New biaxial mixed crystals for frequency conversion of femtosecond pulses

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We have studied a possibility of using some recently investigated biaxial ($LiInS_2$, $LiInSe_2$, $LiGaS_2$, $LiGaSe_2$, and $AgGaGeS_4$) as well as new ($LiIn(S_xSe_{1-x})_2$ and $LiGa(S_xSe_{1-x})_2$) mixed nonlinear crystals as potential frequency converters of femtosecond laser pulses. Main attention is paid to generation of frequency tunable near and middle IR emission in optical parametric oscillators pumped by radiation of Ti:Sapphire lasers available. The investigation includes estimation of phase- and group-velocity matching conditions and potential efficiencies of the conversion.

Introduction

In recent years compact powerful laser systems have been developed, which emit the pulses of femtosecond duration. This made it possible to study substance under extreme conditions that could not earlier be created.[1] First of all, those are solid-state lasers based on wide-band active media: Ti:Sapphire ($\lambda = 0.75–1$ μm) and Cr:Forsterite (1.2–1.32 μm).[2] Frequency conversion of these quite promising and basic sources of super-short pulses into other spectral ranges using non-centrosymmetrical nonlinear crystals seems to be quite attractive, especially if preserving duration of the transformed radiation. Such sources would be an indispensable tool for the study of super-fast semi-conductor elements for the systems of optical communications, key components of lidars of new generation, etc. However, energy of radiation pulses of such lasers converted, directly or in cascade to the mid infrared does not exceed 10 nJ.[3] First of all, the problem is in the absence of appropriate nonlinear crystals capable of using in full measure the properties of group phase matching of the interacting waves.[4]

This study was aimed at search and investigation of nonlinear crystals, in which effective single-stage frequency conversion of Ti:Sapphire and Cr:Forsterite laser radiation could be feasible in the group phase matching mode. Obviously, one should seek such crystals among first of all biaxial nonlinear crystals, because the probability that there exist directions in them along which the phase and group velocity matching is realized simultaneously is higher than in uniaxial crystals.

Information has recently appeared about application of new nonlinear crystals, like $LiInS_2$,[6,7] $LiInSe_2$,[8–10] and $AgGaGeS_4$,[11–14] for conversion of frequency of laser radiation, including, in some cases, radiation of subpicosecond duration. The crystals are considered new, if those are not mentioned in Ref. 5 (last version). Linear and nonlinear optical properties of $LiIn(Se_xS_{1-x})_2$ and $LiGa(Se_xS_{1-x})_2$ nonlinear crystals are described in details in Refs. 15–18.

Conditions of phase and group velocity matching

Traditionally, one select two types of wave interaction in uniaxial crystals: *oo-e* and *oe-e* for negative and *ee-o* and *eo-o* for positive crystals. Appearance of highly effective biaxial nonlinear crystals called for revising the basic concepts used for description of three-frequency interactions in uniaxial crystals.[19] The terms "ordinary" (*o*) and "extraordinary" (*e*) waves have lost their meaning, and the terms "slow" (*s*) and fast (*f*) waves are used instead. One should consider three types of phase matching for arbitrary three-frequency interactions: *ss-f*, *sf-f*, *fs-f*; two types remain in degenerated case (generation of the second harmonics): *ss-f* and *sf-f*.

Besides, biaxial crystals are characterized by two angles of phase matching: polar and azimuth, instead of one polar angle for a uniaxial crystal. The peculiarity of frequency conversion in the femtosecond duration range is the necessity of taking into account the effect of group delay (mismatch of group velocities of the interacting pulses) and the effect of dispersion spread of the pulses. One usually ignores the latter effect at the pulse duration longer than 100 fs.

Selecting the interacting wavelengths so that λ_1, $\lambda_2 > \lambda_3$, and $\lambda_1^{-1} + \lambda_2^{-1} = \lambda_3^{-1}$, we determine the group (quasi-static) length as $L_g = \tau_p / |\Delta u_{ij}^{-1}|$, where i, $j = 1, 2, 3$; $\Delta u_{ij}^{-1} = u_i^{-1} - u_j^{-1}$ is the mismatch of the group velocities, τ_p is the pump pulse duration. Its increase is proportional to the decrease of the group mismatch of the interacting pulses.

