Paper

Growth and study of nonlinear optical crystals at the Hungarian Academy of Sciences

Istvan Földvári, Katalin Polgár, Ágnes Péter, Elena Beregi, and Zsuzsanna Szaller

Abstract — The former Research Laboratory for Crystal Physics continues the growth and defect structure investigation of nonlinear optical single crystals in a new organization, as a part of the Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences. The aim of the activity is to prepare specific crystals for basic and applied research as well as for applications. We improve the quality or modify the properties of well known nonlinear oxide and borate crystals and develop new materials. The principle nonlinear optical crystals in our profile are the followings: Paratellurite (TeO_2), congruent, Mg-doped and stoichiometric lithium niobate ($LiNbO_3$), a variety of sillenite structured crystals ($Bi_{12}MeO_{20}$, Me=Si, Ge, Ti, etc.), bismuth tellurite (Bi_2TeO_5) and nonlinear borates (BBO–β-BaB_2O_4, LBO–LiB_3O_5, LTB–$Li_2B_4O_7$, CLBO–$CsLiB_6O_{10}$ and YAB–$YAl_3(BO_3)_4$). Details of the crystal preparation and the major achievements are discussed in the paper.

Keywords — crystal growth, nonlinear optical materials.

Introduction

The Research Laboratory for Crystal Physics (RLCP) was established in 1976 for continuing the Hungarian tradition in crystal growth and characterization. During the years, the RLCP has earned reputation in growth and investigation of various insulator crystals, first alkali chlorides and fluorides then oxides and borates. The Hungarian Academy of Sciences has recently reorganized its institute network and the RLCP became a part of the Research Institute for Solid State Physics and Optics (RISSPO). The new institute keeps the entire crystal growth profile. The recent program of the Crystal Technology Department covers two sorts of optical materials; nonlinear optical crystals and scintillators. We use here the extended meaning of „nonlinear properties" including electro-optical, acousto-optic and photorefractive properties too. In this paper we want to summarize the state of the art of and the recent achievements on nonlinear optical crystals at RISSPO.

Experimental techniques

Synthesis of the starting materials

Quality requirements and the price of commercial chemicals motivated us to use own raw materials for crystal growth. In addition, some of the binary oxides in our profile, like Bi_2TeO_5 are not available commercially. Table 1 shows a review for the raw materials applied for crystal growth and their preparation methods.

Optical applications require the use of high purity materials (at least 5N). TeO_2, Bi_2O_3 and GeO_2 are prepared from the respective metals by chemical digestion which means a complex acidic oxidation of the metals, often including a purification step too. The other constituents are optical grade commercial materials. The starting material for crystal growth are prepared by multi step solid phase reaction that consists of a few hours treatment of the mixed oxide constituents at a previously determined optimum temperature, grinding of the transition composite, then a second (and further) anneal at higher temperature. The final composition of the synthesized materials was tested by X-ray phase analysis. Some examples for the preparation of starting materials for the individual crystals are presented in [1-2].

Chemical analysis

The chemical analysis directs to determine the actual crystal compositions and the impurity and dopant concentrations. Because of the relative accuracy required, the ratio of the major constituencies in the crystal are followed by wet chemical methods. The impurity and dopant concentrations are determined by atomic absorption spectroscopy (AAS). Appropriate solvents from the crystals are prepared by a chemical digestion specific to the individual crystals. The matrix effect of the host components are taken into account and, occasionally, solvent stabilizer is applied, e.g. [3-4]. The detection limit of the various impurities in the presence of host crystal components is around 1 ppm.

