Methods of control of the initial compositions of melts in internal and external crucibles in Czochralski method have been offered in this work. With their help non-activated and concentration-profiled by some impurities crystals of stoichiometric LiNbO$_3$ (SLN) have been grown by Czochralski method using additional liquid charging.

**Abstract**

Methods of control of the initial compositions of melts in internal and external crucibles in Czochralski method have been offered in this work. With their help non-activated and concentration-profiled by some impurities crystals of stoichiometric LiNbO$_3$ (SLN) have been grown by Czochralski method using additional liquid charging.

**Keywords:** Stoichiometric lithium niobate, optical measurement, temperature measurement, PPLN

1. **Introduction**

For successful development of network of IT communication system and information handling, development and production of new high-performance components of optoelectronics such as periodically polarized micro- and nano-sized domain structures (PPLN) in nonlinear single crystals are required.

Creation and usage of PPLN structures as the components of optoelectronic, laser and telecommunication systems of the new generation is a very perspective area. New optoelectronic systems are so efficient that, for instance, powerful persistent fiber lasers, periodically supplied by polarized domain structure based on SLN single crystals (PPLN), are predicted to be able to exclude completely on the world market avowed and efficient ion lasers of the visible range and solid-state persistent Nd-lasers with traditional increase of the frequency of generation. In this connection, significant efforts to develop and create PPLN-structures are made in the world. The main problems of the development and creation of PPLN are defects of existent nonlinear single crystals, from which they can be made of, and also insufficient methodical level of the study of stability of obtained regular domain walls, and connected with this problem of homogeneity of SLN single crystals for PPLN. Thus, during the process of creation of periodically polarized systems, it's necessary to provide: 1) High optical quality (homogeneity) of the source for PPLN SLN single crystals, 2) low coercive field, applied for reorientation of domains, and 3) high optical stability against laser radiation. Nowadays in Russia and in the technological world, the reception of PPLN structures is targeted on creation of based on them congruous LN with Mg impurity. This method of approach to decision of the problem provides high beam stability against laser radiation PPLN; however the problem of low coercive field, required for increase of the aperture PPLN converters, remains undecided. The majority of the proposed today methods of stoichiometric LN growth is directed to maintenance of the constant composition on the front of the crystallization with conservation of the main advantage of Czochralski method which is extending of single crystal upwards with free surface melt [2, 3].

We offer a brand new method of single crystals growth by Czochralski method using additional liquid charging [4]. In this method the maintenance of the composition on front of the crystallization is provided by division of the melt into two parts: the main composition with concentration of impurity $n_1$ and nourishment composition (with due regard for coefficient of the impurity entry) with concentration of impurity $n_0$. Technically, division of
the compositions was carried out by system of communicating crucibles that were put one in another. Under some conditions of the absence of diffusion between these communicating containers, in measure of extending of a single crystal, concentration of impurity will be changing according to the given by the law of motion of the internal crucible, coefficient of the entry of activators in a single crystal, geometry of the crucible and concentrations of activators in internal and external crucibles. In this work there was offered a new operative method of the control of the melt composition by the means of a direct measurement of the temperature on the front of the crystallization, and there are considered ways of the reception of concentration-profiled single crystals of SLN by means of this method. This work is the first stage in the research and creation of PPLN structures based on SLN single crystals with concentrate profile of different impurities.

2. Experimental procedure

The subject matter of obtainment of SLN single crystals is creation of exact initial composition of the main oxides in a system of crucibles at the beginning of growing. To solve this problem, there was offered the control of the composition melt by measurements of the temperature of crystallization of the test crystal and its comparison with the temperature of the crystallization on the diagram of the condition. Practically the problem was being solved by the following stages: 1) in the main crucible furnace charge was fused with molar correlation of the main oxides Li$_2$O:Nb$_2$O$_5$ 1:1; 2) in the melt of the main crucible the internal crucible was sunk with the given depth (according to the diagram of the condition of the system Li$_2$O:Nb$_2$O$_5$ [5], for growth of SLN crystal from the internal crucible, the composition in it must be with molar correlation of the main oxides 1.38:1); 3) furnace charge enriched with lithium, was being put in the melt in the internal crucible until required correlations were reached between the main oxides. Control of the composition melt in internal and external crucibles was carried out the direct measurement of the temperature on the front of the crystallization of the test single crystal with a diameter 3-5 mm. For this, the thermocouple of the S-type (Pt100% – Pt90%, Rh10%) was fastened on the upper rod together with a chip carrier. The hot junction of the thermocouple was bent in a shape of "П" and was outlined from below on the distance of 3 mm to a seed crystal. After that, submersion of the seed was produced, seeding and growing of a crystal to the diameter 3-5 mm. Signals from the thermocouple and from sensor of the weight, on which chip carrier is fastened together with the crystal, were digitized and displayed on a computer. On the next step, with the constant level of the power, extending of the single crystal was produced. The reading of the thermocouple was corrected on the temperature of the cool ends of the thermocouple. The moment when thermocouple was ice-bound into the growing single crystal, was characterized

