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PERIODICALLY POLED STRUCTURES IN LITHIUM NIOBATE CRYSTALS: GROWTH AND PHOTOELECTRIC PROPERTIES

I. A. Ghambaryan, R. Guo[a], R. K. Hovsepyan, A. R. Poghosyan[*], E. S. Vardanyan, V. G. Lazaryan

Institute for Physical Researches, National Academy of Sciences, Ashtarak-2,
378410, Armenia
[a]Dept. Electrical Engineering and Materials Research Institute, The Pensylvania State University, University Park, PA, 16802, USA

The advantages of producing a periodically poled lithium niobate (PPLN) structure during crystal growth process are the possibility to get thicker and wider structures that leads to greater useful surfaces in addition to the elimination of the subsequent poling process. We report in this paper a new technology of creating bulk periodically poled $LiNbO_3$ single crystals with antiparallel ferroelectric domains, by direct electric field poling during growth processes. Growth system configuration, crystal composition and geometry selection are explored to allow successful control of the direction of spontaneous polarisation using external electric field. PPLN crystal samples with periodicity 10 - 200 μm were grown using this electric field modulated growth technique. The photoelectric and photorefractive properties of PPLN crystals were investigated.

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1. Introduction

Efficient nonlinear optical materials and the related novel enabling nonlinear optical technologies have made it possible to extend availability of laser radiation to certain bands and wavelengths demanded by numerous technological and scientific applications. Second order nonlinear processes become more efficient when both high nonlinear coefficients and phase matching conditions among the interacting waves are satisfied. The most effective way of achieving high efficiency in nonlinear processes is the periodic modulation of the signs of the nonlinear coefficients by what is known as quasi phase matching (QPM) [1]. QPM can be obtained in ferroelectric crystals by periodically alternating the direction of the spontaneous polarisation of their ferroelectric domains, a technique known as periodic poling, where the length of the domain period plays a fundamental role in high efficiency wavelength conversion optical nonlinear processes.

Lithium niobate ($LiNbO_3$) crystal is a well-known excellent nonlinear optical material, which is grown worldwide in large sizes. The motivation for this work has been the existence of an actual need for periodically poled lithium niobate (PPLN) crystals, as it has been shown that PPLN crystals serve as the basis for efficient, widely tuneable parametric oscillators [2] and in highly efficient harmonic generations [3]. The SHG process is of special interests for addressing the increasing demand for compact and efficient laser system emitting in the blue-green region by nonlinear frequency doubling of infrared lasers. PPLN possess significant advantages over conventional birefringent phase-matched bulk $LiNbO_3$ for an extended use in efficient nonlinear processes. The effective nonlinear coefficient for second order nonlinear processes is greatly increased as beams

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[*] Corresponding author: arp@ipr.sci.am

propagating normal to the ferroelectric axis benefit from the high values of the d_{33} nonlinear coefficient, which cannot be accessed by birefringent phase matching. QPM condition also eliminates Pointing vector walk-off. Another advantage is the prospect of QPM at shorter wavelengths (below 1μm), where birefringent phase matching is not possible. The period of domain inversion required for QPM applications lies in the few μm to tens of μm region, whereas photonic band gap [4] devices require sub-μm scale lengths for operation in the visible spectral region.

