Lithuanian Journal of Physics, Vol. **52**, No. 1, pp. 39–43 (2012)

MICROSTRUCTURES IN FERROELECTRIC LITHIUM NIOBATE SINGLE CRYSTALS

N.V. Sidorov [a], M.N. Palatnikov [a], A.A. Janichev [a], P.G. Chufyrev [a], and K. Bormanis [b]

[a] *Institute of Chemistry, Kola Science Centre RAS, Fersman 14, Apatity, 184209 Murmansk Region, Russia*

[b] *Institute of Solid State Physics, University of Latvia, Kengaraga 8, LV-1063 Riga, Latvia*

E-mail: bormanis@cfi.lu.lv

Received 12 October 2011; accepted 1 March 2012

The local fluctuating micro- and nano-structures having the properties different from the rest of the single crystal bulk are found to appear around the laser beam trace in a crystal just after irradiation in the visible range. As the time or intensity of irradiation increases, the number of such micro-structures transforming into static micro- and macro-formations grows and they merge into a continuous track along the laser beam. The photo-refraction in stoichiometric single crystals is shown to be strong enough for the recording and storage of information.

Keywords: lithium niobate, single crystals, photo-refraction, laser radiation, periodic structure

PACS: 77.80.-e, 77.84.Ek, 78.20.Jq, 61.50.Nw

1. Introduction

Recent studies have shown the structural heterogeneities of nano-, micro- and macro-scales emerging inevitably during non-equilibrium crystallisation along with clusters containing localised electrons formed by intrinsic and admixed defects, fractal structures, and laser-induced defects, all being responsible for optical properties of ferroelectric photo-refractive single crystals [1–6]. The studies on the processes creating the structures that affect photo-refraction and other properties of materials are scarce. The issues concerning structural perfectness, homogeneity of single crystals and formation of micro- and macro-structures of pre-determined configurations as well as improving existing or creating new properties are most important for technologies of ferroelectric materials [1].

The optically nonlinear lithium niobate ($LiNbO_3$) single crystal of variable composition is presently one of the most widely used electronic materials [7]. Under certain circumstances, especially during unbalanced crystallisation, macro-, micro- and nano-scale fractal structures may be formed, including layers tens of nanometres thick, sub-micron periodically polarised domains of flat boundaries in the direction perpendicular to the axis of growth [1, 4–6]. Single crystals containing periodically polarised domains are prospective as active nonlinear laser media [1]. By selecting the size of the period of the structure, simultaneous generation of two or more optical harmonics is possible. The stoichiometric lithium niobate (R = Li/Nb = 1) single crystal having a low coercive field value (five times lesser compared with the congruent (R = 0.946) crystal) is one of the most appropriate materials for the purpose [1]. However, stoichiometric single crystals are more vulnerable for optical damage limiting generation and transformation of laser radiation [7, 8].

By now the photo-refraction in lithium niobate single crystals has been well studied experimentally and theoretically [8–10]. The effect, among other factors, depends on the presence of photovoltaic admixtures of multivalent cations (Fe, Cu and others), defects, micro- and nano-structures possessing localised electrons, and ordering particularities of structural units of the cation sub-lattice of the crystal. The photo-refraction effect presents an evident change of the index of refraction of the crystal within a few millimetres around the path of the laser beam and distortion of its structure, which persists for a long time after irradiation is terminated. Despite a number of reports (reviewed in [8–11]) the detailed features of the distortion depending on the composition of the $LiNbO_3$ single crystal have not been examined so far.

In particular, the effects of macro-, micro- and nano-heterogeneity of the single crystal structure on the initial stage of photo-refraction under laser irradiation have not been studied at all. It should be noted that the change of the refraction index in macro- and micro-regions of a crystal having different physical characteristics may proceed differently. Recent studies indicate a pronounced clustered structure changing under external factors in lithium niobate crystals of different compositions [12].

The structural heterogeneity of single crystals may as well affect the formation and dynamics of photo-refraction. The present study is aimed at the dynamics of propagation of laser radiation in photo-refractive lithium niobate single crystals of different compositions.

2. Methods

The single crystals were grown in a number of ways by the Czochralsky technique [1]. The samples were cut from a single crystal ingot and shaped as parallelepipeds of the size of 5×6×7 mm, the edges being parallel to the crystallographic axes *X, Y, Z* (*Z* is the polar axis). The faces of the parallelepipeds were thoroughly polished. A 2018-RM Spectra Physics argon laser generating at 514.5 nm wavelength was used as a source of radiation. All images were taken by a digital camera.

