NEW PERSPECTIVES OF LITHIUM NIOBATE CRYSTALS

E. Kokanyan [a,b], E. Diéguez [a]

[a]Departamento Física de Materiales, Universidad Autonoma de Madrid, 28049 Cantoblanco,
 Spain
[b]Institute for Physical Research, National Academy of Sciences, 378410 Ashtarak-2, Armenia

The growth and characterization of lithium niobate crystals of stoichiometric composition as well as congruent composition with periodic poled domain structure are reviewed. The perspectives of these crystals for fundamental research and optical device applications are discussed.

1. Introduction

Lithium niobate (LN) single crystal has been found to be an excellent material for various optical applications and is under study during last 30 years because of its attractive set of non-linear optical, electro-optical, piezoelectrical, acoustical and photorefractive properties. This crystal is widely used for optical waveguides and photorefractive devices as well as self-frequency doubled and self Q-switched solid state lasers. Nevertheless, recently done two discoveries, that is: i) the growth of stoichiometric LN crystals, and ii) the preparation of bulk periodic poled LN (PPLN) crystals have essentially improved the perspectives of this material.

2. Stoichiometric LN

Commercially available LN crystals are grown from a melt of congruent composition with molar fraction of Li_2O in the range of 48.6-48.35 % [1-4] by the conventional Czochralski technique, and generally have good optical quality and uniformity. Serious disadvantages of congruent LN crystals are the presence of high amount of intrinsic (nonstoichiometric) defects i.e. Nb anti-site defects occupying Li-ion sites and cation vacancies, as well as phenomena called "optical damage". It is obvious that structures and densities of the mentioned intrinsic defects substantially influence the optical properties including photorefraction. This is the reason that the strong interrelation between the subsystems of intrinsic and extrinsic defects as well as relationship between the defects and properties are significant subjects to be studied and are the most important features of LN crystals. Only a complex study of both defect subsystems and properties can lead to the improvement of this material for already existing or possible new applications.

Several attempts have been done to grow LN crystals of stoichiometric composition free of intrinsic defects. Among the techniques for the preparation of LN crystals with stoichiometric composition should be noted the method of vapor transport equilibration (VTE) which is a post-growth method, with annealing a congruent crystal in a Li-rich atmosphere [5,6]. By this method LN crystals close to stoichiometric composition have been obtained. Nevertheless, due to very slow ion transport in LN crystals this procedure is rather long and is thus limited to thin samples. Rather large

and uniform crystals have been grown by the double crucible Czochralski method [7,8]. But they seem to be not stoichiometric [9]. The most promising method of growing stoichiometric LN crystals is that of growth from the potassium-containing melts, firstly reported in [10,11]. In growing the first crystals by this method, a final correction electric current was passed through the crystal-melt system. The method of passing an electric current through the crystal melt system during the LN crystal growth process in order to control its composition and physical properties was reported in [12]. The LN crystals grown by the above mentioned method are free from intrinsic defects and practically free of potassium. The first characterization of the stoichiometry of these crystals by EPR, NMR, Raman spectroscopy [13,14], birefringence [15], precise measurements of lattice parameters [1] and shift of the fundamental absorption edge [16] have been reported in [10,11,17]. The latest characterizations were published in [9,18-20].

Table 1 shows the above mentioned data and compares the results for congruent and stoichiometric crystals.

Table 1. Physical characteristics of stoichiometric LN crystals grown from the potassium-containing melts as well as of congruent LN.

Parameter	Congruent LN	Stoichiometric LN	References
Lattice constants a(Å), c(Å)	5.1497(3) 13.8656(13)	5.1469(3) 13.8594(14)	[17]
Wavelength of fundamental absorption edge (cm^{-1})	320 ($\alpha=15$ cm^{-1}) 319.1 ($\alpha=20$ cm^{-1}) 320.8 ($\alpha=15$ cm^{-1})	305 ($\alpha=15$ cm^{-1}) 303.2 ($\alpha=20$ cm^{-1}) 304 ($\alpha=15$ cm^{-1})	[11] [9] [19,20]
Raman linewidths (cm^{-1}) - for phonon 153 cm^{-1} - for phonon 876 cm^{-1}	9.5 23.7	6.0 18.0	[11] [11]
Optical birefringence n_e-n_o for optical wavelengths λ = 404 nm λ = 633 nm λ = 1176 nm	-0.108 -0.085 -0.075	-0.126 -0.096 -0.09	[11] [11] [11]
Phase matching angle (deg) for SGH at room temperature for $\lambda=1064$ nm	87	66.5	[19,20]
90° phase matching temperature (° C) for SHG	4	243	[19,20]

