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学　位　论　文

光学超晶格LN晶体
生长及其非线性光学
效应

（题名和副题名）

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摘要

本论文对无机非线性光学频率转换晶体作了简要的评述，对光学超晶格 $LiNbO_3$ 晶体的生长工艺、形成机制以及光学超晶格 LN 晶体在非线性频率转换方面的应用进行了实验和理论上的研究。

通过不同的温度场设计，有效的降低了固液界面处的无规温度波动，提高了生长过程中畴结构在 LN 晶体中的响应深度和响应持续长度。首次成功的生长了具有连续畴层数超过 1500，具有稳定周期（周期波动小于 2%）的畴层数超过 500 的，用于倍频 Nd：YAG 激光的光学超晶格 LN 晶体（周期为 6.8μm）。

在接近生长层关于周期性生长速率波动的截止响应频率（相应的空间周期为 1μm）的情况下，通过生长参量的调整，我们首次成功的生长了用于兰光发生的光学超晶格 LN 晶体（周期为 3.4μm），连续周期畴层数达到 460。

我们以坩埚中液面深度为调节参量，成功的证实了光学超晶格中正、负畴层厚度的可调节性，在适当的生长条件下，得到了正、负畴厚度基本相等的光学超晶格 LN 晶体（正负畴层厚度相等可使 SHG 的转换效率达到极大值）。

在畴结构形成机制方面,我们进行了如下的研究：

1).在两种具有典型特征的光学超晶格 LN 晶体样品中（其一是具有正负畴厚度基本相等的畴结构，另一个则是正畴厚度近似为负畴厚度的四倍），利用 X-ray 能量色散谱分析了溶质浓度波动的响应特性。

2).引入临界浓度梯度的概念，定性的解释了粗糙畴界面滞后于浓度波动极大的实验事实，揭示了正、负畴厚度不等的原因。

3).利用固液界面中的温度行波波动所引起的界面失稳解释了周期畴结构中的典型缺陷 （A 型长形岛屿畴）。在该缺陷区域内，周期性的温度调制所引起的浓度波动被界面失稳引起的溶质偏聚所掩盖，因而在该

发周期性畴结构。

研究了光学超晶格 LN 晶体用于非线性倍频。基波光源为

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三级放大的 Nd：YAG 泵浦的光参量振荡器，调谐范围为 0.7～2.2μm。利用光学超晶格 LN 晶体，我们验证了准位相匹配过程中倍频转换效率与畴结构周期数的平方关系，获得了在 500 层畴结构下满足该平方关系的实验结果。

引入了“有效周期数”的概念，计算了有效周期数目和基波波长的关系，通过基波波长扫描和在晶体样品的不同偏角下的基波波长扫描进行倍频转换效率的测试，验证了我们的计算结果，证实了畴结构周期的不稳定是影响转换效率的最主要因素之一。在一定的基波波长下，在品质较差的光学超晶格中，其有效畴周期数可以大大的小于实际畴结构周期数。因此通过对有效片畴数的计算可以作为评估光学超晶格 LN 晶体品质的一种有效方法。

通过在不同的晶体偏角下进行基波波长扫描的倍频效率的测量，给出光学超晶格样品的“允许偏角”(tolerance angle)，超过这个角度，非线性倍频转换效率急剧下降。在我们的实验中，对于无增透膜镀层样品，允许偏角大于 10°。

利用周期为 3.4μm 的光学超晶格 LN 晶体样品,通过直接倍频参量光源 360nm 左右的输出，在两个典型的样品中（样品 A 具有 460 层畴结构，样品 B 具有 290 层畴结构），我们分别获得 4.2%和 3.5%的转换效率，兰光输出波长分别为 430nm 和 435nm。这项工作为利用光学超晶格 LN 晶体研制具有重大应用意义的微型兰光激光器奠定了基础。

本文还首次分析了光学超晶格 LN 晶体在超短脉冲的频率转换中的应用可能性。系统的从理论上论证了光学超晶格 LN 晶体在光参量振荡器中的可行性。

我们首先提出了光学超晶格 LN 晶体用于光参量放大（OPA）和参量振荡（OPO）的新的调谐方法，即通过对晶体样品的转动（改变光学超晶格的周期），在满足新的能量守恒（$\omega_3=\omega_1+\omega_2$）和动量守恒（$\vec{k}_3=\vec{k}_1+\vec{k}_2+\vec{g}$）的条件下，实现光参量过程中的频率调谐。

通过对信号波(或空闲波)波长与光学超晶格周期的相互关系曲线（即调谐曲线）的计算，我们获得了不同周期和不同泵浦频率下 OPO 的调谐范围以及角度灵敏性等重要参数。在泵浦波长为 750nm 到 950nm

之间，从调谐曲线上可以得到一个新的非线性光学现象，即泵浦波可以同时与两组信号光和空闲光满足能量守恒和动量守恒，即可以同时发出两组信号光和空闲光，这个现象如能被实验所证实，不仅具有理论上的意义，而且具有重要的实用价值。

我们论证了光学超晶格 LN OPO 具如下特性：

1).具有很高的非线性频率转换效率和较低的泵浦功率阈值。

2).可以在 LN 晶体的整个范围内获得利用，尤其重要的是可在兰光或兰绿光范围内进行调谐。这是单畴 LN 中所不能达到的。

3).可以灵活的选择 OPO 的角度灵敏性和调谐范围。因而 OPO 可以获得很高的工作稳定性。

4).具有大的调谐范围，在一定条件下（即一定的泵浦频率和光学超晶格周期），几乎可以实现全透光波段的调谐，这时 OPO 具有非常高的角度灵敏性。

Abstract

In this thesis, the development of inorganic nonlinear optical crystal for frequency conversion has been reviewed. The growing technique of $LiNbO_3$ crystal with periodic domain structures (PDS)(i.e. optical superlattice), the PDS's formation mechanism and the material's application in nonlinear optical frequency conversion have been studied both experimentally and theoretically.

THe random temperature fluctuations at the solid-liquid interface(SLI) have been effectively suppressed through our efficient temperature field designs. It results in good reponse of PDS in depth and in length as the periodic temperature fluctuations during the crystal growth in an asymmetry temperature field. We have firstly succeeded in growing LN crystal with a contineous domain structures of over 1500 domain laminas, in which over 500 domain laminas are of good periodicity (the period fluctuation is less than 2%) and in period of 6.8 μm.

We firstly succeeded in growing LN crystal with PDS in period of 3.4 μm which is near the limiting response frequency of the growth striations as the periodic fluctuations of growth rate in an asymmetry temperature field (the spatial period is about 2 μm). The LN crystal with PDS in period of 3.4 μm can be used for the generation of blue light through direct frequency doubling. The number

of domain laminas we achieved in the crystal is 460.

The adjustibility of relative thickness of the positive and the negative domain laminas has been succeedly achieved in our experiments by using the melt depth in crucible as a adjusting parameter. Under suitable conditions, the LN crystals with PDS, in which the thickness of the positive domain laminar is nearly equal to that of the negative, have been obtained. (the SHG efficiency can be maxima in the case of equality between the positive and the negative domain laminas).

We have studied the following aspects on the fomation mechanism of the PDS:

1). The solute concentration distribution in PDS have been measured by energy dispersive X-ray analysis in two typical samples of LN crystal with PDS, in which one has the domain structures in which the thickness of the positive domain is nearly equal to that of the negative, and the another the thickness of the positive domain is 4 times larger than that of the negative. The response characteristics of the PDS as the periodic fluctuations of solute concentration have been systematically studied.

2). The critical concentration gradient has been introduced for discussing the retardation of rough domain boundary as the maxima of solute concentration profile and the origin of the inequality between the thickness of the positive an dthe negative domain laminas has been qualitatively interpreteted.

3). The origin of the typical defects (for example, type

A island-like domain) have been discussed through the SLI instability which is caused by the sinusoidal travelling temperature fluctuations at SLI. Inside the defect, the solute concentration fluctuations which are induced by the periodic modulation of temperature fluctuations has been concealed by the solute aggregation caused by SLI instability, and thus the PDS can not introduced inside the defect.

The frequency doubling of 1.064 μm of Nd:YAG laser and 0.86 μm spectrum by LN crystal with PDS has been studied. The quadratic relationship between the SHG efficiency and number of domain laminas in QPM process was verified up to about 500 domain laminas. The relationship between effective number of domain laminas and the fundamental wavelength was calaulated. The calculation results are in good correspondence with the experimental results which were measured by fundamental wavelength scanning at fixed position of sample or at different rotation angle of the sample. It shows that the calculation of effective number of domain laminas can be an efficient method for evaluating the quality of the domain structures in LN crystals.

The SHG efficiency measurement by fundamental wavelength scanning at different rotating angle can offer the tolerance angle of sample rotation beyond which the SHG efficiency decreases abruptly. In our experiments, it is baout 10 ° with no antireflecting coating on the sample.

The generation of blue light through direct frequency doubling of 860 nm has been achieved in our two typical samples. Sample A and sample B have the number of domain laminas of 460 and 290 respectively, and the SHG efficiency are 4.2% and 3.5% in the two samples. The work for the generation of blue light is very important for our future research of compact, all-solid blue laser.

The possible application of LN crystal with PDS on frequency doubling of short pulse was discussed. The theoretical analysis for optical oscillator (OPO) was systeematically given.

A new tuning method in OPO was proposed firstly, which is through rotating the sample (or changement of the period of the optical superllatice).

The tuning range , angle sensitivity and other useful parameters at different pumping frequency can be obtained through the calculation of the tuning curves. New phenomenon, which is that two groups of signal and idler waves can be generated synchronically when pumping wavelength is between 750 nm to 950 nm, was firstly discovered.

