Morphology of oxide single crystals grown by Czochralski technique at low axial gradients

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Technological factors causing non-cylindrical morphology of $LiNbO_3$, $PbWO_4$ and $Li_6Gd(BO_3)_3$ single crystals grown by Czochralski technique have been considered.

Проанализированы технологические факторы, приводящие к нецилидрической морфологии монокристаллов $LiNbO_3$, $PbWO_4$ и $Li_6Gd(BO_3)_3$ при выращивании методом Чохральского.

The Czochralski technique is of the widely used methods for industrial production of various crystals (garnets, niobates, tungstates, borates, etc.). A modern requirement to the crystal growing technology is to provide large diameter crystals that made it possible to produce a larger number of elements from one single crystal ingot. When growing the large diameter crystals, the axial and radial gradients should be lowered to reduce the thermoelastic stresses and avoid cracking. In practice, the use of low axial gradients causes difficulties in attaining of the preset crystal diameter. For example, the authors observed faceted growth of $LiNbO_3$ (LNO) crystals and helical growth of $PbWO_4$ (PWO) and $Li_6Gd(BO_3)_3$ (LGBO) ones. The helical crystals were highly stressed and cracked under mechanical treatment, thus making it impossible to manufacture the elements. The helical growth of LGBO crystals was observed also in [1]. The spiral-shaped garnet crystals [2] and other ones, e.g., [3], have been reported. To date, it is unclear what technological factors cause such a crystal morphology. Thus, the aim of this work is to establish the correlation between the morphology of LNO, PWO, and LGBO oxide crystals (differing in structure types), the crucible geometry, and the growing thermal conditions.

The PWO and LGBO crystals were grown from stoichiometric charge while the LNO ones, from a charge with $Li_2O/(Li_2O + Nb_2O_5)$ ratio of 0.486. An automated unit ("Analog" type) was used to grow the PWO crystals and vertical resistance furnaces for LNO and LGBO ones. The PWO crystals were grown in an inert atmosphere from platinum crucibles of 100 mm diameter, while LNO and LGBO ones, in air from 90 and 60 mm diameter crucibles, respectively. The pulling and rotation speeds were 3–7 mm/h and 30–60 rpm for LNO; 4–10 mm/h and 25–40 rpm for PWO and 0.7–1 mm/h and 4–20 rpm, respectively. The gradients in the growth zone were varied within wide ranges using platinum heat shields as well as varying the dimensions and shapes of Al_2O_3 or ZrO_2 thermal insulation. The LNO crystals were grown along the <111> direction, PWO along <001>, and LGBO along <122> ones.

The crystals of the preset diameter and with strictly cylindrical surface shape have been obtained at the d_{cryst}/D_{cruc} ratio less than or equal to 0.45 for all the LNO, PWO, and LGBO crystals and the axial gradients $\partial T/\partial z$ of about 15, 25, and 15 K/cm, respec-