Crystal growth

The standard method applied for crystal growth is the diameter controlled Czochralski technique. The growth instruments consists of precision commercial pulling mechanisms, furnaces with resistance heating elements and specific diameter controlling units developed in the RLCP [5]. The open air growth systems use protection for the harmful vapor from the high temperature melts. Among the nonlinear optical crystals, the congruent and Mg-doped $LiNbO_3$, TeO_2, sillenites, Bi_2TeO_5, $CsLiB_6O_{10}$ and $Li_2B_4O_7$ are grown with the Czochralski technique. For the crystals

Table 1
Raw materials and preparation techniques of starting compounds for crystal growth

Crystal	Raw materials	Preparation technique
Paratellurite – TeO_2	Te metal	chemical digestion
Lithium niobate – $LiNbO_3$	Li_2CO_3 + Nb_2O_5	two step solid phase reaction
Bismuth tellurite – Bi_2TeO_5	TeO_2 + Bi_2O_3	two step solid phase reaction
Sillenites – $Bi_{12}MeO_{20}$ (Me = Ge, Si, Ti)	Bi_2O_3 + MeO_2	two step solid phase reaction
β barium metaborate – BaB_2O_4 (BBO)	B_2O_3 + $BaCO_3$	multi step solid phase reaction
Lithium triborate – LiB_3O_5 (LBO)	$Li_2B_4O_7$ + B_2O_3	multi step solid phase reaction
Lithium tetraborate – $Li_2B_4O_7$ (LTB)	commercial	
Cesium-lithium borate – $CsLiB_6O_{10}$ (CLBO)	Li_2CO_3 + Cs_2CO_3 + B_2O_3	multi step solid phase reaction
Yttrium-aluminum-borate – $YAl_3(BO_3)_4$	Y_2O_3 + Al_2O_3 + K_2CO_3 + MoO_3	two step solid phase reaction

having non-congruent melting or phase transition between the melt temperature and room temperature, top seeded flux (TSSG) method and, occasionally, spontaneous nucleation are applied. The flux method is also used for stoichiometric $LiNbO_3$. The actual flux compositions are discussed at the description of the individual crystals.

Orientation, processing and characterization of the crystal samples

The sample preparation from the crystal boules includes an X-ray orientation by a specific single crystal diffractometer (Secasi), cutting by diamond blade and polishing. The orientation and processing technique makes it possible to keep the orientation accuracy of the sample within a few arc minutes that required for some applications like as the acoustic propagation direction for acousto-optic crystals. The crystal processing methods has recently been completed in the RISSPO by the possibility of surface coating.
The single crystal samples are characterized by conventional optical methods and microscopic techniques including chemical etching for developing the characteristic defects like as dislocations, grain boundaries, twinning, etc. Selective etching agents and etching technique have been developed for the specific crystals and surface orientations. Another test method applied is the absorption spectroscopy in the UV-visible and infrared spectral range. If needed, additional investigations were performed in an extended international cooperation.

Materials and achievements

Paratellurite – TeO_2

Single crystals of paratellurite have excellent acousto-optical properties due to their low ultrasound velocity, high refractive indices and large piezo-optic constants [6,7]. The M_2 acousto-optic figure of merit for one of the shear modes in TeO_2 is the highest known value for materials transparent in the visible range [8]. The chemical and mechanical stability of paratellurite promotes also its applications in different acousto-optic devices. Deflectors, modulators and tunable filters are just a few from the realized possibilities.

The TeO_2 crystals are colorless. Impurities are harmful for the crystal growth but not for the coloration since the incorporation of various dopants are extremely, e.g. [1,9]. This is related to the characteristic asymmetric covalent bonding of Te to O that is hard to replace by any impurity of ionic character. Consequently, the absorption edge of the TeO_2 crystal is sharp and it obeys the Urbach rule [10]. The crucial question in the crystal performance is the acoustic attenuation that is closely related with the dislocation density. After a systematic improvement of the growth conditions, the lowest known dislocation density was published for TeO_2 (in specific samples 3000–4000 cm^{-2} on (110) face [11]). Also, it resulted in the lowest observed acoustic attenuation (2.2 db/cm for the slow shear mode in the [110] direction at 100 MHz [12]). The recent progress in the growth of paratellurite is the increased crystal diameter to 5 cm.