A detailed analysis of the peculiarities of the growth processes of LN crystals from potassium containing melts and compositional relationship between crystal and melt have been done in [9,17-20]. On the base of data of LN crystal composition determinated by means of measurements of refractive indexs, lattice constants, fundamental absorption edge as well as second harmonic generation phase-matching angle (Fig. 1, [19,20]), phase-matching temperature, fundamental absorption edge, compositional relationship curves between LN crystal and melt during the growth from potassium containing congruent melts have been presented in [18] and [19,20] (Fig. 2 and Fig. 3 respectively). In the last figure a new presentation, first time reported on ICCG-12, of the melt composition, that is as (Li_2O+K_2O) mol fraction was used. The data were drawn on the well known compositional relationship graph [21,22] for LN crystals replacing the meaning of the abscissa "mol% Li_2O in the melt" by "mol% ($Li_2O + K_2O$) in the melt". The reason for this presentation in the opinion of the authors was the practically identical dependence of the grown crystals composition on the molar fraction of Li_2O and ($Li_2O + K_2O$) in the melt. The potassium in LN melt provides the same chemical medium as lithium does and the melt practically doesn't "sense" the change of Li_2O to

K_2O. The suggestion of the authors was that for growing LN crystals from the potassium-containing melts the pseudo-binary Li_2O-Nb_2O_5 phase diagram can be used as a base, with only a change to the meaning of the abscissa. It should be noted that the compositional relationship data of [9,18] could also be drawn on above mentioned graph with the same success.

Due to high average of intrinsic defects, congruent crystals have very complicated local distribution of crystalline field. As a result unavoidable loss of information about the defect centers appears because of difficulties of analyzing their complex and rich spectra. In spite of this, because of the absence of intrinsic defects and ideal crystalline structure in stoichiometric LN, crystal impurity and defect centers are presented without "masks" and, as a result, high resolution and sensitivity of all kinds of spectra of impurity centers in these crystals are possible [10,11,23-25].
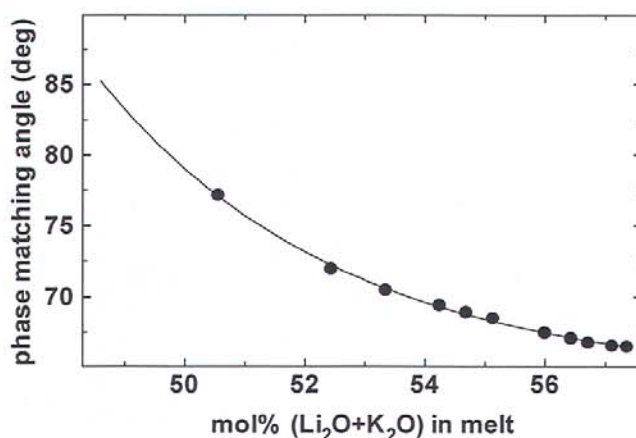

Fig. 1. SHG phase-matching angle of $LiNbO_3$ crystals for fundamental wavelength 1064 nm as a function of (Li_2O + K_2O) mole fraction in the melt.
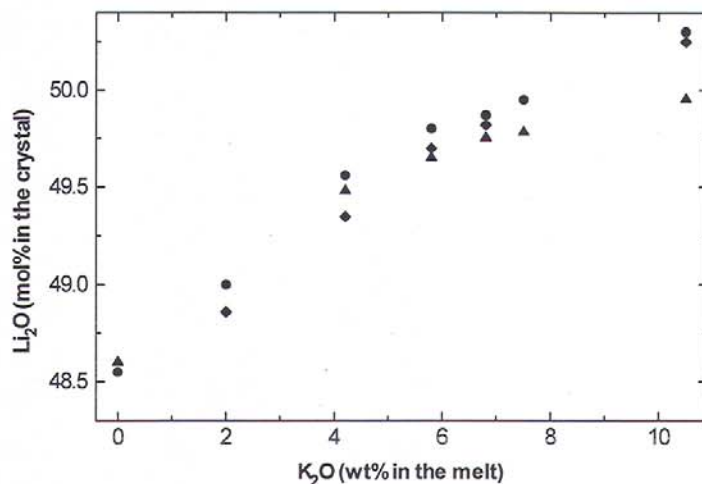

