


Optical properties and structure particularities of LiNbO₃ crystals grown from a boron-doped melt

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ABSTRACT

A series of LiNbO₃:B crystals was grown from the melt doped by boron. It is shown that LiNbO₃:B crystals possess an increased resistance to optical damage. We have found changes according to Raman spectra confirming the ordering of Li⁺, Nb⁵⁺ cations and vacancies along the polar axis. The chemical interactions were studied in the system Li₂O–B₂O₃–Nb₂O₅. Boron cations are unable to incorporate into a cation sublattice of LiNbO₃, but they change the physic-chemical structure of a melt. It contributes to an increased structure and optical uniformity of LiNbO₃:B.

ARTICLE HISTORY

Received 2 October 2018

Accepted 8 February 2019

KEYWORDS

Lithium niobate single crystal; photorefractive effect; Raman spectroscopy; pattern of photoinduced light scattering; boron doping

1. Introduction

Lithium niobate in the single crystal form finds wide application in devices of electronic engineering and nonlinear optics. LiNbO₃ possesses photorefractive effect, which can be regulated in a wide range by doping of crystals by non-photorefractive cations of metals (Mg, Zn, Gd etc). Doping by metallic elements in high concentrations, which can incorporate into crystal structure, leads to an increase of an optical and a structural non-uniformity of a grown crystals [1]. Nonmetal cations, in contrast to metal cations, have both other type of the chemical bond and a different influence on physic-chemical characteristics of the system crystal-melt.

In this paper, we used Raman spectra to study crystals LiNbO₃:B (0.55 ÷ 1.24 mol % in the reaction mixture) in dependence of the boron concentration. Chemical interactions were studied in a system Li₂O–B₂O₃–Nb₂O₅. An optical and structure uniformity of crystals were researched by a photoinduced light scattering (PILS) and a laser conoscopy.

2. Experiment setup

All crystals were grown on air by the Czochralski on an installation “Crystal-2”. The doping was carried out both by a homogeneous doping of the precursor Nb₂O₅ [2] and a direct solid phase doping [3]. Raman spectra were excited by the band 514.5 nm of an argon laser Spectra Physics (model 2018-RM) and were registered by a spectrograph

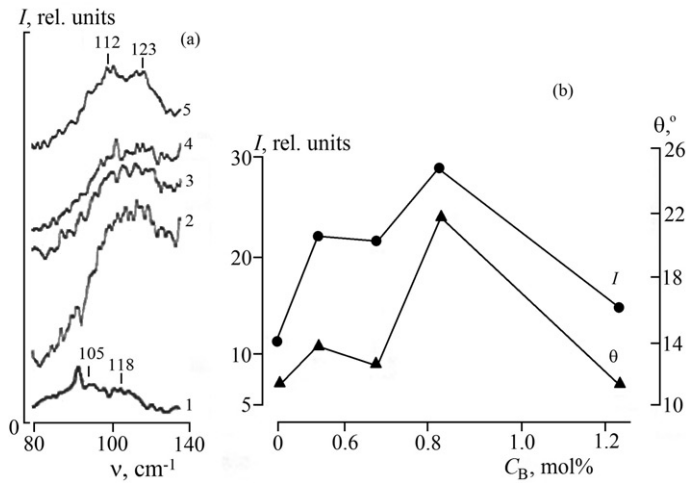


Figure 1. A fragment of a low-frequency Raman spectrum of crystals $\text{LiNbO}_{3\text{cong}}$ (1), $\text{LiNbO}_3\text{:B}$ [0.55 (2), 0.69 (3), 0.83 (4), 1.24 (5) mol % B_2O_3 in the reaction mixture] in the scattering geometry $Y(ZZ)\bar{Y}$ ($A_1(\text{TO})$) (a); concentration dependencies of intensities (I) of band with frequency 630 cm^{-1} in Raman spectra in the scattering geometry $Y(ZX)\bar{Y}$ and PILS opening angle θ of crystals $\text{LiNbO}_{3\text{cong}}$, $\text{LiNbO}_3\text{:B}$ (0.55 ÷ 1.24 mol. % B_2O_3 in the reaction mixture) (b).

