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Review

A review on structure-performance relationship toward the optimal design of infrared nonlinear optical materials with balanced performances

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A B S T R A C T

Infrared (IR) lasers have been widely applied in the many military and civil fields. Nonlinear optical (NLO) crystals have been developed as the critical materials to achieve the efficient IR laser output by the typical frequency-conversion technology. However, commercial IR NLO materials are seriously limited in the IR region because of their low laser-damage thresholds (LDTs) or harmful two-photon absorption (TPA). Therefore, the discovery of new IR NLO materials with optimal key performances (concurrently large NLO coefficient (d_{ij}) and wide optical bandgap (E_g)) has become imperative. Recently, metal chalcogenides have become a rich source for exploration of IR NLO materials and hundreds of them have been discovered. Based on the good balance between experimental E_g ($\geq$3.0 eV) and d_{ij} ($\geq$0.5 × $AgGaS_2$) required for one IR NLO material, to our best knowledge, about 49 chalcogenides satisfy the above condition while limiting the scope to the equal or greater than ternary system. We focus on the structure-performance relationship for 49 compounds and the result shows that alkali or/and alkaline earth metals must be the preferred cations to maintain the wide E_g. Besides, their critical anionic groups are summarized and shown as follows: (i) typical tetrahedral $M^{III}Q_4$ (M^{III} = Ga, In) or/and $M^{IV}Q_4$ (M^{IV} = Si, Ge; Q = S, Se) or PS_4 units; (ii) d^{10} elements-centered ($M^{II}Q_4$: M^{II} = Zn, Cd) and typical $M^{III}Q_4$ or $M^{IV}Q_4$ tetrahedra; (iii) halogen-centered polyhedral ligands. So the combination of above anionic groups and alkali or/and alkaline earth metals into crystal structures produces the feasible design strategy to explore new IR NLO materials with excellent performances.

Contents

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1. Introduction

Nonlinear optical (NLO) materials are of great importance in producing the laser output from UV/DUV to infrared (IR) wavelengths by the frequency-conversion technology [1–5]. Recently, crystals have been attracted the increasing attentions and several famous NLO crystals have been achieved the laser output in the range from UV to visible regions, such as KH_2PO_4 (KDP) [6], $KTiOPO_4$ (KTP) [7], $LiNbO_3$ (LN) [8], β-BaB_2O_4 (β-BBO) [9], $YCa_4O(BO_3)_3$ (YCOB) [10] and LiB_3O_5 (LBO) [11], *et al.* Meanwhile, some interesting materials including glasses, nanocomposite films, and polymer composites have also been achieved the second and third-order harmonic generation (SHG and THG) as the laser operated devices [12–29]. However, achieving the output of DUV (<200 nm) and IR (3–20 μm) lasers is still a huge challenge [30–48]. Among them, IR lasers have been widely applied in the military and civil fields including the telecommunication, remote sensing, laser guidance and biological medicine. However, only several commercially available IR NLO materials have been discovered, such as $AgGaQ_2$ (Q = S, Se) and $ZnGeP_2$ so far [49–51]. Although they possess the wide IR transmission ranges (>10 μm) and strong second-order harmonic generation (SHG) responses, their application prospects are seriously hindered by inherent performance defects, such as low laser damage threshold (LDT) for $AgGaS_2$ (AGS), harmful two photon absorption (TPA) at 1 μm for $ZnGeP_2$, and non-phase matching (NPM) behavior for $AgGaSe_2$. Therefore, the prerequisite in the exploration of new IR NLO materials is to eliminate the above performance defects of commercial IR NLO materials, in other words, an outstanding IR NLO material should satisfy the following conditions: long IR absorption edge, large SHG response (d_{ij}), wide optical bandgap (E_g), high LDT and easy to grow large-size single crystal. In order to obtain the long

Table 1
Space groups and optical performances among the $AgGaS_2$ (AGS) and 49 chalcogenides with balanced performances ($E_g \geq 3.0$ eV and $d_{ij} \geq 0.5 \times$ AGS).