Several techniques have been applied to obtain the PPLN structures [5], either the oppositely poled ("head-to-head" and "tail-to-tail") domain structures directly during the growth process [6] or after growth for antiparallel or opposite domain structures [7, 8]. The after growth processes is realised by electric field poling using patterned electrodes, which has become the established method for achieving high quality periodically poled structures in $LiNbO_3$. Using this method, periods down to ~3 μm are routinely produced, by applying an electric field with magnitude exceeds the coercive field between the +z and -z faces, usually at elevated temperatures. Although conceptually simple, this method requires access to photolithographic patterning facilities and subsequent high voltage and/or high temperature applications. The quality of the resultant periodically-poled material depends on a number of factors, including the definition of the patterned photoresist and hence electrodes, the mark-to-space ratio used, the type of liquid or gel electrodes used, the exact procedure for high voltage applications and displacement current monitoring, etc. Periodicities below ~3 μm are difficult to produce, particularly with simultaneously large aspect ratios. The after-growth poling technique requires application of electric fields in the order of 200 kV/cm to the samples that leads at best to devices with useful thickness about 0.3-0.5 mm. Such devices are too thin to allow for wide angle tuning of QPM parametric oscillators and also the use of crystals in lasers with high energies and high average powers, thus limit their utilities in a large numbers of applications (medicine and technology, lidars, colour TV and information systems, etc.).

PPLN structures obtained during crystal growth, on the other hand, effectively overcome the above limitations and provide the possibility of obtaining thicker or wider structures, greater useful surfaces, and being free from the subsequent poling process. Lithium Niobate crystals with periodic structures have been obtained [6] by the Czochralski crystal growth technique with the rotational axis displaced from the symmetry axis of the temperature field. This situation creates a periodic temperature fluctuation, which leads to growth striations. The crystals were grown along c-axis, which was displaced several mm away from the rotational symmetry axis of the temperature field. In this method the addition of the dopant in the crystal is necessary for charge compensation and the period length of the PPLN structures is essentially defined by the correlation between pulling and rotational rates. The crystal grown by this way has head-to-head and tail-to-tail polarisation configuration or opposite domain structures that is mostly suited for acoustic devices.

However, to our knowledge, direct production of $LiNbO_3$ crystals with periodically poled antiparallel domain structure, which is most suitable for the second harmonic generation and optical parametric oscillations, have not been available. In this paper a new technology of producing $LiNbO_3$ crystals with a periodically poled antiparallel domain structure by direct electric field modulation during growth is reported.

2. Experimental procedure

Using the traditional growth methods for lithium niobate crystals, without applying an electrical current through the crystallisation front, the direction of the spontaneous polarisation P_S is determined randomly and thus a multidomain crystal usually results. If a bias voltage is applied to a seed-melt system, the direction of P_S will be stipulated by polarity of this voltage. For a certain selected geometry of a growth system it is found possible (in our preliminary researches) to switch the direction of spontaneous polarisation when the polarity of the external applied voltage is switched. For the production of PPLN crystals it is necessary to grow them along [010] direction, with the c-domains antiparallel to each other periodically. The efficiency of switching depends on boundary conditions, thermal asymmetries, magnitude of bias voltage, variety of dopant in melt, to name a few.

It is necessary to take into account also that a lithium niobate crystal grows from melt in its paraelectric phase and the formation of ferroelectric phase takes place in grown crystal pulled away above the melt level (the distance depending on the temperature gradient of the growth system), where crystal temperature is reduced below its Curie point. It is the horizontal component of the applied electric field, which will be effectively higher when the melting point and the ferroelectric phase transition point are closer to each other, crucial for the creation of PPLN structures. Therefore, a system configuration that minimises the temperature difference and position separations between the ferroelectric phase transition point and the melt-growth surface is of critical importance to obtain and strengthen the effect of the applied bias voltage. The introduction of potassium impurity in the melt has shown to be an effective approach [9] that leads to a modification of the melt composition and hence to a modification of melting and Curie temperatures differences by bring the temperatures of ferroelectric phase transition and Solidus-Liquidus transition closer. To minimise the temperature difference between growth and polarisation, it is also necessary to grow crystals from its congruent melt compositions for the reason illustrated in a later figure (Fig. 2).

Based on the Czochralski method, the PPLN growth system is modified with the capability of applying an electric current during growth. One electrode is the crystal seed itself, another electrode is a conducting ring, encircles the growth and floats on the melt surface. Orientation of seed is selected to be [010] and the c-axis is perpendicular to the growth direction but parallel to the modulating electric field. Under such conditions the period length of PPLN structure is defined by the crystal pulling rate and the frequency of an applied voltage. A schematic of the PPLN growth configuration is presented in Fig. 1, the relation between the ferroelectric Curie temperature T_C and the crystal growth temperature T_G along growth dimension L is also illustrated.