T64000 by Horiba Jobin Yvon using of a confocal microscope. The investigation methods of PILS and a laser conoscopy are described in detail in [4].

3. Results and discussion

Figure 1 demonstrates a fragment of Raman spectra of lithium niobate crystals in the scattering geometry $Y(ZZ)\bar{Y}$. The 120 cm^{-1} band corresponding to a two-particle state of acoustic phonons with a zero total wave vector is absent in the Raman spectra of $\text{LiNbO}_{3\text{stoich}}$. An increase in the intensity of this band indicates an increase in the amount of Nb_{Li} structural defects. At the same time, split of the band into two components indicates high structural perfection of the crystals. From Figure 1 it can be seen that the 120 cm^{-1} band is divided into two components 112 and 123 cm^{-1} in the Raman spectra of $\text{LiNbO}_3\text{:B}$ (1.24 mol % B_2O_3 in the reaction mixture), in which Nb_{Li} defects present, and $\text{LiNbO}_{3\text{cong}}$ crystals.

A 630 cm^{-1} band is forbidden in the Raman spectrum by the selection rules in the $Y(ZX)\bar{Y}$ scattering geometry. This band corresponds to the vibration of oxygen octahedra of an $A_1(\text{TO})$ symmetry type. This band is usually used as an analytical one in order to determine a photorefractive effect magnitude. Figure 1 demonstrates that the intensity of the 630 cm^{-1} band in the Raman spectra of $\text{LiNbO}_3\text{:B}$ crystals (0.55 ÷ 1.24 mol % B_2O_3 in the reaction mixture) correlate well with the concentration behavior of PILS opening angle θ . It indicates the fact that distortion of oxygen octahedra in the structure and photorefractive effect in the $\text{LiNbO}_3\text{:B}$ crystals depend on boron concentration in the reaction mixture.

Figure 2 demonstrates that $\text{LiNbO}_3\text{:B}$ bandwidths corresponding to vibrations of cations inside octahedra ($150\text{ ÷ }300\text{ cm}^{-1}$) are narrower than that in a spectrum of $\text{LiNbO}_{3\text{cong}}$ crystal. At the same time widths of bands 152 and 240 cm^{-1} in the

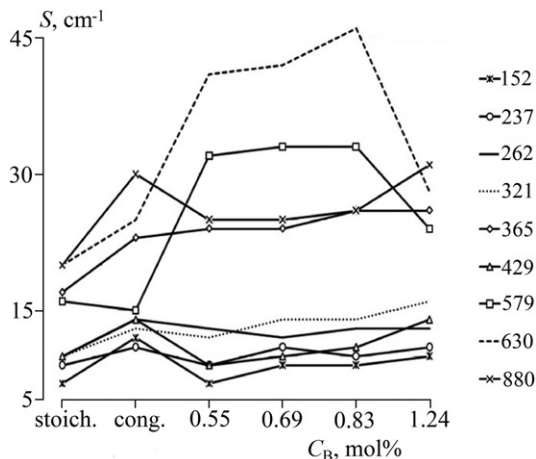


Figure 2. Widths dependence of basic Raman lines in the scattering geometry $Y(ZX)\bar{Y}$ of nominally pure crystals of LiNbO_3 (1), LiNbO_3 (2), and LiNbO_3 :B: 0.55 (3), 0.69 (4), 0.83 (5), 1.24 (6) mol % B_2O_3 in the reaction mixture.

