

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Recent Advances in Infrared Nonlinear Optical Crystal

*Senthil Kumar Chandran, Chinnakannu Elavarasi,
Srinivasan Manikam and John James Gnanapragasam*

Abstract

The search and growth of nonlinear optical (NLO) crystals in the infrared (IR) area are significant and of high importance in the fields of NLO, signal communication, solid-state chemistry, and laser frequency conversion. Infrared NLO crystals have a wide IR transparent range, high laser damage threshold (LDT) value, and large NLO coefficients. This chapter presents the recent advances in IR-NLO crystals and especially emphasizes their crystal growth method, crystal structures, band gap value, LDT, and NLO properties. Based on its structural variety, it is categorized into chalcogenides, chalcogen halides, oxides, halides, and oxyhalides. This chapter describes several kinds of IR-NLO crystals and their structural, band gap value, thermal, optical, LDT, and NLO properties and also describes the significance of these crystals in laser frequency conversion, optical parameter oscillator, and other optical applications.

Keywords: crystal growth, laser-induced damage thresholds, infrared crystal, transmittance, optical parameter oscillator

1. Introduction

Nonlinear optical (NLO) crystals are important for frequency conversion and are widely used in different laser-oriented applications. High-efficiency NLO crystals need in high-efficiency laser methods, so it is essential to growing novel NLO crystals with good properties. In the past five decades, many valuable NLO crystals in the near-infrared (NIR), visible, and ultraviolet areas have been commercialized, such as LiNbO_3 , LiB_3O_5 (LBO), $\beta\text{-BaB}_2\text{O}_4$ ($\beta\text{-BBO}$), KTiOPO_4 (KTP), and KH_2PO_4 (KDP). These crystals are commonly used in basic science and technology, such as laser generation, artificial nuclear fusion, and so on. However, due to the increasing practical or market necessities, only a few crystals can be successfully used in deep-UV (DUV) and mid/far-IR areas. Nevertheless, NLO crystals that can powerfully produce high-power mid-IR lasers in the spectral area of 2–25 μm are very rare. Up to now, several useful NLO crystals have been originated and used in DUV, UV-Vis, and near IR, but they cannot be implemented in mid-infrared spectra because they have two atmospheric transparent regions, 3–5 and 8–14 μm , owing to strong absorption [1–5].

Second-order nonlinear optical (NLO) crystals are significant for producing coherent energy in the IR region (3–20 μm). IR lasers have several vital applications in various devices, such as optical parametric oscillators (OPO), remote sensing, optical sensing, instrumental spectroscopy, industry, military, analytical devices optical imaging, laser guidance, telecommunication, medical diagnostics, and long-distance communications. Such instruments are used to identify various elements and precise vibrational spectra [6–9]. Even after several years of deep research, only three unresolved NLO crystals have been commercially accessible in the mid and far-IR areas, namely, AgGaSe_2 , AgGaS_2 , and ZnGeP_2 . However, some inadequacies still exist in these IR-NLO crystals, such as the inherent efficiency loss arising from dual photon absorption, low MIR cut-off edge, non-phase matchable behavior, and low laser damage threshold. Already commercial ones cannot meet the commercial conditions because of their inherent disadvantages. Hence, it is essential to find out new efficient MIR NLO crystals with more stable efficiency [3, 7, 8, 10].

The large size high-quality mid-IR-NLO crystals for laser device applications are grown by Bridgman-Stockbarger (BS) method and molecular beam epitaxy (MBE) growth method [5]. The IR-NLO crystal can be separated into five categories: chalcogenides, chalcogenides, oxides, oxyhalides, halides, and chalcogenides [4]. This chapter will emphasize second-order NLO inorganic crystals in the MIR region. We did not focus on the commercially accessible LiNbO_3 , LiB_3O_5 (LBO), $\beta\text{-BaB}_2\text{O}_4$ ($\beta\text{-BBO}$), KH_2PO_4 , and KTiOPO_4 NLO crystals, these crystals have absorption bands in this region. Instead, this chapter focus on the chalcogenides, chalcogenides, oxides, halides, and oxyhalides. These crystals are promising materials for MIR applications due to they have wide transmittance in the MIR region [11].

2. Main conditions at NLO crystal select for changing coherent energy in the IR region

The selection of high-quality crystals is mainly tough when designing new, appropriate NLO crystals for the IR region. It should be highlighted that the balance between SHG coefficients and energy gap is an important feature to attain noble optical functioning in a mid-IR-NLO crystal [3]. The mid-IR-NLO crystals are significant to develop high-power tunable laser output extending the two atmospheric bands (3–5 μm and 8–14 μm) [4]. The accessibility of bulk-size single crystals is vital for the production of NLO devices. It is a great task to grow novel mid-IR-NLO crystals with desirable properties for useful applications. The good mid-IR-NLO crystals should satisfy the following basic criteria [2, 3, 6, 10, 12, 13]:

1. High second harmonic generation (SHG) responses
2. High laser damage threshold
3. Wide IR optical transparency range
4. Moderate birefringence
5. Good thermal stability
6. Good mechanical properties

7. Good facile growth of big size crystals
8. Splendid chemical stability
9. Crystal with non-centrosymmetric space group
10. Congruent-melting performance to enable single-crystal growth
11. Low absorption loss at suitable laser wavelengths

3. Chalcogenides

Chalcogenides are new kind of material denoting the chalcogen elements (sulfide, selenide, and telluride) of the group VIA. The chalcogenides are designed by covalent bonding and originate in a variety of structures, mostly formatted in octahedral or trigonal geometry. Chalcogenides are useful in many fields, such as photocatalyst, thermoelectric, MIR-NLO, photovoltaic, sensor, fuel cell, and battery [6, 14, 15]. Chalcogenides are suitable crystals for MIR-NLO as they exhibit wide transparency in IR regions and can obtain large SHG responses in this region [16]. Normally, chalcogenides are capable materials for MIR-NLO devices owing to their many benefits, such as large optical nonlinearity, broad transparency range, and large birefringence. II-IV-V₂ and I-III-VI₂ chalcopyrites are now the leading functional MIR-NLO crystals in the market and laboratory. In the past two decades, more consideration has been given to discovering chalcogenides as MIR-NLO crystals for their structural diversity. Quaternary chalcogenide crystals own a high bandgap (E_g) and high LDT. But the small nonlinearity coefficients slowed down their use in high-power laser generation. Though such kinds of crystals have many MIR-NLO benefits, many of them also have some inadequacies. To meet the requirement of laser device manufacture, some advanced growth methods are adopted to produce high purity and high-quality big size crystals of the chalcogenide. But, quaternary chalcogenide crystals, such as Li₂Ga₂GeS₆, LiGaGe₂Se₆, AgGaGeS₄, and Ba₂GaGeS₆, are grown in bulk-sized crystals, which is desirable for optical devices [5, 6, 10, 16]. There are different kinds of chalcogenides, generally, alkali metal chalcogenides and transition metal chalcogenides (TMCs), which again can be categorized into binary, ternary, and quaternary chalcogenides. The chalcogenides have weaker interatomic bonds than the oxides, resulting in good optical transparencies in the IR regions. Meanwhile, the chalcogenides exhibit adjustable structure and optical properties [6, 14, 15, 17].

3.1 Cataloguing of chalcogenides based on number of components

Chalcogenides are classified based on their number of components, such as binary, ternary and quaternary structures, number of metals, number of chalcogen ions, and so on though, both ternary and quaternary elements of chalcogenides are systematically analyzed compared to binary chalcogenides [18, 19].

3.1.1 Binary chalcogenides

Binary chalcogenides contains two kinds of ions (metal ions and chalcogen anion). The CdS, CdSe, Ga₂S₃, GaS, In₂S₃, GaSe MnS, SnS, SnS₂, ZnS, and ZnSe are

an example of binary chalcogenides. For instance, CdS is one of the most considered chalcogenides. It has an energy gap value of 2.3 eV and is comparatively active under visible light. Its special size and structure-based optical and electronic properties are desirable for various kinds of applications. Owing to its numerous possible applications CDS chalcogenides are assumed to be the most significant materials [18, 19].