3. Results and discussion

Considerable bulk heterogeneity, i. e. domains and clustered structures, a large number of charged defects, and an index of refraction obviously varying along the axis of growth, is typical of lithium niobate single crystals, particularly of stoichiometric composition [7–9, 12]. As examples, the fractal domains in $LiNbO_3$:Tm (1.8% mass) and the regular nano-size domain structure in $LiNbO_3$:Gd (0.44% mass) grown from congruent melt under imbalanced conditions are shown in Figs. 1 and 2 [5, 6].

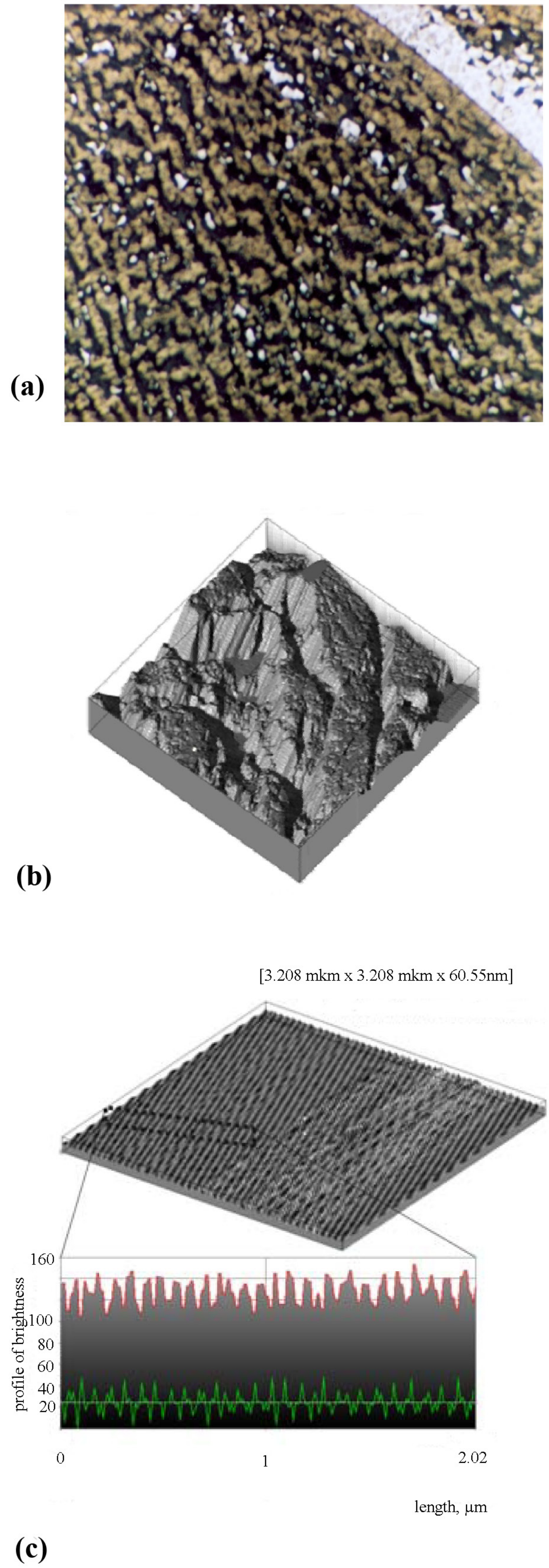

Fig. 1. (a, b) Fractal domains in the $LiNbO_3$:Tm (1.8% mass) single crystal. (c) Regular structure of nano-size domains in the $LiNbO_3$:Gd (0.44% mass) single crystal.