Lithium niobate – $LiNbO_3$

Lithium niobate is one of the most widely used nonlinear optical materials. Besides its nonlinear optical applications, the outstanding electro-optical and electro-acoustic properties are also employed (e.g. electro-acoustic transducers, acoustic surface wave filters, integrated optical elements). The achievements in study and application of LiNbO3 have been published in more than 8000 papers and dozens of reviews. Some recent books cover the major results [13,14]. LiNbO3 is a typical nonstoichiometric material. Homogeneous single crystals can only be grown from the congruent melt composition (48.6 mole% Li_2O and 51.4 mole% Nb_2O_5), e.g. [15,16]. The quality of the undoped congruent crystals is excellent. One exception is the limited resistance to visible laser light („laser hardness"). A major breakthrough in the laser hardness problem was the application of Mg dopant [17,18]. Mg doping pushes away the „antisite„ Nb ions from the lithium position and shifts the absorption edge of $LiNbO_3$ toward the shorter wavelengths. This enhanced absorption range looks to be the major reason of the increased laser resistance [19]. There were several attempts to get stoichiometric $LiNbO_3$ in which there are no antisite Nb ions without using dopants. Growth from Li reach melt did not produce homogeneous crystal composition. Remarkable progress was only achieved

by the double crucible method (with abs.edge position at 308 nm [20]). The annealing of the congruent crystals in Li rich vapor resulted in only a surface layer of stoichiometric $LiNbO_3$. It was shown that the composition of the $LiNbO_3$ crystals grown from melt with a large K_2O content approached the stoichiometric composition [21]. We have improved this technique and pointed out that the heavy K_2O containing melt was actually a flux that reduced the growth temperature [22]. By the developed flux technique we published the growth of the $LiNbO_3$ crystals that was closest to the stoichiometric composition [22]. We introduced also a simple, non-destructive test method for determine the crystal composition based on the absorption edge position of the crystal [23]. This method has recently been improved [24]. The state of art of our stoichiometric crystal is represented by the 303 nm abs. edge position (at 20 cm^{-1} abs. coeff.). The technical conditions were the followings: top seeded flux with K_2O. The Li/Nb ratio was 1 and the K_2O content corresponded to the K/Nb ratio of 0.38 in the melt. The actual growth temperature was in the 1030–1075°C range.

Sillenites – $Bi_{12}MeO_{20}$ (Me = Si, Ge, Ti)

The first use of sillenites related to the acoustic surface wave applications. Their outstanding photorefractive properties were first reported in [25]. The subsequent comprehensive studies of the photorefractive effects are summarized in topical books and reviews e.g. [26,27]. The single crystals grown from the melt exhibit yellow-brown coloration that was studied by several authors and reviewed in [28,29]. The color is related to an absorption shoulder near the intrinsic absorption edge and there are still debate on the origin of the coloration. It was recently pointed out that photochromic effect contribute to the color through generation of color centers stabile at room temperature [31]. The color of the sillenites grown from heavily doped melt with Al or Ga are pale and the absorption shoulder is missing [30,31]. Growth of undoped, colorless sillenite crystals has recently been reported by hydrothermal method [32].

We optimized the solid phase reaction and crystal growth of various sillenite crystals. The $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ crystals are grown by the Czochralski technique while the $Bi_{12}TiO_{20}$ by flux method. Ge–Si mixed sillenites and exotic sillenite structured crystals were also grown [33].

It was pointed out that various impurities modify physical parameters that play role in the photorefractive properties of sillenites [34,35]. Fast photorefractive response of Al-doped sillenites was predicted [35].