3.1.2 Ternary chalcogenides

When selecting a crystal for laser energy conversion in the IR, it is essential to have an ideal mixture of various considerations like birefringence value not less than 0.03 and LDT value of around 100 M cm^{-2} , energy gap value of more than 3.3 eV and the NLO coefficient should be more than 4 pm V $^{-1}$ [20]. The Li- and Ba-having chalcogenides meet these desires. The ZnGeP $_2$, AgGaSe $_2$, CdSiP $_2$, and AgGaTe $_2$ crystals have high NLO susceptibility, but their forbidden energy band is too low. The most commonly used nonlinear crystals for the MIR are AgGaS $_2$, AgGaSe $_2$, and ZnGeP $_2$. However, they all own serious disadvantages [6, 21, 22]. In recent times, consideration was given to chalcogenide crystals, such as alkali and alkali-earth metals (Li and Ba) (Table 1). These crystals permit one to resolve some difficulties in the MIR region. The birefringence value in Li-comprising crystals is significantly larger. LiBC $_2$ (B = Ga; C = S, Se) crystals can be applied for SHG applications wavelengths between 1.4 and 12 μm [23, 24]. Telluride crystals also have MIR properties, especially LiGaTe $_2$ has phase-matching in the entire transparency region. The SHG conversion efficiency of LiGaTe $_2$ is 10.6 μm , which is higher than that of AGSe [25]. To enhance the energy gap, Ag cation is to be substituted with alkali/alkaline earth metal (Li, Ba). Adding

Crystal	Point group	Transparency range (μm)	Band gap (ev)	Nonlinear coeff. (pm V $^{-1}$)	Laser damage threshold (MW cm $^{-2}$)
AgGaS $_2$	42 m	0.47–13	2.7	d32 = 8, 1.06 d36 = 19, 1.06	34 at 10 ns, 1064 nm
ZnGeP $_2$	42 m	0.74–12	2	d36=75, 9.6	100 at 10 ns, 2000 nm
AgGaSe $_2$	42 m	0.76–18	1.8	d32 = 19.6, 3.4 d36 = 39, 1.06	13 at 30 ns, 2000 nm
LiGaTe $_2$	42 m	0.52–20	2.31	d36 = 43, 4.5	—
LiGaS $_2$	mm2	0.32–12	4.15	d31 = 5.8, 2.3 d24 = 5.1, 2.3	240 at 14 ns, 1064 nm
LiGaSe $_2$	mm2	0.37–14	3.57	d31 = 9.9, 2.3 d24 = 7.7, 2.3	80 at 5.6 ns, 1064 nm
LiInS $_2$	mm2	0.34–13.2	3.57	d31 = 7.25 d24 = 5.66, 2.3	40* 14 ns, 1064 nm
LiInSe $_2$	mm2	0.46–14	2.86	d31 = 11.78 d24 = 8.17, 2.3	40* 10 ns, 1064 nm
BaGa $_4$ S $_7$	mm2	0.35–13.7	3.54	d32 = 5.7, 2.3	250 at 14 ns, 1064 nm
BaGa $_4$ Se $_7$	m	0.47–18	2.64	d11 = 18.2, 2.3 d13 = -0.6, 2.3	—

Table 1. Point group, transparency range, band gap, and LDT value of ternary chalcogenides.



Figure 1.
Single crystals of $BaGa_4S_7$.

these metal, we can get $LiBC_2$ ($B = In, Ga; C = S, Se, Te$) and $BaGa_4C_7$ ($C = S, Se$) group crystals. These crystals own a high bandgap value [26–28]. A little mass of Li is the reason for high thermal conductivity and high vibrational frequencies. The thermal conductivity of Li mixtures is around five times higher than that of AGS (Se) [29] and four to eight times more than that of $BaGa_4S_7$ (Se) (**Figure 1**) [6, 28]. The laser damage threshold for LGS is 3.5 Jcm^{-2} , which is five times larger than LiSe [30]. A similar result has been obtained when the Ag ion is substituted with Ba. $BaGa_4S_7$ crystal has high LDT and NLO susceptibility. Though, Ba cation slightly drops the band gap value. The point group is mm_2 and m for $BaGa_4S_7$ (**Figure 1**) and $BaGa_4Se_7$, respectively. Wide transparency regions of $0.35\text{--}12$ and $0.47\text{--}15.0 \mu\text{m}$, and energy gaps of 3.54 and 2.64 eV were found for both $BaGa_4S_7$ and $BaGa_4Se_7$ crystals, respectively. Both crystals have strong absorption peak at $15 \mu\text{m}$. The $BaGa_4Se_7$ showed high nonlinear susceptibility of $d_{11} = 18.2 \text{ pm V}^{-1}$ [6, 31, 32].

3.1.3 Quaternary chalcogenides

Quaternary chalcogenides have four kinds of ions together with a chalcogen anion. These kinds of materials have different applications, such as MIR-NLO, solar cell absorbers, photocatalysts, and so on. Quaternary materials adopt different kinds of elements, which permits comparatively complex structural, electronic, and optical properties [6, 33]. Using the quaternary crystals, the IR-NLO parameters can be enhanced with a high content of NLO-active parts [6]. A compact organization of the microscopic NLO-active parts increases high macroscopic NLO outcomes [6]. The birefringence value of $AgGaSe_2$ is 0.05 and this value for $AgGaGe_3Se_8$ is 0.11 . The enhanced LDT value of $AgGaGeS_4$ shows that it is a potential alternative crystal to the generally used $AgGaS_2$ for IR-NLO applications. $Li_2In_2SiSe_6$, $Li_2In_2GeSe_6$, $Li_2Ga_2GeS_6$, and $LiGaGe_2Se_6$ are the Li-having quaternary chalcogenides crystals (**Table 2**) [6, 34–37]. All these crystals have non-centrosymmetric crystal structures. $Li_2Ga_2GeS_6$ (**Figure 2**), $LiGaGe_2Se_6$ (**Figure 3**) crystals have orthorhombic crystal systems with space group Fdd_2 and $Li_2In_2GeSe_6$, $Li_2In_2SiSe_6$ crystals own monoclinic crystal systems with space group Cc . Ba-having quaternary $BaGa_2GeS_6$, $BaGa_2GeSe_6$ structures, which are promising crystals for NLO applications [37]. The NLO susceptibilities of $Li_2Ga_2GeS_6$ are 16 pm/V , which is significantly higher than $LiGaS_2$ (5.8 pm/V). A similar result was noted for $LiGaGe_2Se_6$. $BaGa_2GeS_6$ and $BaGa_2GeSe_6$ crystals also have improved NLO parameters. The SHG experiments showed that both materials have phase-matched behavior. The calculated SHG coefficient is ~ 2.1 and

Crystal	Point group	Transparency range (μm)	Band gap (eV)	Nonlinear coeff., (pm V^{-1})	Optical damage threshold (MW cm^{-2})
AgGaGeS_4	mm2	0.42–12	2.8	$d_{31} = 15, 1.06$	50 at 15 ns, 1064 nm
$\text{AgGaGe}_3\text{Se}_8$	mm2	0.6–18	2.4	$d_{31} = 33.4$	–
$\text{Li}_2\text{Ga}_2\text{GeS}_6$	mm2	0.35–14	2.51	$d_{\text{eff}} = 16, 1.06$	>50 at 15 ns, 1064 nm
$\text{LiGaGe}_2\text{Se}_6$	mm2	0.47–18	2.64	$d_{15} = 18.6, 2.09$	50 at 10 ns, 1064 nm
$\text{Li}_2\text{In}_2\text{GeS}_6$	m	0.36	3.45	$\approx d_{36} = 12.6, 10.6$	–
$\text{Li}_2\text{In}_2\text{GeSe}_6$	m	0.54	2.30	$\approx d_{36} \text{ AGSe}$	–
$\text{Li}_2\text{In}_2\text{SiS}_6$	m	0.34	3.61	$\approx d_{36} \text{ AGS}$	–
$\text{BaGa}_2\text{GeS}_6$	3	0.38–14	3.26	$d_{\text{eff}} = 26.3, 2.09$	–
$\text{BaGa}_2\text{GeSe}_6$	3	0.44–18	2.81	$d_{\text{eff}} = 43.7, 2.09$	–

Table 2.
Point group, transparency range, band gap, and LDT value of quaternary chalcogenides.



Figure 2.
Crystal of $\text{LiGaGe}_2\text{Se}_6$.

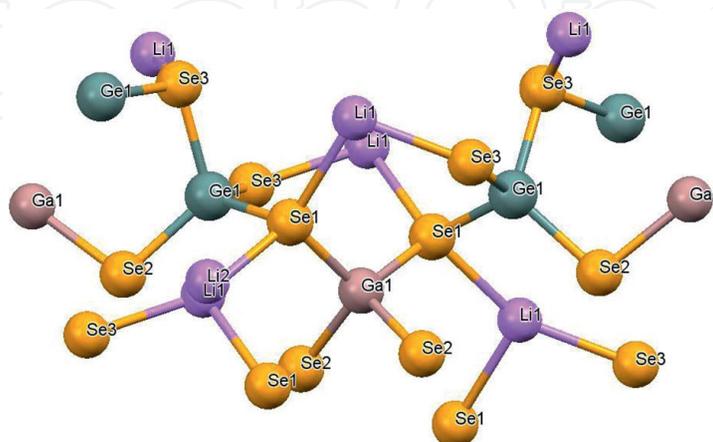


Figure 3.
Crystal structure of $\text{LiGaGe}_2\text{Se}_6$.