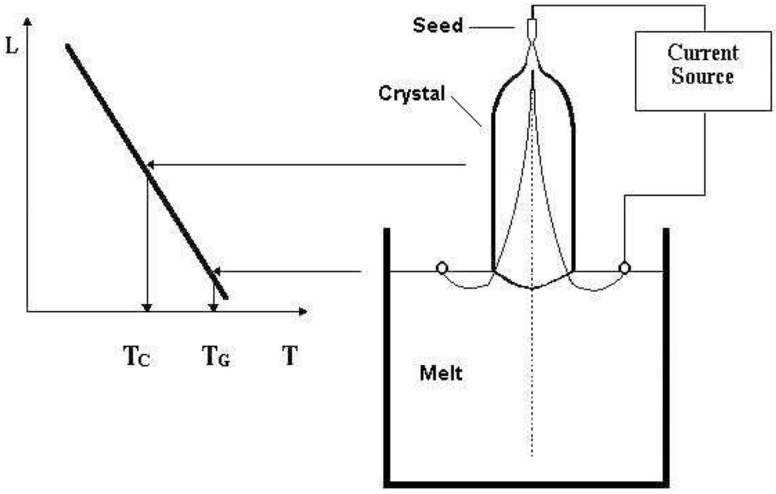

Fig. 1. Schematic of the PPLN crystal growth experimental setup.

Horizontal component of an electric current (field) will dictate the direction of polarisation vectors. Vertical component will influence on the electrochemical processes at crystallisation front and probably on composition of the grown crystal. To achieve polarisation inversion and obtain the antiparallel domains it is necessary to work around the temperature difference between T_C, when spontaneous polarisation direction is set, and T_G, when the crystal grows, while electric field is applied using the melt and the grown crystal as part of the circuit. Although only small electric field strength is needed to dictate the polarisation directions at T_C, the horizontal component of the electric field near the T_C, which is Δx above the melt surface at T_G, can be rather small for large Δx (see Fig. 1).

Clearly the Δx is determined by both the composition of the melt (because of T_c-T_g) and the temperature gradient of the system. The increase of temperature gradient for any growth system has practical restrictions thus increasing efficiency of the applied electric filed by the diminution of (T_c-T_g) is necessary. In an earlier work [9] T_c and T_g dependence on the composition of the crystal was determined that (T_c-T_s) decreases with increasing oxides ratio of lithium to niobium, R = Li_2O/Nb_2O_5 (see Fig. 2).

It is possible to grow crystals with R close to 1 from a melt with R as high as 1.38, but this conjugates with known difficulties. Therefore we grow from congruent melting composition with addition of potassium dopant. This technique was applied by us for the first time in 1985, when we showed that the addition of potassium impurity in $LiNbO_3$ melt increased a synchronism temperature (1.06 to 0.53), as a corollary of a modification of composition of the grown crystal (by increasing the Li:Nb ratio).

