INORGANIC
CHEMISTRY
FRONTIERS

Accepted Manuscript

Designing Syntheses and Photophysical Simulations of

Noncentrosymmetric Compounds

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Abstract

In this paper, we describe the preparations of inorganic noncentrosymmetry (NCS) chalcogenides and their infrared nonlinear optical properties. We present a reasonable synthesis of inorganic NCS compounds by thinking of genetic development processes of a living organism. The basic unit having NCS structure is selected as a chromophore of NCS materials. The NCS compounds will be obtained from NCS chromophore development of normal growth. The chromophore development will be an alienation process of growth if the NCS compound is not formed by NCS chromophore. The normal developments of the NCS chromophores (SnS_4) and (Sn_2S_3) obtain the NCS crystal of $Ba_7Sn_5S_{15}$; and the normal developments of the NCS chromophores of (BiS_5) and (InS_4) obtain a compound of Ba_2BiInS_5 keeping in NCS structure. Both of them, the Ba^{2+} ions are a charge-compensating agent. The NCS crystals $SnGa_4Q_7$ (Q = S, Se) were obtained by NCS chromophores of (GaQ_4) and (SnQ_4). However, the centrosymmetry (CS) compound of $Ba_6Sn_7S_{20}$ was obtained because the developments of NCS chromophores of the (SnS_4) and (SnS_5) alienate from the normal process of growth. We give more examples of NCS chromophore developments of normal and alienable processes in this paper. For NCS compounds, we have searched their nonlinear optical (NLO) properties of micro-crystals (powders) and electronic origin of NLO response. The intensity of second harmonic generation (SHG), laser-induced damage threshold (LIDT), and infrared transparency were measured, and the conversion efficiency, figure of merit (FOM), and energy band structure were calculated for these NCS compound materials. It is found that the NCS materials of $SnGa_4Q_7$ (Q = S, Se) appear with large conversion efficiencies, high damage threshold and wide transparencies in the mid-infrared region. And, the study of micro-mechanism elucidate that the stereochemically active lone-pair electrons of Sn^{2+} can significantly improve the polarity of the $[SnQ_4]$ chromophore. Large NLO responses of them originate from the covalent interactions of Sn−Q and the cooperative effects of polarities between the chromophore $[SnQ_4]$ and $[GaQ_4]$. It is also found that the $Ba_7Sn_5S_{15}$ material is type-I phase-matchablility, and that the SHG conversion efficiency and FOM is about twice of that of $AgGaS_2$ at the saturated particle size (particle size of 150−212 μm). The $Ba_8Sn_4S_{15}$ is not phase-matching material. The SHG intensity and conversion efficient of $Ba_8Sn_4S_{15}$ are separately about 250 times than those of α-SiO_2, and the SHG intensity and conversion efficient

are separately about 10 times than those of AgGaS$_2$ at the particle size of 25−45 μm.

Introduction

The noncentrosymmetric (NCS) compounds and their crystals can exhibit a variety of technologically important physical properties, and the NCS crystals may become the materials of piezoelectricity, pyroelectricity, ferroelectricity, and second-order nonlinear optical (NLO) response[1]. The structural symmetry of material affects its property. There are the crystallographic interrelationships between the NCS crystal classes[2,3] and physical properties, and among 32 crystal point groups[4], 20 NCS groups (21 NCS crystal classes excluding point group 432 (O group)) can exhibit the piezoelectric or NLO effect. It is noted that all pyroelectric materials have NLO behavior but the converse is not true. The NLO material can be made into optical frequency conversion device, and it can broaden the wavelength coverage ranges of laser spectrum. As well known, one can distinguish between two classes of laser sources[5]. One class includes sources which generate tunable laser radiation directly from gain in gas discharge, solid-state bulk materials or optical fibers, i.e. direct laser radiation sources. The longest wavelength coverage of direct solid state laser source is only limited under 3.5 microns. The other class of laser sources is based on frequency conversion of basic laser sources by using NLO crystal. It is for this purpose that many NLO crystals have been developed to broaden the wavelength coverage of laser spectrum. Scientists and engineers constantly explore new NLO material to solve the development of optical technology demand and twenty-first century scientific and technologic challenges. The main progress took place in the last two decades following the advancement in near-infrared solid state laser technology and NLO crystals. The second harmonic generation (SHG), parametric down-conversion and up-conversion processes in NLO crystals as well as combinations of them have been widely used to fill in gaps in the laser spectrum, in which the direct laser radiations do not exist or certain operational regimes are impossible from the vacuum ultraviolet (~150 nm) to the deep mid-IR (middle infrared) [6-9]. The coherent mid-IR sources have important applications in sciences and technology, including the detection and quantification of molecular trace gases[10], medical diagnostics and military systems[11-12], free space optical communication and deep space exploration, etc [5,13-14].