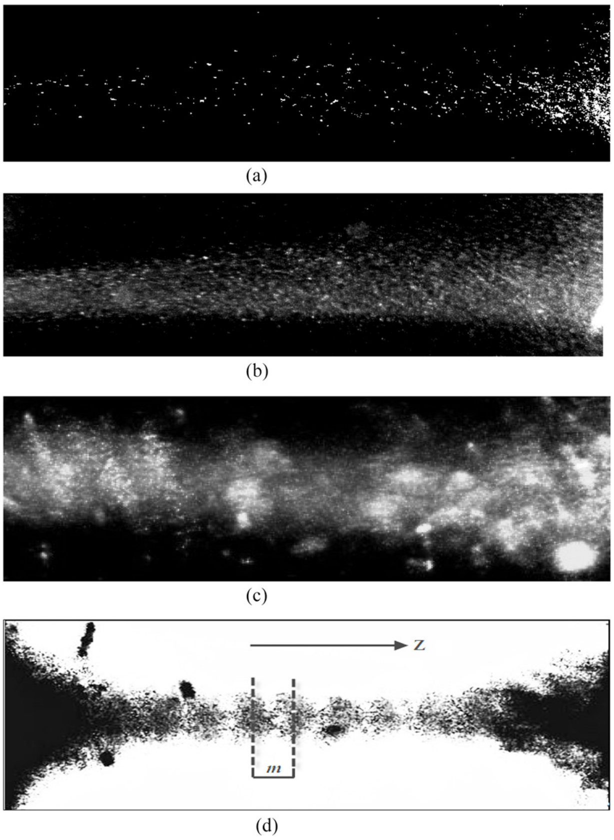

Fig. 2. (a, b, c) Laser beam propagating in the stoichiometric lithium niobate single crystal grown from 58.6 mole % Li_2O melt. (d) Periodic structure of the beam.

In the single crystals of such heterogeneity and in the presence of a large number of charged defects, considerably imbalanced conditions may arise in the places where interaction with radiation takes place [2]. The structure of a crystal may obtain the ability of self-organisation when the necessary precondition, i. e. energy flow from an external source to dissipate, is present. Due to energy flow, the imbalanced system becomes active and allows laser-induced macro-, micro- and nano-structures to form in addition to the structures produced during imbalanced crystallisation [2]. The type and size of micro- and nano-structures may essentially affect photo-refraction, its dynamics, and the physical characteristics of the optical single crystal materials [13]. Under conditions of strong imbalance at irradiation of the crystal in the vicinity of the laser beam, the system may become unstable and the structures of different scales obviously featuring spatial self-organisation emerge. The structures may have properties of self-resemblance and can be identified as fractals at different scale levels.

The following has been observed during experiments of propagation of linearly polarised laser radiation in different photo-refractive lithium niobate single crystal compositions. The laser track does not form immediately after irradiation or at low intensity irradiation: distinct local fluctuating micro- and macro-structures (Fig. 2(a)) with the refraction index different from that of the rest of the crystals develop at the initial stage of irradiation. As the time or intensity of irradiation increases, the number of such micro-structures grows (Fig. 2(b)) transforming into a continuous track (Fig. 2(c)). The track may remain in the crystal for a long time determined by Maxwell's relaxation (up to a year in dark). The existence of the track is an evidence of possibility to use the material for storage of information (Fig. 3). The step-wise appearance and development (fluctuating micro-structures–static

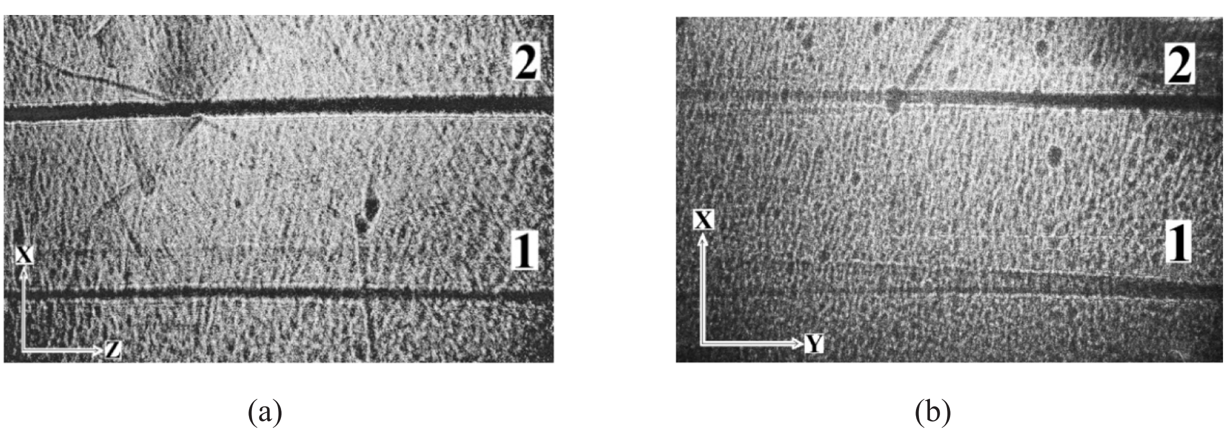

Fig. 3. Images of a laser beam in the stoichiometric lithium niobate single crystal after 5 min (1) and 12 min (2) since the beginning of irradiation in (a) *ZX* and (b) *YX* planes. Vector **E** of the light wave is directed along the polar axis.

