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Influence of gas phase composition on the defects formation in lithium niobate

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Lithium niobate, $LiNbO_3$ (LN), is widely used as a material for electro-optical devices. The process of formation of wave-guides in LN is usually performed by the high-temperature diffusion of some element, usually Ti, previously patterned by conventional photolithography techniques on LN substrate. As a result of the process, shallow surface patterns of higher refraction index (wave-guides) are formed on the LN single crystal. The characteristics of the obtained wave-guides, including optical stability and power losses, depend mainly on the sizes of the diffusion zones, their contour and concentration profiles of the components in the zones.

The composition of the gas phase has an appreciable influence on the diffusion process. This is related to the influence of the gas environment on the balance of defects in the sub-surface zone of LN and, hence, on its kinetic characteristics. Thus, the elucidation of the mechanism of interaction of the crystal surface layer with gas phases of various compositions at high txemperatures is of considerable interest for the development of optimal technologies of electro-optical devices.

At the same time, no data are available in the literature relevant to the equilibrium of LN with gas phases of various compositions at the temperatures usually used in the diffusion process. In this paper we present some results that may be useful for the understanding of the parameters involved.

A computer modeling of the equilibrium in LN-gas phase systems was carried out with calculations for the following gas phases: (a) inert gas (Ar) or vacuum with LN, (b) oxygen, and (c) a mixture of oxygen with water vapor. The modeling of equilibrium was carried out using the "Astra-4" code [1]. The code algorithm is based on the maximization of the system entropy by the iteration method. Thermo-chemical data for $LiNbO_3$ were taken from the literature [2–4]. No data were found for the thermo-chemical characteristics of $LiNb_3O_8$. This phase is conjugated with $LiNbO_3$ in quasi-binary Li_2O-Nb_2O_5 system. Besides, we have not found in the literature the thermo-chemical characteristics of $LiNbO_3$ within its homogeneity range. Obviously, the published data [2] concern LN stoichiometric composition.

Thus, two possibilities arise:

1. There is a minimum on a curve pressure—composition within a homogeneity range of LN. Naturally, this composition should evaporate congruently. So, the calculations of the equilibrium taking into account only data concerning the stoichiometric LN corresponds to the reaction of dissociation (1):

$$LiNbO_{3s} \rightarrow 1/2Li_2O_g + 1/2Nb_2O_{5s}, \qquad (1)$$

However, two important experimental facts exclude presence of such minimum. First, primary evaporation of Li on heating LN [5], and, second, is formation of the second phase—lower lithium niobate-$LiNb_3O_8$ during such heating (see, e.g., [6, 7]).

2. Therefore to date it is generally accepted the model of primary evaporation of lithium. Hence, the assumption of composition displacement from stoichiometric LN up to two-phases (LN-$LiNb_3O_8$) equilibria is more plausible. Hence, a thermal dissociation of LN can be described by the following reaction (2):

$$LiNbO_{3S} \rightarrow Li_2O_g + LiNb_3O_{8S}, \qquad (2)$$

where $LiNb_3O_8$ is the lower lithium niobate ($1/2Li_2O_3/2Nb_2O_5$) on the upper (with respect to Li_2O) border of its homogeneity range at a given temperature, and $LiNbO_{3s}$ on the lower (with respect to Li_2O) border of its homogeneity range. Obviously, the pressure values obtained by calculation according reaction (1) should exceed equilibrium ones.

Due to these circumstances, the results of our calculations are somewhat approximate. Nevertheless, a comparison of the results of such calculations enables us to find the quantitative differences in mechanisms of LN behavior in various gaseous environments and to shed light on some earlier experimental results.

The basic component of the gas phase in equilibrium with LN is atomic lithium (Fig. 1). Partial pressure of Li slightly changes with temperature and surpasses partial pressures of lithium oxide, Li_2O, by 5–6 orders in the range of 1000–1600 K. These results are in satisfactory qualitative agreement with experimental data obtained by mass-spectrometric technique [8].

The partial pressures of Li-containing gas components in the equilibrium with LN are reduced sharply (approximately by 5 orders) at the introduction of oxygen into the system (Fig. 2). The main component of gaseous phase in this case is LiO. Having in mind an extremely low pressure of LiO at temperatures used during the diffusion process, incongruent evaporation of lithium may be neglected.

It is apparent from the data shown in Fig. 3 that the addition of water to oxygen results in a considerable increase the pressures of Li-containing components. The

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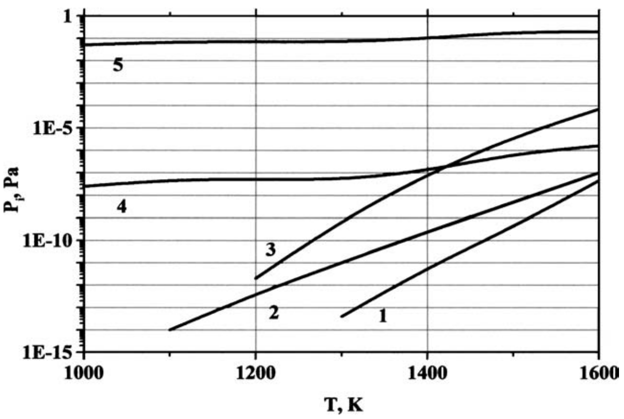

Figure 1 Equilibrium partial pressures in $LiNbO_3$-Ar system: 1-O, 2-LiO, 3-NbO_2, 4-Li_2O, 5-Li.