At present, nonlinear frequency down-conversion is still a powerful method to transform the wavelength of near-IR laser sources to the mid-IR spectral range and generate coherent radiation in all time zones from 3μm up to 20 μm and above. Non-oxide NLO crystals play key role, in particular above 5 μm, such as unary, binary, ternary and quaternary arsenides, phosphides, sulfides, selenides or tellurides, and they have been used in such down-conversion devices. During the past ten years, many compounds with large NLO coefficients and wide transparencies in IR regions have been prepared, and they are K$_2$P$_2$Se$_6$ [15], Na$_2$Ge$_2$Se$_5$ [16], K$_4$GeP$_4$Se$_{12}$ [17], Na$_{0.5}$Pb$_{1.75}$GeS$_4$ [18], LiGaGe$_2$Se$_6$ [19], α- and β-A$_2$Hg$_3$M$_2$S$_8$ (A = K, Rb; M = Ge, Sn) [20], Li$_2$In$_2$GeSe$_6$ [21], Li$_2$CdMS$_4$ (M = Ge, Sn) [22], Ba$_6$Sn$_6$Se$_{13}$ [23], [Zn(H$_2$O)$_4$][Zn$_2$Sn$_3$Se$_9$(MeNH$_2$)] [24], K$_6$Cd$_4$Sn$_3$Se$_{13}$ [25], K$_{14}$Cd$_{15}$Sn$_{12}$Se$_{46}$

[26], $A_6Sn[Zn_4Sn_4S_{17}]$ (A = K, Rb, Cs) [27], $BaGa_2GeQ_6$ (Q = S, Se) [28], $Pb_4Ga_4GeQ_{12}$ (Q = S, Se) [29], $Ba_4CuGa_5Q_{12}$ (Q = S, Se) [30], $Ag_2In_2Si(Ge)S_6$ [31], $Ag_{0.5}Pb_{1.75}Ge(S_{1-x}Se_x)_4$ [32], $Zn_xBa_2B_2S_{5+x}$ (x ≈ 0.2) [33], $CsCd_4X^{III}_5Q_{12}$ (X^{III} = Ga, In; Q = S, Se) [34], and $Rb_2CdBr_2I_2$ [35]. All of them have their specific advantages but also some drawbacks. The crystals of $AgGaS_2$, $AgGaSe_2$, $ZnGaP_2$, GaSe and CdSe also have some drawbacks although they can be obtained from the commercial market [36]. The crystals of $AgGaS_2$ and $AgGaSe_2$ have residual absorption, poor thermal conductivity and anisotropic thermal expansion. The crystal of $ZnGaP_2$ has a limited transparency due to multi-photon and residual absorption. GaSe crystal is very low damage threshold, and CdSe has quite modest birefringence and nonlinearity. Accordingly, the development of new and improvement of existing nonlinear crystals are critical for advancing mid-IR coherent source，at particular, with increasing conversion efficiency and the output power.