![Fig. 1. The dependence of the weight of SLN crystal and the temperature in the field of crystallization.](image-url)
by the sharp jump on the curve of weight Fig. 1. The reading of the thermocouple at that moment is matched to the composition of the crystal according to phase diagram of the system Li$_2$O-Nb$_2$O$_5$ [5]. If experimentally determined composition does not match with theoretically laid one, then correction of the composition with pouring carbonate lithium in reactor is produced. After creation of the required compositions in external and internal crucibles, there was included a shift of the internal crucible under computer control with such velocity that mass velocity of SLN-crystal extending was equal the mass velocity of the arrival in the internal crucible of the melt from external crucible with a composition of Li$_2$O:Nb$_2$O$_5$ 1 mole: 1 mole. Obtained this way non-activated single crystal SLN with diameter 2 inches for making PPLN structures is on Fig. 2.

![Fig. 2. The morphology of as-grown SLN crystal.](image)

![Fig. 3. The dependence of the concentration Mg$^{2+}$ in SLN:Yb,Mg single crystal.](image)

The need for such crystals is conditioned by possibility of the creation of high-performance laser medium with longitudinal diode pumping, and also discrete photoinduced structures based on these crystals. During the process of creating the concentrate profiles, the impurity (one or several) was added in the given correlations either in internal crucible only, or only in external crucible (Mg on Fig. 3). To make a homogeneous alloying along the length of an ingot impurity was added both in internal and in external crucible with due regard for its coefficient of the entry in crystal.

### 3. Discussion

To estimate homogeneity by composition of single crystals grown along an ingot, indirect methods of the estimation were used. In this work there was used a method of study of the IR-type spectrum of the absorption OH-groups in SLN single crystals [6], and research spectrum of the combinational dispersion (CD) spectrum and positions of UV edges of the band of the fundamental absorption. With homogeneous composition of the ingot (both by the main oxides, and by impurity ions such as Mg$^{2+}$) the view of IR-spectrum and correlation of intensity and half-width of lines must remain constant along the ingot, as it was observed in the experiment. It means that correspondence between the initial correlations of the main oxides with a process of stoichiometric LN single crystal growth with a diagram of the condition. To estimate accuracy of the offered method there were created concentrate profiles of photorefractive impurities of Mg along the ingot with constant concentration of laser ions and constant correlation of the main oxides along the ingot. This way there were grown single crystals of SLN with constant concentration of Cr$^{3+}$ and concentrate profile of Mg$^{2+}$, as well
as single crystals of SLN with constant concentration of Yb$^{3+}$ and profile of the change of concentrations of Mg$^{2+}$. With some certain threshold concentration of magnesium in SLN (depending on a correlation of the main oxides in a crystal) qualitative shift of many characteristics of the crystal occurs, including the IR-type of spectrum of the absorption OH-groups and CD spectrum (Fig. 4, 5). Appearance of the band in IR-spectrum with maximum at 3521 cm$^{-1}$ indicates entry of magnesium into crystallographic position of Nb. Shifts also exists in IR-spectrum, in which the additional band in the field of 120 cm$^{-1}$ appears. Estimation of homogeneity of the distribution of impurities along the ingot was carried out by other indirect signs such as position of the edge of UV-bands of the absorption, half-width of lines in spectrum of the combinational light dispersion, and also by the size of half-wave voltage. Indirect studies of the composition of a growth crystal SLN:Yb$^{3+}$,Mg$^{2+}$ confirm that correlation between the main oxides is very close to unity, but concentrate profiles of Mg and Yb along the ingot correspond to theoretically given ones.

4. Conclusion
Offered in this work methods of temperature control of the crystal composition for the method of growth of incongruous crystals of SLN has allowed to create the exact initial compositions in internal and external crucibles by the main oxides. System of crystal growth based on a signal of the sensor of the crystal weight and set shift of the crystal weight in time, supported the given mass increase of the crystal

Fig. 4. IR spectra of the SLN:Yb,Mg crystal.

Fig. 5. The fragment of CD spectra of the SLN:Yb,Mg crystal.
and realized exactly the same velocity of the entering of nourishment melt of the composition into internal crucible. Thus there was reached constancy of concentrations of the main oxides in the internal crucible and there was provided constancy of the crystal composition along the length of the ingot.

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References