The group velocities u_i and u_j were calculated by the following formula

$$u_i = \left(\frac{\partial \omega}{\partial k}\right)_{\omega=\omega_i} = c\left[n_i - \lambda_i\left(\frac{\partial n}{\partial \lambda}\right)_{\lambda=\lambda_i}\right]^{-1}$$

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using Sellmeier dispersion equations $n_i = n(\lambda_i)$. The group length values impose restrictions on the length of the crystals used, $L < L_g$.

In the case of non-degenerate three-frequency interaction one can match the group velocities only for a pair of interacting pulses.[4] However, the schemes are experimentally tested now, which use the femtosecond pump pulse (λ_3) and long (nanosecond duration) seeding pulse at idler frequency (λ_2) in order to obtain the pulses at the signal frequency (λ_1) with time parameters of the pump pulse.[20] In some cases the conditions of the conditions of group phase-matching along the direction of the phase matching can be accurately satisfied, and here $L_g \to \infty$. As the condition $L_g \to \infty$ can be realized only at some fixed wavelengths, it is reasonable to use mixed crystals (solid solutions) for controlling these wavelengths.

Simulation results

As the ratio between the real crystal lengths and the group length is determining for the effective frequency conversion of short-pulse radiation, the group lengths were calculated for the parametric light generation by mixing radiation of the Ti:Sapphire-laser ($\lambda_3 = 0.82$ μm) and the signal wave at $\lambda_1 = 4$ μm in the main planes of the crystal. The results of calculations are presented in the Table, the angle of phase matching θ and the parameter $d^2_{\text{eff}}/n_1n_2n_3$, determining the efficiency of conversion are also shown here (d_{eff} is the coefficient of nonlinear susceptibility proportional to the square of the field strength, n_i are the refractive index values at the wavelengths of interacting waves).

Interactions in the *YZ* plane are not of practical interest because the wavelength range, within which the phase matching occurs is too narrow, that, in its turn, is related to low birefringence. It follows from the data presented in the Table that crystals of finite but quite large lengths (fractions of millimeter) can be used for practical realization of femtosecond frequency converters.

The calculated spectral dependences of the group lengths are shown in Fig. 1 for generation of the second harmonics in one of the main planes of the $LiIn(Se_xS_{1-x})_2$ crystal, and Fig. 2 shows the directions of simultaneous phase and group phase matching for interactions of the type *ss-f* in the volume (out of the main planes) of the $LiIn(S_{1-x}Se_x)_2$ crystal.

It is seen that simultaneous realization of the group and phase matching for the mixed crystals with the constant mixing ratio *x* is observed along some direction, which moves with the change of the mixing ratio.

The dependences of λ_1 and λ_2 on λ_3 ($\lambda_3^{-1} = \lambda_1^{-1} + \lambda_2^{-1}$) for which the condition of group phase matching is fulfilled along the direction of the phase matching for interactions of the *sf-f* type (curves *1–3*) and the *fs-f* type (*4–6*) in the *XY* plane in the crystals $LiGaS_2$ and $LiGaSe_2$, are shown in Fig. 3.