~3.5 times higher than that of AgGaS_2 . The nonlinear susceptibilities are 26.3 pm/V and 43.7 pm/V for $\text{BaGa}_2\text{GeS}_6$ and $\text{BaGa}_2\text{GeSe}_6$, respectively [37]. The transparency region in $\text{Li}_2\text{Ga}_2\text{GeS}_6$ and $\text{LiGaGe}_2\text{Se}_6$ is 0.35–12 and 0.37–14 μm , respectively. For $\text{BaGa}_2\text{GeS}_6$ and $\text{BaGa}_2\text{GeSe}_6$, the transparency regions are 0.380–13.7 μm and 0.44–18 μm , respectively. Band gaps of $\text{BaGa}_2\text{GeS}_6$ and $\text{BaGa}_2\text{GeSe}_6$ are 3.26 and 2.81 eV, respectively. $\text{Li}_2\text{In}_2\text{GeSe}_6$ and $\text{Li}_2\text{In}_2\text{SiSe}_6$ crystals have the energy gap values of 2.30 and 3.61 eV, respectively [6].

4. Chalcogenides

Chalcogenides could be considered potential materials for mid-IR applications. The chalcogenides contain a combination of sulfur and halogen. Chalcogenides have non-centrosymmetric coordinated surroundings that can stimulate mid-IR-NLO efficiency. Based on the chemical compounds present in the chalcogenides, it can be divided into [4]:

1. Alkali/alkaline-earth metal chalcogenides
2. Adduct-type chalcogenides
3. Lewis acid adducts chalcogenides
4. Main group element clusters chalcogenides
5. Other group main metal chalcogenides
6. Transition metal chalcogenides

4.1 Alkali/alkaline-earth metal chalcogenides

The $\text{Ba}_4\text{Ge}_3\text{S}_9\text{Cl}_2$ chalcogenide has excellent mid-IR-NLO properties [38]. It has a space group $P6_3$. The bandgap energy of $\text{Ba}_4\text{Ge}_3\text{S}_9\text{Cl}_2$ was 2.91 eV. The SHG response of $\text{Ba}_4\text{Ge}_3\text{S}_9\text{Cl}_2$ was 2.4 times higher than that of AGS [38]. The bandgap of $\text{Ba}_4\text{Ge}_3\text{S}_9\text{Cl}_2$ is 2.67 eV, which was calculated by the DFT method. NLO coefficients are found to be $d_{15} = d_{24} = 7.61$ and $d_{33} = 13.81$ pm/V. The bandgap of $\text{NaBa}_4\text{Ge}_3\text{S}_{10}\text{Cl}$ was 3.49 eV and SHG efficiency was 0.3 times that of AgGaS_2 (AGS) [39]. The theoretically calculated bandgap of this crystal is 2.94 eV. Then, the NLO coefficients are calculated to be $d_{15} = d_{24} = 3.89$ and $d_{33} = 9.32$ pm/V. The mid-IR-NLO crystals $[\text{A}_3\text{X}][\text{Ga}_3\text{PS}_8]$ ($\text{A} = \text{K}, \text{Rb}; \text{X} = \text{Cl}, \text{Br}$) were synthesized and reported by B.W. Liu et al. in the year 2016 [40]. Two Cl-crystals $[\text{K}_3\text{Cl}][\text{Ga}_3\text{PS}_8]$ and $[\text{Rb}_3\text{Cl}][\text{Ga}_3\text{PS}_8]$ are having isostructural with space group Pmn_{21} , while the other two Br-crystals $[\text{Rb}_3\text{Br}][\text{Ga}_3\text{PS}_8]$ and $[\text{K}_3\text{Br}][\text{Ga}_3\text{PS}_8]$ belong to Pm space group. These four compounds showed outstanding mid-IR-NLO behavior and the energy gaps of $[\text{K}_3\text{Cl}][\text{Ga}_3\text{PS}_8]$, $[\text{Rb}_3\text{Cl}][\text{Ga}_3\text{PS}_8]$, $[\text{K}_3\text{Br}][\text{Ga}_3\text{PS}_8]$, and $[\text{Rb}_3\text{Br}][\text{Ga}_3\text{PS}_8]$ are 3.60, 3.65, 3.85, and 3.50 eV, respectively. All four compounds showed large SHG responses of 4.0, 5.0, 7.0, and 9.0 times that of AgGaS_2 (AGS) at 1064 nm [39]. Moreover, these four compounds have higher laser threshold damage (LTD) of 37, 35, 31, and 29 times than that of AGS (Table 3).

Crystal	Space group	Band gap (ev) (DFT)	SHG AgGaS ₂ (AGS) times	Nonlinear coefficients (pm/V)	Laser threshold damage (LDT) AgGaS ₂ (AGS)
Ba ₄ Ge ₃ S ₉ Cl ₂	P6 ₃	2.67	2.4	d ₁₅ = d ₂₄ = 7.61 and d ₃₃ = 13.81	–
NaBa ₄ Ge ₃ S ₁₀ Cl	—	3.49	0.3	are d ₁₅ = d ₂₄ = 3.89 and d ₃₃ = 9.32	–
[K ₃ Cl][Ga ₃ PS ₈]	Pmn21	3.60	4.0	–	37
[Rb ₃ Cl][Ga ₃ PS ₈]	Pmn21	3.65	5.0	–	35
[K ₃ Br][Ga ₃ PS ₈]	Pm	3.85,	7.0	–	35
[Rb ₃ Br][Ga ₃ PS ₈]	Pm	3.50	9.0	–	29

Table 3.

Space group, band gap, and LDT value of alkali/alkaline-earth metal chalcogenides.

Crystal	Space group	Band gap (ev)	SHG AgGaS ₂ (AGS) times	IR transparent ranges (μm)	NLO coefficients (pm/V)
(SbI ₃). (S ₈) ₃	R _{3m}	2.52	1.0	2.5–25.0	d ₁₅ = 9.21, d ₂₂ = 9.22, d ₃₃ = 6.91
(AsI ₃). (S ₈) ₃	R _{3m}	2.31 eV	0.8	0.4–25.0	d ₁₅ = 3.40, d ₂₂ = 6.21, d ₃₃ = 0.73
(SnI ₄). (S ₈) ₂	Fdd ₂	2.17 eV	0.5	2.5–25.0	–

Table 4.

Space group, band gap, SHG, and transparency range value of adduct-type chalcogenides.

4.2 Adduct-type chalcogenides

The (SbI₃). (S₈)₃ and (SnI₄). (S₈)₂ are the adduct-type of chalcogenides. The (TI₃). (S₈)₃ (T = As, Sb) [4, 41–44] adduct-type chalcogenides have isostructural with R_{3m} space group (**Table 4**). The (SbI₃). (S₈)₃ and (AsI₃). (S₈)₃ chalcogenides have reasonable energy gap value of 2.52 and 2.31 eV and their theoretical energy gaps are 2.69 and 2.21 eV, respectively. SHG responses of these two chalcogenides have 1.0 and 0.8 times that of AgGaS₂. They also have wide IR transparent wavelengths around 2.5–25.0 μm and 0.4–25.0 μm [41, 42]. The calculated NLO coefficients are d₁₅ = 9.21, d₂₂ = 9.22, d₃₃ = 6.91 pm/V for (SbI₃). (S₈)₃ and d₁₅ = 3.40, d₂₂ = 6.21, d₃₃ = 0.73 pm/V for (AsI₃). (S₈)₃. The chalcogenides (SnI₄). (S₈)₂ has space group Fdd₂ [44] and a wide IR window in the range of 2.5–25.0 μm. The energy gap of (SnI₄). (S₈)₂ is 2.17 eV. The SHG response of (SnI₄). (S₈)₂ is 0.5 times stronger than that of AgGaS₂ at 2.1 μm.

4.3 Lewis acid adduct chalcogenides

Lewis acid adduct chalcogenides have sulfur-nitrogen rings with a variety of structures. These chalcogenides have moderate band gaps and IR-NLO properties (**Table 5**). A new chalcogenide (NSF)₄ [45] has a space group of P-421c. The calculated energy gaps are 4.57 eV (HSE06 method) and 3.58 eV (GGA method). For a high LDT, the large bandgap is more advantageous. The birefringence for (NSF)₄ is 0.220 at 1064 nm and the calculated NLO coefficient for (NSF)₄ is d₁₄ = 3.20 pm/V. Increased bandgap occurs due to the large electronegativity of F atoms in the

Crystal	Space group	Band gap (HSE06) (ev)	NLO coefficient (pm/V)
(NSF) ₄	P-421c	4.57	d ₁₄ = 3.20
S ₃ N ₅ PF ₂	R ₃ m	3.49	d ₁₅ = 1.71, d ₂₁ = 0.19 and d ₃₃ = 3.69

Table 5.
 Space group and band gap, and value of Lewis acid adduct chalcogenides.

compound. S₃N₅PF₂ crystal [46] has an R₃m space group. It has a wide bandgap of 3.49 eV (HSE06). The estimated birefringence is around 0.110 at 1064 nm and NLO coefficients are d₁₅ = 1.71, d₂₁ = 0.19 and d₃₃ = 3.69 pm/V. The d₃₃ coefficient is around 9.2 times stronger than that of KDP.