Fig. 2. Li_2O content in the crystals as a function of the K_2O content in the melt; ● -- lattice volume calculated on the base of measurements of lattice parameters by X-ray diffraction; ▲ -- fundamental absorption edge position; ◆ -- (n_o^2-n_e^2) obtained by photorefractive measurements.

The evolution of EPR spectra of Cr^{3+} ions in LN crystals from congruent composition to stoichiometric one is well demonstrated in Fig. 4 [24]. And at last the discovery of new centers of well known impurities, such as Cr, Fe, Yb in stoichiometric LN [25-27] which were not observable in congruent one brightly illustrates the above mentioned advantages of the stoichiometric LN crystals.
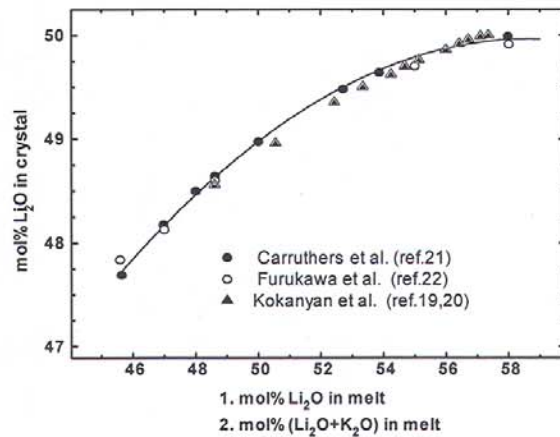

Fig. 3. The variation of the crystal composition as a function of Li_2O and $(Li_2O + K_2O)$ mole fraction in the melt. The points ($\bullet$; O) correspond to the abscissa 1. mol % Li_2O in melt and the triangles ($\blacktriangle$) to the abscissa 2. mol % $(Li_2O + K_2O)$ in melt.
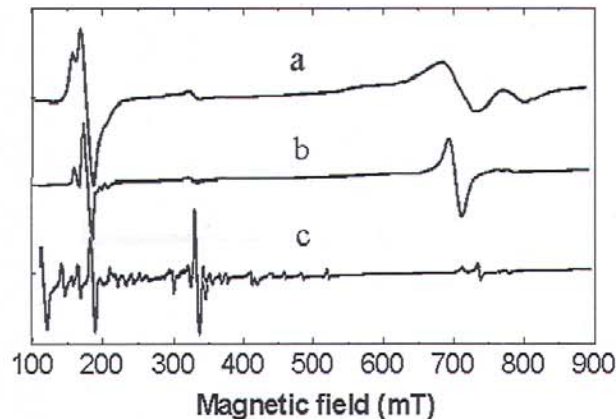

Fig. 4. Dependence of Cr^{3+} EPR spectra on crystal composition: a – 48.5 mol% Li_2O; b – 49.85 mol% Li_2O; c – 50.0 mol% Li_2O. B||y, Cr = 0.02 wt%, T = 4.2 K.

The problem of "optical damage" in congruent LN crystals, which essentially limits the possible applications of this material, is solved by heavily doping (about 5 mol%) of LN with MgO. The heavy doping with MgO remarkably increases the laser damage threshold, but at the same time the high concentration of MgO required to achieve the sufficient damage resistance subsequently gives rise to a difficulty in growing high optical quality crystals, which, as a result, limits the usage of these crystals for optical device applications. In spite of this, stoichiometric LN crystals, while

showing higher photorefractive sensitivity when doped with MgO in concentration about three times less than the above mentioned value, exhibit four orders of magnitude increased optical damage resistance as compared to that of the congruent crystals [28].

