveguide formation in LT is a proton exchange reaction. Proton exchanged layers in LT (H:LT) with chemical composition $H_xLi_{1-x}TaO_3$ are the promising waveguide mediums for electrooptical modulators, frequency converters and integrated lasers [1,2] because of apparent simplicity of their fabrication and relatively low temperature of ion exchange reaction, far below the Curie temperature of LT crystal. However, the applicability of H:LT waveguide layers in modern integrated optic devices is limited by noticeable refractive index instabilities [3-7]. Earlier, it has been supposed that the refractive index variation with time at room temperature can be related to relaxation of high temperature phases (HTP) to equilibrium phases at T=20°C [5]. More recently, this supposition has been confirmed for H:LT layers with low x values [8] but H:LT waveguides with high hydrogen concentrations, which are most valuable for present practical applications, were not investigated up to now. In this study the sources of refractive index instabilities in H:LT layers with high hydrogen contents have been revealed. To this aim the variation of refractive index in hydrogen doped layers was measured as a function of quenching temperature. Moreover, the evolution of refractive index due to HTP relaxation was traced for δ-phase of H:LT.

Experimental setup

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 layer to the level that belongs to the composition range of desired equilibrium phase. As a criteria of phase assignment, the surface value of refractive index increase $\Delta n_e(0)$ was used. The intervals of $\Delta n_e(0)$ related to selected equilibrium phase at *T=20°C* were taken from [9]. To search for the HTP formation the quenching technique was applied. With this aim the samples were subjected to

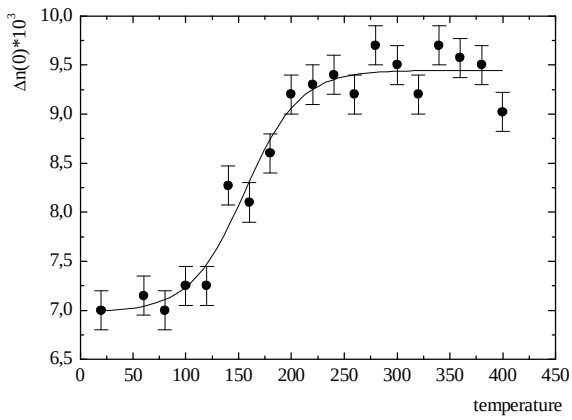

Fig.1: Refractive index on surface of waveguide layer vs. quenching temperature from near room to 400°C.

annealing for 10 min at different temperatures over the range 20°C< T<400°C. After this, two cooling regimes (α-H:LT) were applied: slow cooling for 2-3 hours together with the furnace or quick cooling for 5-7 minutes (quenching) by taking the samples out from the furnace to room. Waveguide mode effective indices N_m were measured by prism coupling method with possible error of ±0.0002 at wavelength λ=0.6328μm. Then, taking a set of N_m values as a basis, the profile of Δn_e over the waveguides depth was reconstructed by the inverse WKB method [10].

Results and discussion

Typical dependence of Δn(0) on quenching temperature is shown in Fig.1. As it is seen, the temperature interval of Δn(0) jump increase (ΔT=125-200°C) can be revealed. Those intervals are related to interphase transitions between the phase equilibrium at room conditions and the high temperature phase. It is principal that after short annealing at any particular temperature in the range up to 400°C and slow cooling the refractive index value returns to the initial value related to the equilibrium phase. This fact confirms the absence of noticeable hydrogen diffusion under the experimental conditions and allows to connect the

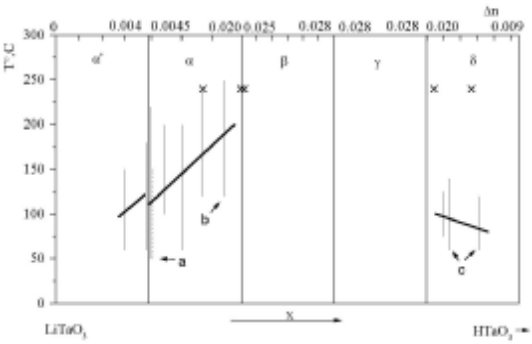

Fig.2: Phase diagram of $LiTaO_3$-$HTaO_3$ system, including HTP properties. Lines a, b, c are drawing using data from [11-13] correspondingly. Sign × mark Δn value where HTP formation were observed in [14], but no additional date was traced.

observed variations of Δn(0) with HTP formation. Thereby, the formation of HTP in H:LT compound is evident in Fig.1.

The quenching curves similar to that shown in Fig.1 were measured for a number of samples with different hydrogen content. The results were used as a basis for reconstruction of $LiTaO_3$-$HTaO_3$ phase diagram for the layers. The diagram accounting the HTP existence is presented in Fig.2. Here vertical segments show the temperature intervals of interphase transition between equilibrium and HTP and the hard dark lines, connecting the middles of vertical segments, depict the appropriate interphase boundaries. The existence of HTP was detected for a wide range of hydrogen concentration in H:LT system. Regrettably, the intervals of β- and γ-phases of $H_xLi_{1-x}TaO_3$ solutions were not investigated in this study because the Δn(0) value is not vary on x variation for the equilibrium phases and precise identification of equilibrium H:LT phase is not possible by waveguide mode spectroscopy. Observed HTP are metastable at room temperature and refractive indices variation for the states is induced by continuous transition to the relating equilibrium phase. When the temperature rises from T=20°C, the typical temperature of the interphase transition beginning is ~ 50-100°C. This is typical working temperature range for high frequency electrooptical modulators [15]. So, the HTP formation is possible by technological heat treatments during integrated device fabrication or due to device working temperature fluctuations and involves long time drift of optical characteristic.