4.4 Main group element clusters chalcogenides

The chalcogenides (Bi₄S₄)(AlCl₄)₄ belong to the space group I-4 (**Figure 4**) [47] and it has two classes of main group component clusters that are in AlCl₄ tetrahedron and Bi₄S₄ cube. The energy gap of (Bi₄S₄)(AlCl₄)₄ is calculated to be 3.59 eV. (Bi₄S₄)(AlCl₄)₄ is the largest main group element cluster chalcogenide, which has an NLO coefficient value of d₁₄ = 1.52 pm/V and it is 3.8 times stronger than that of KDP. The DFT method showed that the main group component cluster chalcogenides has insignificant NLO coefficients.

4.5 Other main groups of metal chalcogenides

Both In₅S₅Cl [48] and In₅S₅Br [49] have isostructural properties, which are having the space groups Pmn21. The In₅S₅Cl and In₅S₅Br materials have band gap of 1.76 and 1.84 eV, respectively (**Table 6**). The estimated NLO coefficients are found to be d₁₅ = 0.36, d₂₄ = 2.83, d₃₃ = 13.38 pm/V for In₅S₅Cl and d₁₅ = 2.07, d₂₄ = 2.21, d₃₃ = 7.38 pm/V for In₅S₅Br. When compared with the NLO coefficients of AGS, the main group metal chalcogenides In₅S₅Cl and In₅S₅Br have d₃₃=1.0 and 0.5 times than that of AGS. The (CS₃N₂Br)Br₃ main group metal chalcogenides [50] crystallizes in space group Pna21. The estimated energy gap for (CS₃N₂Br)Br₃ is 2.21 eV (HSE0₆), and the NLO coefficients of (CS₃N₂Br)Br₃ are d₁₅ = 8.90, d₂₄ = 5.40, d₃₃ = 1.00 pm/V. From the NLO coefficient result, d₁₅ has a good NLO coefficient, which is about 0.6 times that of AGS.

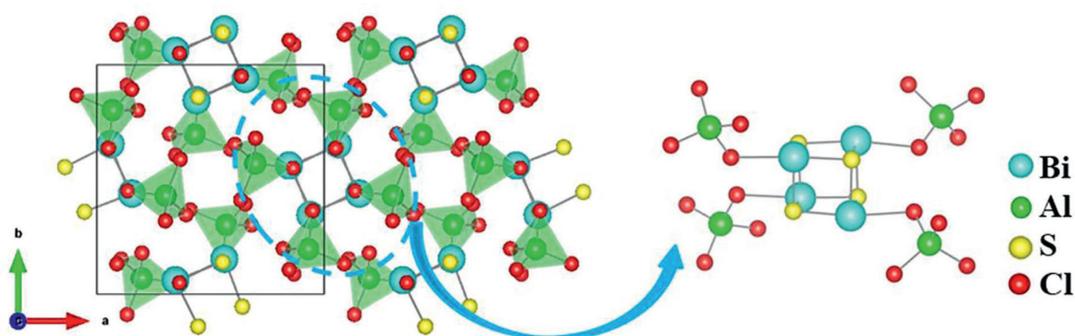


Figure 4.
 Crystal structure of (Bi₄S₄)(AlCl₄)₄.

Crystal	Space group	Band gap (HSE06) eV	NLO coefficient (pm/V)	NLO coefficient (AGS) times
In ₅ S ₅ Cl	Pmn21	1.76	d ₁₅ = 0.36, d ₂₄ = 2.83, d ₃₃ = 13.38	1.0
In ₅ S ₅ Br	Pmn21	1.84	d ₁₅ = 2.07, d ₂₄ = 2.21, d ₃₃ = 7.38	0.5
(CS ₃ N ₂ Br)Br ₃	Pna ₂₁	2.21	d ₁₅ = 8.90, d ₂₄ = 5.40, d ₃₃ = 1.00	0.6

Table 6. Space group, band gap, and SHG value of other main groups of metal chalcogenides.

4.6 Transition metal chalcogenides

Asymmetric distribution of electron clouds is generally caused by polyhedron with the d₁₀ transition metals because of the dp orbital hybridization and group distortion, so it produces high SHG behavior. Due to the dp hybridization, the compound has a red-shifted absorption edge, this might reduce the bandgap of IR-NLO materials. To enhance the chalcogenides energy gap, halogen elements are introduced, that is, by combining cations with d₁₀ configuration, which led to the equilibrium among energy gaps and SHG behavior in the IR-NLO crystals. So, they separated the asymmetric chalcogenides with a d₁₀ electronic configuration. The transition metal chalcogenide Ag₂HgSI₂ has the space group Cmc₂₁ [51]. The bandgap of Ag₂HgSI₂ is 2.65 eV and it is compared with AGS of (2.70 eV). The SHG of Ag₂HgSI₂ is 4.2 times stronger than that of KDP. The theoretical birefringence of Ag₂HgSI₂ is 0.210 at 1064 nm. The crystal (P₄S₃)₃(CuCl)₇ belongs to the space group P_{31c} [52]. The bandgap of (P₄S₃)₃(CuCl)₇ is 2.77 eV (HSE0₆ method) and NLO coefficients of (P₄S₃)₃(CuCl)₇ are d₃₃ = 3.34 and d₁₅ = d₂₄ = 1.81 pm/V. In the NLO coefficients, the d₃₃ value is about 8.5 times that of KDP and has a birefringence value of 0.150 at 1064 nm.

5. Oxide crystal

Normally, oxide-based materials have a high laser damage threshold and many of them have limited IR transparency within the range of 6 μm. Here, we would like to explain the new oxide-based NLO materials, which are very important for the development of IR transparent regions beyond 6 μm. Several new NLO oxide crystals were identified, which have high IR cutoff wavelengths that are up to 6 μm. For instance β-BaTeMo₂O₉ [53], MnTeMoO₆ [54], Cs₂TeW₃O₁₂ [55], V₂Te₂O₉ [56], Li₃VO₄ [57], M₂LiVO₄ (M = Rb, Cs) [58], Li₂K₄TiOGe₄O₁₂ [59], and Rb₄Li₂TiOGe₄O₁₂ [60]. Moreover, for the oxide-based NLO material, IR transparent range is a difficult factor to attain. Pb₁₇O₈Cl₁₈ was new IR-NLO material discovered by Pan and Poeppelmeier et al. [61] in 2015. Pb₁₇O₈Cl₁₈ single crystal was synthesized by modified spontaneous crystallization in an open model. Tao's et al. [62] reported a new LiNbO₃-type NLO crystal. Li₂ZrTeO₆ crystal (size: 16 × 15 × 12 mm³) is grown by top-seeded solution growth (TSSG) method. To maintain the structural qualities of LiNbO₃, Zr⁴⁺ and Te⁶⁺ were substituted for Nb⁵⁺ to form Li₂ZrTeO₆ and it crystallized in the trigonal crystal system with space group R3 (Figure 5). LiNbO₃ belongs to the space group, R_{3c}, which has a close structural feature with Li₂ZrTeO₆ [63]. La₃SnGa₅O₁₄ is a new

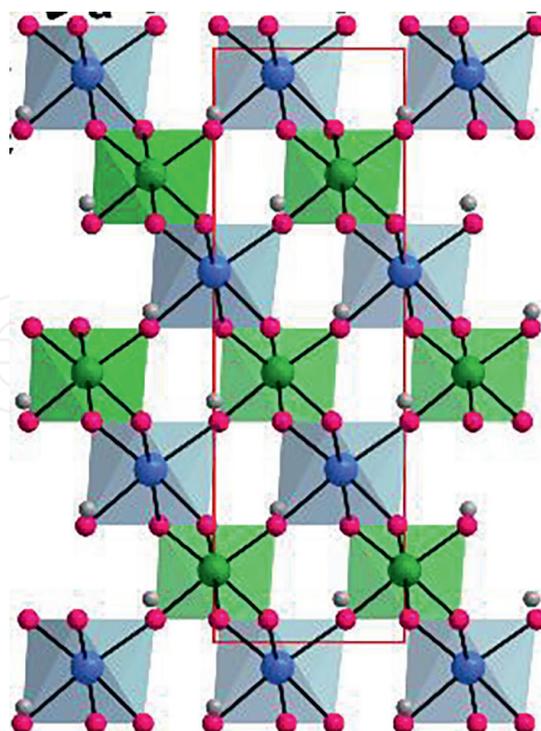


Figure 5.
 Crystal structures of $\text{Li}_2\text{ZrTeO}_6$.