Some characteristics of the optical superllatice LN OPO have been summarized as follows:

1). High efficiency and low pumping power threshold.
2). Phase-matchable in entire transparent range(QPM).
3). Easy adjustibility of angle sensitivity and the tuning range.
4). Large tuning range.

Contents

Chapter 1. Introduction to the development of nonlinear optical crystals

1. Introduction

Considerable progress has been made in the area of nonlinear optics because of its wide applications in optical communications, integrated optics and optical information systems. Both classes of materials, inorganics and organics, have been developed and have advantages and disadvantages. Inorganic crystals are good candidates for high power laser applications in far-infrared region. Organic crystals have shown high-order polarities many times larger than their inorganic counterparts in short wavelength region. Hundreds of materials have been discoverd in the past. To date, only a handful of these materials are routinely used in lasers and nonlinear optics. Some inorganic crystals for different applications are briefly listed below:

A. Laser crystals(numbers given below are wavelengthes in µm)

(1). Untunable laser crystals

0.6943: ruby($Cr:Al_2O_3$)

1.060: Nd:YAG, Nd/Cr:GSGG, Nd:YLF, Nd:YAP

1.08+1.34(double wavelengthes): Nd:YAP

0.53(self-doubling of frequency): NAB, NYAB

2.08: CTH:YAG (where CTH=Cr,Tm,Ho)

2.94: Er:YAG, Er:YAP

(2). Tunable laser crystals

0.66-1.20: $Ti:Al_2O_3$

0.71-0.82: $Cr:BeAl_2O_4$

1.75-2.5: $Co:MgF_2$

(3). Semiconductive laser materials

0.70-0.91: GaAs/GaAlAs

1.1-1.6: InGaAsP

(4). Colour center laser crystals

LiF:(including F_2, F_2^+, F_3^+, F_2^-)

B. Linear and nonlinear optical crystals

(1). Frequency conversion crystals

KTP, BBO, LBO, $LiNbO_3$, $MgO:LiNbO_3$, LAP, Urea,$LiIO_3$, KDP, KD*P,CDA

(2). Photorefractive crystals

$BaTiO_3$, $KNbO_3$, $Fe:LiNbO_3$, KNSBN, BSO, BGO, Fe:KN

(3). Electro-optical crystals

$LiNbO_3$, KD*P, $LiTaO_3$

(4). Magneto-optical crysrtals

TGG, YIG

(5). Others: including photoconductive, opto-elastic, infrared, acoustic-optical crystal, etc.

C. Substrate crystals

(1). Used in SAW: $LiTaO_3$, $LiNbO_3$

(2). Integrated circuit (IC): Si, α-Al_2O_3

(3). Opto-electric integrated circuit: Si, $LiNbO_3$, GaAs

(4). High T_c superconductive film: $LaAlO_3$, $SrTiO_3$, MgO, ZrO_2

2. Growth and characterization of nonlinear optical crystals suitable for frequency conversion

Since the discovery of second-harmonic generation with a ruby by Franken et al(1), nonlinear optical mixing has been widely recognized as an effective method for generation of the high power coherent radiation in spectral regions where the general laser sources are unavailable. With a single fixed frequency laser, the frequency mixing and optical parametric oscillation can provide fully tunable radiation throughout the UV to the IR(2)(3). The widespread use of nonlinear optical devices has been limited by the lack of materials with suitable characteristics. Substantial progress has been made in the development of nonlinear optical materials recently. Novel materials having attractive properties are being discovered at a rapid pace(4-8), with advances in crystal growth technology which makes possible the commercial development of promising materials such as Urea, magnesium-oxide doped lithium niobate(MgO:LiNbO$_3$), potassium niobate(KNbO$_3$), potassium titanyl phosphate(KTP), and barium metaborate(BBO), etc. Preliminary experiments performed on these materials have been very encouraging(9-10) and will undoubtly lead to wide-spread applications of these crystals in nonlinear optics and relevant devices.

In what follows, we shall concern with bulk materials and especially with materials of modulated structures(11-12) which is the subject of this paper. The growth and applications of crystal fibers(13), though important, will not be discussed. Likewise, we shall not concern ourselfs with organic materials. A comprehensive review of it can be found in the work by Chemla and Zyss(14).

2.1. Material consideration and characterization

Characterization of nonlinear optical crystals can be devided into two types: the measurement of optical properties and the investigation of growth defects. The former includes the measurements of intrinsic physical properties which are directly relevant to optical ferquency conversion. The latter includes the study of growth defects, such as twinning, phase homogeneity, mechanical stresses, inclusions.... etc. Many standard techniques such as trace chemical analysis, etching and decoration, x-ray topology, electron microprobe analysis....etc, can be used for defect charactrization. The use of these techniques for crystal characterization has been reviewed by Landise(15). We here shall primarily concern with the characterization of the optical and other relevant physical properties of nonlinear crystals.

The characterization of a nonlinear optical material includes the quantitative and qualitative specification of these parameters. A general set of such parameters are given below. The underlying physical principles for the selections of these parameters have been discussed in standard references[16,17].

d_{eff}^2/n^3 is the nonlinear figure-of-merit($(pm/v)^2$). The nonlinear coefficient d is defined by the expression $P=2\varepsilon_0 dE^2$.

Γ_{max} is the single shot optical damage threshold. It is usually given as an intensity(GW/cm^2) or an energy fluence(j/cm^2). For certain materials(e.g. Urea) which have a accumulative damage property that depends on the duration of irradiation, this is not a useful charactrization. For CW operation, a corresponding CW damage threshold can be defined.

$n_x(\lambda), n_y(\lambda), n_z(\lambda)$. are the refractive indices along the principal dieletric axes. They define the material dispersion and birefringence. In a phase-matched nonlinear optical process in a crystal, birefringence is used to compensate for material dispersion. A large birefringence is needed for phase-matching near the obsorption cut off.

ρ is walk-off angle. It is the angle between the phase velocity direction and energy propagation direction of the extraordinary wave in an anisotropic medium. A large birefringence implies a large walk-off angle. In certain experimental configurations, it places an upper limit on the length of the crystal that can be used for ferquency conversion. In uniaxial crystals, the angle peaks at about

45° from the optical axis.

β_T is the temperature sensitivity, $\partial(\Delta K)/\partial T\,[\mathrm{cm}^{-1}/^{\circ}\mathrm{C}]$. where K stands for wave vectoer. It is an intrinsic parameter which describes the material tolerance to temperature variation for a particular frequency conversion process. It is related to the temperature bandwidth(FWHM) by $1\Delta T=4A/\beta_t$, where A=1.39.

β_θ is the angular sensitivity, $\partial(\Delta K)/\partial\theta\,[\mathrm{cm}^{-1}/\mathrm{mrad}]$. It is analogous to the temperature sensitivity given above. For critically phase-matched process, a large birefringence implies a small angular bandwidth. Phase-matched frequency conversion processes of low angular sensitivity can be obtained in a crystal which has a broad transparancy and a small birefringence.

β_λ is the spectral sensitivity, $\partial(\Delta K)/\partial\lambda\,[\mathrm{cm}^{-1}/\mathrm{A}]$. It gives the spectral bandwidth that can be efficiently converted. It is useful in designing ferquency convertors of broad bandwidth radiation such as picosecond or femtosecond pulses.

ΔV_g^{-1} is the reciprocal group velocity mismatch(fs/mm), $\partial K_s/\partial\omega_s - \partial K/\partial\omega_f$, where s and f stand for the second-harmonic and fundamental frequency. It represents approximately the temporal broadening of the second-harmonic pulses in a 1mm thick nonlinear crystal caused by the nonlinear interaction. It is usually significant only in frequency conversion of subpicosecond pulses.

$\sigma(\lambda)$ is the optical absorption of the material(cm^{-1}) within its transparancy range. It is a measure of the intrinsic passive loss of laser light in the material. A largr absorption at the pumping wavelength generally implies signicant heating of the material by the pumping laser.

ΔT_F is the fracture temperature as discussed in reference(18). It is the temperature difference at which an ideal thin plate with 100 µm defect fractures. It gives a quantitative measurement of the thermal loading capacity of a crystal and is of extreme importance in high average power applications.

Other intrinsic and extrinsic parameters should be specified in the comparison of different nonlinear optical crystals. The mechanical properties can be specified by the fracture toughness(K_c), Mohs hardness and elastic constant. Physical and Chemical charateristics that worth considering are the presence of ferroelectric phase transitions which may lead to domain formations, compositional inhomogeneity, melting point and susceptibility to attack by moisture and common solvents. Crystal availability can be assessed by considering the crystal growth technique, growth run time, typical crystal yield(i.e. crystal size), predominent growth defects and post-growth processing(such as poling and detwinning). Crystal that is difficult to growth with high yield will not provide sufficient economic incentive for its commercial development unless it possesses unusually good optical characteristics. A case in point is KDP where despite the enormous expenses, sustained international efforts were devoted to its development. By the same token, favorable growth characteristics can go a long way in bringing a nonlinear optical material with modest characteristics into everyday use. The longevity and popularity of KDP(and its isomorphs) is a typical example.

The full characterization of a nonlinear optical material will involve the proper documentation of these parameters. Techniques for the measurement of these parameters are numerous and can readily be found in literature. The review of these techniques will not be presented here.