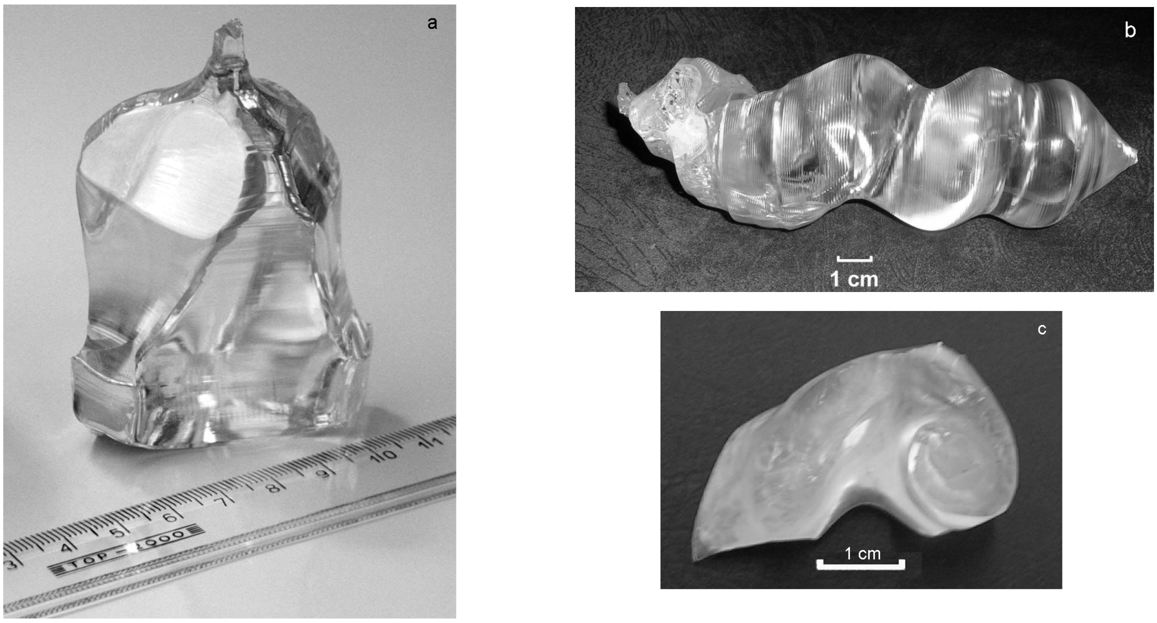

Fig. 1. Crystals grown at low gradients: LNO (a), PWO (b), LGBO (c).

tively. The crystals have characteristics similar to those described before [4-6]. When the inequality $0.45 < d_{cryst}/D_{cruc} < 0.65$ is valid, the crystal takes cylindrical shape at the initial growth stages but later, the growing crystal is always deformed. At the mentioned d_{cryst}/D_{cruc} ratio and the corresponding gradients, the faceted growth is realized for LNO (Fig.1a) and helical for PWO (Fig.1b) and LGBO (Fig.1c).

The crystal growth speed along the corresponding direction is in proportion with therma[flow along that direction $V_z \sim \lambda_z \partial T/\partial z$ [7] where λ is the thermal conductivity coefficient and $\partial T/\partial z$, the temperature gradient. If the crystal is anisotropic, the thermal conductivity coefficient is a 2nd order tensor. However, taking into account that PWO crystals are tetragonal (space group $I4_1/a$) and LGBO crystals are monoclinic (space group $P2_1/c$), it can be transformed to the following form: $\begin{matrix} \lambda_{11} & \lambda_{12} & 0 \\ -\lambda_{21} & \lambda_{22} & 0 \\ 0 & 0 & \lambda_{33} \end{matrix}$ for PWO and $\begin{matrix} \lambda_{11} & \lambda_{12} & 0 \\ \lambda_{21} & \lambda_{22} & 0 \\ 0 & 0 & \lambda_{33} \end{matrix}$ for LGBO [7]. In the case of LNO crystal, the situation is complicated by a series of phase transitions resulting in the crystal lattice rebuilding and, as a consequence, in significant changes of the crystal properties [8]. The thermal conductivity tensor components may differ considerably from each other. For example, the growth speed of InSb crystal along various directions are different by several orders [9]. Moreover, the thermal conductivity coefficient is influenced considerably by impurities (both intentional and unintentional) and by the structure of growing crystal (extrinsic phase inclusions, dislocations, blocks, etc.) [10].

As mentioned above, the axial and radial gradients should be reduced when growing a crystal of relatively large diameter. In particular, a relationship for the maximum axial gradient for a preset crystal diameter is given in [11]. For example, to grow an LNO crystal of 12 mm in diameter, the maximum axial gradient should not exceed 100 K/cm and for a 20 mm diameter one, 50 K/cm. The growing of LNO, PWO, and LGBO crystals of 50, 50, and 30 mm in diameter, respectively, forced us to provide low axial gradients (15–25 K/cm), thus comparable with the radial gradients. Moreover, the heat removal along the growth axis may become reduced considerably as the crystal volume increases due to the crystal absorption in IR region. The set of factors defining the thermal conditions of the growth and the crystal anisotropy results in the fact that the direction of maximum heat removal may not coincide with the growing direction. In the case of LNO crystal, those conditions have caused the face output onto the surface. In PWO and LGBO, the same conditions resulted in strong stresses, dislocations, and blocks. The mechanical damage of a growing crystal (that is, dislocations) provoke directly the helical growth, the mechanism thereof being described within the frame of Burton-Cabrera-Frank theory [12].

Thus, it has been shown that the morphology of LNO, PWO, and LGBO crystals (belonging to different structure types) grown by Czochralski technique under low axial gradients, is non-cylindrical. The factors causing the non-cylindrical morphology have been discussed.

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Морфологія оксидних монокристалів, вирощених за методом Чохральського при малих аксіальних градієнтах

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Проаналізовано технологічні фактори, що призводять до нециліндричної морфології монокристалів $LiNbO_3$, $PbWO_4$ і $Li_6Gd(BO_3)_3$ при вирощуванні за методом Чохральського.