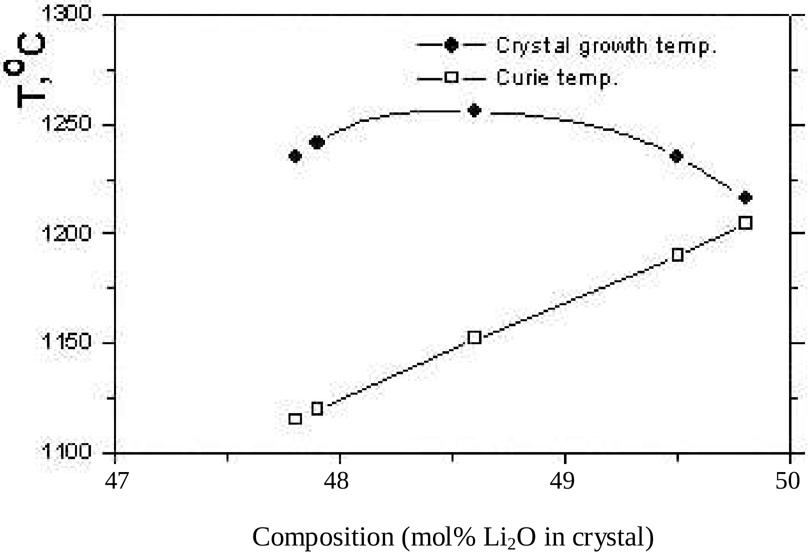

Fig. 2. Dependence of Curie temperature and crystal growth temperature versus $LiNbO_3$ solid solution composition

In Fig. 3 the measured values of the phase-matching temperature T_m and the temperature T_g, that is the temperature at which congruent seed with melt are in equilibrium condition, are plotted as functions of the amount of potassium oxide added in the initially congruent-melt composition. Phase-matching temperature is equivalent to the Curie temperature. It is, therefore, clear, that the addition of potassium oxide in melt results in the same diminution of T_g-T_c, as that of growth from melt with the large excess of lithium.

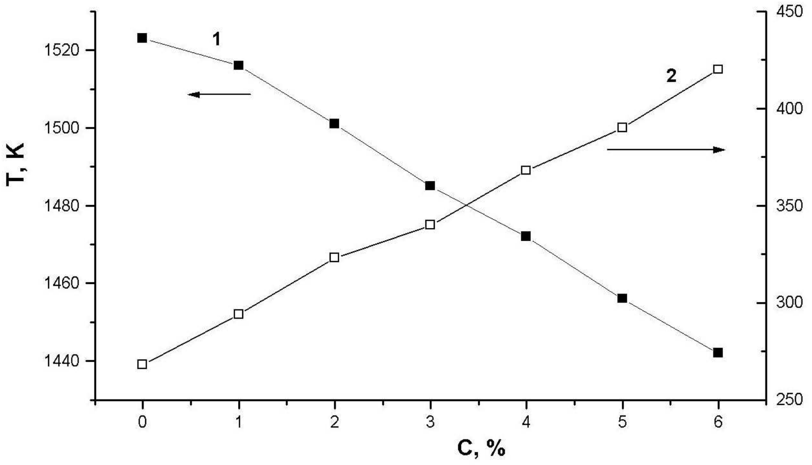

Fig. 3. Dependence of crystal growth temperature (1) and phase-matching temperature (2) versus K_2O concentration.

Thus for effective influence of an electric field on polarisation inversion of domains in lithium niobate growing in [010] direction, the growth from *congruent melt with proper addition of potassium oxide in melt,* constitutes the necessary conditions in our current approaches.

3. Results and discussion

To compare the electric field effect on the growth of PPLN, several crystals were grown using the same growth rate (typically 2 mm/hour). From the grown crystals plates parallel to twin planes were cut out and etched after polishing by a known technique ($HF:NO_3$, 1:2, at T= 90C, 10 min). Without applying alternating electric field, no regular domain structures were found on the crystals which have been grown from congruent composition, nor on the crystals which have been grown from congruent composition with 4 mol. % of potassium oxide addition. But in the crystals grown with application of alternative electric field (the c*urrent polarity is switched every 1-9 min during the growth)* from congruent melt composition with 4 mol. % potassium oxide addition there are well formed domain structures. The modulating electric field was switched on after stabilisation of the crystal growth diameter (beginning of a cylindrical part) and maintained till the end of the growth. At the same time there is no domain structure in a last part of crystal (~ 1-2 mm). This shift corresponds to distance Δx (see. Fig. 1).