2.2. Criteria for useful nonlinear crystals

There is no "ideal" nonlinear crystal in our desired applications. The applicability of a particular crystal depends on the nonlinear interaction process used, the characteristics of desired device and the pumping laser. For a given application, special material properties are required but it may not be significant in other applications. For instance, efficient doubling of very high power lasers having poor quality requires a crystal with large angular bandwidth(18). A crystal which has a smaller nonlinearity but allows noncritical phase-matching will perform better than one which is more nonlinear but is critically phase-matched. On the other hand, for the doubling of fetmosecond optical pulses, the prefered crystal will be the one with large nonlinearity so that a very thin crystal can be used to avoid dispersive broadening of the second-harmonic output pulses.

For a material that has favorable features such as large nonlinearity, high damage threshold, favorable crystal growth habits etc., an application can always be found that uses the crystal efficiently. From the material point of view, only general criteria can be established to gauge the usefullness of a nonlinear crystal. For specialized applications where device performance requirements are well estabilished, quantitative criteria for the selection of a suitable nonlinear crystal can be obtained(18). The fully qualitative requirements of the criteria for the nonlinear frequency conversion material for various device applications are listed in table 1.

Table 1. The criteria of nonlinear crystals for various applications

Applications	*Requirements for crystal properties*
Efficient SHG and up-conversion:	*Easy to phase match, high nonlinearity.*
Optical parametric oscillation:	*Broad tranparency, large refringence and high damage threshold.*
Short pulse generation:	*High nonlinearity.*
High average power frequency conversion:	*Good thermal characteristics and large angle acceptance.*
Low average power and CW devices:	*High nonlinearity, easy to phase match and good optical quality.*
Laser fusion:	*Low threshold power, good UV transparency and high damage threshold.*

2.3. Recent advances of nonlinear crystals for frequency conversion

Some new nonlinear crystals suitable for frequency conversion using second-order nonlinearity have been recently explored for the generation of coherence light ranging from UV to mid-IR. In table 2, we have listed some properties of several new nonlinear crystals.

Table 2. Some properties of several nonlinear crystals(all data is for 1064 nm)

crystal:	KDP	BBO*	KTP
point group	42m	3m	mm2
birefringence	n_e=1.4599	n_e=1.5425	n_a=1.7367
	n_o=1.4938	n_o=1.6551	n_b=1.7395
			n_c=1.8305
transparency(um)	0.2-1.4	0.19-3.3	0.35-4.4
Γ_{max}	3.5 GW/cm^2	13.5 GW/cm^2	15.0 GW/cm^2
nonlinearity	d_{36}=0.39	d_{33}=1.6	d_{31}=6.5
(Pm/V)		d_{31}=0.08	d_{32}=5.0
			d_{24}=7.6
			d_{15}=6.1
			d_{33}=13.7

(continuing Table 2)

crystal	KNbO$_3$	LiNbO$_3$	BNN
point group	mm2	3m	mm2
birefringence	n_a=2.2200	n_e=2.2325	n_a=2.2567
	n_b=2.1196	n_o=2.1560	n_b=2.2580
	n_c=2.2574		n_c=2.1700
transparency(um)	0.4-5.5	0.35-5.0	0.37-5.0
Γ_{max}(MW/cm^2)	----	120	40
nonlinearity	d_{31}=11.3	d_{22}=2.3	d_{31}=-12.8
(Pm/V)	d_{32}=-12.9	d_{31}=-4.8	d_{32}=-12.8
	d_{24}=11.9	d_{33}=-29.7	d_{24}=-12.8
	d_{33}=-19.6		d_{33}=-17.6

**: Datas are taken from" Tech. Digest Seri." v.8(1988) 285*

We shall present here a critical review on some of the most important crystals including BBO,KTP and KNbO$_3$, etc. Novel devices using wave-quide and the self-frequency-doubling crystal of NYAB are discussed briefly. Quasi-phase-matching theory in LiNbO$_3$ which is the main topic of our research will be discussed in detail in a seperate section in this chapter.

BBO crystal: It was discovered by the Fujian Institute of Research on the Structure of Matter in 1985(19). Since then, it has been widely used for the generation of UV sources from the up-conversion of dye lasers and Nd:YAG lasers. BBO has promising features of wide transmission ranges(189nm-3000nm), high nonlinearity (about 4 times of

KDP), high damage threshold and it is phase-matchable within its whole transparent regime. Furthermore, BBO has very wide tunability in optical parametric oscilltor which makes BBO to be an excellent crystal for tunable solid-state lasers in UV,Visible and near IR.

BBO crystal is an uniaxial crystal with an effective nonlinearity given by $d_{eff}=d_{22}\cos Q$(for type I, optimal value) which represents a vanishing d_{eff} when 90° angle is achieved. This unfavorable 90 degree phase-matching of BBO limits its applications in deep UV (189-219 nm) sources generation.

KTP and $KNbO_3$ crystals: KTP is a superior material for various nonlinear optical applications. It is not hydroscopic and has large nonlinear optical coefficients, high damage threshold, has small beam walkoff and large temperature and angular bandwidths. In addition KTP has large electrooptic coefficients and low dielectric constants which make it potentially useful for electrooptic applications. $KNbO_3$ has the same symmetry, mm2, with that of KTP. It is high nonlinearity but difficulty to growth. Noncritical phase-matching may be achieved in these two crystals. They are good condidates for the generation of blue light and the tunable mid-IR solid-state lasers.(20-24)

Self-frequency-doubling crystals: There are two crystals which have been recently studied as self-frequency-doubling materials, $Nd:MgO:LiNbO_3$ and neodymium yttrium aluminum borate(NYAB). The NYAB crystal particularly has the borate(NYAB). The NYAB crystal particularly has the potential application for miniature lasers. It has a nonlinear coefficient 3 times than that of KDP and has the comparable emision gain and mechanical properties as that of Nd:YAG. Flash-lamp and dye-laser pumped NYAB oprated in pulsed mode and Diode-pumped CW and Q-switched NYAB are reported(25-26).

Wave-guide SHG: Direct frequency doubling of diode laser was reported in wave-guide $LiNbO_3$ using Cherenkov effect(27) and guasi-phase-matching method.(28-29)

3. Quasi-phase-matching (QPM)

Quasi-phase-matching (QPM) was the first technique suggested by Bloembergen and Armstrong in 1962 for compensating refractive index dispersion(30). This technique may be applied to isotropic materials for nonlinear interactions or to anisotropic materials in which some nonlinear process are not phase-matchable. By modulating the sign of the nonlinear coefficient at odd multiples of the coherence length in LN with PDS, the phase matching may be achieved with the effective coupling reduced by a factor of $2/\pi$ in comparison to that of the common phase-matching crystal. However conversion efficiency may be largely enhanced by the number of modulating periods in LN crystal and by the usage of the largest nonlinear coefficent, d_{33}, of crystal (it is not usable in uniform LN crystal). Thus an enhancement factor of $23N^2$ for periodic domains may be achieved theoretically, where N is the number of domains in the crystal(31).

3.1. *The QPM theory*

Two ways for presentation of the QPM theory in LN crystal were given by Xue(32) and Van der poel(28). The first is the comparison of SHG intensity in both QPM technique and that in the e+e—>e process in single domain LN crystal.(32) It gives the relation of :

$$I(2\omega)/I_0(2\omega)=N^2 \qquad \ldots(1.1)$$

Where $I(2\omega)$ is the intensity of second-harmonic wave for QPM technique and the $I_0(2\omega)$ indicates the SHG intensity for a crystal of one coherence length, $I(2\omega)$ is given by:

$$I(2\omega)=\frac{8\pi c d_{33}^2}{(n_{2\omega}^2-n_\omega^2)^2} T^2R^4E_\omega^4 \left|\sin\left(\frac{\pi l'}{2l_c}\right) \sum_{m=1}^{N} (-1)^{m-1}\exp\left\{-i(m-1)\frac{\pi l'}{l_c}\right\}\right|^2 \qquad \ldots(1.2)$$

for the case of $l'=l_c$, we have:

$$I(2\omega)=\frac{8\pi c d_{33}^2}{(n_{2\omega}^2-n_\omega^2)^2} T^2R^4E_\omega^4 N^2 \qquad \ldots(1.3)$$

The second way is the SHG output power comparison between the QPM technique and the hypothetical phase-matching process using d_{33} in single domain LN crystal of equal interacting length, the results is:(28)

$$P(2\omega)/P_h(2\omega)=I^2\cdot G^2 \qquad \ldots(1.4)$$

In the case when the QPM condition which is satisfied in LN crystal with periodic domain structures, T=1, and $G=2/\pi$. Thus equation(1.4) shows that the effective nonlinear optical coefficient, through the QPM technique in LN crystal using d_{33}, is $2/\pi d_{33}$.

3.2. Applications of LN crystal with periodic domain structure

QPM in $LiNbO_3$ crystal with periodic laminar ferroelectric domain structures has many advantages in some nonlinear optical interactionss:

1). It has high nonlinearity, d_{eff} = 22pm/V, which is the largest in crystals listed in table 2. Thus the interacting length can be reduced to about 1/4 that of using d_{31}.

2). It's optical damage threshold can reach to several GW/cm^2 with doping of MgO(33). It is comparable with that of KDP.The improvement of optical damage threshold of $LiNbO_3$ with the periodic domain structures has also been reported(34). Therefore, with the careful choice of dopant and the formation of such domain structures, it is possible that the great improvement in optical damage threshold could be achieved.

3). In its entire transparency range of $LiNbO_3$, The QPM can be achieved. Whereas in the case of single domain, it is not phase-matchable by the birefringence in short wavelength near absorption cutoff. Quasi-phase-matching method enlarges the applicable frequency range of $LiNbO_3$ in which the most important is in blue, and blue green wavelength range.