IR-NLO crystal, it belongs to the langasite family and has a space group $P321$ [64]. Polycrystalline $\text{La}_3\text{SnGa}_5\text{O}_{14}$ was produced using a solid-state reaction and a single crystal were grown by Czochralski method. The single crystal of $\text{Pb}_{17}\text{O}_8\text{Cl}_{18}$ has a bandgap of 3.44 eV and it has high IR transparency ($13.9 \mu\text{m}$). $\text{La}_3\text{SnGa}_5\text{O}_{14}$ has a wide energy gap value of 4.60 eV and transparency of $10 \mu\text{m}$.

The SHG responses of $\text{Pb}_{17}\text{O}_8\text{Cl}_{18}$ showed a response at 2090 nm and 1064 nm, which is phase-matchable, and it is two times stronger than that of AgGaS_2 and four times higher than that of KDP. $\text{Li}_2\text{ZrTeO}_6$ showed a huge powder SHG behavior at 1064 nm, which is 2.5 times higher than that of KDP [63]. For $\text{Li}_2\text{ZrTeO}_6$ and LiNbO_3 , there is a variation in the SHG responses, which is closely correlated, and it is due to the different sizes of octahedral distortions in their crystal structure. The SHG efficiency of $\text{La}_3\text{SnGa}_5\text{O}_{14}$ is 0.4 times that of AgGaS_2 and when compared to AgGaS_2 ($13 \mu\text{m}$) it has wide IR transparency. $\text{Pb}_{17}\text{O}_8\text{Cl}_{18}$ has an LDT of 12.8 MW/cm^2 (Table 7). These characteristics reveal that $\text{Pb}_{17}\text{O}_8\text{Cl}_{18}$ is one of the good mid-IR-NLO crystals for the next generation. $\text{Li}_2\text{ZrTeO}_6$ has an outstanding optical performance and a very high LDT greater than 1.3 GW/cm^2

Crystal	Space group	Bandgap (eV)	IR range	SHG	LDT (\times AGS, MW/cm ²)
$\text{Li}_2\text{ZrTeO}_6$	$R3$	4.06	$7.4 \mu\text{m}$	2.5 times (KDP)	$> 1300 \text{ MW/cm}^2$
$\text{La}_3\text{SnGa}_5\text{O}_{14}$	$P321$	4.60 eV	$10 \mu\text{m}$	0.4 times that of AgGaS_2	$28 \times \text{AGS}$, 846 MW/cm^2
$\text{Pb}_{17}\text{O}_8\text{Cl}_{18}$	$Fmm2$	3.44 eV	$13.9 \mu\text{m}$	2 times (AgGaS_2) and 4 times (KDP)	$12.8 \times \text{AGS}$ (on powder)

Table 7.
 Space group, band gap, transparency range, and SHG value of oxide crystal.

and it was more than 22 times that of LiNbO_3 . It has a higher IR transparent range that is up to $7.4 \mu\text{m}$. $\text{La}_3\text{SnGa}_5\text{O}_{14}$, which has the highest LDT of 846 MW/cm^2 , is an alternative NLO crystal in the mid-IR region. It is transparent beyond $10 \mu\text{m}$. The langasite family provided valuable information to design a new NLO crystal in the IR area.

6. Halides

A halide has a binary form in which one region is a halogen and the other region is a component or radical that is less electronegative/electropositive than the halogen [65]. For preparing NLO halides, the physical, chemical, and crystallographic aspects are important. In halides, hyperpolarizabilities were used to find out the NLO susceptibilities. Moreover, these crystals have high LDT and good mechanical properties. HgBr_2 crystal was grown using a lowering temperature technique with a size of about $15 \times 15 \times 1.5 \text{ mm}^3$ [66]. Tl_3PbBr_5 , Tl_4PbI_6 , Tl_4HgI_6 , and Tl_3PbI_5 were grown by the vertical Bridgman method [5]. The 3:1:5 ratio showed orthorhombic symmetry and the 4:1:6 ratio indicated tetragonal symmetry. In this method, they maintained the temperature gradients in the range from 20 K/cm to 30 K/cm and cooling rates were in the range from 5 to 10 K/h, which showed a growth of 1 cm/day and 3–5 cm/day. Tl_3PbCl_5 [67] and Tl_3PbBr_5 [68] single crystals were grown by Bridgman-Stockbarger technique. Tl_3PbI_5 is colorless and Tl_3PbBr_5 (Figure 6) crystal is a yellow color and transparent. Tl_4HgI_6 crystal is grown using Bridgman-Stockbarger method [69, 70] and they melt consistently at 396°C . The crystal was red and when the iodine concentration increases in the stoichiometric ratio, the crystal becomes changed to black. It belongs to the point symmetry group C_{4v} . BaMgF_4 crystal was grown using the Czochralski technique [71]. It belongs to the pyroelectric fluoride group BaMF_4 ($M = \text{Mg, Co, Ni, Zn}$) and it has space group Cmc_{21} . SrAlF_5 crystal belongs to the class of uniaxial ferroelectric [72] and is grown using Czochralski technique [71]. Tl_3PbCl_5 and Tl_3PbBr_5 are nonhygroscopic. In Tl_3PbBr_5 , the phase transition is observed at $\sim 237^\circ\text{C}$, and for Tl_3PbCl_5 , phase transition is noted at 171°C . Tl_2HgI_4 compound has a melting point temperature of 318°C .

HgBr_2 crystal showed good phase matchable SHG efficiency, which is 10 times greater than that of KDP and has transparency between 2.5 and 25 mm. It covers the whole mid-IR range. Tl_3PbCl_5 and Tl_3PbBr_5 have transparency of 0.5–20 mm and 0.65–24 mm, respectively. The Tl_4HgI_6 crystal is optically positive and transparent from 1.2 to 40 mm. BaMgF_4 is a ferroelectric fluoride due to its wide transparency between 125 nm and 13 mm, and it can be used for UV and mid-IR optical applications [71, 72]. In the UV region, the shortest band is noted at 368 nm, which represents the potential behavior of BaMgF_4 as a nonlinear material. It can be used for the production of all solid-state lasers and mid-IR wavelength areas. BaMgF_4 and SrAlF_5 crystals are promising crystals for solid-state lasers. The LDT value of the HgBr_2 crystal is 0.3 GW/cm^2 .



Figure 6.
Crystal of Tl_3PbBr_5 .

7. Oxyhalides

To develop high efficiency in mid-IR-NLO crystals, it is important to have an oxide-based system with an expandable IR transparent range. Many NLO oxides have a range from 3 to 5 μm atmospheric windows. When compared with the AgGaS_2 (13 μm), the oxide-based materials, such as $\text{La}_3\text{SnGa}_5\text{O}_{14}$ and $\text{Pb}_{17}\text{O}_8\text{Cl}_{18}$, have wide IR transparency between 12 and 13.9 μm . In this lead oxyhalide, NLO crystal $\text{Pb}_{17}\text{O}_8\text{Cl}_{18}$ plays an outstanding overall property. To obtain high LDT, halide and oxide-based crystals with high bandgaps are used. Nowadays, the mixture of heavy metal lone pair cation, Pb^{2+} , and mixed oxyhalides are focused on IR applications. Xinglong Chen et al. discovered the lead mixed oxyhalides, such as $\text{Pb}_{13}\text{O}_6\text{C}_9\text{Br}_5$, $\text{Pb}_{13}\text{O}_6\text{C}_{17}\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{C}_{14}\text{Br}_{10}$ [73], which have broad IR transparency up to 14 μm , high SHG behavior ($0.6\text{--}0.9 \times \text{AgGaS}_2$) and wide bandgaps from 3.05 to 3.21 eV. $\text{Pb}_{13}\text{O}_6\text{C}_9\text{Br}_5$ single crystal has the size of $2.9 \times 1.3 \times 0.5 \text{ cm}^3$, which was grown using the top-seeded solution growth (TSSG) method. It has a wide transparent range from 0.384 to 14.0 μm and a high LDT value ($14.6 \times \text{AgGaS}_2$). Many crystals, such as APbCO_3F ($A = \text{Rb}, \text{Cs}$), $\text{Pb}_2\text{BO}_3\text{Cl}$, $\text{Cs}_3\text{VO}(\text{O}_2)_2\text{CO}_3$, Bi_3TeBO_9 , and BiFSeO_3 [74–78], have been reported with outstanding properties and it is a very good material for visible/near-IR non-linear optical applications. $\text{Pb}_{13}\text{O}_6\text{C}_{14}\text{Br}_{10}$, $\text{Pb}_{13}\text{O}_6\text{C}_{17}\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{C}_9\text{Br}_5$ have orthorhombic crystal structures with space group $Fmm2$ (Table 8). These three crystals are isomorphous.

