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New Non-Linear Single Crystals for a Broad Spectral Region

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Abstract

A brief review is presented of modern non-linear crystals allowing to broaden the range of coherent radiation in solid laser systems till 155 nm in the vacuum ultraviolet region and till 18 μm in the middle infrared region. Special attention is paid to periodic structures in ferroelectrics that are developed for the quasi-phase matching (QPM), and to polyfunctional elements based on KTA and $LiInS_2$ doped by rare earth ions.

INTRODUCTION

The use of single crystal non-linear convertors is one of the most efficient and economic ways to broaden the available spectral region of coherent radiation. Wavelength-tuned laser systems allow to solve many important scientific and technological problems. In spite of the continuous broadening of the spectral range in which the radiation with the necessary wavelength can be directly generated in a solid active element (this range being now extended from the blue region of the visible spectrum to 3 μm), an urgent problem exists to obtain coherent radiation in the vacuum ultraviolet (VUV) and middle IR regions. The former is extremely important primarily for UV lithography in the production of semiconductor devices with a high element density while in the latter case many analytical tasks are solved using the characteristic properties of the rovibronic absorption spectrum.

CRYSTALS FOR VACUUM ULTRAVIOLET, ULTRAVIOLET AND VISIBLE REGIONS

Non-linear crystals transparent in the VUV region are rather widely represented first of all by the borate systems (Table 1). The structure of the new compounds is based on the planary borate group (BO_3) that provides a maximum non-linear susceptibility. The cations of Be, Al, *etc.* while interacting with the oxygen atoms of this group affect the structure of energy levels of the borate group; so, by selecting proper cations one can achieve a shift of the edge of fundamental absorption to shorter wavelengths at the conservation of non-linear properties. Thanks to the efforts of the researchers from China, Japan and Russia, the first successive crystals of this class have been developed. They include β-BaB_2O_4 (BBO) and LiB_3O_5 (LBO) which are characterized by the parameters providing their promising importance as non-linear materials. These parameters include high efficiency of non-linear conversion, broad range of transparency, the presence of phase matching, high chemical and mechanical stability, high threshold of optical damage, and technological convenience of preparation and use of the laser elements.

The mentioned crystals can be used in the regimes of both the simple doubling, mixing, and parametric generation. The main parameters for the most promising crystals are shown in Tables 1 and 2; the crystals grown in the Design

TABLE 1
Major parameters of non-linear crystals for the region from VUV to mid-IR

Crystal	Symmetry	Non-linear susceptibility, 10^{-12} m/V	Transparency range, nm	The edge of SHG region, nm	Walk-off angle (matching type)
KBBF	D_3	d_{11} = 0.76	155–3600	184.7	–
SBBO	D_3	d_{22} = 1.62	165–3780	< 200	
TBO	D_{3h}	–	175–3780	< 200	
BABO	D_3	d_{11} = 0.75	–	–	
LBO*	*mm*2	d_{32} = 1.16	160–2600	555	0.43(I) 0.22(II)
BBO*	3*m*	d_{22} = 1.8	189–2500	411	4.8
CLBO*	42*m*	d_{36} = 0.96	180–2750	471	1.83
4LB*	4*mm*	d_{31} = 0.18	180–2800	–	
YCOB		d_{SHG} = 1.1	220–		8.5
GdCOB		d_{SHG} = 1.3	220–		
$Gd_xY_{1-x}COB$		NPM SHG NPM SHG			0 0
KTP*	*mm*2	d_{33}=13.7	350–4400	990	0.06
KTA*	*mm*2	d_{33} = 16.2	350–5500	1083	0.06

Note. The crystals grown at the DTIM, SB RAS, are marked with asterisks. NPM – non-critical phase matching.

and Technological Institute of Monocrystals (DTIM) are marked with asterisks.