Bismuth tellurite Bi_2TeO_5

Bismuth tellurite is a new nonlinear optical material that became interesting when its unique photorefractive properties were discovered [36,37]. The crystal exhibits a long-living photorefractive signal component that develops in the four-wave mixing write process and lasts for years without any fixing [38]. Thus Bi_2TeO_5 is a good candidate for holographic memory substrate. The technical details for growth of Bi_2TeO_5 single crystals were first described in our laboratory [2]. There is only one other known source for bismuth tellurite so far (Dniepropetrovsk University, Ukraine). After developing the growth technique, several physical properties of the crystals were determined in the RLCP like the absorption and reflectivity spectra [39], refractive indices and their temperature dependence [40,41] and the nonlinear absorption [42]. The photorefractive investigations were extended to the short pulse (ps) excitation [43,44]. A recent review summarizes the photochromic and photorefractive properties of Bi_2TeO_5 [45]. Another interesting observation was that various dopants build in the crystal with segregation coefficients close to unity [4,46]. This allows to use Bi_2TeO_5 as a host for dopants like rare earth ions and Cr.

Nonlinear borates

Borates applied in nonlinear optics (e.g. BBO–β-BaB_2O_4, LBO–LiB_3O_5, CLBO–$CsLiB_6O_{10}$, LTB–$Li_2B_4O_7$), exhibit broad optical transparency range (160–3500 nm), excellent laser damage threshold and adequate birefringence for phase matching in a wide range of visible and UV wavelengths. The huntite type double borates, $(RM_3(BO_3)_4$ where R^{3+} = Sc, Y, La, Ln, In, Bi and M^{3+} = Al, Cr, Ga, Fe, Sc), can easily be doped with rare earth and transition metals.

BBO is used for generation of higher harmonics of the laser frequency, including the fifth harmonic of the Nd:YAG, for frequency mixing and optical parametric oscillation. This crystal is grown in our laboratory by high temperature top seeded solution growth (HTTSSG) from BaB_2O_4–Na_2O FLUX [47]. The maximum dimensions of the BBO crystal was successfully increased to about 60 mm in diameter and 130 g in weight. A chemical etching technique was developed to test the quality of the crystals [48]. The FLUX method resulted in good optical quality but, occasionally, the crystal contained inclusion.

LBO is used for the generation of non-critical phase matching second and third harmonics of Nd:YAG and frequency mixing down to the far UV range [49]. It is an excellent material for parametric generation of ultrashort pulses. Due to its incongruent melting, LBO is grown also by HTTSSG from LiB_3O_5+B_2O_3 flux [50]. The maximal dimension of the LBO crystals grown in our laboratory was 60 mm ϕ. The main problem in the preparation of LBO is the frequent cracking of the crystal during cooling.

CLBO can be grown by both Czochralski and TSSG methods [51,52]. Its advantage is the high yield in forth and fifth harmonic generation of Nd:YAG laser emission [53]. The major drawback in the application of CLBO is its hygroscopic nature. We grow CLBO by the Czochralski method. The maximal dimension achieved was 40 mm ϕ and 40 mm long.

LTB is applied as temperature independent SAW-filter and as soft-tissue-equivalent thermoluminescent (TL) dosime-

ter. The effective generation of fourth and fifth harmonic of Nd:YAG laser light is recently reported [54]. The congruently melting material can be grown by the Czochralski or Bridgman technique. We used the Czochralski method and crystals of 25 mm ϕ and 40 mm long were grown. The crystal is hard to dope by simply adding dopants to the melt. The low incorporation of Cu, however, was enough to generate detectable thermoluminescence in LTB:Cu [55]. Planar waveguides were prepared by He^+ ion implantation and the properties of the waveguide was presented in [56].