By using Czochralski and flux method, oxide-based crystals can be obtained. The $\text{Pb}_{13}\text{O}_6\text{C}_{14}\text{Br}_{10}$, $\text{Pb}_{13}\text{O}_6\text{C}_{17}\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{C}_9\text{Br}_5$ crystals were grown by flux method and the self-flux method was adopted for $\text{PbCl}_2\text{-PbBr}_2$. The crystals obtained by this method were optically transparent and they showed a good growth rate. $\text{Pb}_{13}\text{O}_6\text{C}_9\text{Br}_5$ was used to grow large-size crystals using the TSSG technique. After many technical optimizations, two big size crystals (Dimensions up to $2.9 \times 1.3 \times 0.5$ and $3.7 \times 0.4 \times 0.7 \text{ cm}^3$) were grown using the [001] and [100] oriented seeds. They have good transparency and good growth speed. Therefore, to get a better quality crystal the growth parameters (cooling rate, rotation speed, and temperature gradient) are very important in the crystallization process. DSC curves of $\text{Pb}_{13}\text{O}_6\text{C}_{14}\text{Br}_{10}$, $\text{Pb}_{13}\text{O}_6\text{C}_{17}\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{C}_9\text{Br}_5$ show that each of them has one endothermic peak at 501°C , 504°C , and 508°C , respectively, which belongs to the melting point and these crystals have two exothermic peaks, which indicate the decomposing of the compounds. Due to the volatility of the halide materials, there is no weight loss before 490°C in the TGA curves. From the DSC and TGA, it was concluded that these compounds have high thermal stability up to 490°C . $\text{Pb}_{13}\text{O}_6\text{C}_9\text{Br}_5$, $\text{Pb}_{13}\text{O}_6\text{C}_{17}\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{C}_{14}\text{Br}_{10}$ have high reflectance wavelengths in the region between 500 and 2500 nm. When compared with AgGaS_2 (2.67 eV, 0.53–13 μm) and ZnGeP_2 (1.68 eV, 0.74–12 μm), the crystals of $\text{Pb}_{13}\text{O}_6\text{C}_{14}\text{Br}_{10}$, $\text{Pb}_{13}\text{O}_6\text{C}_{17}\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{C}_9\text{Br}_5$ own greater energy gaps and good transparency in IR region [79, 80].

Crystal	Space group	SHG (AgGaS_2)	LDT (AgGaS_2)
$\text{Pb}_{13}\text{O}_6\text{C}_{14}\text{Br}_{10}$	$Fmm2$	0.6	3.0
$\text{Pb}_{13}\text{O}_6\text{C}_{17}\text{Br}_7$	$Fmm2$	0.8	3.2
$\text{Pb}_{13}\text{O}_6\text{C}_9\text{Br}_5$	$Fmm2$	0.9	4.0

Table 8.
Space group and SHG value of oxyhalides.

In the application of high-power laser systems, the NLO crystal with laser-induced damage is one of the biggest problems. The crystals which have wider bandgaps are subjected to higher LDTs. Polycrystalline samples are used for the laser-induced damage threshold evaluation, and the polycrystalline material of AgGaS_2 was used as reference material. The $\text{Pb}_{13}\text{O}_6\text{C}_{14}\text{Br}_{10}$, $\text{Pb}_{13}\text{O}_6\text{C}_{17}\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{C}_{19}\text{Br}_5$ have large LDTs values, which are 3.0, 3.2, and 4.0 times higher than that of AgGaS_2 . The $\text{Pb}_{13}\text{O}_6\text{C}_{19}\text{Br}_5$ crystal has LDT of 439 MW/cm^2 this is 14.6 times higher than that of the AgGaS_2 crystal (30 MW/cm^2). The second harmonic generation intensity is 0.5 times higher than that of AgGaS_2 . The SHG value of $\text{Pb}_{13}\text{O}_6\text{C}_{14}\text{Br}_{10}$, $\text{Pb}_{13}\text{O}_6\text{C}_{17}\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{C}_{19}\text{Br}_5$ are found to be 0.6, 0.8, and 0.9, respectively. From this, we concluded that SHG responses of each material have all phase-matchable when it is under the 2090 nm wavelength. Due to the increase in particle size, it showed a positive movement in SHG response.

8. Conclusion

In summary, significant progress has been attained in the search for new, favorable IR nonlinear crystals, such as chalcogenides, chalcogen halides, oxides, halides, and oxyhalides, for producing coherent energy in the MIR. For a good NLO crystal, the crystals must have good physical and chemical properties, such as wide transparency range, LDT, chemical stability, birefringence, and nonlinear susceptibility. Nevertheless, for practical applications, the crystals should have high qualities with promising properties. For promising optical applications, accurate optical properties should be measured. For MIR applications, high bandgap value, LDT, and NLO susceptibility optical transparency are important. Various IR crystals fulfill the basic conditions of IR-NLO applications. The significant behavior of these crystals recommends that this crystal can be used in different optical applications.

IntechOpen

IntechOpen

Author details

Senthil Kumar Chandran^{1*}, Chinnakannu Elavarasi², Srinivasan Manikam³
and John James Gnanapragasam⁴

1 Department of Physics, Government Arts and Science College, Hosur, Tamil Nadu, India

2 Sri Vijay Vidyalaya College of Arts and Science, Dharmapuri, Tamil Nadu, India

3 Department of Physics, Center for Crystal Growth, SSN College of Engineering, Kalavakkam, Tamil Nadu, India

4 Department of Physics, Government Arts College, Trichy, Tamil Nadu, India

*Address all correspondence to: senthilkumarchandran89@gmail.com

IntechOpen

© 2022 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Yan M, Xue HG, Guo SP. Recent achievements in lone-pair cation-based infrared second-order nonlinear optical materials. *Crystal Growth & Design*. 2020;**21**(1):698-720
- [2] Chen X, Ok KM. Recent advances in oxide-based nonlinear optical materials with wide infrared transparency beyond 6 μm . *Chemistry, an Asian Journal*. 2020;**15**(22):3709-3716
- [3] Liang F, Kang L, Lin Z, Wu Y. Mid-infrared nonlinear optical materials based on metal chalcogenides: Structure-property relationship. *Crystal Growth & Design*. 2017;**17**(4):2254-2289
- [4] Gao L, Huang J, Guo S, Yang Z, Pan S. Structure-property survey and computer-assisted screening of mid-infrared nonlinear optical chalcogenides. *Coordination Chemistry Reviews*. 2020;**421**:213379
- [5] Jiang XM, Guo SP, Zeng HY, Zhang MJ, Guo GC. Large crystal growth and new crystal exploration of mid-infrared second-order nonlinear optical materials. *Structure-Property Relationships in Non-Linear Optical Crystals II*. 2012;**2012**:1-43
- [6] Isaenko LI, Yeliseyev AP. Recent studies of nonlinear chalcogenide crystals for the mid-IR. *Semiconductor Science and Technology*. 2016;**31**(12):123001
- [7] Shi ZH, Chi Y, Sun ZD, Liu W, Guo SP. $\text{Sn}_2\text{Ga}_2\text{S}_5$: A type of IR nonlinear-optical material. *Inorganic Chemistry*. 2019;**58**(18):12002
- [8] Nguyen V, Ji B, Wu K, Zhang B, Wang J. Unprecedented mid-infrared nonlinear optical materials achieved by crystal structure engineering, a case study of $(\text{KX})\text{P}_2\text{S}_6$ ($\text{X} = \text{Sb, Bi, Ba}$). *Chemical Science*. 2022;**13**(9):2640-2648
- [9] Wu C, Lin L, Jiang X, Lin Z, Huang Z, Humphrey MG, et al. $\text{K}_5(\text{W}_3\text{O}_9\text{F}_4)(\text{IO}_3)$: An efficient mid-infrared nonlinear optical compound with high laser damage threshold. *Chemistry of Materials*. 2019;**31**(24):10100-10108
- [10] Yu T, Wang S, Zhang X, Li C, Qiao J, Jia N, et al. MnSiP_2 : A new Mid-IR ternary phosphide with strong SHG effect and ultrabroad transparency range. *Chemistry of Materials*. 2019;**31**(6):2010-2018
- [11] Guo SP, Chi Y, Guo GC. Recent achievements on middle and far-infrared second-order nonlinear optical materials. *Coordination Chemistry Reviews*. 2017;**335**:44-57
- [12] Guo Y, Liang F, Yin W, Li Z, Luo X, Lin ZS, et al. BaHgGeSe_4 and SrHgGeSe_4 : Two new Hg-based infrared nonlinear optical materials. *Chemistry of Materials*. 2019;**31**(8):3034-3040
- [13] Li MY, Ma Z, Li B, Wu XT, Lin H, Zhu QL. HgCuPS_4 : An exceptional infrared nonlinear optical material with defect diamond-like structure. *Chemistry of Materials*. 2020;**32**(10):4331-4339
- [14] Kushwaha AK, Kalita H, Suman S, Bhardwaj A, Ghosh R. Two-dimensional (2D) thermoelectric materials. *Thermoelectricity and Advanced Thermoelectric Materials*. 2021:233-260
- [15] Muslih EY, Munir B, Khan MM. Advances in chalcogenides and chalcogenides-based nanomaterials such as sulfides, selenides, and tellurides. *Chalcogenide-Based Nanomaterials as Photocatalysts*. 2021:7-31