4). The walkoff angle, which existed in critical phase-matching in general crystals, could be not considered in quasi-phase-matching. The upper limit on the length of the crystal due to walkoff angle thus does not exist.

5). The growth characteristics of the $LiNbO_3$ with periodic ferroelectric domain structures is the same as that of growing $LiNbO_3$ crystal. Twins, inclusions and cracks are avoidable, and that crystal growth parameters are easy to control. Though there are additional difficulties in the formation of the periodic domain structures in response to the periodic temperature fluctuations.

The potential applications of the $LiNbO_3$ with periodic domain structures can be summarized as following as compared with table 1:

1). High efficient harmonic generation and up-conversion. High nonlinearity in LN crystal through using d_{33} makes it more competitive with other nonlinear optical materials in the visible and the mid-IR.

2). Low average power/ CW devices

Miniaturized sources of coherent blue or/ blue green radiation can be produced by frequency up-conversion of the infrared radiation of diode laser. Direct upconversion of diode laser radiation and the method using the diode laser to pump a solid-state laser which is then upconverted are possible. In each case, the challenge is to find small size and economic combination of nonlinear materials and lasers for efficient frequency upconversion. The QPM in LN crystal, with its high nonlinearity, low angular sensitivity and relative short interacting length of the crystal, is very efficient in direct frequency doubling of diode laser for the generation of blue light. In table 4 has listed the nonlinearity of some nonlinear crystals and the LN crystal with PDS which were used for the generation of blue light.

Table 4. Nonlinear crystals for compact blue laser$^{(35)}$

Crystal:	KTP	KN	LN(QPM)
Nonlinearity:	d_{31}=6.5	d_{31}=16	d_{33}=22
(pm/V)	d_{32}=5.0	d_{32}=20.5	

3). Optical parametric oscillator

As aforementioned, quasi-phase-matching can be achieved in entire tranparency range of $LiNbO_3$. Its damage threshold can also be improved by carefully choice of dopant and the formation of domain structures. It gives the possibility of the LN crystal with PDS for optical parametric oscillation through QPM method. Its high nonlinearity can reduce the pump power threshold and the tuning range of this kind of OPO can be made down to blue or blue green region with carefully choice of pumping. (it is very difficulty for tuning range down to 600 nm in single domain LN OPO).

4). Short pulse generation

Two factors which limit the doubling of ultrashort pulses are the phase-matching bandwidth of the crystal and the group velocity broading of the SHG pulse via nonlinear interaction. Reduction of crystal length will allow a larger portion of the pump spectrum to be converted. Thus the high nonlinearity of material is very important for short pulse frequency conversion.

In the following, we shall systematically discusse our present researches on the growth of $LiNbO_3$ crystal with good periodic domain structures with large number of domain layers, and its applications in high efficient frequency conversion, blue light generation and optical parametric oscilltor. Each subject is given in a separate chapter in this thesis, and the review on each topic is presented in the corresponding chapter.

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Chapter 2. Growth of $LiNbO_3$ crystal with periodic ferroelectric domain structures

1. Introduction

2. The formation of periodic domain structures in LN crystal

  2.1 The formation of periodic striations

  2.2 Growth straitions and ferroelectric domain structures

  2.3 The limitting frequency of PDS response to the tempreature fluctuations

3. The grougth of LN crystal with PDS

  3.1 Requirements for tempreature field and tempreature field design

  3.2 The response of the PDS as the interface fluctuations

4. The perfection of the PDS in LN crystal

  4.1 The achievement of the equality between the thickness of positive and negtive domains

  4.2 The defects in the PDS in LN domains

5. Conclusion remarks

1. Introduction

We have discussed the QPM method in chapter 1, in this chapter we shall discuss the growth of LN crystal with periodic domain structures (PDS) in detail. Some features of the crystal, such as the number of domain laminas, the regularity of the period and the equality between the thickness of positive and the negative domain laminas, are very important for characterizing LN crystal with PDS for nonlinear optical applications. Thus the growth of the crystal with PDS has been the main topic in our group since 1980. We have listed in table 1 the progress in the growth of LN crystal with PDS till 1991. The numbers of the domain laminas in the figure are those in which the period fluctuation is less than 2%.

Table 1. The progress in number of domain laminas.

Units	*Number*	*Wavelength(nm)*	*Year*
Nanjing Univer.	*50*	*1064*	*1980*
Nanjing Univer.	*200*	*1064*	*1982*
Franhofer Inst.	*50*	*1064*	*1985*
Stanford Univer.	*230*	*860*	*1990*
Nanjing Univer.	*500*	*1064*	*1990**
Nanjing Univer.	*460*	*860*	*1991**

*: In this paper.

2. The formation of periodic domain structures in LN crystal

The growth striations are harmful to most melt-grown single crystals and therefore should be eliminated growth striations for obtaining a crystal with high degree of homogeneity. But it was found that the direct relation between growth striation and the structure of the ferroelectric domain in LN crystal is existed.(1,2) In this section, we will give an account on our experimental results on the growth striations and the PDS investigations in LN crystal.

2.1. The formation of growth striations

The solute concentration at solid-liquid interface(SLI), during crystal growing, is equal to the product of the average solute concentration in liquid and the effective distribution coefficient,(3) where the latter is determined by the growth rate and the boundary layer thickness.

The fluctuation of microscopic growth rate will cause the fluctuation of solute concentration. Thus, the growth striations give a useful built-in record of the interface shape at any point within the crystal and are widely employed in the study of the microscopic growth rate and the morphology of solid-liquid interface.(4)

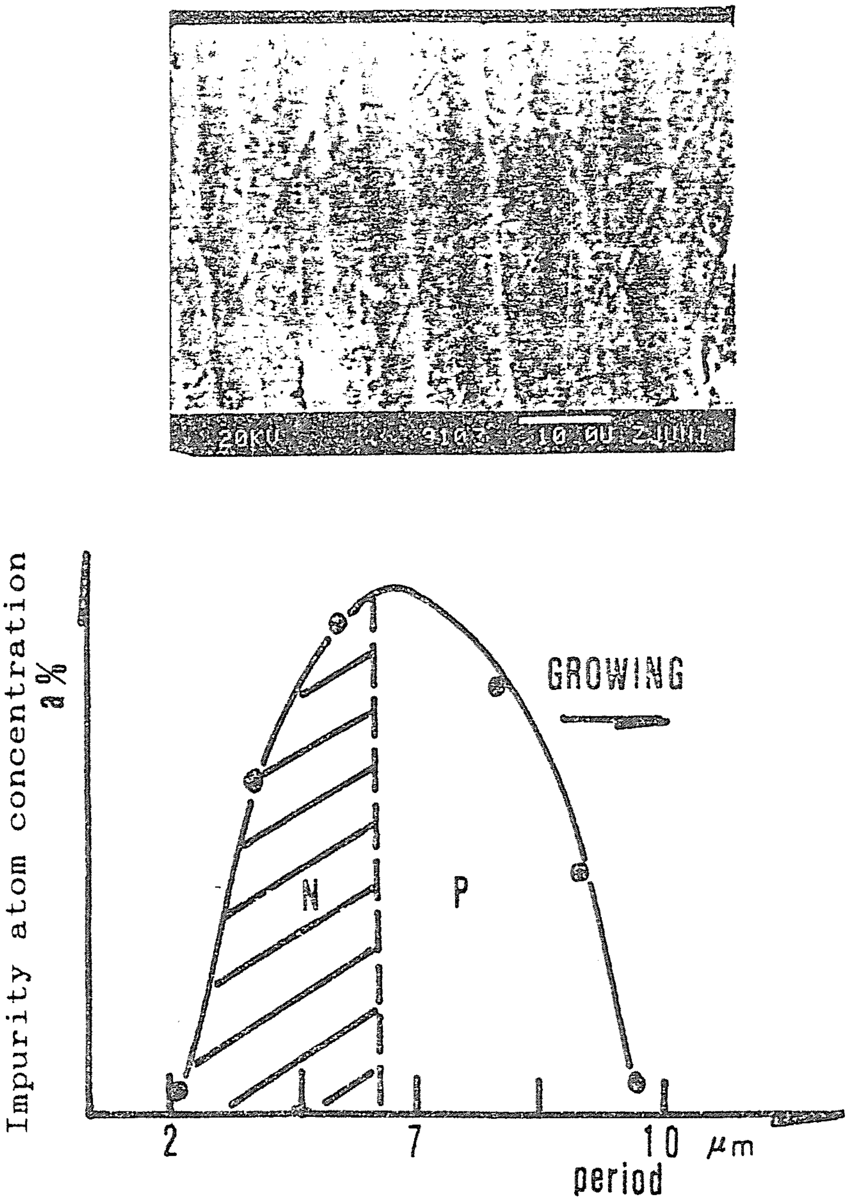
The rotational growth striations are caused by the displacement of the rotational axis of the growing crystal from the symmetry axis of the temperature field in which the periodic fluctuations of temperature are existed during crystal growth, thus the fluctuations of growth rate and solute concentration within the crystal are produced. In all discussions given in this chapter, we will only refer to the relation between the rotational growth striations and the PDS in LN crystal growth.

2.2. Growth striations and ferroelectric domain structures

Perhapes for the reasons of the valence of solute ion and its radius which is different from that of the base material ion, the spatial solute concentration profile induces the spatial charge field distribution in the as-grown LN crystal. The spatial charge field then induces the orientation of spontanieous polarization along the polar axis which is c-axis in LN crystal. The previous works in our group(2) have shown the one-to-one correspondence between the striations and the temperature fluctuations. The relation between the solute concentration profile and the ferroelectric domain structures is also demonstrated by energy dispersive X-ray analysis.