All above mentioned characteristics in addition to the single domain nature of stoichiometric LN crystals [9,29], and compared to larger electro-optic coefficient r_{33} [30], shorter fundamental absorption edge [9,11,18], smaller electric field required for ferroelectric domain switching [31] of congruent LN, illustrate the excellent potential of stoichiometric LN both for fundamental research and various optical device applications.

3. Periodic poled LN

The idea of quasi-phase-matching (QPM) was first proposed by Armstrong et. al. [32]. It predicts that the nonlinear optical effects can be enhanced in both birefringent or non-birefringent crystals with periodic modulation of nonlinear susceptibilities, that is in optical superlattice crystals. Compared with birefringent phase matching QPM permits access to longer components of the nonlinear tensor of the material and to wider wavelength ranges. QPM can be achieved by an appropriate periodic modulation of nonlinearity, thus compensating for the phase mismatch between the generated field and its corresponding induced nonlinear polarization. In LN crystals this is realized by means of periodic inversion of the ferroelectric domains since the sign of the nonlinear coefficient is related to direction of the spontaneous polarization. Since d_{33} for LN crystal is about 7.5 times larger than the ordinary used d_{31}, for PPLN crystals one can expect a QPM enhancement factor of $(d_{33}/d_{32})^2(2/\pi)^2 \approx 23$.

A lot of post-growth methods such as direct electron-beam writing [33], corona discharge [34], proton exchange and rapid heat treatment [35], applying external electric fields to patterned electrodes prepared by photolithography [36,37], as well as direct growth methods such as laser heat pedestal [38], and Czochralski (CZ) methods [39] are used for obtaining PPLN crystals. The most extensively used electric field poling technique giving excellent results of high uniformity of domain lengths is restricted to obtain domain inversion depth no more than 0.5 mm and therefore is insufficient for some applications, such as angle tuning optical parametric oscillators. According to the above mentioned comments, the CZ technique has advantages of obtaining thick periodic poled structures in LN crystals with greater useful surfaces. This is the reason that the authors of the present paper focus their attention to this method as the most perspective one.

During the last 5 years this technique connected with rotation-induced growth striations during center-off growth process was used for obtaining PPLN crystals doped with Y, Yb, Eu, Er, Nd:MgO, Yb:MgO, Cr and Hf ions [40-47]. In [46,47] beside the center-off growth, the periodic structures were obtained by using the growth striations caused by the influence of the applied periodic electric current to the crystal-melt system. The addition of impurities besides the role of helping in creation of periodic structure in the crystals offers the potential of combining nonlinear processes taking place in the host crystal and optical processes originated by the ion. In this case Nd, Eu, Er and Yb ions are introduced as trivalent rare earth active optical ions [41-45], Er for emission of green light through upconversion [43], and Hf for strong suppression of phofotorefractive effect in PPLN crystals [46-48].