Drs. I. Chung and M. G. Kanatzidis considered that the metal chalcogenides are the most promising source of potential NLO materials with desirable properties, particularly in the IR region[37]. A general strategy is suggested to employ NCS chromophore as building units in the design syntheses of NLO crystals [38-40]. The NCS chromophore include the distorted polyhedron with a d^0 cation center resulting from a second-order Jahn-Teller (SOJT) effect [41-44], polar displacement of a d^{10} cation center [45], and stereochemically active lone pair (SCALP) effect of cation [46-48], and the distorted triangle and tetrahedron [49-52a]. The NLO crystal materials can be also constructed by the multifold NCS chromophore with different coordinate environments [52b,53]. In this paper, we present the reasonable designs of mid-IR NCS crystals by thinking of gene development process.

Designs and Syntheses of Noncentrosymmetric Compounds

Optimization of material chromophore

NCS chromophore is a fundamental building block (FBB) toward a NCS material. The development of NCS chromophore will produce an instrument device, which is along the processes: chromophore→ cluster→…→unit cell→single crystal→device. In bio-system, genetic development is along the processes: gene→genome→…→cell→tissue→organ. There are some common factors between a gene and NCS chromophore; both are the developments from a basic unit toward a larger purpose of dimension and function. However, their natures are different. A gene is the molecular unit of heredity of a living organism, and it holds the information to build and maintain an organism's cell and pass genetic traits to offspring. The word gene, when applied in non-biological contexts, connotes a FBB toward a larger purpose [54]. Here, we must have a clear understanding that the material chromophore is not life activity and the gene in bio-system is consisted in vital organ. By thinking of gene development in biosystem, we present the reasonable designs of NCS inorganic materials originating from NCS chromophores. A NCS chromophore of material has different coordinate structures, and they are the distorted triangle, pentagon, n-polygon (n is odd number with ≠1), tetrahedron, octahedron, square pyramid, pentagonal pyramid, triangular bipyramid, pentagonal bipyramid, and other NCS structure geometry, as shown in Figure 1.1.
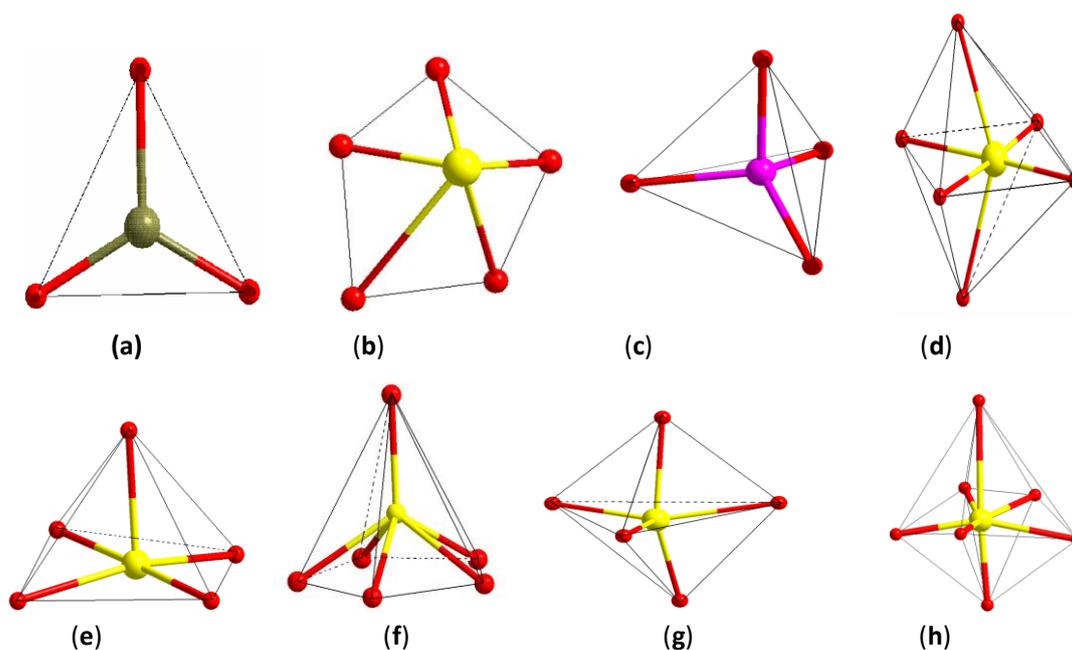
Figure 1.1 Noncentrosymmetric chromophore structures. (**a**) non-equilateral triangle (or triangular pyramid), (**b**) non-equilateral pentagon, (**c**) tetrahedron, (**d**) distortion octahedral, (**e**) square pyramid, (**f**) pentagonal pyramid, (**g**) triangular bipyramid, (**h**) pentagon bipyramid.