In our works, we choiced two typical samples for experiments. Sample A has a structure in which the thickness of positive domain laminar is nearly equal to that of the negative, as the photograph shown in fig.1. Sample B has a structure in which the thickness of positive domain laminar is about 4 times larger than that of the negative, which are shown in fig.2. The solute concentration distributions were measured by energy dispersive X-ray analysis . For the two samples, their corresponding solute concentration are also shown in fig.1 and fig.2 respectively.

In fig.1, the concentration profile is similar to that given in our previous works.(2) Domain boundaries are found near the maxima and the minima of the curve. In positive domain area, the concentration decreases and its gradient



1. The photograph and solute concentration distribution sample A.

is negative; in the negative domain area, however, the concentration increases and its gradient is positive. But in fig.2, the above conclusions is not exactly correct. In the positive domain area, the concentration gradient is not always negative near the maximal scope of the curve. The deviation of the boundary from the maxima is certainly existed.

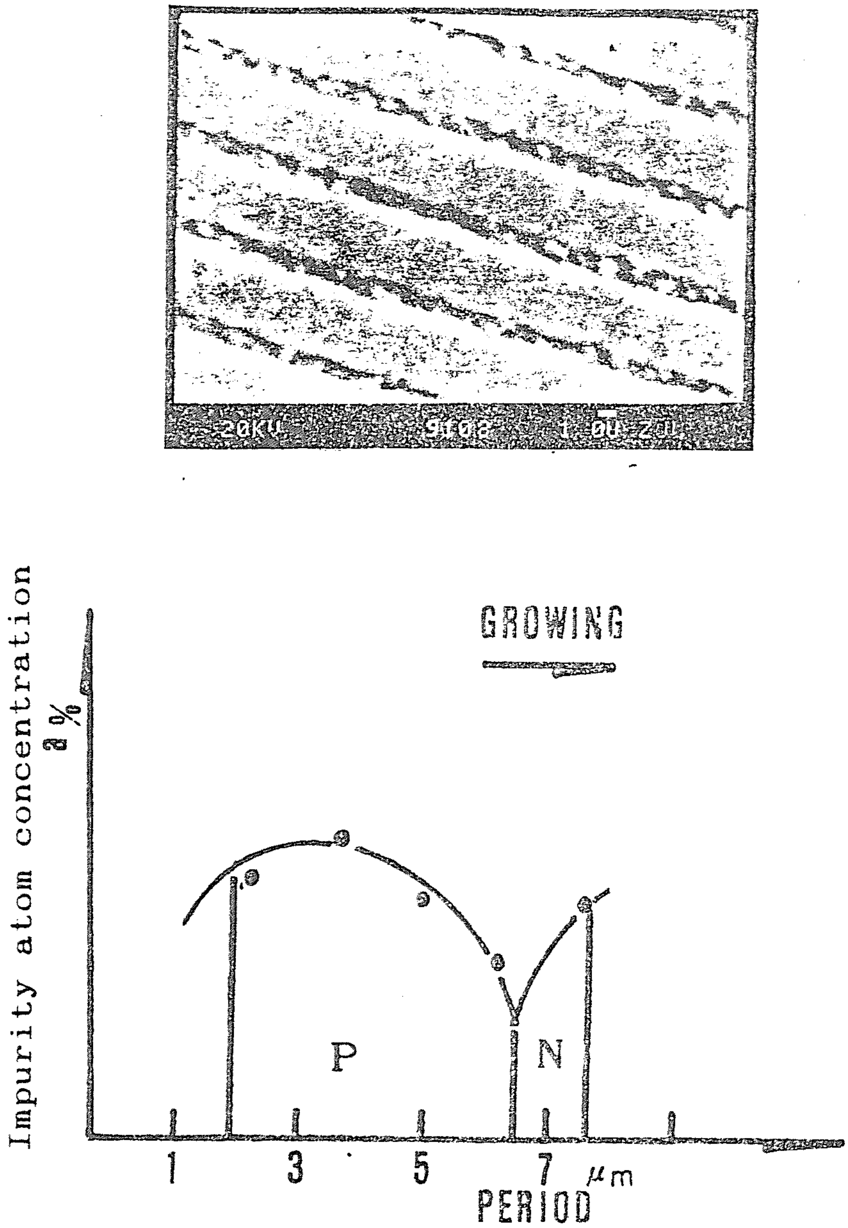


Fig. 2. The photograph and solute concentration distribution in sample B.

To interprete the results, the so-called " critical concentration gradient" where the domain boundary occurs will be introduced here. Two types of sign inversion of concentration gradient, i.e., the abrupt change of concentration gradient at the minima and the gradual change at the maxima, are existed in the profile. An abrupt change corresponds to a smooth domain boundary and the gradual change corresponds to a rough boundary, as shown in fig.3.

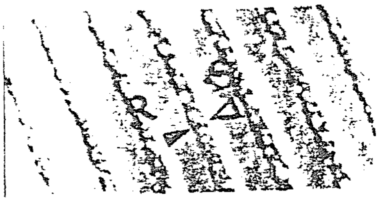


Fig. 3. The photograph of the smooth and rough domain boundaries.(1500X)

For gradual change of concentration gradient, the energy barrier for achieving the reversal of the domain must be overcome by the spatial charge electric field at where it corresponds to certain concentration gradient, i.e., is the critical concentration gradient. The rough boundary can not occured exactly at the maxima of the profile because at where the concentration gradient is zero. So the retardation from the maxima during the formation of rough boundary exists. This retardation is determined by the convature at the maxima of the concentration profile. In fig.1, sample A has a small convature at its solute concentration maxima and thus the deviation or retardation is also small, but in fig.2, sample B has a large convature at the maxima due to its relative wider thickness of the positive domain and thus the retardation is large also.

2.3. The limiting frequency of PDS response to about the temperature fluctuations[5]

In general, the amplitude of solute concentration fluctuations decreases as the frequency of growth rate fluctuations increases. When the latter increases to certain extent, the former approachs to zero and thus no growth striations are introduced. The limiting response frequency can be expressed as:

$$f_L=D/\delta_c^2$$

here δ_c is the boundary layer thickness. D is the diffusion coefficient. For the rotation rate of 10 rot./min. and pulling rate of 2 mm/hr, the limiting response frequency is about 0.9 to 1.0 µm, this corresponds to the responsable minimal thickness of domain laminar.

3. The growth of LN crystal with PDS

For growing LN crystal with PDS, three methods have been used for introducing the periodic temperature fluctuations at solid-liquid interface. The first is the crystal growth in an asymmetry temperature field or the crystal growth at a position deviated from the symmetry center of asymmetry temperature[6]. The second is the periodic electric field modulation during crystal growth according to Peltier effect[2] and the last is with the periodic heating power fluctuations in growing of small diameter crystal using laser heated pedestal growth method[7]. In present works, LN crystal with PDS was grown in an asymmetry temperature field.

2.1. Requirements of temperature field and temperature field designs

Crystals were grown by the Czochralski technique using mid-frequency induction heating system including automatic control through electric weighing the crucible and the melt to ensure identical growing conditions and crystal sizes. The melt was prepared in air from Li_2CO_3 and Nb_2O_5 at congruent composition and was doped with 0.5% yttrium. It was contained in a 60 mm diameter platinum crucible and 10 mm to 25 mm crystals were grown with a length between 10 mm to 30 mm. Fig. 4 shows the crystal growing system. The temperature field can be adjusted by different furnace designs.

The requirements of temperature field designs for growing LN crystal with PDS are as follows:

a). Reasonable temperature gradient conditions.

b). Easy to suppress the random temperature fluctuations at the solid-liquid interface caused by the convections in melt or in air.

In our works, we have designed three temperature field systems which are marked A, B and C. The thickness of thermal insulating layer in the three systems keeps the sequence of C > B > A. Measurements on vertical temperature