For PPLN crystals obtained by the above mentioned method, a conventional CZ method is used with growing of the crystal along the a-axis (in [49] along the normal to the (0 1 $\bar{1}$ 2) face), which is displaced about 5 mm away from the rotational symmetry axis of the temperature field. The period of the domain structure is controlled by the change of rate ratio of pulling to rotation. SEM micrograph of PPLN crystals doped with Er and preliminary etched in HF:HNO$_3$ mixture is shown in Fig. 5 [51] and brightly illustrates the good uniformity of the domains. SHG experiments were used for characterization of the homogeneity of the periodic structures [47,50,51]. Fig. 6 shows QPM SHG tuning curve for a PPLN crystal doped with Er ions [51].
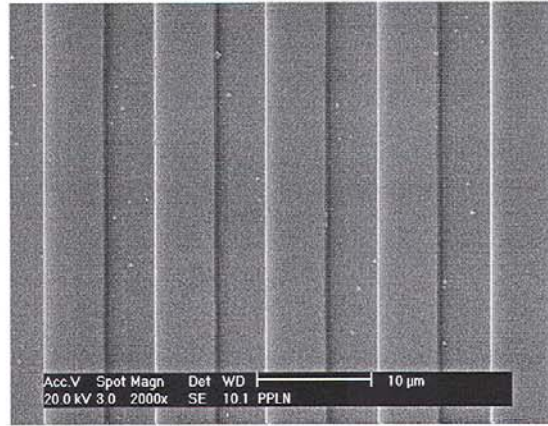
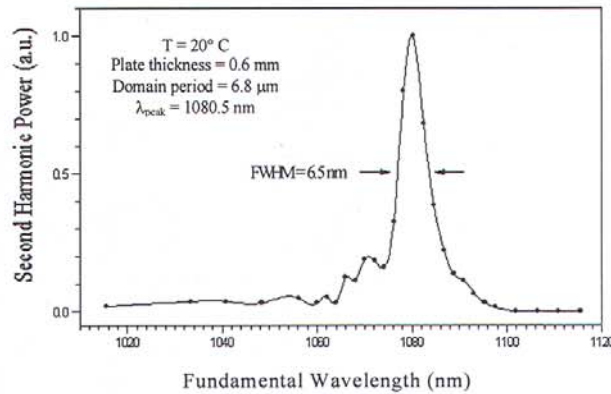Fig. 5. SEM micrograph of periodic domain structure in LN crystal doped with Er.

Fig. 6. Quasi-phase-matching second harmonic generation tuning curve for PPLN crystal
doped with Er.

The little change of the form of the curve from sinc^2 was due to the dispersion of the domain lengths. The measurement of SHG efficiency at the wavelength peak shows for the effective nonlinear coefficient a value of about 15 pm/V which was close to the theoretical one (21 pm/V). The comparison of the obtained and expected values of FWHM (full bandwidth at half maximum) shows a few percent dispersion errors in domain lengths for the above mentioned crystal. The average scattering of domain lengths for PPLN crystals grown by this method is about 5% [41,47,50,51].

There are some disagreements in the literature concerning the mechanism of formation of periodic domain structure in as grown LN crystals. In [39,40,42] it is shown the existence of one to one correspondence between a periodic domain structure and the variation of the dopant concentration, where the domain walls of the periodic structures are always located in the maximum and minimum of dopant concentration gradient, which is in agreement with [52] where was suggested that an impurity gradient concentration in LN crystals influence the orientation of the polarization vector. In [53] a convex solid-liquid interface was introduced to be beneficial for generating the periodic domain structures. Nevertheless, in opposition to the facts mentioned in [54] it has been reported that the dopant concentration remains constant along the domain structure and the periodic

structures are directly related to the variation in the Nb ion composition (Fig. 7, [54]), which has been shown to be in one to one correspondence with the domain structure.
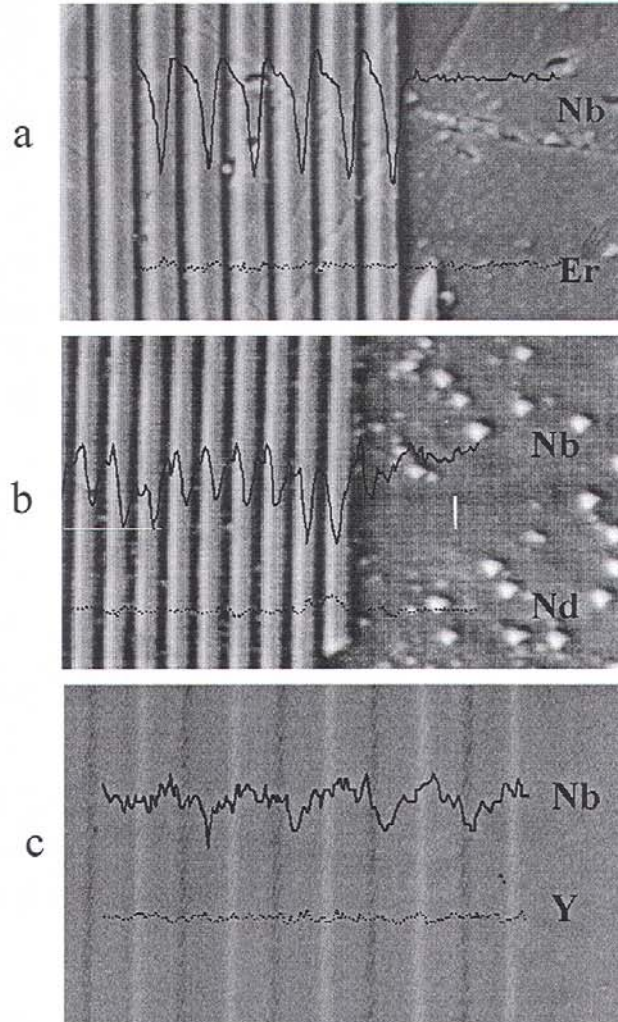