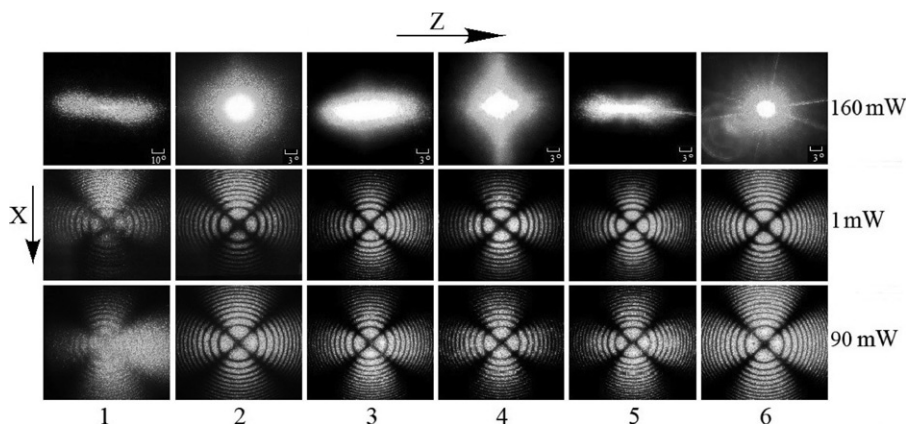


Figure 3. Speckle-structure of the PILS indicatrix ($P = 160$ mW) and conoscopic pictures ($P = 1$ and 90 mW) of crystals LiNbO_3 (1), LiNbO_3 (2), LiNbO_3 :B (0.55 (3), 0.69 (4), 0.83 (5), 1.24 (6) mol % B_2O_3 in the reaction mixture). A complete PILS indicatrix opening time is 60 seconds for all researched crystals.

LiNbO_3 :B spectra coincide with the bandwidths in the LiNbO_3 spectrum within the error of the experiment. However, it is noteworthy that bands with frequencies 578 ($E(\text{TO})$) and 630 ($A_1(\text{TO})$) cm^{-1} corresponding to twice degenerate and totally symmetric vibrations of oxygen atoms are significantly expanding, Figure 2. Thus, even a small change of a boron concentration in the melt leads both to a noticeable increase in ordering of structure units of cation sublattice along the polar axis in LiNbO_3 :B crystals and a distortion of oxygen octahedra of the structure.

Conoscopic pictures confirm high optical uniformity of LiNbO_3 :B crystals, Figure 3. The LiNbO_3 :B containing 1.24 mol % B_2O_3 in the reaction mixture has the best optical damage resistance according to the PILS data. For crystals LiNbO_3 :B (0.55 ÷ 1.24 mol % B_2O_3 in the reaction mixture) an angle θ does not exceed 22° , Figure 1C. At the same

time, an opening angle θ of a PILS speckle-structure is higher for LiNbO_3 and it is equal to 56° .

Boron is unable to influence the crystal structure, defectiveness and physical characteristics of crystals due to a trace amount ($\sim 10^{-4}$ wt. %) in the LiNbO_3 :B crystals, according to mass spectrometry data. Therefore, significant differences between LiNbO_3 :B, LiNbO_3 and LiNbO_3 could be caused only by dopant influence on the melt structure. The authors [5] have considered triple system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Nb}_2\text{O}_5$. They believe that borates are able to be a flux at LiNbO_3 crystals growth. We may assume that polyanions containing boron form stable covalent bonds with polyanions containing niobium in the melt. This process binds the excess of niobium and increases the ratio Li/Nb in the melt. As a result, the grown crystal becomes close to a stoichiometric one in a cation sublattice order. Such crystal is characterized by a lower concentration of Nb_{Li} defects and lithium vacancies.

4. Summary

Oxide compound of boron as strong complexing agents and solvents have significant influence on the structure and physical characteristics of a melt and grown from this melt crystal. This approach allows us to use direct structuring of the melt to obtain nominally pure LiNbO_3 crystals with properties as in a doped crystal. The cation sublattice units order and a Nb_{Li} defects amount in such crystals is close to a crystal of stoichiometric composition.

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