Table. Some characteristics of optical parametric oscillation

Crystal		Plane	L_g, mm			θ, deg.	$d^2_{\text{eff}}/n_1n_2n_3$, (pm/V)^2
			Δ_{31}	Δ_{32}	Δ_{21}		
$LiIn(S_{1-x}Se_x)_2$	x = 0	*XY*	0.10991	0.75306	0.12869	55.908	3.1569
		XZ	0.13496	0.59894	0.17422	28.357	0.87533
	x = 0.2	*XY*	0.09859	0.66315	0.1158	60.705	4.27064
		XZ	0.1198	0.52418	0.15528	24.8415	0.92805
	x = 0.4	*XY*	0.09038	0.60512	0.10625	65.475	5.40001
		XZ	0.10899	0.47473	0.14147	21.2226	0.89139
	x = 0.6	*XY*	0.08414	0.56402	0.09889	70.641	6.63014
		XZ	0.10088	0.44002	0.1309	17.3991	0.75706
	x = 0.8	*XY*	0.07926	0.53381	0.09308	76.734	8.01876
		XZ	0.09462	0.41436	0.12262	13.0771	0.52196
	x = 1	*XY*	0.07535	0.51149	0.08836	89.019	9.22371
		XZ	0.08964	0.39461	0.11598	7.25309	0.19169
$LiGa(S_{1-x}Se_x)_2$	x = 0	*XY*	0.14934	1.20464	0.17047	51.12	2.88275
		XZ	0.18744	0.99288	0.23106	40.4195	1.4396
	x = 0.2	*XY*	0.13418	0.95189	0.15619	51.309	3.46068
		XZ	0.16543	0.80739	0.20806	40.5016	1.81179
	x = 0.4	*XY*	0.12284	0.82433	0.14436	51.93	4.04306
		XZ	0.14966	0.70699	0.18986	40.2608	2.17564
	x = 0.6	*XY*	0.11403	0.74177	0.13474	52.677	4.62826
		XZ	0.13768	0.6397	0.17544	39.915	2.53686
	x = 0.8	*XY*	0.10689	0.67976	0.12683	53.424	5.21634
		XZ	0.12828	0.58863	0.16403	39.5474	2.89862
	x = 1	*XY*	0.10113	0.63319	0.12035	54.135	5.81039
		XZ	0.12083	0.55029	0.15482	39.1878	3.26391
$AgGaGeS_4$	–	*XY*	0.10548	0.71807	0.12364	55.602	3.41103
		XZ	0.12885	0.51382	0.17197	43.0636	9.63026

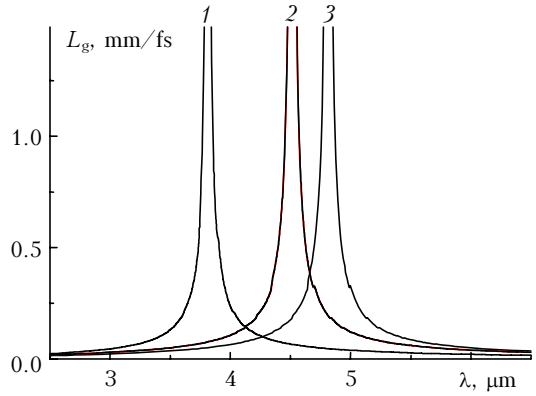

Fig. 1. Dispersion of phase matching for second harmonics generation in the $LiIn(Se_xS_{1-x})_2$ crystal in *XZ* plane following the interaction of the *ss-f* type: x = 0 (*1*); 0.5 (*2*); 1 (*3*).

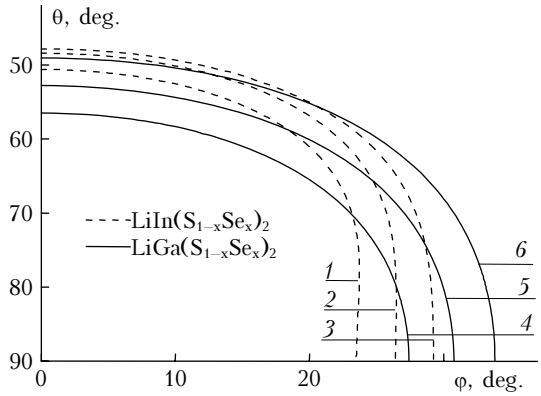

Fig. 2. Directions of simultaneous phase and group-matching for interaction of the *ss-f* type out of the main planes of the $LiIn(S_{1-x}Se_x)_2$ crystal: x = 1 (curve *1*); 0.5 (*2*); 0 (*3*) and $LiGa(Se_xS_{1-x})_2$ crystal: x = 1 (curve *4*); 0.5 (*5*); 0 (*6*).

Interaction of the *ss-f* type in *XY* plane cannot be realized because the effective nonlinear susceptibility d_{eff} vanishes there.[17] It follows from the shape of the curves in Fig. 3 that frequency conversion of femtosecond pulses is possible in a wide wavelength range.