Fig. 7. SEM images along with the Nb (-) and dopant (---) concentration profiles measured by WDX (wavelength dispersive X-ray) for the PPLN crystals doped by: (a) Er 0.7 mol%; (b) Nd and (c) Y.

The combination of nonlinear optical properties of PPLN and spectral properties of Er^{3+} in this host gives the possibility of simultaneous emission of second harmonic light through QPM and green light through upconversion at room temperature. The mentioned result was well demonstrated in [43] by generation of violet-and-green and blue-and-green light while pumping by infrared diode laser the PPLN:Er crystal.

Self-frequency doubling (SFD) is one of the most important techniques for constructing compact and reliable short wavelength light sources. The best LN crystal for this purpose in the past was LN:Nd:MgO, which requires for SFD operation a temperature higher than 100 °C and was limited only to generate green light.

SHG measurements indicate that PPLN crystals co-doped with Nd:MgO and Yb:MgO both are suitable for self-frequency-doubling operation using high-gain π polarization at room temperature [45,50]. The blue and green SFD operation were both achieved in optical superlattice LN:Nd:MgO [50]. About 18% of overall efficiency of green output power during SFD performance for the PPLN crystal co-doped with Yb:MgO was achieved [45] (Fig. 8). The mentioned value is comparable with those one for other well known SFD laser systems [55,56].
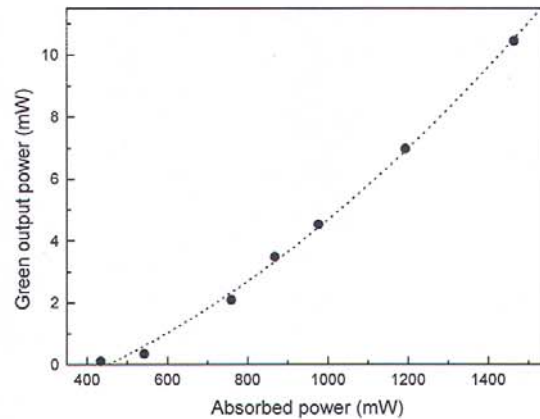

Fig. 8. Self-frequency-doubling performance in PPLN crystal co-doped with MgO:Yb.

4. Conclusion

All the above mentioned results brightly illustrate that CZ technique might be successfully used for obtaining PPLN crystals with uniform and controlled domain structure, thus recommending PPLN crystals as an excellent material for sum and mixed harmonics generation for blue-green laser technology and optical parametric oscillators both throughout the QPM technique and as a media for compact polifunctional laser systems.

Acknowledgements

References

[1] C. Lerner, Legras and J. P. Dumas, J. Crystal Growth, **3**, 231 (1968).
[2] N. M. O'Bryan, P. K. Gallagher, C. D. Brandle, J. Am. Ceram. Soc., **68**, 493 (1985).
[3] R. Bordui, G. Norwood, C. D. Bird, G. D. Calvert, J. Cryst. Growth, **113,** 61 (1991).
[4] R. L. Holman, Mater. Sci. Res., **11**, 343 (1978).
[5] D. N. Jundt, M. M. Fejer, R. L. Byer, IEEE J. Quantum Electr., **26**, 135 (1990).
[6] Y. S. Luh, M. M. Fejer, R. L. Byer, R. S. Feigelson, J. Crystal Growth, **82**, 264 (1987).
[7] J. K. Kitamura, I. K. Yamamoto, N. Jyi, S. Kimura, T. Hayashi, J. Crystal Growth, **116**, 327 (1992).
[8] J. K. Kitamura, Y. Furukawa, N. Jyi, Ferroelectrics, **202**, 21 (1997).
[9] K. Polgar, A. Peter, L. Kovacs, G. Corradi, Zc. Saller, J. Crystal Growth, **177**, 211 (1997).