microstructures–continuous trail) of the laser track revealed in single crystals by the study correlate with the development of triple-layer speckled patterns at photo-refractive light scattering (undesirable at recording) in a lithium niobate single crystal [3].

We have observed the periodic structure of a laser beam directed along the polar axis (*Z*) of a stoichiometric lithium niobate single crystal grown from melt of 58.6 mole % Li_2O (Fig. 2(d)). The period *m* of the structure is about 0.33 mm. The periodicity is absent at the beginning and is not observed in laser beams directed along axes *X* and *Y*. Similar experiments were made with congruent single crystals ostensibly pure and containing admixtures grown from congruent melt, and with ostensibly pure stoichiometric single crystals grown from congruent melt containing admixture of K_2O. Regardless of the direction, no periodicity in the laser beam was observed in any of these crystals. The observed periodic structure of a laser beam might be related to the gyrotropy of a stoichiometric lithium niobate single crystal. A detailed description of the effect is given in the case of the single crystal of paratellurite [14].

The gyrotropy of stoichiometric lithium niobate single crystals grown from melt of 58.6 mole % Li_2O might be related to the features of growth typical of such crystals [1]. Under conditions the crystals are grown they have a considerable heterogeneity of composition along the axis of growth [1, 7, 8]. As the results of our study show, the index of refraction of lithium niobate single crystals of compositions close to stoichiometric grown from congruent melt with added K_2O is more homogenous and gyrotropy is absent. It has to be noted that adding K_2O to the melt does not provide strongly stoichiometric single crystals [1].

One may suppose that the presence of the periodic structure of a laser beam propagating along the polar axis of a lithium niobate single crystal suggests the crystal being of stoichiometric composition. Together with the absence of the 120 cm^{-1} Raman band [2] it can serve as evidence of stoichiometry. Our studies show the absence of periodicity of a laser beam in the visible range in lithium niobate single crystals of compositions close to stoichiometric grown from congruent melt with admixture of K_2O. At the same time the 120 cm^{-1} band is always present in the Raman spectra of such crystals [8] pointing to the complicatedness of obtaining a strongly stoichiometric composition from congruent melt by adding K_2O [15, 16].

Finally, it should be noted that the kind of fluctuating and static microstructures and the speckle patterns of photo-refractive light scattering represent different compositions of lithium niobate crystals, either ostensibly pure or containing admixtures. Nevertheless, the light scattered by the defects and the defects themselves exhibit specific features the studies of which provide information about the structure and micro- and macro-heterogeneity of single crystals. Further studies of the specific features observed at propagation of laser radiation in lithium niobate crystals of different compositions grown in different ways under different conditions are of doubtless interest when designing materials with preset optical properties.

References

[1] M.N. Palatnikov, *Materials of Electronic Techniques based on Ferroelectric Niobate-tantalate Solid Solution Single Crystals and Ceramics of Alkali Metals with Micro- and Nanostructures*, Doct. thesis (IHTREMS KSC RAS, Apatity, 2011) [in Russian].

[2] N.V. Sidorov, A.A. Janichev, P.G. Chufyrev, B.N. Mavrin, M.N. Palatnikov, and V.T. Kalinnikov, Micro- and nanostructures in photorefractive lithium niobate single crystals induced by laser radiation, Doklady Akademii Nauk **428**(4), 492–495 (2009) [in Russian].

[3] N.V. Sidorov, A.V. Syuy, M.N. Palatnikov, and V.T. Kalinnikov, Speckle-layer structure in photorefractive lithium niobate single crystals, Doklady Akademii Nauk **437**(3), 352–355 (2011) [in Russian].

[4] M.N. Palatnikov, O.B. Shcherbina, I.V. Biryukova, N.V. Sidorov, and V.T. Kalinnikov, Study of $LiNbO_3$:Gd crystal structure depending on grown conditions, Bulletin of KSC RAS **3**, 40–46 (2010) [in Russian].