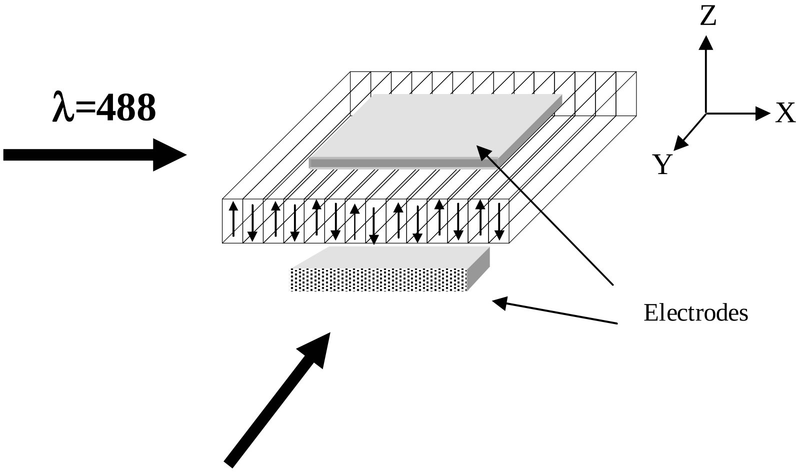

Fig 4. Experimental setup for study of PPLN crystal photoelectric and photorefractive properties. Period of PPLN structure: 50 μm; power of ion-argon laser radiation: 70-100 mW; crystal dimensions: 4.0, 4.3 and 1.7 mm.

The periodicity of the domains corresponds to the alternating frequencies of the applied electric current, becoming larger with a shift apparently with the increase of distance Δx that is related to the temperature gradient in the growth system. As the crystal length increases, the periodic domain pattern eventually disappears in the last mm of the growth, due to the reduction of the effective horizontal field strength. It is anticipated that the ‘chirping’ of the periodic domain structure may be corrected by adjusting the frequency of the driving electric field to compensate for the temperature gradient to obtain uniform periodic structures.

A gradient of temperatures in this growth system was nominally $100^oC\ cm^{-1}$. The actual gradient in the crystal (calculated from Δx) can be estimated to be ~ $50^oC\ cm^{-1}$. The crystals were grown with the speed of 2 mm/hour and at a rotation rate of 12 rpm. The growth bands due to rotation would have period < 3 μm. There is no such strips observable in any grown crystals.

Thus the carried out experiments have shown, that periodically poled structure in lithium niobate crystals is formed during growth process due to direct influence of the applied electric field, instead of perturbations of growth system. The developed technique has allowed to receive PPLN samples with a period 10-200 μm and with useful thickness up to 3-4 mm, which is practically unattainable with traditional techniques. Limitation of the period dimension is determined by several parameters (growth velocity, rotation speed, temperature accuracy and etc.) and is ~3 μm.

3.1. Photoelectric and photorefractive properties

Periodically poled ferroelectric media are useful for the high efficiency and low threshold frequency conversion devices. In addition to this advantage, experiments [10, 11] have shown that periodically poled $LiNbO_3$ crystals are more resistant to photorefractive beam degradation than homogeneously poled crystals. Lithium niobate crystals have a large photovoltaic effect along the polar axis; this effect dominates their photorefractive behavior. In periodically-poled photovoltaic media, neighboring domains generate photovoltaic currents in opposite directions. Thus reduction of the total photovoltaic space charge field can be expected. Because it is this electric space charge field that is responsible for changes in the refractive index through the electro-optic effect, high resistance to photorefractive beam degradation can be expected in periodically-poled photovoltaic media.

The investigations of photoelectric (conductivity, photovoltaic and pyroelectric currents) and photorefractive properties of the obtained PPLN structures (in the sample with 50 μm domain structure) have been carried out using Ar-ion laser (λ=488 nm, P= 70-100 mW). Experimental scheme is shown in Fig. 4. The measurements were carried out using DAQ-system I/O board (AT-MIO-16E10, "National Instruments").