[10] G. I. Malovichko, V. G. Grachev, L. P. Yurchenko, V. Ya. Proshko, E. P. Kokanyan, V. T. Gabrielyan, phys. stat. sol. (a), **133**, K29 (1992).

[11] G. I. Malovichko, V. G. Grachev, E. P. Kokanyan, O. F. Schirmer, K. Betzler, B. Gather, F. Jermann, S. Klauer, U. Schlarb, M. Wöhlecke, Appl. Phys. A, **56**, 103 (1993).

[12] R. Balasanyan, V. T. Gabrielyan, E. P. Kokanyan, J. Földvari, Sov. Kristallografia, **35**, 1540 (1990).

[13] A. E. Balavenskaya, L. I. Pyatigorskaya, Z. I. Shapiro, L. N. Margolin, E. A. Bovina, J. Appl. Spectroscopy, **38**, 491 (1983).

[14] U. Scharlb, S. Klauer, M. Wesselmann, K. Betzler, M. Wohlecke, Appl. Phys. A, **56**, 311 (1993).

[15] E. Born, E. Willibald, R. Veith: Proc. IEEE Ultrasonic Symposium, ed. by B.R.McAvoy (IEEE, New York) 1984, p.268.

[16] J. Földvari, K. Polgar, R. Voszka, R. N. Balasanyan, Cryst. Res. and Techn., **19**, 1659 (1984).

[17] G. Malovichko, O. Cerclier, J. Estienne, V. Grachev, E. Kokanyan, C. Boulesteix, J. Phys. Chem. Solids, **56**, 1285 (1995).

[18] M. D. Serrano, V. Bermudez, L. Arizmendi, E. Dieguez, J. Crystal Growth, **210**, 670 (2000).

[19] E. P. Kokanyan, R. S. Feigelson, to be published.

[20] E. P. Kokanyan, Abstracts of ICCG-12, Jerusalem (1998) p. 228.

[21] J. R. Carruthers, G. E. Peterson, M. Grasso, P. M. Bridenbaugh, J. Appl. Phys., **42**, 1846 (1971).

[22] Y. Furukawa, M. Sato, K. Kitamura, Y. Yajima, M. Minakata, J. Appl. Phys., **72**, 325 (1992).

[23] G. Malovichko, V. Grachev, O. Schirmer, J. Phys. Condens. Matter, **5**, 3971 (1993).

[24] G. Malovichko, V. Grachev, E. Kokanyan, O. Schirmer, Phys. Rew. B, **59**, 9113 (1999).

[25] F. Lhomme, P. Bourson, M. Fontana, G. Malovichko, M. Ailerie, E. Kokanyan, J. Phys.: Condens. Matter, **10**, 1137 (1998).

[26] G. Malovichko, V. Grachev, O. Schirmer. Solid State Commun., **89**, 195 (1994).

[27] G. Malovichko, V. Grachev, E. Kokanyan. O. Schirmer, Ferroelectrics, **239**, 357 (2000).

[28] K. Niwa, Y. Furukawa, S. Takekawa, K. Kitamura, J. Crystal Growth, **208**, 493 (2000).

[29] V. Bermudez, P .S. Dutta, M. D. Serrano, E. Dieguez, Appl. Phys. Lett., **70**, 729 (1997).

[30] T. Fujiwara, M. Takahashi, A. J. Ikushima, Y. Furukawa, J. K. Kitamura, Electron. Lett., **35**, 1 (1999).

[31] V. Gopalan, T. E. Mitchell, Y. Furukawa, K. Kitamura, Appl. Phys. Lett., **72**, 1981 (1998).

[32] A. Armstrong, N. Blombergen, J. Ducuing, P. S. Pershan. Phys. Rev., **127**, 1918 (1962).