Huntite type double borates

Among the huntite borates, prospective results have been published for rare-earth doped yttrium-aluminum borate (YAB)–$YAl_3(BO_3)_4$ single crystals [57, 58]. The Nd-doped crystals (Nd:YAB or NYAB) show good laser efficiency with broad excitation range. The optical arrangement for self-frequency doubling (SFD) laser was shown to be free from quenching effects. Note that YAB is transparent to the far UV (down to 165 nm). Laser effects were also shown in Er, Cr and Cr + Ga doped crystals [59]. Microchip lasers made from huntite borates have recently been reported [60-62]. Because of the incongruent melting, YAB and related crystals can be grown from high temperature solution.
We grow YAB and $Nd_xY_{1-x}Al_3(BO_3)_4$ (NYAB) crystals with spontaneous nucleation and top seeded methods. The FLUX used is: K_2MoO_4+B_2O_3 (80%), YAB or NYAB (20%). The Nd content of the melt for NYAB was 3-12 mole%. The maximum dimension for the HTTSSG grown crystals was $17 \times 15 \times 15$ mm^3. We have preliminary results in the growth of $Er_xY_{1-x}Al_3(BO_3)_4$ and $Y_1Al_{3-y}Cr_y(BO_3)_4$ crystals too.

Conclusion

The Research Institute for Solid State Physics and Optics conducts an extended program for growth and characterization of nonlinear optical crystals. These crystals have been studied in a broad international cooperation involving institutes from USA, France, Germany, Italy, Spain, Great Britain, Portugal, Mexico, Poland, Ukraine, Russia and Armenia. We are open for further, mutually interesting joint programs in basic and applied research. Upon request we can provide specific crystals and characterized samples from our profile.

Acknowledgment

This work was supported by the Hungarian Research Found OTKA under the projects T-029756 and T-024091.

References

[1] I. Földvári, K. Raksányi, R. Voszka, E. Hartmann, and Á. Péter, *J. Cryst. Growth*, vol. 52, p. 561, 1981.

[2] I. Földvári, Á. Péter, R. Voszka, and L. A. Kappers, *J. Cryst. Growth*, vol. 100, p. 75, 1990.

[3] L. F. Bencs, O. Szakács, *Spectrochim. Acta B*, vol. 52, p. 1483, 1997.

[4] Á. Péter, O. Szakács, I. Földvári, L. Bencs, and A. Munoz F, *Mater. Res. Bull.* vol. 31, p. 1067, 1996.

[5] F. Schimdt and R. Voszka, *Cryst. Res. Technol.*, vol. 16, p. K-127, 1981.

[6] G. Arlt and M. Schweppe, *Solid State Commun.*, vol. 6, p. 783, 1968.

[7] N. Uchida and Y. Omachi, *J. Appl. Phys.*, vol. 41, p. 2307, 1970.

[8] T. Yano and A. Watanabe, *Appl. Phys. Lett.*, vol. 24, p. 256, 1974.

[9] I. Földvári, R. Voszka, L. A. Kappers, D. S. Hamilton, and R. H. Bartram, *Phys. Lett. A*, vol. 109, p. 303, 1985.

[10] A. Mecseki, I. Földvári, and R. Voszka, *Acta Phys. Hung.*, vol. 53, p. 15, 1982.

[11] J. Janszky, Á. Péter, A. Mecseki, R. Voszka, I. Tarján, I. Földvári, I. M. Silvestrova, and Yu. V. Pisarevskii, *Sov. Phys. Crystallogr.*, vol. 27, p. 90, 1982.

[12] I. M. Silvestrova, Yu. V. Pisarevskii, I. Földvári, Á. Péter, R. Voszka, and J. Janszky, *Phys. Stat. Sol. A*, vol. 66, p. K-55, 1981.

[13] *Properties of Lithium Niobate, EMIS Datareviews Series No. 5*. London: INSPEC Publ., 1989.

[14] A. M. Prokhorov and Yu. S. Kuzminov, *Physics and Chemistry of Crystalline Lithium Niobate*. New York: Hilger, 1990.

[15] P. Lerner, C. Legras, and J. P. Dumas, *J. Cryst. Growth*, vol. 3, p. 231, 1968.

[16] J. R. Carruthers, G. E. Peterson, M. Grasso, and P. M. Bridenbaugh, *J. Appl. Phys.*, vol. 42, p. 1846, 1971.

[17] D. A. Bryan, R. Gerson, and H. E. Tomaschke, *Appl. Phys. Lett.*, vol. 44, p. 847, 1984.