- [16] Shi W, Ding YJ, Fernelius N, Vodopyanov K. Efficient, tunable, and coherent 0.18-5.27-THz source based on GaSe crystal. *Optics Letters*. 2002;**27**(16):1454-1456
- [17] Abudurusuli A, Li J, Pan S. A review on the recently developed promising infrared nonlinear optical materials. *Dalton Transactions*. 2021;**50**(9):3155-3160
- [18] Nitsche R, Bölsterli HU, Lichtensteiger M. Crystal growth by chemical transport reactions—I: Binary, ternary, and mixed-crystal chalcogenides. *Journal of Physics and Chemistry of Solids*. 1961;**21**:199-205
- [19] Bajpai PK, Yadav S, Tiwari A, Virk HS. Recent advances in the synthesis and characterization of chalcogenide nanoparticles. *Solid State Phenomena*. 2015;**222**:187-233
- [20] Jiang X, Kang L, Luo S, Gong P, Lee MH, Lin Z. Development of nonlinear optical materials promoted by density functional theory simulations. *International Journal of Modern Physics B*. 2014;**28**(27):1430018
- [21] Ohmer MC, Goldstein JT, Zelmon DE, Saxler AW, Hegde SM, Wolf JD, et al. Infrared properties of AgGaTe₂, a nonlinear optical chalcopyrite semiconductor. *Journal of Applied Physics*. 1999;**86**(1):94-99
- [22] Schunemann PG, Setzler SD, Pollak TM, Ohmer MC, Goldstein JT, Zelmon DE. Crystal growth and properties of AgGaTe₂. *Journal of Crystal Growth*. 2000;**211**:242-246
- [23] Isaenko L, Yelisseyev A, Lobanov S, Titov A, Petrov V, Zondy JJ, et al. Growth and properties of LiGaX₂ (X= S, Se, Te) single crystals for nonlinear optical applications in the mid-IR. *Crystal Research and Technology: Journal of Experimental and Industrial Crystallography*. 2003;**38**:379-387
- [24] Yelisseyev A, Isaenko L, Lovanov S, Zondy JJ. Advanced solid state lasers. *OSA Trends in Optics and Photonics Series*. 2000;**34**:561-569
- [25] Zondy JJ, Bielsa F, Douillet A, Hilico L, Acef O, Petrov V, et al. Frequency doubling of CO₂ laser radiation at 10.6 μm in the highly nonlinear chalcopyrite LiGaTe₂. *Optics Letters*. 2007;**32**(12):1722-1724
- [26] Yao J, Mei D, Bai L, Lin Z, Yin W, Fu P, et al. BaGa₄Se₇: A new congruent-melting IR nonlinear optical material. *Inorganic Chemistry*. 2010;**49**(20):9212-9216
- [27] Yao J, Yin W, Feng K, Li X, Mei D, Lu Q, et al. Growth and characterization of BaGa₄Se₇ crystal. *Journal of Crystal Growth*. 2012;**346**(1):1-4
- [28] Isaenko L, Yelisseyev A, Lobanov S, Krinitsin P, Petrov V, Zondy JJ. Ternary chalcogenides LiBC₂ (B= In, Ga; C= S, Se, Te) for mid-IR nonlinear optics. *Journal of Non-Crystalline Solids*. 2006;**352**:2439-2443
- [29] Yelisseyev AP, Drebushchak VA, Titov AS, Isaenko LI, Lobanov SI, Lyapunov KM, et al. Thermal properties of the mid-infrared nonlinear crystal LiInSe₂. *Journal of Applied Physics*. 2004;**96**(7):3659-3665
- [30] Petrov V, Yelisseyev A, Isaenko L, Lobanov S, Titov A, Zondy JJ. Second-harmonic generation and optical parametric amplification in the mid-IR with orthorhombic biaxial crystals LiGaS₂ and LiGaSe₂. *Applied Physics B*. 2004;**78**(5):543-546
- [31] Badikov V, Badikov D, Shevyrdyaeva G, Tyazhev A, Marchev G,

- Panyutin V, et al. BaGa₄S₇: Wide-bandgap phase-matchable nonlinear crystal for the mid-infrared. *Optical Materials Express*. 2011;1(3):316-320
- [32] Tyazhev A, Kolker D, Marchev G, Badikov V, Badikov D, Shevyrdyaeva G, et al. Midinfrared optical parametric oscillator based on the wide-bandgap BaGa₄S₇ nonlinear crystal. *Optics Letters*. 2012;37(19):4146-4148
- [33] Medina-Ramírez I, Hernández-Ramírez A, Maya-Trevino ML. Synthesis methods for photocatalytic materials. In *Photocatalytic Semiconductors*. 2015:69-102
- [34] Isaenko LI, Yelisseyev AP, Lobanov SI, Krinitsin PG, Molochev MS. Structure and optical properties of Li₂Ga₂GeS₆ nonlinear crystal. *Optical Materials*. 2015;47:413-419
- [35] Yelisseyev AP, Isaenko LI, Krinitsin P, Liang F, Goloshumova AA, Naumov DY, et al. Crystal growth, structure, and optical properties of LiGaGe₂Se₆. *Inorganic Chemistry*. 2016;55(17):8672-8680
- [36] Yin W, Feng K, Hao W, Yao J, Wu Y. Synthesis, structure, and properties of Li₂In₂Mq₆ (m = Si, Ge; q = S, Se): A new series of IR nonlinear optical materials. *Inorganic Chemistry*. 2012;51(10):5839-5843
- [37] Lin X, Guo Y, Ye N. BaGa₂GeX₆ (X = S, Se): New mid-IR nonlinear optical crystals with large band gaps. *Journal of Solid State Chemistry*. 2012;195:172-177
- [38] Liu PF, Li YY, Zheng YJ, Yu JS, Duan RH, Chen H, et al. Tailored synthesis of nonlinear optical quaternary chalcogenides: Ba₄Ge₃S₉Cl₂, Ba₄Si₃Se₉Cl₂ and Ba₄Ge₃Se₉Cl₂. *Dalton Transactions*. 2017;46(8):2715-2721
- [39] Feng K, Kang L, Lin Z, Yao J, Wu Y. Noncentrosymmetric chalcogenide NaBa₄Ge₃S₁₀Cl with large bandgap and IR NLO response. *Journal of Materials Chemistry C*. 2014;2(23):4590-4596
- [40] Liu BW, Zeng HY, Jiang XM, Wang GE, Li SF, Xu L, et al. [A₃X][Ga₃PS₈] (A = K, Rb; X = Cl, Br): Promising IR non-linear optical materials exhibiting concurrently strong second-harmonic generation and high laser-induced damage thresholds. *Chemical Science*. 2016;7(9):6273-6277
- [41] Guo SP, Sun ZD, Chi Y, Xue HG. Adduct-type IR nonlinear-optical crystal SbI₃·(S₈)₃ with a large second-harmonic generation and a high laser-induced damage threshold. *Inorganic Chemistry*. 2018;57(17):11282-11288
- [42] Samoc A, Samoc M, Prasad PN, Krajewska-Cizio A. Second-harmonic generation in the crystalline complex antimony triiodide-sulfur. *JOSA B*. 1992;9(10):1819-1824
- [43] Lu ZT, Sun ZD, Chi Y, Xue HG, Guo SP. Balanced second-order nonlinear optical properties of adducts CHI₃·(S₈)₃ and AsI₃·(S₈)₃: A systematic survey. *Inorganic Chemistry*. 2019;58(7):4619-4625
- [44] Guo SP, Chi Y, Xue HG. SnI₄·(S₈)₂: A novel adduct-type infrared second-order nonlinear optical crystal. *Angewandte Chemie*. 2018;130(36):11714-11717
- [45] Wiegers GT, Vos A. Refinement of the structure of tetrathiazylfluoride (NSF)₄. *Acta Crystallographica*. 1963;16(2):152-153
- [46] Weiss J, Ruppert I, Appel R. Die Kristall- und Molekülstruktur von S₃N₅PF₂. *Zeitschrift für Anorganische*

und Allgemeine Chemie.
1974;**406**:329-336

[47] Beck J, Schlueter S, Zotov N. The cube-shaped main group element clusters (Bi₄S₄)⁴⁺ and (Bi₄Se₄)⁴⁺-synthesis from chloroaluminate melts, crystal structures and vibrational spectra. *Zeitschrift für Anorganische und Allgemeine Chemie*. 2004;**630**:2512-2519