Numerical simulations have also been carried out in the frameworks of the standard three-wavelength model, and the dynamics of conversion of femtosecond pulses was studied taking into account the variance of group velocities and the dispersion spread of the pulses.

The system of the initial equations for the amplitudes of pump waves, as well as the signal and idler waves obtained in the plane wave approximation has the following form[5]:

$$\frac{\partial A_1}{\partial z} + \frac{1}{u_1}\frac{\partial A_1}{\partial t} + \delta_1 A_1 + i\frac{\beta_1}{2}\frac{\partial^2 A_1}{\partial t^2} = -i\sigma_1 A_3 A_2 \exp(-i\Delta kz),$$

$$\frac{\partial A_2}{\partial z} + \frac{1}{u_2}\frac{\partial A_2}{\partial t} + \delta_2 A_2 + i\frac{\beta_2}{2}\frac{\partial^2 A_2}{\partial t^2} = -i\sigma_2 A_3^* A_1 \exp(-i\Delta kz),$$

$$\frac{\partial A_3}{\partial z} + \frac{1}{u_3}\frac{\partial A_3}{\partial t} + \delta_3 A_3 + i\frac{\beta_3}{2}\frac{\partial^2 A_3}{\partial t^2} = -i\sigma_{31} A_3^* A_1 \exp(-i\Delta kz),$$

where $\Delta k = k_1 - k_2 - k_3$ is the wave mismatch, k_i are the wave numbers of the pump, signal, and idler waves, β_i, δ_i, σ_i are the variance parameters, coefficients of the optical losses and nonlinear relation, respectively. The diffraction and walk off of radiation were not taken into account in calculations, because real apertures of the beams should be great (on the order of fractions of mm^2) to avoid destruction of crystals. Linear and two-photon absorption at the corresponding wavelengths were also considered negligible. The pulse duration of 100 fs and intensity of 10 GW/cm^2 were chosen as input parameters, the crystal lengths were taken to correspond to the group lengths. The conversion efficiency was 12 to 67% depending on the type of crystal and the type of the interaction considered.

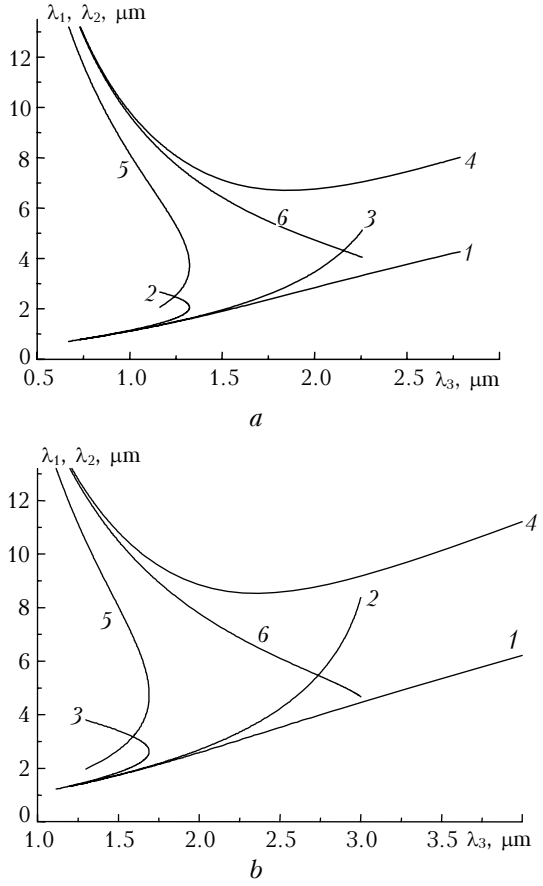

Fig. 3. Wavelength dependence of the group velocity matching of the waves of the s_1-f_2 (*1*), f_2-s_3 (*2*), s_1-f_3 (*3*), f_1-s_2 (*4*), s_2-f_3 (*5*), and f_1-f_3 type (*6*) for the *sf-f* (*1–3*) and *fs-f* type (*4–6*) of interaction in nonlinear crystals $LiGaS_2$ (*a*) and $LiGaSe_2$ (*b*).