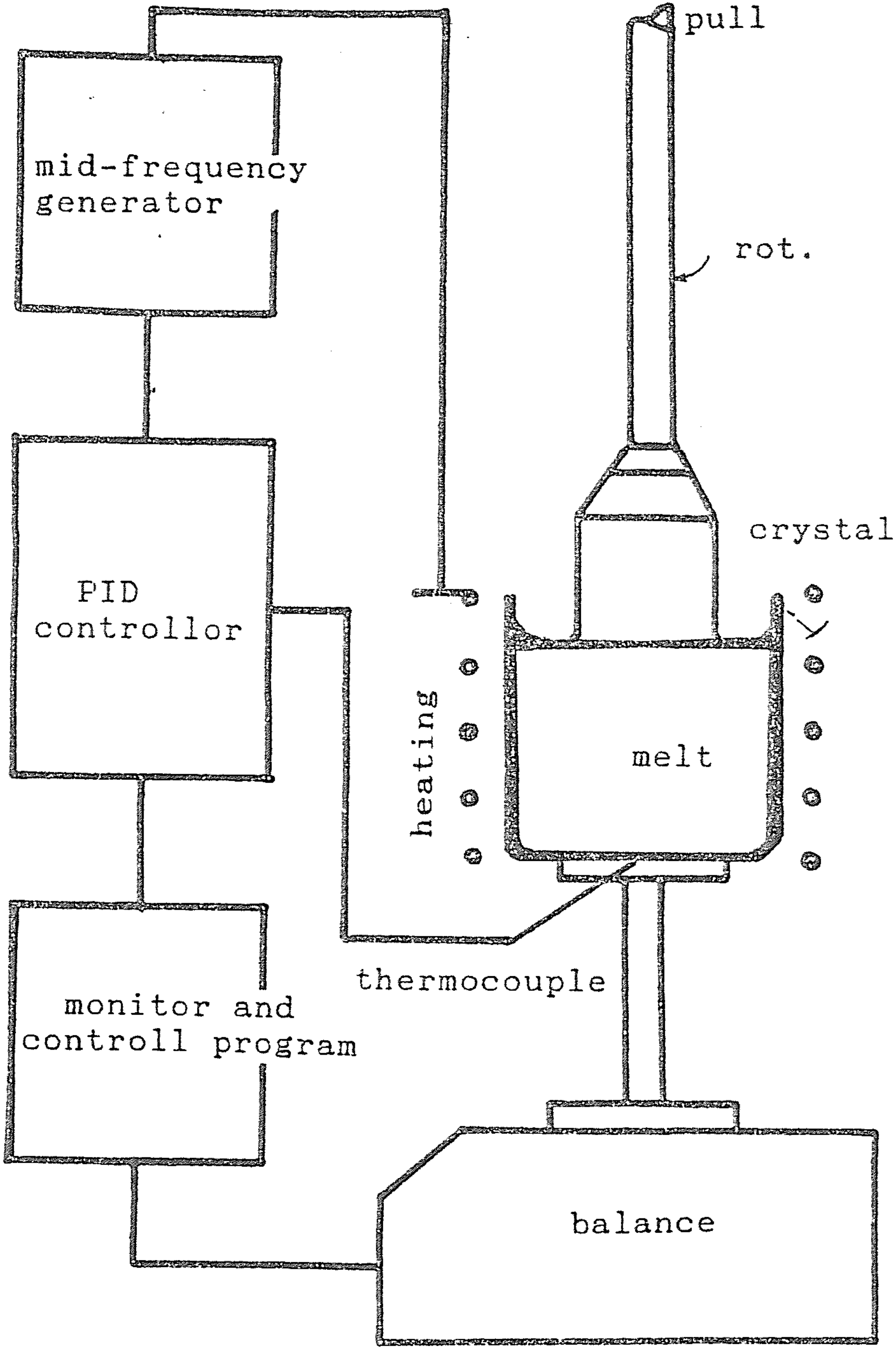


Fig. 4. The crystal growing system.

gradients were performed with a fine thermocouple of 0.5 mm in diameter and covered with a ceramic cappilary to keep the measurements stable. In fig.5 we show the vertical gradients above and below the melt surface in the three temperature systems. System A, B and C were marked according to their their thickness of thermal insulating layer in the figure's

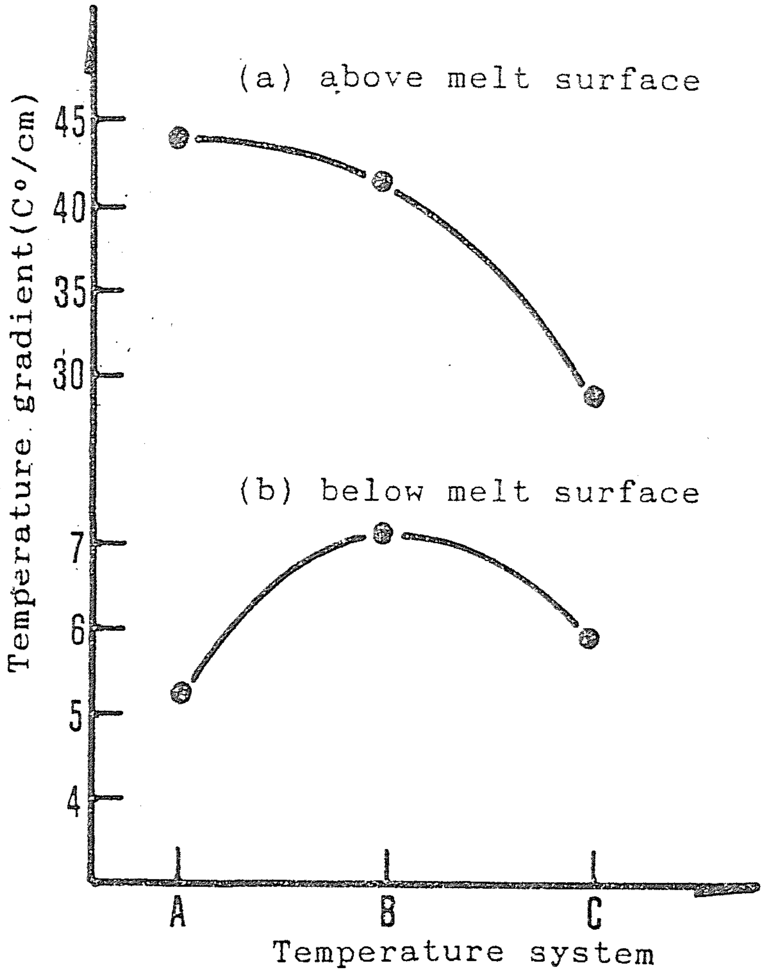


Fig. 5. The vertical temperature gradients above and below the surface of the melt in three temperature systems (A, B and C).

abscissa. In our experiments, system A has a very bad responce for the formation of the PDS and thus is discarded. The vertical temperature gradient below and above the melt surface in system B and C were ahown in fig. 6 and 7. System B has a relatively higher temperature gradient than that of system C. our works indicate that the system B is the best suitable for the responce of the PDS in LN crystal as the interface periodic temperature fluctuations.

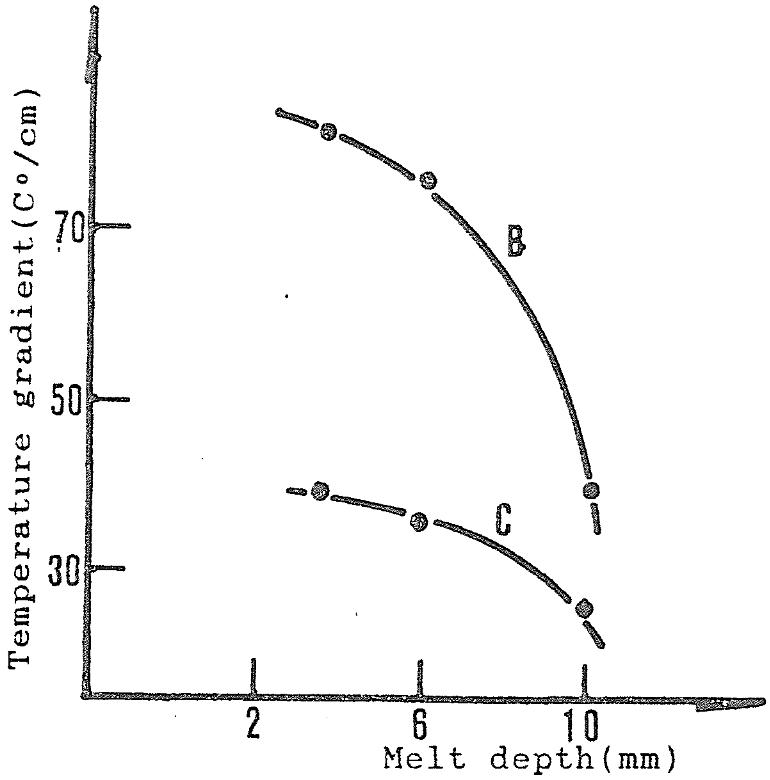


Fig. 6. The variation of the vertical temperature gradients above the melt surface vs the melt depth which is the distance between the mouth of the crucible and the melt surface.

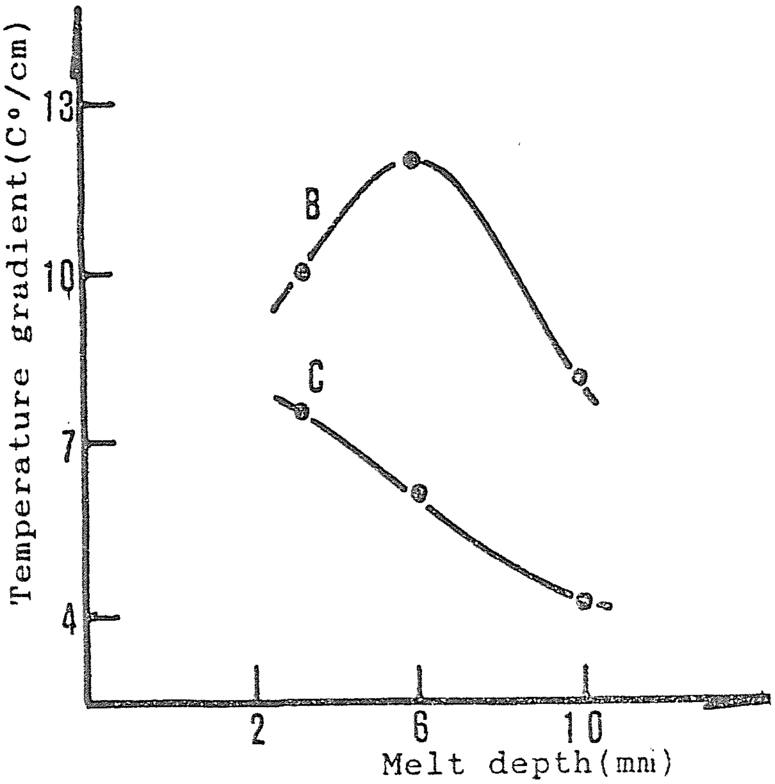


Fig. 7. The variation of the vertical temperature gradients below the melt surface vs the melt depth.