[5] M.N. Palatnikov, O.B. Shcherbina, N.V. Sidorov, and K. Bormanis, Micro- and nanostructures in lithium niobate single crystals doped with lanthanides, Crystallography Reports **55**(5), 811–814 (2010).

[6] M.N. Palatnikov, O.B. Shcherbina, V.V. Efremov, N.V. Sidorov, and V.T. Kalinnikov, Periodic micro- and nanostructures in single crystals $LiNbO_3$:Gd grown at nonstationary conditions, Proc. RAS, Inorganic Materials **46**(4), 479–484 (2010) [in Russian].

[7] Yu.S. Kuz'minov, *Lithium Niobate – Electrooptical and Nonlinear Optical Crystal* (Science, Moscow, 1987) [in Russian].

[8] N.V. Sidorov, T.R. Volk, B.N. Mavrin, and V.T. Kalinnikov, *Lithium Niobate: Defects, Photorefraction, Vibrational Spectrum, Polaritons* (Science, Moscow, 2003) [in Russian].

[9] T. Volk and M. Wohlecke, *Lithium Niobate. Defects, Photorefraction and Ferroelectric Switching* (Springer, Berlin, 2008).

[10] B.I. Sturman and V.M. Fridkin, *Photogalvanic Effect and Related Phenomena in Substances without a Centre of Symmetry* (Science, Moscow, 1992) [in Russian].

[11] M. Goulkov, M. Imlau, and Th. Woleke, Photorefractive parameters of lithium niobate crystals from photoinduced light scattering, Phys. Rev. B **77**, 235110–235115 (2008).

[12] V.M. Voskresenskii, O.R. Starodub, N.V. Sidorov, M.N. Palatnikov, and B.N. Mavrin, Modeling of clusters, Crystallography Reports **56**(2), 221–226 (2011).

[13] N.V. Sidorov, A.V. Syuy, M.N. Palatnikov, D.V. Evstratova, and B.N. Mavrin, N.V. Sidorov, A.V. Syuy, M.N. Palatnikov, D.V. Evstratova, and B.N. Mavrin, Photorefractive and Raman scattering, Opt. Spectrosc. **110**(6), 864–870 (2011).

[14] E.Yu. Vorontsova, R.M. Grechishkin, I.A. Kaplunov, F.I. Kolesnikov, V.Ya. Molchanov, I.V. Talyzin, and S.A. Tretyakov, Manifestation of gyrotropy upon light scattering in paratellurite, Opt. Spectrosc. **104**(6), 886–889 (2008).

[15] N.V. Sidorov, P.G. Chufyrev, M.N. Palatnikov, and V.T. Kalinnikov, Raman spectra and photorefraction of pure and alloyed crystals $LiNbO_3$, Proc. RAS, Inorganic Materials **41**(2), 210–218 (2005) [in Russian].

[16] N.V. Sidorov, P.G. Chufyrev, M.N. Palatnikov, and V.T. Kalinnikov, Defects, photorefraction and vibrational spectrum of lithium niobate crystals with different composition, Nano Microsyst. Technique **3**, 12–17 (2006) [in Russian].

MIKRODARINIAI FEROELEKTRINIUOSE LIČIO NIOBATO MONOKRISTALUOSE

N. V. Sidorov [a], M. N. Palatnikov [a], A. A. Janichev [a], P. G. Chufyrev [a], K. Bormanis [b]

[a] *Rusijos MA Kolos mokslinio centro Chemijos institutas, Apatitai, Rusija*

[b] *Latvijos universiteto Kietojo kūno fizikos institutas, Ryga, Latvija*

Santrauka

Nustatyta, kad aplink lazerio pluošto taką kristale iškart po jo apšvitos regimojo ruožo spinduliuote susidaro lokalūs fliuktuojantys mikro- ir nanodariniai, savo savybėmis besiskiriantys nuo monokristalinės aplinkos. Didėjant apšvitos trukmei ar intensyvumui, šių mikrodarinių, virstančių statinėmis mikro- ir makroformacijomis, kiekis didėja ir jie susilieja į ištisinį pėdsaką išilgai lazerio pluošto. Parodyta, kad stechiometriniuose monokristaluose yra pakankamai didelė fotorefrakcija, tinkama informacijos įrašymui ir kaupimui.