	Compounds	Space group	Bandgap	SHG response, d_{ij} (pm/V)	PM/NPM	Refs.
1	**$AgGaS_2$**	***$I\bar{4}2d$***	**2.64**	**$d_{14} = 13$**	**PM**	[49]
2	$LiGaS_2$	$Pna2_1$	4.15	$d_{31} = 5.8$, $d_{24} = 5.1$, $d_{33} = -10.7$	PM	[66]
3	$LiInS_2$	$Pna2_1$	3.59	$d_{31} = 7.25$, $d_{24} = 5.66$, $d_{33} = -16$	PM	[66]
4	$LiGaSe_2$	$Pna2_1$	3.34	$d_{31} = 9.9$, $d_{24} = 7.7$, $d_{33} = -18.2$	PM	[66]
5	$BaGa_4S_7$	$Pmn2_1$	3.54	1.0 × AGS @ 2.05 μm	PM	[69]
6	$SnGa_4S_7$	Pc	3.10	1.3 × AGS @ 2.05 μm	PM	[70]
7	$PbGa_4S_7$	Pc	3.08	1.2 × AGS @ 2.09 μm	–	[71]
8	$BaAl_4S_7$	$Pmn2_1$	3.95	0.5 × AGS @ 1.06 μm	PM	[74]
9	$BaAl_4Se_7$	Pc	3.40	0.5 × AGS @ 1.06 μm	–	[75]
10	$Cd_xHg_{1-x}Ga_2S_4$	$I\bar{4}$	3.22	$d_{14} = 27.2$	PM	[103]
11	$AgGaGeS_4$	$Fdd2$	3.0	$d_{31} = 15$	PM	[80]
12	$Li_2Ga_2GeS_6$	$Fdd2$	3.65	1.2 × AGS @ 1.06 μm	PM	[82]
13	$LiGaGe_2S_6$	$Fdd2$	3.52	1.2 × AGS @ 1.06 μm	PM	[83]
14	$Na_2Ga_2GeS_6$	$Fdd2$	3.10	0.8 × AGS @ 1.91 μm	PM	[88]
15	$Li_2In_2SiS_6$	Cc	3.61	1.0 × AGS @ 2.09 μm	–	[84]
16	$Li_2In_2GeS_6$	Cc	3.45	1.0 × AGS @ 2.09 μm	–	[84]
17	$BaGa_2SiS_6$	$R3$	3.75	1.0 × AGS @ 2.09 μm	PM	[86]
18	$BaGa_2GeS_6$	$R3$	3.26	2.1 × AGS @ 2.05 μm	PM	[85]
19	$Ba_2Ga_8GeS_{16}$	$P6_3mc$	3.0	0.9 × AGS @ 1.95 μm	PM	[87]
20	Li_2CdGeS_4	$Pmn2_1$	3.15	2.0 × AGS @ 1.55 μm	PM	[91]
21	Li_2MnGeS_4	$Pna2_1$	3.069	2.0 × AGS @ 2.70 μm	PM	[92]
22	Li_2ZnSiS_4	$Pna2_1$	3.90	1.1 × AGS @ 2.09 μm	PM	[93]
23	α-Cu_2ZnSiS_4	$Pmn2_1$	3.0	1.2 × AGS @ 1.55 μm	PM	[94]
24	β-Cu_2ZnSiS_4	Pn	3.2	1.2 × AGS @ 1.55 μm	PM	[94]
25	$InPS_4$	$I\bar{4}$	3.12	$d_{14} = 25$	–	[89]
26	$Zn_3(PS_4)_2$	$P\bar{4}n2$	3.07	1.6 × AGS @ 2.09 μm	PM	[42]
27	$LiZnPS_4$	$I\bar{4}$	3.44	0.8 × AGS @ 2.09 μm	PM	[42]
28	$LiGa_2PS_6$	Cc	3.15	0.5 × AGS @ 1.91 μm	–	[90]
29	$Ba_6Li_2CdSn_4S_{16}$	$I\bar{4}3d$	3.02	7.6 × AGS @ 2.05 μm	NPM	[77]
30	$Ba_6Zn_7Ga_2S_{16}$	$R3$	3.50	0.5 × AGS @ 2.05 μm	PM	[104]
31	$RbCd_4Ga_5S_{12}$	$R3$	3.02	11.1 × AGS @ 2.05 μm	NPM	[105]
32	$CsCd_4Ga_5S_{12}$	$R3$	3.09	9.8 × AGS @ 2.05 μm	NPM	[105]
33	$KZn_4Ga_5S_{12}$	$R3$	3.65	1.4 × AGS @ 2.05 μm	NPM	[106]
34	$RbZn_4Ga_5S_{12}$	$R3$	3.65	1.3 × AGS @ 2.05 μm	NPM	[106]
35	$CsZn_4Ga_5S_{12}$	$R3$	3.65	1.2 × AGS @ 2.05 μm	NPM	[106]
36	$Na_2ZnGe_2S_6$	Cc	3.25	0.9 × AGS @ 2.09 μm	PM	[107]
37	$Na_2CdGe_2S_6$	Cc	3.21	0.8 × AGS @ 2.09 μm	PM	[108]
38	$Sr_5ZnGa_6S_{15}$	$Ama2$	3.15	1.2 × AGS @ 2.05 μm	PM	[109]
39	$K_3Ga_3PS_8Cl$	$Pmn2_1$	3.60	1.0 × AGS @ 1.95 μm	PM	[113]
40	$K_3Ga_3PS_8Br$	Pm	3.85	1.1 × AGS @ 1.95 μm	PM	[113]
41	$Rb_3Ga_3PS_8Cl$	$Pmn2_1$	3.65	1.2 × AGS @ 1.95 μm	PM	[113]
42	$Rb_3Ga_3PS_8Br$	Pm	3.50	2.0 × AGS @ 1.95 μm	PM	[113]
43	$Ba_3KGa_5Se_{10}Cl_2$	$I\bar{4}$	3.22	10 × AGS @ 2.05 μm	NPM	[114]
44	$Ba_3RbGa_5Se_{10}Cl_2$	$I\bar{4}$	3.23	20 × AGS @ 2.05 μm	NPM	[114]
45	$Ba_3CsGa_5Se_{10}Cl_2$	$I\bar{4}$	3.25	100 × AGS @ 2.05 μm	NPM	[114]
46	$Ba_4ZnGa_4Se_{10}Cl_2$	$I\bar{4}$	3.08	59 × AGS @ 2.05 μm	NPM	[114]
47	$Ba_6Cs_2InGa_9Se_{20}Cl_4$	$I\bar{4}$	3.01	64 × AGS @ 2.05 μm	NPM	[114]
48	Na_2BaSnS_4	$I\bar{4}2d$	3.27	0.5 × AGS @ 2.09 μm	PM	[76]
49	Li_2BaSnS_4	$I\bar{4}2m$	3.07	0.7 × AGS @ 2.09 μm	PM	[56]
50	Li_2BaGeS_4	$I\bar{4}2m$	3.66	0.5 × AGS @ 2.09 μm	PM	[56]