To determine the life-time of HTP phases in H:LT the sample with Δn(0)=0.018, corresponding to concentration interval of δ-H:LT was subjected to quenching at 400°C, 10 min. The refractive index of HTP formed by this way was equal 0.029 and slowly decreases with time under room condition (Fig.3).

As one can see, the additional refractive index, induced by HTP formation on quenching, decreases by a half for ~26000 hours (~3 years). The function governing the evolution of refractive index can be

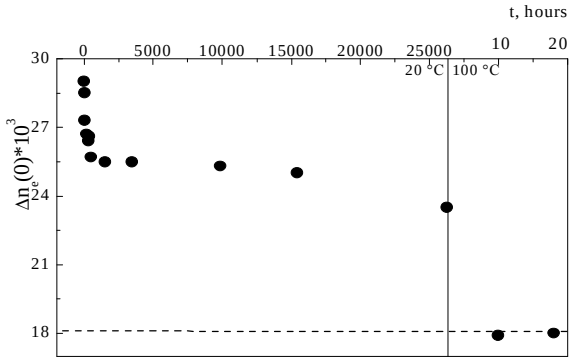

Fig.3: Refractive index evolution due HTP relaxation in concentration interval of δ-H:LT.

written as $\Delta n_e = \Delta n_e(0)\cdot(e^{\frac{-0.693\cdot t}{\tau_1}} + e^{\frac{-0.693\cdot t}{\tau_2}})$ with two significantly different components, characterized by τ_1~100 hours, τ_2~70000 hours. Under the temperature ~100°C the process of HTP decay is faster and phase transition to an equilibrium state finishes during 20 hours.

In our resent investigations [16], we observed that the HTP decay in α-H:LT is a single process, and half-life period is ~1500 hours. Above this, the interphase transition in H:LN system is more quick, and totally finishs after ~250 hours at room conditions.

Taking into account the shape of functions of refractive index evolution the nature of high-temperature states in $H_xLi_{1-x}MO_3$ (M=Nb, Ta) can be suggested. The high-temperature phase formation could be related to the existence of several proton positions in crystal lattice. For $H_xLi_{1-x}NbO_3$ system in [17] the total energy of crystal was calculated as a function of the displacement of proton It was estimated, that the total energy structure of the hydrogen displacement along the O-O line has a double well energy structure. The one site is more stable by 0.27 eV then second site and these sites are separate by 0.9 Å in space. It may be supposed that the variations of refractive index during the high-temperature phase formation can be induced by partial displacement of hydrogens from stable site with low energy to metastable site with higher energy. Then, on the high-temperature phase relaxing, the protons returns back from metastable site to stable one. This is a single process, that's why the refractive index decreasing during the hightemperature phase relaxation in $H_xLi_{1-x}NbO_3$ is described by one exponent. Perhaps, in $H_xLi_{1-x}TaO_3$ the lattice energy dependence on the hydrogen displacement along the O-O bond line have a triple well energy structure, and the hydrogens redistribute between three nonequal sites when the high-temperature state formation takes place. In this case, on high-temperature phase relaxation, protons rmove to stable site from two metastable sites simultaneously but with different probability. It explains why the double exponent function of refractive index variation with time during high-temperature phase relaxation is observed. In this

function one exponent describes proton replacement from one metastable site to stable site, and second exponent - from another site.

However, this simple model is not able to describe existence more then one high-temperature phase, which is not in agreement with experimental data. Moreover, in [18] authors obtain the six nonequivalent positions of protons in $LiNbO_3$ crystal lattice. The six positions could explain formation of four high-temperature states, described in [16], and suggest undetected fifth phase.

Four mechanisms of refractive index variation are known. The absence of chemical composition under high-temperature phase formation-decay processes was shown in [8] and we can neglect by molar refraction changes. The spontaneous polarization change also unclear. It was shown using X-ray diffractometry [18] that one crystal cell parameter (c) changes under phase transition. Therefore, only the molar volume variation and elastooptic effect can be considered as causes for refractive index variation. Using experimental data from [18] ($\Delta n_e(0)^{room}$=0.1088, $\Delta n_e(0)^{hightemperature}$=0.1164 => $\delta\Delta n_e(0)$=0.0076, $\delta\Delta c$=0,26%), and using expression $\delta\Delta n_e^V = \frac{\delta\Delta c}{6\cdot n_e}\cdot(n_e^2+2)\cdot(n_e^2-1)$ we get $\delta\Delta n_e(0)$=0.0060, which is in good enough agreement (23%) with experimental value.

Conclusions

The existence of high-temperature, metastable at room conditions phases in $H_xLi_{1-x}TaO_3$ waveguide layers was observed over wide range of hydrogen content. The refractive index jumps and temperature intervals of phase transitions between equilibrium and high-temperature states were traced. It was shown, that the relaxation of HTP in concentration interval of δ-H:LT occurs for a long time period. The nature of HTP in $H_xLi_{1-x}TaO_3$ and $H_xLi_{1-x}NbO_3$ is discussed.

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