It is no guarantee to predict a macroscopically NCS material which is the development from NCS chromophore. A NCS chromophore will develop gradually with a normal process of growth if the NCS crystal is constructed by using NCS chromophore. The chromophore development will be an alienation process of growth if the NCS structural crystal is not formed by NCS chromophore. Such cases have been carefully studied by several groups. Dr. Poeppelmeier *et al.*[55-59] synthesized and examined the crystallographically ordered transition-metal oxyfluorides $[MO_xF_{6-x}]^{n-}$ (M=d^0 transition metal, x = 1-3, and n = 2, 3) and determined that the polar or no polar symmetry originates from the changes in the bond network. Dr. Halasyamani *et al.* studied another series of analogues $A_2Ti(IO_3)_6$ (A=Li, Na, K, Rb, Cs, Tl) and considered that the polarity results only from the Li and Na phases of cation-size, coordination requirements, and bond valence concept arguments [60]. Our group synthesized CS crystal of Ba_2BiGaS_5 and NCS crystal of Ba_2BiInS_5 and they are constructed by tetrahedron (Ga/InS$_4$) chromophore and square-pyramidal (BiS$_5$) chromophore [61], and we consider that the different crystal symmetries result from the distorted tetrahedron or cation size effect in these two compounds.

CS materials of $Ba_6Sn_7S_{20}$, Ba_2BiGaS_5 and NCS materials of $Ba_7Sn_5S_{15}$, Ba_2BiInS_5

Compound $Ba_7Sn_5S_{15}$ was prepared by a solid-state reaction method from stoichiometric amounts of BaS, Sn, and S. It crystallizes in NCS space group $P6_3cm$ of the hexagonal system, and is constructed by the material chromophores of tetrahedron (SnS$_4$) and triangular pyramid (SnS$_3$) [62]. The Sn-S distances vary from 2.361 to 2.407 Å in the SnS$_4$ tetrahedron, and the calculated bond valence sums (BVS) of the Sn is 4.27 or 4.14, which is close to the oxidation state +4 of Sn. In the triangular pyramidal (SnS$_3$), the Sn is a threefold coordination with Sn-S distances