3.2. The response of the PDS to the interface fluctuations

For a efficient SHG process in LN crystal with PDS, the thickness of each domain laminar must be equal to the coherence length of the corresponding fundamental wavelength. The coherence length is about 3.4 µm for the fundamental wavelength of 1064 nm of Nd:YAG laser and is 1.7 µm for 860 nm of diode laser. The 1.7 um is near the theoretical limiting response frequency of 0.9 to 1 µm, as we have discussed in last section. Thus more difficulties are existed for the response of the PDS in laminar thickness of 1.7 μm than that of 3.4 μm.

The period domains number of the PDS, the ratio of the thickness of the positive and the negative domain laminas and the period stability are important for characterizing the quality of LN crystal with PDS for nonlinear optical applications. We have succeeded in growing the crystal with contineous laminar domain number of over 1500, in which over 500 laminas with period fluctuations less than 2%. We have also succeeded in growing the crystal in period of 3.4 μm with the number of domain laminas over 460, which was used for the generation of blue light. Their photographes were shown in fig.8.

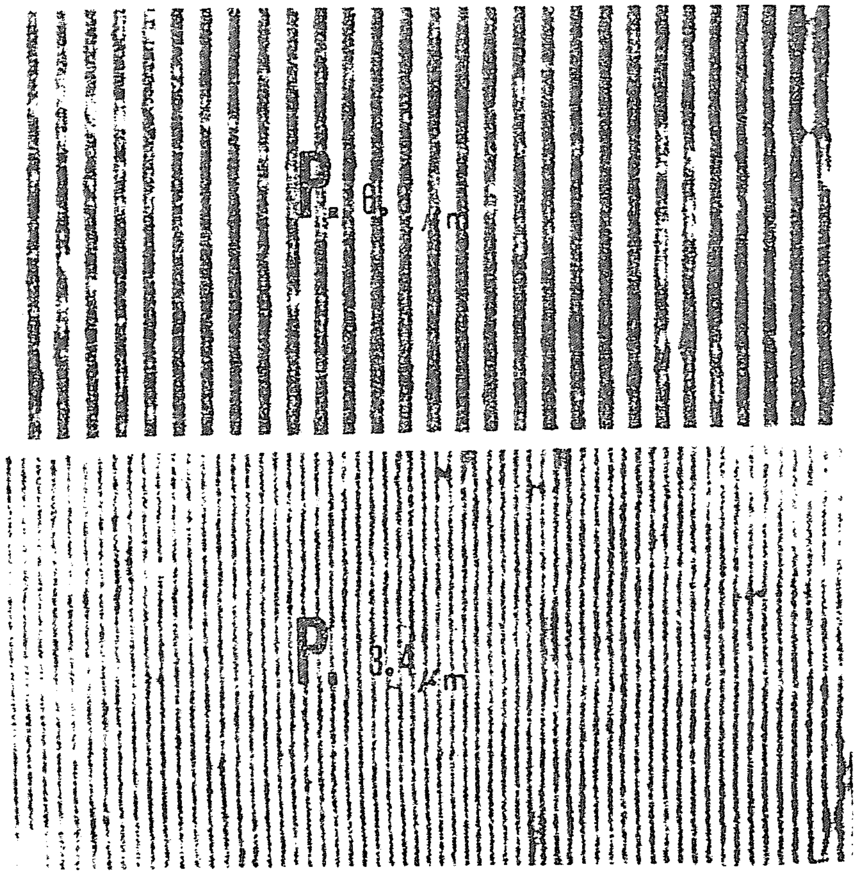


Fig. 8. The photographes of LN crystals with PDS at different period. (450X)

4. The perfection of the PDS in LN crystal

4.1 The achievement of the equality between the thickness of positive and negative domain laminas

The inequality of the thickness of positive and negative domain laminas causes the incomplete phase matching when the second-harmonic wave and the fundamental wave pass through one period of domain structures and thus decreases the SHG efficiency.

We have succeedly achieved the equality between the thickness of positive and negative domain laminas by adjusting the depth of melt surface (which is the distance between the mouth of crucible and the melt surface). Fig. 9 shows the dependence of the relative thickness of the positive and the negative domains as the melt depth in crystal growing. The relative thickness is defined as $|(d_p-d_n)|/(d_p+d_n)$. In some range of of the depth the melt surface, the relative thickness can be nearly equal to zero. System B has a relatively broad range than that of system C.

The relative thickness of the positive and the negative domains is determined by the solute concentration fluctuations, as we have discussed in section 2. In solute concentration profile, the critical concentration gradient determines the position of rough boundary. Thus the deviation of the rough boundary from the maxima of the concentration profile, can be adjusted by changing the growing conditions such as the vertical and horizontal temperature gradients, etc. Theoretical analysis about this problem is difficulty due to its complexity.

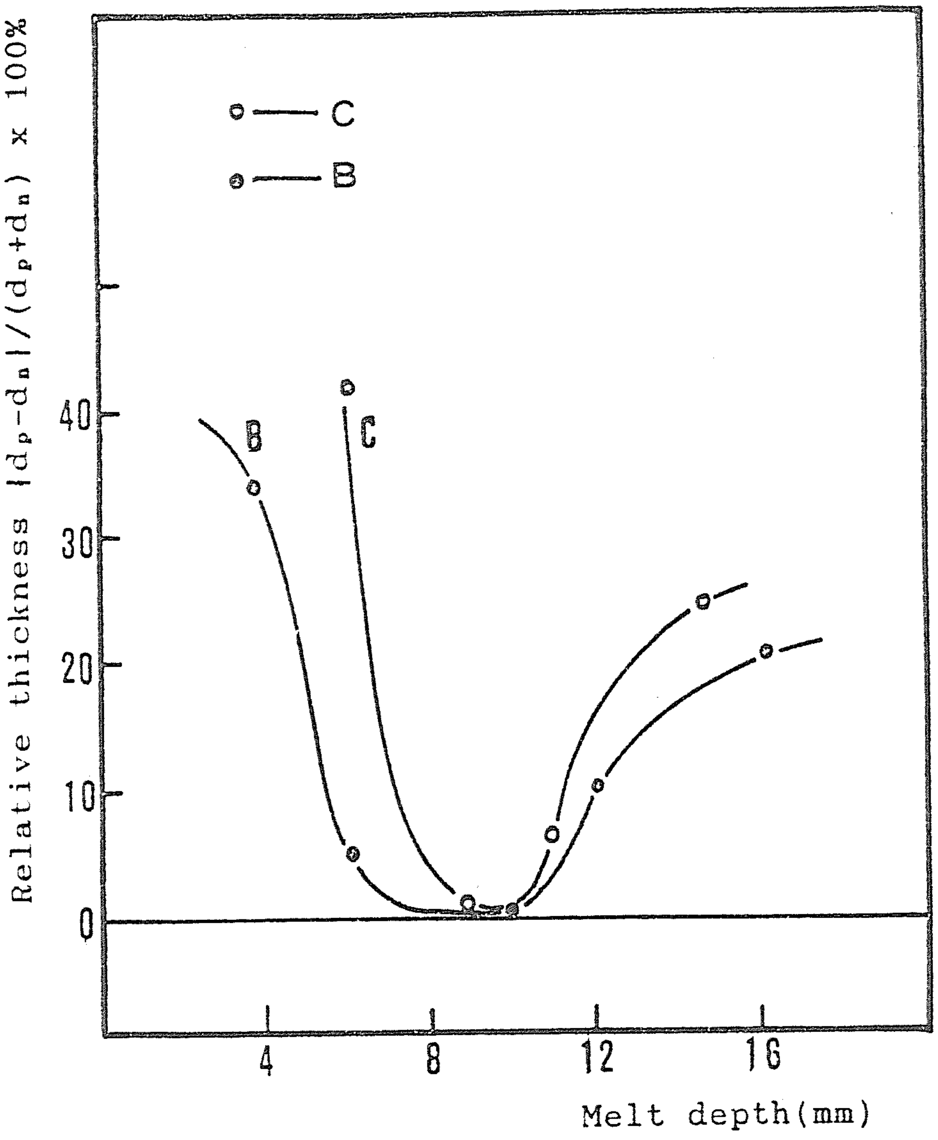


Fig. 9. The variation of the relative thickness vs the melt depth.

4.2. The defects in the PDS in LN crystal

The defects in periodic domain structures have many origins and different morphologies. We show in fig. 10 the photograph of various defects in LN crystal with the PDS. The photograph was taken at the face of x-z plane in LN crystal. These defects can be classified as following types according to their morphology:

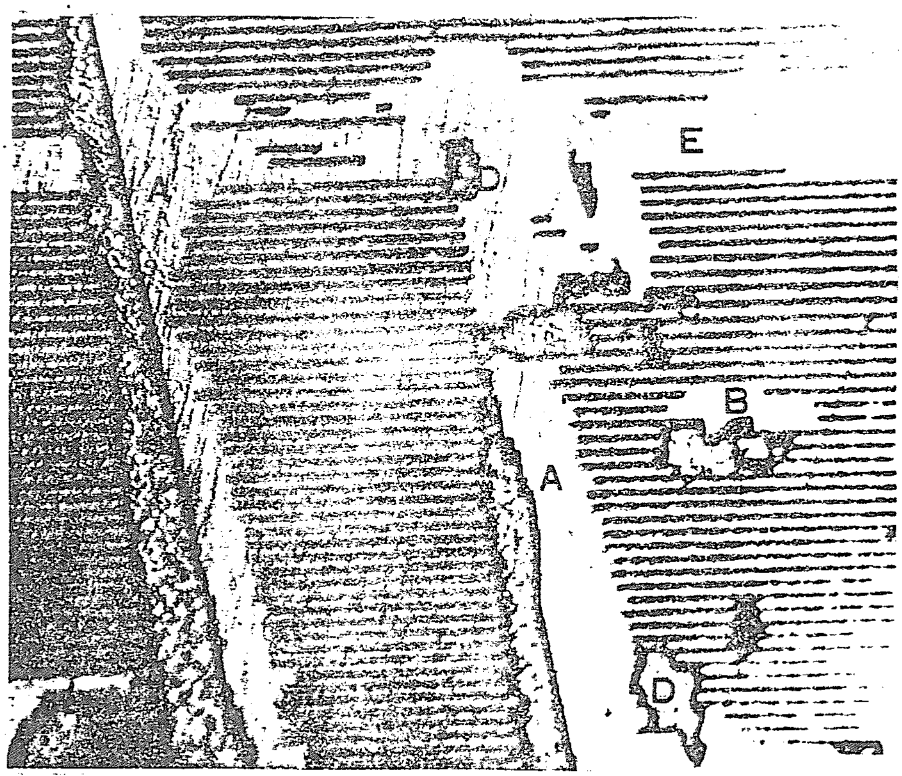


Fig. 10. The photograph of the defects in PDS. (400x)

Type A has a long morphology and has a charateristic angle with the growing direction (from the inner toward the outer of the melt during the crystal growth), the positive and the negative domains are at each side of it, as shown in fig. 10. A.