A large group of new borate compounds was presented by the authors of [1] as a result of theoretical analysis of the features that determine non-linear parameters in the borate structure. The shortest wavelengths were obtained with $KBe_2BO_3F_2$ (KBBF) [1] which is transparent till 155 nm in the VUV region and the edge of the region of direct generation of the second harmonics (SHG) at 184.7 nm. Even higher nonlinearity is exhibited by the $Sr_2Be_2B_2O_7$ (SBBO) crystal with better mechanical properties and the edge of SHG at $\lambda < 200$ nm. This row is continued by the crystals $Ba_2Be_2B_2O_7$ (TBO) and $BaAl_2B_2O_7$ (BABO) that are now under thorough investigation. Another group of new borates including $CsLiB_6O_{10}$(CLBO), $YCa_4O(BO_3)_3$ (YCOB) and $Gd_xY_{1-x}COB$ was proposed by the authors of [2]. The advantage of CLBO is the possibility to obtain the 4th and 5th harmonics from the YAG : Nd laser radiation. Midlle birefringence and, as a result, small walk-off angle allowing to provide better overlapping of the interacting beams in comparison with BBO, and high angular, spectral and temperature width of the matching make this crystal preferable for the generation of radiation at 213 and 266 nm using powerful YAG : Nd lasers. It is expected that the crystals YCOB and $Gd_xY_{1-x}COB$ will be competitive to generate the 2nd and 3rd harmonics from the YAG : Nd radiation due to the possibility to realize a very profitable mode, *i. e.* non-critical phase matching with the zero walk-off angle and especially large width of angular matching for $Gd_{0.275}Y_{0.725}COB$ (2nd harmonics) and $Gd_{0.28}Y_{0.72}COB$ (3rd harmonics) in combination with higher optical damage threshold which is characteristic of borates.

Nevertheless, at present the crystals of the well known group $KTiOPO_4$ (KTP) are used to

TABLE 2
Main parameters of promising non-linear crystals for the mid-IR region

Crystal	Symmetry	Non-linear susceptibility, 10^{-12} m/V	Transparency range, μm	Optical damage threshold, GW/cm^2
$LiInS_2$*	*mm*2	d_{33} = 18	0.45–12	> 100 (20 ns)
$LiInSe_2$*	*mm*2	d_{33} = 37	0.6–15	–
$AgGaS_2$*	42*m*	d_{36} = 13.6	0.45–12	75 (10 ns)
$AgGaSe_2$*	42*m*	d_{36} = 33	0.65–18	
$ZnGeP_2$	42*m*	d = 65	0.75–12	50 (20 ns)
GaSe*	62*m*	d_{22} = 70	0.7–18	180 (20 ns)

*See Note to Table 1.

generate medium-power radiation in the visible region. The next step in their development is the $KTiOAsO_4$ (KTA) crystals with higher optical damage threshold and transparency region broadened to longer wavelengths which allow to obtain coherent radiation in the range 3 to 5 μm [3].

NON-LINEAR DEVICES WITH PERIODIC STRUCTURES

It was found to be extremely important that the crystals of the KTP group crystallize in the space group *mm*2 which relates to one of the ten groups with pyroelectric properties. The crystals of this group are characterized by relatively friable structure with soft cation sublattice which is exhibited in high ion conductivity at temperatures above 200 K. High pyroelectric coefficient γ (about 10^{-5} C/m^2), especially in the region of lattice rearrangement and phase transitions, leads to the appearance of strong electric fields (hundreds kV per centimetre) within the crystal volume [4]. According to the definition, these crystals are characterized by the presence of spontaneous polarization P_s. For the case of the KTP group, the direction of the polarization can be changed to the opposite by applying the external electric field. So, these crystals are ferroelectrics.

The growth of polar crystals was found to exhibit some specific features. First of all, it is the trend to self-organization of real structure which is generally directed to the compensation of tremendous pyroelectric fields arising during the growth and cooling of crystals. This is exhibited in the formation of twinning or domain structures, as well as prolonged defects of the channel type. At high P_s, this can take place directly during the growth when a crystal, growing as a monodomain till a definite stage, begins to build up additional domain blocks with the opposite direction of P_s. As far as the channel defects are concerned, they are directed towards the polar axis and filled with more easily melting phases that serve till a definite moment of time as a kind of conductor intended for the compensation of fields arising in the ideal lattice.

At present, the possibility of domain re-orientation is used in non-linear crystals to create periodic structures with alternating layers in which P_s direction is opposite. A specific matching mode is realized in these structures which is called quasi-phase matching (QPM) [5]. The major advantages of QPM are the following:

1) the realization of any interaction with the participation of beams from the transparency region of non-linear material at a definite temperature in the regime of non-critical phase matching;

2) the interaction regime can be organized so that the maximum (in value) element of the non-linear susceptibility tensor $\chi^{(2)}$ will work [5]. It is important that for QPM, due to non-critical phase matching, the walk-off angle is zero and the dependence of the output energy on pumping energy exhibits no saturation effects at high energies.

