Short Communication

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Broad Band Nonlinear Crystals of Multicomponent Chalcogenides for the Mid-Ir Applications

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Abstract

The main trends in change of functional characteristics are considered as crystal composition is varied.

Keywords: Nonlinear crystals, Chalcogenides, Main linear and Nonlinear properties.

In the present review main attention is focused on Li-containing nonlinear optical (NLO) crystals which are transparent in the UV-to-mid-IR spectral range. We show how to optimize a crystal composition in order to improve the nonlinear output parameters. Crystals under examination are important for the obtaining of tunable coherent radiation in the mid-IR: this is necessary for the detecting of different chemical compounds with specific vibrational spectra. When choosing a material for laser radiation conversion in the IR it is necessary to have an optimal combination of different parameters: birefringence not less than 0.03 and optical damage threshold of about 100M/cm^2 at ns regime, this can be reached at band gap near 3.3 eV while nonlinear coefficient should be not lower than 4pm/V. Some of our crystals meet this requirement.

Ternary $LiBC_2$ (B=Ga, In, C=S, Se, Te) crystals possess a large band gap which results in low two-photon absorption and high laser damage threshold when using commercial solid state lasers operating in the near IR, for pumping. However, an increase of the band gap energy is accompanied usually by the decrease of the NLO response. Optimal combination of these two parameters takes place in tellurides, for example in $LiGaTe_2$ with d=43pm/V [1]. Therefore, it is a very important issue to achieve the balance between band gap energy, high SHG coefficient and transparency further in the mid-IR.

An adding of Ge, Si, Cd, Sn to $LiBC_2$ allows us to create new NLO materials, quaternary compounds, and analyze the trends in changes of composition and of characteristics responsible for nonlinear efficiency. Such quaternary chalcogenides include the tetrahedron building units $[LiC_4]$, $[BC_4]$, and $[MC_4]$, where B=Ga, In; M=Ge, Si; C=S, Se, Te. The bond lengths in the last two tetrahedrons grow evenly in the S→Se→Te set. The $[LiC_4]$ distortion increases when passing from ternary compounds to quaternary ones and one of Li ions is considerably remote of the center in the quaternary compounds. Crystal structure becomes more distorted in the later case. In In-containing quaternary crystals both Li and in occupy two crystallographically nonequivalent sites.

As a result nonlinear parameters of $Li_2Ga_2GeS_6$, $LiGaGe_2Se_6$, $Li_2In_2GeSe_6$, $Li_2In_2SiSe_6$ are higher in comparison with ternary analogues [2]. For example, nonlinear susceptibility of $Li_2Ga_2GeS_6$ is 16 pm/V: it is considerably higher in comparison with that of $LiGaS_2$ which is d31 = 5.8 pm/V. Moreover, the long-wave edge of the transparency range is red-shifted as the fourth component is added. Earlier maximum nonlinear susceptibility was reported for tellurides [3]. $LiInTe_2$ was found more stable, but its band gap is considerably smaller compared with $LiGaTe_2$ (1.5 and 2.41 eV, respectively). Adding Ge or Si to $LiInTe_2$ we found that band gap increases to 2.3 and 2.54 eV, respectively. Simultaneously nonlinear coefficients dij grow up to values known for AGSe.

Ge, Si atoms in quaternary chalcogenides were established to increase three important parameters: birefringence, band gap and efficiency of nonlinear conversion [4]. IR transparency edge considerably shifts to longer wavelengths, especially for LGGS, LGGSe relative to ternary LGS, LGSe **(Table)**.

The Ge or Si adding was found to shift down the melting temperature Tm and this effect is more pronounced for Ga compounds. Tm changes from 1050°C for $LiGaS_2$ to 900°C for $Li_2Ga_2GeS_6$ and from 915° C for $LiGaSe^2$ to 750°C for $Li_2Ga_2GeSe_6$. This lowers the risk of incongruent evaporation during the crystal growth. As a result a composition deviation from the stoichiometric value and concentration of inclusions of side phases becomes smaller.

Table: Main parameters of promising nonlinear crystals for the mid-IR

Crystal	Point group	Transparency range, μm	Band gap, eV	Nonlinear coeff., pm/V@μm	Optical damage threshold, MW/cm^2
AgGaGeS$_4$ (AgGaS$_2$)	mm2 (-42m)	0.42-12 (0.47 – 13)	2.8 (>2.7)	d31=15@1.06 (d32=8@1.06 d36=19@1.06)	50at 15ns1064nm (>34at10ns @ 1064nm)
AgGaGe$_3$Se$_8$ (AgGaSe$_2$)	mm2 (-42m)	0.6 – 18 (0.76 – 18)	2.4 ! (>1.8)	d31 = 33.4 (d32=19.6@3.4 d36=39@1.06)	- (13 at 30 ns @2000)
Li$_2$Ga$_2$GeS$_6$ (LiGaS$_2$)	mm2 (mm2)	0.35 -14 (0.32-12)	2.51 (<4.16)	deff=16@1.064! (d31=5.8@2.3 d24=5.1@2.3)	>50 at15ns 1064 (>240 at 14ns @1064nm)
LiGaGe$_2$Se$_6$ (LiGaSe2)	mm2 (mm2)	0.47 - 18 (0.37 - 14)	2.64 (<3.57)	d15=18.6@2.09! (>d31=9.9@2.3 d24=7.7@2.3)	50 at 10ns @1064 (80 at 5.6ns)
Li$_2$In$_2$GeS$_6$ (LiInS$_2$)	m (mm2)	0.36- (0.34 – 13.2)	3.45 (3.57)	≈d36=12.6@10.6! (d31=7.25 d24=5.66@2.3)	- (40* 14 ns@1064 nm)
Li$_2$In$_2$GeSe$_6$ (LiInSe$_2$)	m (mm2)	0.54- (0.46 - 14)	2.30 (2.86)	≈ d36 AGSe! (d31=11.78 d24=8.17@2.3)	- (40* 10 ns@1064 nm)
Li$_2$In$_2$SiS$_6$ (Li$_2$In$_2$SiSe$_6$)	m (m)	0.34- (0.49)	3.61 ! (2.54)	≈ d36 AGS (≈ d36 AGSe)!	- (-)

Conclusions

The algorithm of nonlinear crystals search is directed on optimization of their structure and linear/nonlinear optical properties taking into account specific applications and technological peculiarities of growth of high quality crystals.

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