[48] Nickel V, Deiseroth HJ, Kienle L, Duppel V, Reiner C. Polymorphism of In₅S₅Cl–X-ray and HRTEM-Investigations. *Allgemeine Chemie*. 2010;**636**:79-84

[49] Deiseroth HJ, Reiner C, Xhaxhiu K, Schlosser M, Kienle L. X-Ray and transmission electron microscopy investigations of the new solids In₅S₅Cl, In₅Se₅Cl, In₅S₅Br, and In₅Se₅Br. *Zeitschrift für Anorganische und Allgemeine Chemie*. 2004;**630**:2319-2328

[50] Wolmershäuser G, Krüger C, Tsay YH. [CS₃N₂Br]⁺ Br⁻-ein Produkt der Bromierung von S₄N₄ in Schwefelkohlenstoff. *Chemische Berichte*. 1982;**115**(3):1126-1131

[51] Keller HL, Wimbert L. Über Münzmetall-Quecksilber-Chalkogenidhalogenide. III Zur Kristallstruktur von Ag₂HgSI₂. *Zeitschrift für Anorganische und Allgemeine Chemie*. 2003;**629**(12-13):2337-2340

[52] Biegerl A, Brunner E, Gröger C, Scheer M, Wachter J, Zabel M. The unexpected versatility of P₄S₃ as a building block in polymeric copper halide networks: 2, 3-P, 1, 2, 3-P and all-P coordination. *Chemistry – A European Journal*. 2007;**13**(33):9270-9276

[53] Zhang W, Tao X, Zhang C, Gao Z, Zhang Y, Yu W, et al. Bulk growth and

characterization of a novel nonlinear optical crystal BaTeMo₂O₉. *Crystal Growth & Design*. 2008;**8**(1):304-307

[54] Jin CG, Li Z, Huang LX, He MZ. Top-seeded solution growth and characterization of a novel nonlinear optical crystal MnTeMoO₆. *Journal of Crystal Growth*. 2013;**369**:43-46

[55] Zhang J, Tao X, Sun Y, Zhang Z, Zhang C, Gao Z, et al. Top-seeded solution growth, morphology, and properties of a polar crystal Cs₂TeMo₃O₁₂. *Crystal Growth & Design*. 2011;**11**(5):1863-1868

[56] Zhang W, Wang X, Shen G, Shen D. Top-seeded growth, optical properties and theoretical studies of noncentrosymmetric Te₂V₂O₉. *Crystal Research and Technology*. 2012;**47**:163-168

[57] Chen Z, Zhang Z, Dong X, Shi Y, Liu Y, Jing Q. Li₃VO₄: A promising mid-infrared nonlinear optical material with large laser damage threshold. *Crystal Growth & Design*. 2017;**17**:2792-2800

[58] Han G, Wang Y, Su X, Yang Z, Pan S. Growth, properties, and theoretical analysis of M₂LiVO₄ (M = Rb, Cs) crystals: Two potential mid-infrared nonlinear optical materials. *Scientific Reports*. 2017;**7**:1901

[59] Xu J, Wu H, Yu H, Zhang W, Hu Z, Wang J, et al. Li₂K₄TiOGe₄O₁₂: A stable mid-infrared nonlinear optical material. *Chemistry of Materials*. 2020;**32**:906-912

[60] Xi M, Tang C, Li R. Rb₄Li₂TiOGe₄O₁₂: A titanyl nonlinear optical material with the widest transparency range. *Angewandte Chemie, International Edition*. 2019;**58**:18257-18260

[61] Zhang H, Zhang M, Pan S, Dong X, Yang Z, Hou X, et al. Pb₁₇O₈Cl₁₈: A

promising IR nonlinear optical material with large laser damage threshold synthesized in an open system. *Journal of the American Chemical Society*. 2015;**137**:8360-8363

[62] Lu W, Gao Z, Liu X, Tian X, Wu Q, Li C, et al. Rational design of a LiNbO₃-like nonlinear optical crystal, Li₂ZrTeO₆, with high laser-damage threshold and wide Mid-IR transparency window. *Journal of the American Chemical Society*. 2018;**140**:13089-13096. DOI: 10.1021/jacs.8b08803

[63] Ok KM, Halasyamani PS, Casanova D, Llundell M, Alemany P, Alvarez S. Distortions in octahedrally coordinated d₀ transition metal oxides: A continuous symmetry measures approach. *Chemistry of Materials*. 2006;**18**:3176-3183

[64] Lan H, Liang F, Jiang X, Zhang C, Yu H, Lin Z, et al. Pushing nonlinear optical oxides into the mid-infrared spectral region beyond 10 μm: Design, synthesis, and characterization of La₃SnGa₅O₁₄. *Journal of the American Chemical Society*. 2018;**140**:4684-4690

[65] Hagemann M, Weber HJ. Are ternary halides useful materials for nonlinear optical applications? *Applied Physics A*. 1996;**63**(1):67-74

[66] Zhu T, Chen X, Qin J. Research progress on mid-IR nonlinear optical crystals with high laser damage threshold in China. *Frontiers of Chemistry in China*. 2011;**6**(1):1-8

[67] Singh NB, Suhre DR, Green K, Fernelius N, Hopkins FK. Periodically poled materials for long-wavelength infrared (LWIR) NLO applications. *Journal of Crystal Growth*. 2005;**274**:132-137

[68] Ferrier A, Velázquez M, Pérez O, Grebille D, Portier X, Moncorgé R.

Crystal growth and characterization of the non-centrosymmetric compound Tl₃PbCl₅. *Journal of Crystal Growth*. 2006;**291**(2):375-384

[69] Ferrier A, Velázquez M, Portier X, Doualan JL, Moncorgé R. Tl₃PbBr₅: A possible crystal candidate for middle infrared nonlinear optics. *Journal of Crystal Growth*. 2006;**289**(1):357-365

[70] Badikov DV, Badikov VV, Kuz'micheva GM, Panyutin VL, Rybakov VB, Chizhikov VI, et al. Growth and X-ray diffraction study of Tl₄HgI₆ crystals. *Inorganic Materials*. 2004;**40**:314-320

[71] Shimamura K, Villora EG, Muramatsu K, Ichinose N. Advantageous growth characteristics and properties of SrAlF₅ compared with BaMgF₄ for UV/VUV nonlinear optical applications. *Journal of Crystal Growth*. 2005;**275**:128-134

[72] Ravez J, Simon A, Chaminade JP. Ferroelectric behavior and phase transition at 715 K in SrAlF₅. *Journal of Applied Physics*. 1981;**52**:4740-4743

[73] Chen X, Jo H, Ok KM. Lead mixed oxyhalides satisfying all fundamental requirements for high-performance mid-infrared nonlinear optical materials. *Angewandte Chemie*. 2020;**132**(19):7584-7590

[74] Zou G, Lin C, Jo H, Nam G, You TS, Ok KM. Pb₂BO₃Cl: A Tailor-Made polar lead borate chloride with very strong second harmonic generation. *Angewandte Chemie*. 2016;**128**(39):12257-12261

[75] Zou G, Lin Z, Zeng H, Jo H, Lim SJ, You TS, et al. Cs₃VO(O₂)₂CO₃: An exceptionally thermostable carbonatoperoxovanadate with an extremely large second-harmonic

generation response. *Chemical Science*.
2018;**9**(48):8957-8961

[76] Xia M, Jiang X, Lin Z, Li R.
“All-three-in-one”: A new bismuth–
tellurium–borate Bi_3TeBO_9
exhibiting strong second harmonic
generation response. *Journal of
the American Chemical Society*.
2016;**138**(43):14190-14193

[77] Zou G, Ye N, Huang L,
Lin X. Alkaline-alkaline earth fluoride
carbonate crystals ABCO_3F (A= K,
Rb, Cs; B= Ca, Sr, Ba) as nonlinear
optical materials. *Journal of the
American Chemical Society*.
2011;**133**(49):20001-20007

[78] Liang ML, Hu CL, Kong F, Mao JG.
 BiFSeO_3 : An excellent SHG material
designed by aliovalent substitution.
*Journal of the American Chemical
Society*. 2016;**138**:9433-9436

[79] Kubelka P. Ein Beitrag zur Optik
der Farbanstriche (Contribution to the
optic of paint). *Zeitschrift fur technische
Physik*. 1931;**12**:593-601

[80] Tauc J. Absorption edge and
internal electric fields in amorphous
semiconductors. *Materials Research
Bulletin*. 1970;**5**(8):721-729