During the recent decade, the development of this approach allowed to create periodic structures in a series of ferroelectrics including $LiNbO_3$, $LiTaO_3$, $RbTiOAsO_4$, and $KTiOPO_4$ [5].

NON-LINEAR CRYSTALS FOR THE MIDDLE INFRARED REGION

At present, the list of used non-linear crystals for this region is short and includes only several titles: $AgGaS_2$, $AgGaSe_2$ and $ZnGeP_2$ (see Table 2). So, the search and development of the methods to prepare new non-linear crystals with better parameters become very urgent. We were the first to grow single crystals $LiInS_2$ and $LiInSe_2$ of the optical quality with a diameter up to 20 mm and length up to 50 mm [6], as well as mechanically strong and volume-uniform GaSe crystals distinguished by maximum non-linear susceptibility (see Table 2), though there are some problems connected with their mechanical treatment. The crystal $ZnGeP_2$ should also be noted. It possesses high non-linear parameters ($\chi^{(2)} = 65$ pm/V) and increased (compared to other IR materials) heat conductance (36 W/(m·K)). However, the presence of absorption bands in the short wavelength region of the transparency range due to cation vacancies allows practical use of the crystal only within the range 2 to 8 μm.

The crystals under development $LiInS_2$ and $LiInSe_2$ are crystallized, like KTP, in the *mm*2 group, belong to pyroelectrics (possibly also to

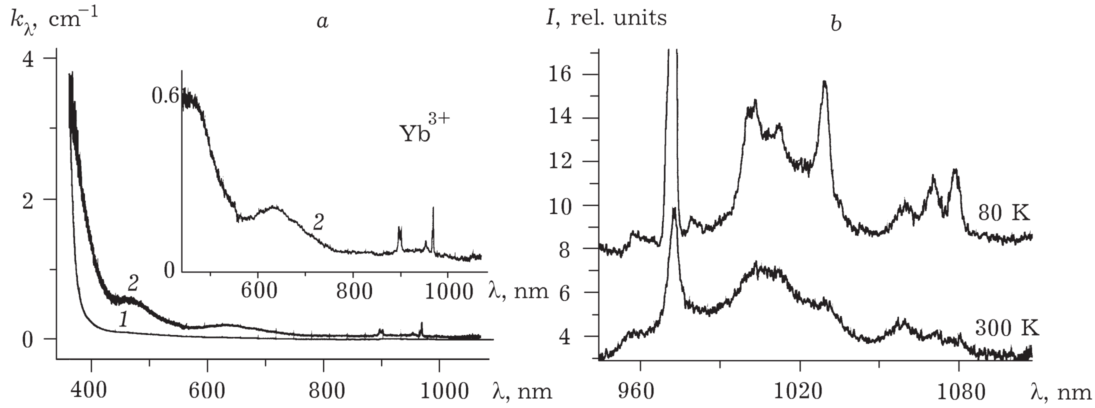

Fig. 1. Absorption (*a*) and photoluminescence (*b*) spectra of pure (*1*) and Yb^{3+}-doped (*2*) KTA single crystals.

ferroelectrics), have a broad transparency range similarly to $AgGaS_2$ but are characterized by higher non-linearity (see Table 2); due to the presence of Li instead of heavy silver ion, vibration frequencies somewhat increase, so one can expect an elevation of the optical damage threshold.

The attempts have been made for a long time to create crystal media appropriate as polyfunctional elements of laser schemes combining the functions of an active medium and non-linear convertor and allowing to pass to more compact devices. We were the first to obtain the KTA crystals activated with ytterbium (KTA : Y) [6], and $LiInS_2$ activated with neodymium [7]. Absorption and photoluminescence spectra for the mentioned crystals are shown in Figs. 1 and 2. They correspond to the incorporation of the ions of rare earths (3+). Cross sections are $1.2\cdot10^{-20}$ cm^2 for KTA : Yb and $2\cdot10^{-20}$ for $LiInS_2$: Nd; no luminescence quenching was observed at 300 K.