Pyroelectric current was measured when laser radiation (beam diameter <100 μm) propagates along Y axis and scans crystal along X axis. So the light propagates practically only in one domain. Thus the sign of pyroelectric current indicates a direction of spontaneous polarization of the given domain. The investigations of pyroelectric properties of PPLN structures showed the change of sign of pyroelectric current according to change of direction of spontaneous polarization in the domains (see Fig. 5).

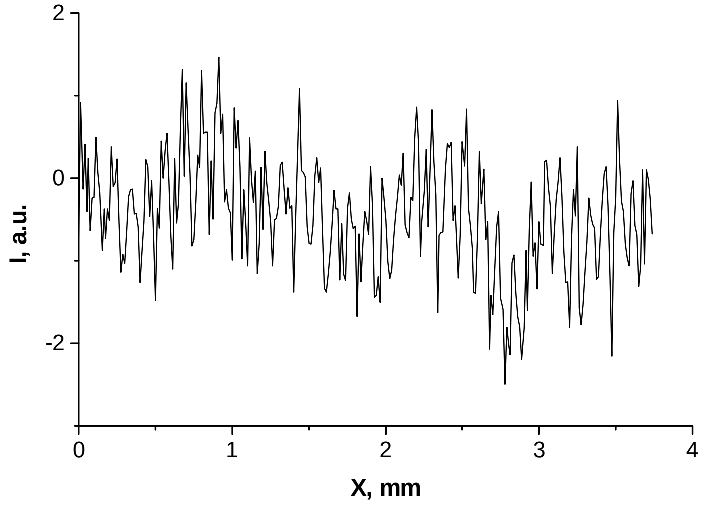

Fig. 5. Pyroelectric current when laser radiation scans crystal along X axis.

Investigations of photovoltaic and photorefractive effects were carried out, when light propagates along Y and X directions. In the first case we actually have a single domain crystal, and in the second case the light propagates through all domains and, thus, the peculiarities of periodic structure become apparent. It was found the significant decreasing of photovoltaic current in PPLN crystals (see Fig. 6.).

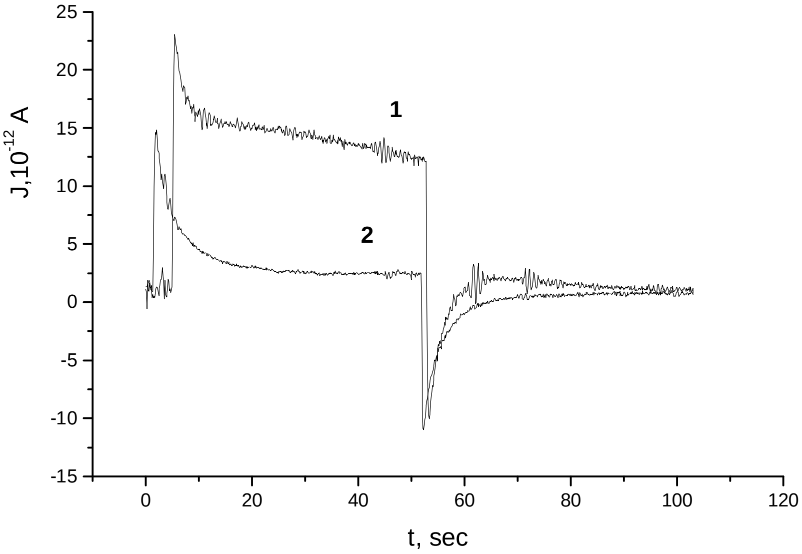

Fig. 6. Photovoltaic current when laser radiation propagates along Y axis (curve 1) and along X axis (curve 2).

For photorefractive effect the direction of photoinduced electric field is determined by a direction of spontaneous polarization of each domain, however photoinduced change of a refractive index does not change a sign as Δn is determined by a direction of an electric field relative to the direction of spontaneous polarization. Nevertheless, it was found significant decreasing of photorefractive effect in PPLN structure as electric fields of the neighbor domains suppress each other due to the small size of the domain (Fig. 7).