[33] A. C. G. Nutt, V. Gopalan, M. C. Gupta, Appl. Phys. Lett., **60**, 2828 (1992).

[34] A. Harada, Y. Nihei, Appl. Phys. Lett., **69**, 2629 (1996).

[35] Shi-ning Zhu, Yong-yuan Zhu, Zhi-yong Zhang, Hong Shu, Jing-fen Hong, Chuan-zhen Ge, Nai-ben Ming, J. Phys.: Condens. Matter, 7, 1437 (1995).

[36] M. Yamada, N. Nada, M. Saitoh, K. Watanabe, Appl. Phys. Lett., **62**, 435 (1993).

[37] J. Webjorn, V. Pruneri, St. P. J. Russel, J. R. M. Barr, D. C. Hanna, Electron. Lett., **30**, 894 (1994).

[38] G. A. Magel, M. M. Fejer, R. L. Byer, Appl. Phys. Lett., **56**, 108 (1990).

[39] Nai-Ben Ming, Jing-feng Hong, Duan Feng, J. Mater. Sci., **17**, 1663 (1982).

[40] Ya-lin Lu, Yan-qing Lu, Xiang-fei Cheng, Gui-peng Luo, Cheng-cheng Xue, Nai-ben Ming, Appl. Phys. Lett., **68,** 2642 (1996).

[41] J. Capmany, V. Bermudez, E. Dieguez, Appl. Phys. Lett., **74**, 1534 (1999).

[42] I. I. Naumova, N. F. Evlanova, S. V. Lavrishchev, Ferroelectrics, **190**, 107 (1997).

[43] Jian-jun Zheng, Yan-qing Lu, Gui-peng Luo, Jing Ma, Ya-lin Lu, Appl. Phys. Lett., **72**, 1808 (1998).

[44] Ya-lin Lu, Yan-qing Lu, Cheng-cheng Xue, Nai-ben Ming, Appl. Phys. Lett., **68,** 1467 (1996).

[45] J. Capmany, E. Montoya, V. Bermudez, D. Callejo, E. Dieguez, L. E. Bausa, Appl. Phys. Lett., **76**, 1 (2000).

[46] E. P. Kokanyan, V. G. Babajanyan, G. R. Badalyanc, R. G. Manucharyan, R. S. Feigelson, Proceedings of Conf. on Laser Physics "LP-99" Ashtarak, (Armenia) Oct. 1999, p.121.

[47] E. P. Kokanyn, V. G. Babajanyan, G. G. Demirkhanyan, R. S. Feigelson, to be published.

[48] A. M. Petrosyan, R. K. Hovsepyan, E. P. Kokanyan, R. S. Feigelson, Proc. SPIE, **4060**, 106 (2000).

[49] I. I. Naumova, N. F. Evlanova, O. A. Gliko, S. V. Lavrishchev, J. Crystal Growth, **181,** 160 (1997).

[50] Y. Q. Lu, J. J. Zheng, Y. L. Lu, N. M. Ming. Appl. Phys. B, **67**, 29 (1998).

[51] V. Bermudez, J. Capmany, J. Garsia Sole, E. Dieguez, Appl. Phys. Lett., **73**, 593 (1998).

[52] M. Tasson, H. Legal, J. C. Gay, J. C. Peuzin, F. C. Lissalde, Ferroelectrics, **13**, 479 (1976).

[53] Ya-lin Lu, Yan-qing Lu, Xiang-fei Cheng, Gui-peng Luo, Cheng-cheng Xue, Nai-ben Ming, Appl. Phys. Lett., **68**, 2781 (1996).

[54] V. Bermudez, D. Callejo, F. Caccavale, F. Segato, F. Agullo-uenda, E. Dieguez, Solid State Com., to be published.

[55] J. Bartschke, R. Knappe, K. J. Boller, R. Wallenstein, IEEE J. Quantum Electronics, **33,** 2295 (1997).

[56] J. M. Eichenholtsz, D. A. Hammons, L. Shah, Q. Ye, R. E. Peale, M. Richardson, B. H. T. Chai, Appl. Phys. Lett., **74**, 1954 (1999).