A tendency of the recent moment should be specially noted: Yb^{3+} ions become real competitors for Nd^{3+} as a classic dopant. This is connected with a very simple scheme of energy levels in Yb^{3+} which lacks only one electron for the 4*f*-shell to be completed; as a consequence, there are only two manifolds, $^2F_{7/2}$ (the ground state) and $^2F_{5/2}$ (excited state) separated by a gap of about 10 000 cm^{-1}. Absorption bands with the transition to the levels of $^2F_{5/2}$ state split in the crystal field are observed at 900–970 nm and well agree with the InGaAs diodes while the emission is observed at 970–1030 nm (see Fig. 1). The absence of high-energy excited states for the case of Yb^{3+} leads to the absence of concentration saturation effects, up-conversion and excited absorption

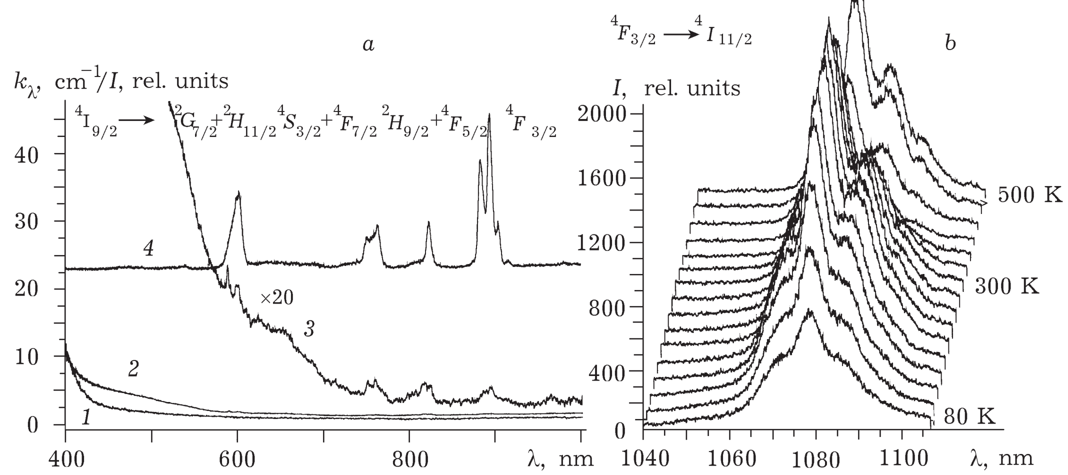

Fig. 2. Absorption (*1–3*) and luminescence excitation (*4*) spectra at 1077 (*a*) and 820 nm (*b*) for pure and Nd^{3+}-doped $LiInS_2$ single crystals. Temperature, K: *a* – 300 (*1–3*), 80 (*4*); *b* – 80–500.

characteristic of Nd^{3+} and Er^{3+}. It should be noted that the Yb^{3+} ion is one of the smallest among the rare earths, so doping goes on easier. Besides, the use of laser diodes allows to carry out the longitudinal excitation; this lowers the demands to the concentration of the dopant and decreases heat stresses inside the active medium [8]. All these considerations function also in the construction of polyfunctional media.

CONCLUSION

So, the element base developed at the DTIM, SB RAS, at present provides the solution of many urgent problems put forward by the researchers developing new quantum electronic devices. The investigations have been fruitful, also due to the collaboration with the Livermore National Laboratory (USA) and the Observatory of Paris.

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REFERENCES

1 C. T. Chen, N. Ye, B. Wu *et al.*, Proc. Int. Symp. “Laser and Nonlinear Optical Materials”, Singapore, 1997, p. 103.
2 T. Sasaki, Y. Mori and M. Yoshimura, *Ibid.*, p. 126.
3 L. Isaenko, A. Merkulov, V. Tyurikov and V. Atuchin, *J. Cryst. Growth*, 171 (1997) 146.
4 L. Isaenko and A. Yelisseyev, Proc. Int. Symp. “Laser and Nonlinear Optical Materials”, Singapore, 1997, p. 155.
5 L. E. Myers, R. C. Eckardt, M. M. Fejer *et al.*, *JOSA, B*, 12 (1995) 2102.
6 A. Yelisseyev, L. Isaenko, A. Belov and A. Merkulov, *J. Cryst. Growth*, 198/199 (1999) 555.
7 A. Yelisseyev, L. Isaenko, S. Lobanov *et al.*, Proc. E-MRS Spring Meeting (1st Europ. Mat. Conf.), Strasbourg, 1999, p. 158.
8 L. DeLoach, S. Payne, L. Chase *et al.*, *IEEE J. Quantum Electronics*, 29/4 (1993) 1179.