[18] K. L. Sweeney, L. E. Halliburton, D. A. Brysan, R. R. Rice, R. Gerson, and H. E. Tomaschke, *Appl. Phys. Lett.*, vol. 45, p. 805, 1984.

[19] K. Polgár, L. Kovács, I. Földvári, and I. Cravero, *Solid State Commun.*, vol. 59, p. 375, 1986.

[20] K. Kitamura, J. K. Yamamoto, N. Iyi, and S. Kimura, *J. Cryst. Growth*, vol. 116, p. 327, 1992.

[21] G. Malovichko, V. G. Grachev, L. P. Yurchenko, V. Ya. Proshko, E. P. Kokanyan, and V. T. Gabrielian, *Phys. Stat. Sol. A*, vol. 133, p. K-29, 1992.

[22] K. Polgár, Á. Péter, L. Kovács, G. Corradi, and Zs. Szaller, *J. Cryst. Growth*, vol. 177, p. 211, 1997.

[23] I. Földvári, K. Polgár, R. Voszka, and R. N. Balasanyan, *Cryst. Res. Technol.*, vol. 19, p. 1659, 1984.

[24] L. Kovács, G. Russchhaupt, K. Polgár, G. Corradi, and M. Wöhlecke, *Appl. Phys. Lett.*, vol. 70, p. 2801, 1997.

[25] J. P. Huignard and F. Micheron, *Appl. Phys. Lett.*, vol. 29, p. 591, 1976.

[26] P. Günter, *Phys. Rep.*, vol. 93, p. 199, 1982.

[27] P. Günter and J. P. Huignard, Eds. *Photorefractive Materials and their applications*. Vols I and II. Berlin: Springer Verlag, 1988 and 1989.

[28] B. C. Grabmayer and R. Oberschmidt, *Phys. Stat. Sol. A*, vol. 96, p. 199, 1986.

[29] L. Arizmendi, J. M. Cabrera, and F. Agullo-Lopez, *Intern. J. Optoelectr.*, vol. 7, p. 149, 1992.

[30] J. J. Martin, I. Földvári, and C. A. Hunt, *J. Appl. Phys.*, vol. 70, p. 7554, 1991.

[31] S. L. Hou, R. B. Lauer, and R. E. Aldrich, *J. Appl. Phys.*, vol. 44, p. 2652, 1973.

[32] M. T. Harris, J. J. Larkin, and J. J. Martin, *Appl. Phys. Lett.*, vol. 60, p. 2162, 1992.

[33] C. Zaldo, C. Moya, J. L. G. Fierro, K. Polgár, L. Kovács, Zs. Szaller, *J. Phys. Chem. Solids*, vol. 57, p. 1667, 1996.

[34] I. Földvári, J. J. Martin, C. A. Hunt, R. C. Powell, R. J. Reeves, and S. A. Holmstrom, *Opt. Mater.*, vol. 2, p. 25, 1993.

[35] I. Földvári, L. E. Halliburton, G. J. Edwards, and L. Ötsi, *Solid State Commun.*, vol. 77, p. 181, 1991.

[36] I. Földvári, M. P. Scripsick, L. E. Halliburton, and Á. Péter, *Phys. Lett. A*, vol. 154, p. 84, 1991.

[37] I. Földvári, H. Liu, R. C. Powell, and Á. Péter, *J. Appl. Phys.*, vol. 71, p. 5465, 1992.

[38] I. Földvári, H. Liu, and R. C. Powell, *SPIE Proc.*, vol. 162, p. 9, 1992.

[39] I. Földvári, Á. Péter, L. A. Kappers, O. R. Gilliam, and R. Capelletti, *J. Mat. Sci.*, vol. 27, p. 750, 1992.

[40] G. Mandula, L. Kovács, Á. Péter, and E. Hartmann, *Opt. Mat.*, vol. 1, p. 161, 1992.