Type B is typical island-like domains. From fig. 10. B, it has a morphology that the upper part is positive domain and the lower part (along the growing direction) is the negative. But the interface between them is not a plane.

Type C is only the negative domain which makes the periodic domain laminas undividable.

Type D is also the negative domain in the form of distorted rectangle, it always appears along with defect of the type A.

Type E is the interuptions of periodic domain structures and is always the positive domain.

The type A defects may be caused by the planar interface instability. There are two kinds of perturbations which cause this instability, according to the works by Ming (8). One is quasi-sinusoid and the other is the quasi-sinusoidal travelling wave. The quasi-sinisoidal travelling wave causes a radial solute concentration fluctuations in growing interface and moves outer when the interface advances. The radial solute concentration fluctuations give the morphology of the negative and the positive domains at each side of the type A on the x-z plane of LN crystal. The characteristic angle of type A, then, is determined by the phase velocity of the travelling wave and the growth rate.

For verifying the results above, we have measured the concentration distributions along the growing direction

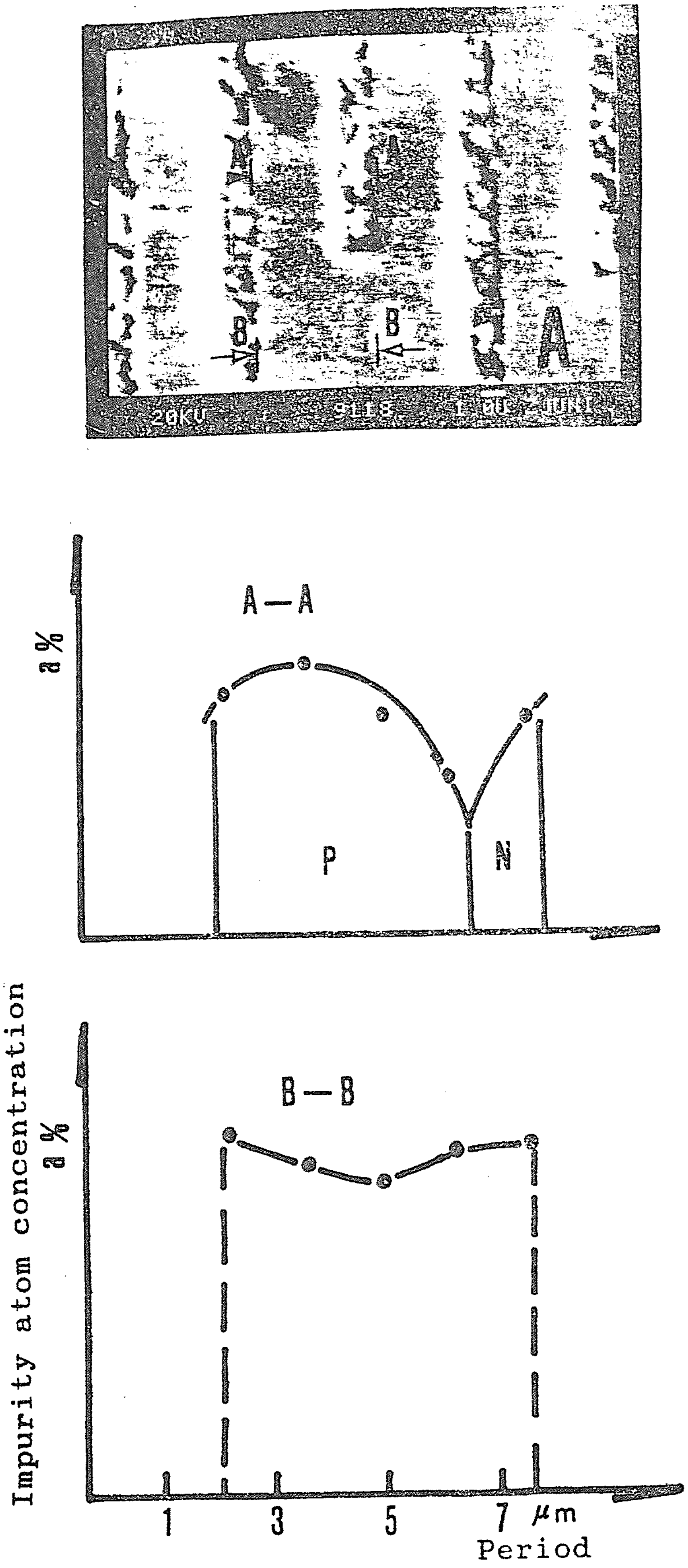


Fig. 11. The photograph and solute concentration variations: (A-A is in the PDS, B-B is inside the island-like domains).

using energy dispersive X-ray analysis both in the periodic domain structures and inside the type A, as what were shown in fig.11. The photograph of the measured area was shown in fig. 11.A, which corresponds to the area marked by a square in fig. 12. The concentration profile for one period in periodic domain structures is marked by A-A in fig.11. That inside thetype A is marked by B-B. It is easily seen that the periodic solute concentration fluctuations (A-A) is very typical as what we have shown in section 2. But the B-B profile which was measured inside the type A is not periodic and has small amplitude of fluctuations. It has the relatively higher average solute concentration than that in

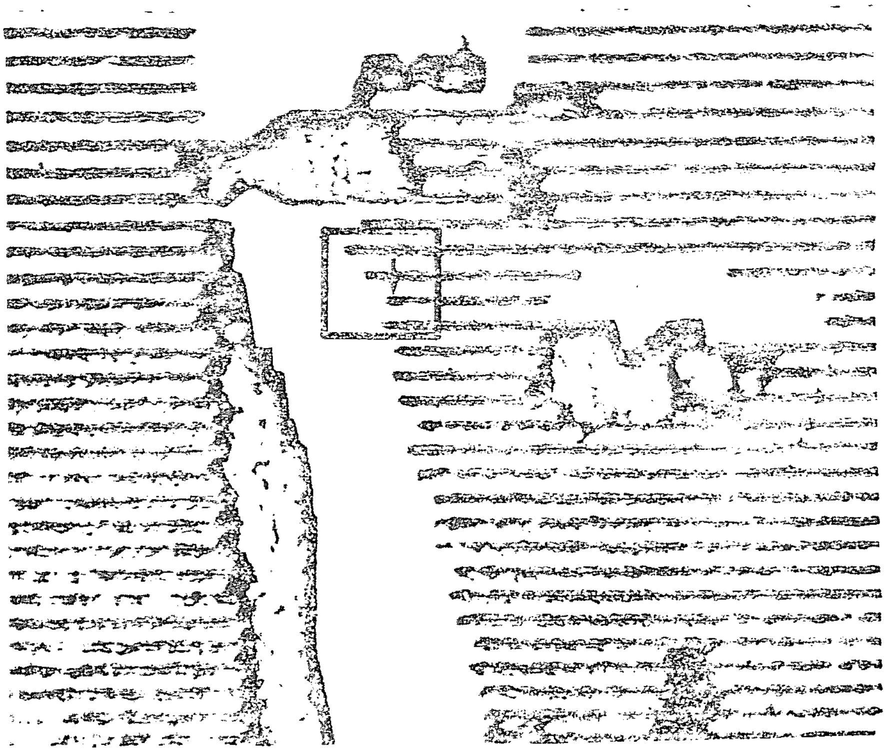


Fig. 12. Enlarged area for measurement in Fig. 11. (850x)

A-A profile. It shows the solute aggregation is exactly existed in type A, But the relative small amplitude of concentration fluctuations makes the concentration variation unable to reach the critical concentration gradient to cause the reversal of domains. So the PDS can not be produced by this periodic modulation in concentration.

We have no experimental results about the defect B to E. Different origins might be existed. Systematical research about the aspect is required for our future works.

5. Conclusion remarks

We have designed the suitable temperature field system for the response of the PDS as the periodic interface temperature fluctuations In LN crystal growth. The LN crystals with the number of domain laminas over 1500 have been succeedly grown, in which the number with period fluctuations less than 2% is over 500. We have also succeedly grown the LN crystal with PDS in period of 3.4 μm for the generation of blue light. The number of the domain laminas is about 460. The technique which can be used to adjust the relative thickness of the positive and the negative domains has been developed in our works.

The formation of PDS and defects inside the PDS have been systematically discussed in this chapter. We have firstly introduced the critical solute concentration gradient for the analysis of the formation mechanism of the PDS.

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