One of the possible modes of frequency conversion of femtosecond pulses is the mode, in which the differences of group velocities for two pairs of interacting waves have contrary signs. At a proper choice of the starting delay between the pulses at the crystal input, the pulse intensities, and the crystal length, one can reach conversion with compression of

the pulse duration. In the case of realization of the pulse compression mode, as the estimates show, the peak power of the frequency converted radiation increases compared to the pump due to the decrease of the pulse duration up to 10 times.

Conditions of the frequency conversion of femtosecond pulses also can be realized in the biaxial $AgGaGeS_4$ crystal (solid solution of the crystals $AgGaS_2$ and GeS_2). At the frequency conversion under conditions of phase matching of ultrashort pulses (duration $\tau < 10^{-13}$ s) their dispersion spread at propagation inside the crystal becomes significant. The following characteristic parameters are used for estimating effect of this spread: the dispersion spread length

$$L_{\rm d} = 0.5\tau^2\left(\frac{\partial^2 k}{\partial\omega^2}\right)^{-1}$$

and the dispersion spread time

$$\tau_{\rm d} = 4L^2\left(\frac{\partial^2 k}{\partial\omega^2}\right)^2,$$

where L is the crystal length. One should take into account this effect if $L > L_{\rm d}$ or $\tau_{\rm p} < \tau_{\rm d}$.[21] The spectral dependences of the dispersion lengths are shown in Fig. 4 for the case of propagation of the pulse of duration $\tau_{\rm p} = 100$ fs along the main axes of the $AgGaGeS_4$ crystal.

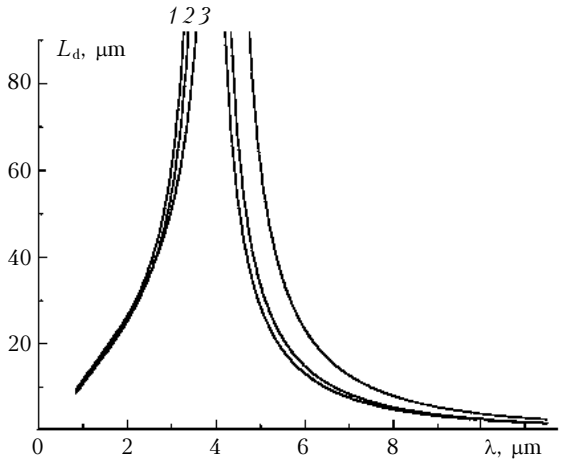

Fig. 4. Dependences of the dispersion wavelengths of the waves polarized orthogonal to the planes *YZ* (*1*); *XZ* (*2*); *XY* (*3*).

Besides, the mode of conversion with compression is realized for generation of the second harmonics of the *fs-f* type, i.e., when the condition $(u_2^f - u_1^s) = -(u_2^f - u_1^f)$ is fulfilled between the group velocities of pump u_1 and the second harmonics u_2. Let us note that generation of the second harmonics is possible in the $AgGaGeS_4$ crystal under conditions of group phase matching in the range 4.1–4.26 μm. Besides, this crystal can be used in the scheme of effective parametric generation of femtosecond radiation by mixing pump radiation of a Cr:Forsterite laser under conditions of accompanying phase matching between the pulses of pump and generated radiation.

Conclusion

Thus, the estimates show that the biaxial crystals $LiInS_2$, $LiInSe_2$, $LiGaS_2$, $LiGaSe_2$, and $AgGaGeS_4$ under study are real candidates for frequency converters of ultrashort radiation pulses. To convert the frequency of femtosecond pulses in biaxial crystals, the *ss-f* type of interaction is preferable against the *fs-f* and *sf-f* types because of weaker group mismatch of the pulses. Of course, in choosing the type of interaction one should also take into account other characteristics, for example, spatial dependence of the effective nonlinear susceptibility.

The data obtained on the group lengths and their variances can serve the reference point for preliminary choice of the appropriate nonlinear crystal for the specific conversion scheme. Tuning over two angles of phase matching (θ and φ) in biaxial crystals provides for additional possibilities of adjustment of group matching for the required wavelengths.

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