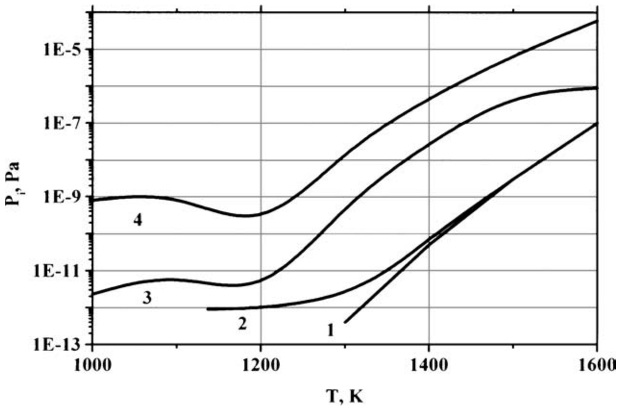

Figure 2 Equilibrium partial pressures in $LiNbO_3$-O_2 system: 1-NbO_2, 2-Li_2O, 3-Li, 4-LiO.

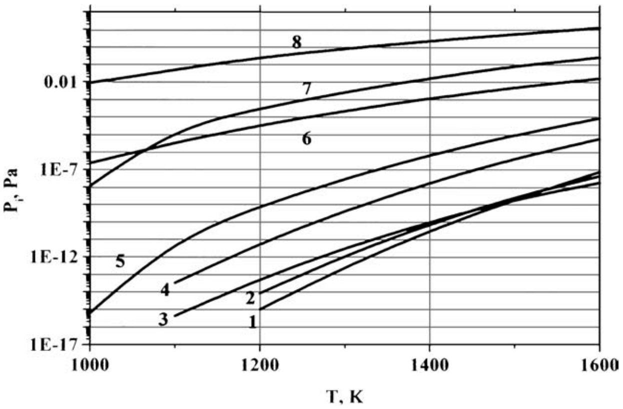

Figure 3 Equilibrium partial pressures in $LiNbO_3$-O_2-H_2O system: 1-NbO_2, 2-Li_2O, 3-Li_2O_2, 4-Li, 5-LiO, 6-LiOH, 7-H_2, 8-OH; $P_{O_2} = 0.98 \times 10^5$ Pa, $P_{H_2O} = 2 \times 10^3$ Pa.

basic Li-containing component is LiOH, whereas a prevailing component of gas phase is a neutral OH group. Calculations also show that as the partial pressure of water is increased, the equilibrium LiOH pressure increases, as well. So, it might seem that water vapor introduction should result in an opposite effect, namely, in an intensification of the process of Li evaporation.

On the other hand, O_2-H_2O mixture has been experimentally found [9–12] to be a favorable gas environment for the realization of the Ti in-diffusion process. Traditional interpretation of this effect is a decrease in the rate of incongruent evaporation of lithium under the influence of water vapor [11]. Furthermore, on the basis of their experimental data, the authors [11] came to the conclusion that the increase in humidity, Li evaporation rate decreases. Besides, an acceleration of Ti in-diffusion in LN under the influence of water vapor had been established in [12]. It is obvious that results of calculation of equilibrium in the system Li-O_2-H_2 contradict the given conclusions. Therefore experimental data demand other interpretation. We believe that this seeming contradiction is caused by the neglect of the role of hydrogen in the process.

It is known that LN obtained by Czochralski method contains appreciable concentration of hydrogen in the form of OH groups. The typical H contents in LN is $\sim 1.5 \times 10^{20}$ cm^{-3} (∼0.5–0.7% at.) [13]. The source of hydrogen is the moisture present in the chamber during the growth process. This circumstance is a key for the understanding of the processes occurring on the crystal surface at its subsequent heat treatment in dry oxygen. In fact, the conditions for the formation of molecules LiOH having a high vapor pressure (see Fig. 3) are created in O_2 environment. The consequences of the said process are:

1. removal of Li from the surface and occurrence of a flow of lithium and hydrogen ions from the matrix to the surface;
2. inclusions of the second phase, $LiNb_3O_8$, formation in the sub-surfaces Li-depleted zone, obviously, these effects result in surface degradation and the formation of a superficial zone with an increased refraction index in comparison with the initial crystal (so called surface wave-guide formation).

Introduction of H_2O in a gaseous phase, for unclear reasons, partially mollifies the situation. The probable reason is the presence in the gas phase of H_2 and OH group (the products of water dissociation), which create a barrier for the transition of H_2 and LiOH from the crystal into the gas and, hence, hinder their migration from the bulk of crystal to the surface. Besides, presence water vapor causes change structure of defects in LN. Oxygen loss of LN at high temperatures, e.g., as LiOH in the O_2-H_2O environment, causes, in particular, formation of oxygen vacancies and their directional flow (and also flow of oxygen ions) in the course of the diffusion process. The presence of appreciate oxygen conductivity in LN [14, 15] testifies to the important role of oxygen vacancies and/or F-centers in the mass transfer process.

Thus, the mechanism of water vapor influence on LN containing hydrogen is still far from being understood as yet and demands additional studies. In particular, a phenomenon of nonmonotonic interconnection between pressure of a water vapor and the second phase formation on a surface Ti-LN diffusion zone [7] demands adequate explanation.

Despite some inhibition of the undesirable processes described above, the introduction of moisture into a gas phase cannot prevent them completely. Thus, it is necessary to admit that the mixture O_2-$2H_2O$ as a standard gas environment for high-temperature treatment of $LiNbO_3$ is rather far from an ideal one.

The obvious solution of the problem is to remove hydrogen from as-grown crystals. This idea was elegantly realized [10] by annealing the crystals in dry oxygen (dew point below −70 °C) at high temperatures with the subsequent mechanical removal of the sub-surface "bad" multiphase Li-depleted layer (∼50 microns). Naturally, optimal environment for heat treatment of the crystals obtained after said treatment is dry oxygen.

As follows from the data given in Fig. 2, partial pressures of all Li-containing species components are insignificant, and the evaporation of Li can be neglected in this case.

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