[41] G. Mandula, Á. Péter, and E. Hartmann, *Pure and Appl. Opt.*, vol. 3, p. 839, 1994.

[42] I. Földvári, B. Taheri, R. J. Reeves, and R. C. Powell, *Opt. Commun.*, vol. 99, p. 245, 1993.

[43] I. Földvári, R. C. Powell, H. Liu, and Á. Péter, *Opt. Mat.*, vol. 2, p. 175, 1993.

[44] I. Földvári, Á. Péter, R. C. Powell, and B. Taheri, *Opt. Mat.*, vol. 4, p. 299, 1995.

[45] I. Földvári, L. A. Kappers, and R. C. Powell, *Mat. Sci. Forum*, vol. 239–241, p. 315, 1997.

[46] I. Földvári, Á. Péter, L. A. Kappers, R. H. Bartram, and R. Capelletti, *Mat. Sci. Forum*, vol. 239–241, p. 231, 1997.

[47] K. Polgár, Á. Péter, and F. Schmidt, *Cryst. Properties and Preparation*, vol. 36–38, p. 209, 1991.

[48] K. Polgár and Á. Péter, *J. Cryst. Growth*, vol. 134, p. 219, 1993.

[49] C. T. Chen, Y. Wu, A. Jiang, B. Wu, G. You, and S. Liu, *J. Opt. Soc. Am. B*, vol. 6, p. 616, 1989.

[50] S. Zhao, Ch. Huang, and H. Zhang, *J. Cryst. Growth*, vol. 99, p. 805, 1990.

[51] Y. Mori, I. Kuroda, S. Nakigama, A. Taguchi, T. Sasaki, and S. Nakai, *J. Cryst. Growth*, vol. 156, p. 307, 1995.

[52] Y. Mori, I. Kuroda, S. Nakigama, T. Sasaki, and S. Nakai, *Appl. Phys. Lett.*, vol. 67, p. 25, 1995.

[53] Y. K. Yap, M. Inagaki, D. Nakijama, Y. Mori, and T. Sasaki, *Opt. Lett.*, vol. 21, 1996.

[54] R. Komatsu, T. Sugawara, K. Sassa, N. Sarukura, Z. Liu, S. Izumida, Y. Segawa, S. Uda, T. Fukada, and K. Yamanouchi, *Appl. Phys. Lett.*, vol. 70, p. 3492, 1997.

[55] M. Martini, F. Meinardi, L. Kovács, and K. Polgár, *Rad. Prot. Dosimetry*, vol. 65, p. 343, 1348, 1996.

[56] A. Boudriona, P. Moretti, J. C. Loulerque, and K. Polgár, *Phys. Stat. Sol. A*, vol. 153, p. 553, 1996.

[57] J. T. Lin, *Lasers and Opt.*, p. 34, December 1990.

[58] S. T. Jung, D. Y. Choi, J. K. Kang, and S. J. Chung, *J. Cryst. Growth*, vol. 148, p. 207, 1995.

[59] M. Iwai, Y. Mori, T. Sasaki, S. Nakai, N. Sarukura, Z. Liu, and Y. Segawa, *Jap. J. Appl. Phys.*, vol. 34, p. 2338, 1995.

[60] B. Braun, F. X. Kartner, U. Keller, J. P. Meyn, and G. Huber, *Opt. Lett.*, vol. 21, p. 405, 1996.

[61] T. Omatsu, Y. Kato, M. Shimosegawa, A. Hasegawa, and I. Ogura, *Opt. Commun.*, vol. 118, p. 302, 1995.

[62] Y. F. Chen, S. C. Wang, C. F. Kao, and T. M. Huang, *IEEE Phot. Technol. Lett.*, vol. 8, p. 1313, 1996.

Istvan Földvári, Katalin Polgár, Ágnes Péter, Elena Beregi, and Zsuzsanna Szaller
Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Konkoly-Thege u. 29–33, 1525 Budpaest, P.O. Box 49, Hungary