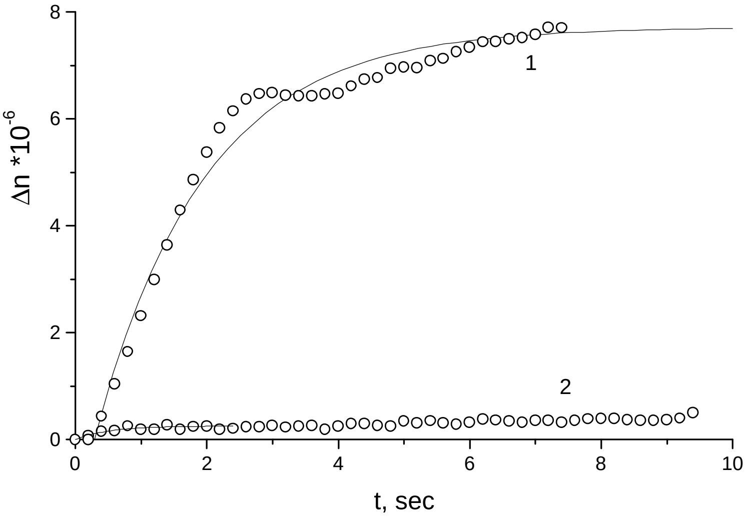

Fig. 7. Photorefractive effect when laser radiation propagates along Y axis (curve 1) and along X axis (curve 2). One can see the considerable suppression of optically induced change of refractive index.

The anisotropy of dark conductivity (up to 2 orders) in Z and X directions has been obtained (ρ_x=2.4 × 10^{14}ohm.cm, ρ_y=3.1 × 10^{12} ohm.cm, and ρ_z=1.5 × 10^{12} ohm.cm). The characteristic times for photovoltaic and photorefractive effects correspond to conductivity in X direction.

4. Conclusion

Periodically poled $LiNbO_3$ single crystals with antiparallel domain configurations have been successfully grown with a [010] oriented seed from a congruent melting composition with 4 mol % potassium addition using a modified Cz geometry. The experiments reported in this paper showed that the polarisation antiparallel domain structure in lithium niobate crystals can be created during growth process by a direct poling technique with electric field of alternating polarity. PPLN structures with period length 10 - 200 μm were demonstrated by this method.

Acknowledgements

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References

[1] J. Armstrong, N. Bloembergen, J. Ducuing, P. Persham, Phys. Rev. **127**, 1918 (1962).
[2] M. Ebrahimzadeh, P. J. Phillips, S. Das, Applied Physics B **72**, 793 (2001).
[3] D. Richter, D. G. Lancaster, R. F. Curl, W. Neu, F. K. Tittel, Applied Physics B **67**, 347 (1998).
[4] J. D. Joannopoulos, R. D. Meade, J. N. Winn, Photonic Crystals: Molding the Flow of Light, Princeton University Press, Princeton (1995).
[5] M. Houe, P. D. Townsend, J. Phys. D **28**, 1747 (1995).
[6] J. Capmany, V. Bermudez, E. Dieguez, Appl. Phys. Lett. **74(11)**, 1535 (1999).
[7] P. T. Brown, G. W. Ross, R. W. Eason, A. R. Poghosyan, Optics communications **163**, 310 (1999).
[8] V. Gopalan, M. Gupta, Appl. Phys. Lett. **68**, 888 (1996).
[9] E. S. Vardanyan, L. M. Kazaryan, R. K. Hovsepyan, A. R. Poghosyan, P. R. Rusyan, Crystallography **44**, 1 (1999).
[10] G. A. Magel, M. M. Fejer, R. L. Byer, Appl. Phys. Lett. **56**, 108 (1990).
[11] D. H. Jundt, G. A. Magel, M. M. Fejer, R. L. Byer, Appl. Phys. Lett. **59**, 2657 (1991).