ranging from 2.583 to 2.687 Å, and the calculated BVS is 2.30 or 2.25 which is close to oxidation state of +2. The two triangular pyramids ($2SnS_3$) are the arrangements against each other. They are share with a basal plane and form a triangular bipyramid (Sn_2S_3). The isolated $[SnS_4]^{4-}$ tetrahedra and $[Sn_2S_3]^{2-}$ triangular bipyramids held together by the Ba^{2+} cations [62]. The NCS chromophores of (SnS_4) and (Sn_2S_3) develop normally into NCS crystal, the skeleton frame is plotted in Figure 1.2a. Compound $Ba_6Sn_7S_{20}$ was prepared with the molar ratio of stoichiometric amounts from Ba, Sn, and S. It crystallizes in CS space group $C2/c$ of the monoclinic system, and is constructed by the material chromophores of tetrahedron (SnS_4) and triangular bipyramid (SnS_5) [62]. In the triangular bipyramid, the Sn atom is coordinated by five S atoms with Sn-S distances ranging from 3.339 to 3.812 Å, and the calculated BVS of Sn is 4.09 or 3.96 which is close to oxidation state +4 of Sn. In the SnS_4 tetrahedron, the Sn-S distances vary from 2.327 to 2.481 Å and the calculated BVS of Sn is 3.99 or 4.04, which is also close to the oxidation state +4 of Sn. Three (SnS_4) tetrahedrons are connected to each other by corner sharing to form a kind of basic structural unit $[Sn_3S_8]^{4-}$, and four (SnS_5) triangular bipyramids are connected to each other by edge sharing to form another basic structural unit $[Sn_4S_{14}]^{12-}$. Both of the structural units $[Sn_3S_8]^{4-}$ and $[Sn_4S_{14}]^{12-}$ are connected to each other by corner sharing to form a three-dimensional framework with the Ba cations in the cavities in the configuration of the $Ba_6Sn_7S_{20}$ [62]. The developments of NCS chromophores of the (SnS_4) and (SnS_5) alienate from the normal process of growth, and the CS crystal is obtained as shown in Figure 1.2b. By the comparisons between these two processes, we consider that the different crystal symmetries between the $Ba_6Sn_7S_{20}$ and $Ba_7Sn_5S_{15}$ result from the different oxidation states of Sn ion. We believe that the low oxidation state of Sn ions in the material chromophore (Sn_2S_3) will be favorable for growing NCS crystal.

（a）

(b)
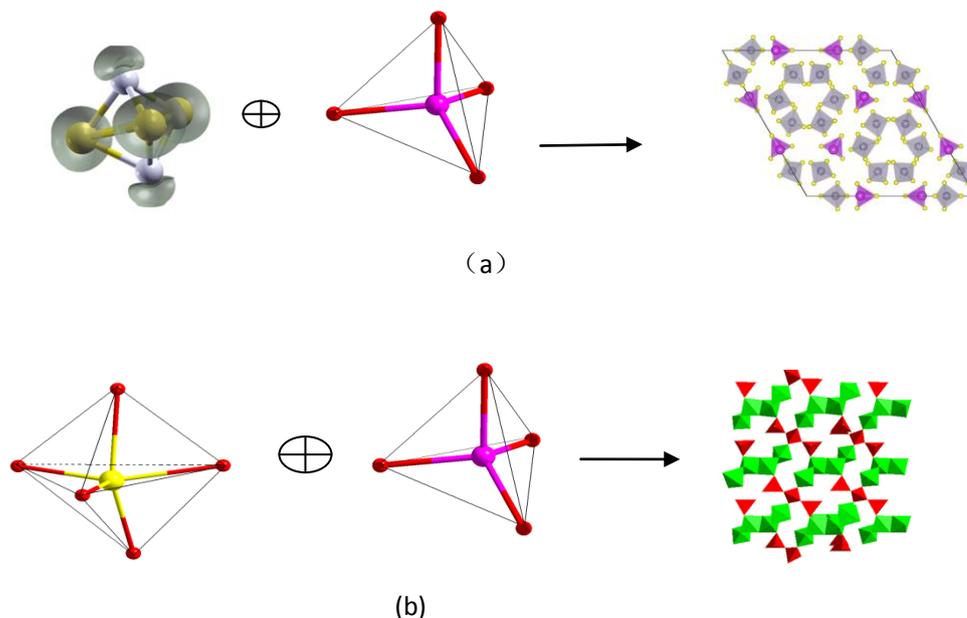
Figure 1.2. The skeleton frame of NCS chromophore developments (no shown Ba^{2+} ions), (a) normal process of chromophores (SnS_5) and (SnS_4) into $Ba_7Sn_5S_{20}$; (b) alienated process of growth into material $Ba_6Sn_7S_{20}$ from chromophores (SnS_5) and (SnS_4).

Compound Ba_2BiInS_5 was prepared by a solid-state reaction method from stoichiometric amounts of BaS, Bi, In, and S. It crystallizes in NCS space group *Cmc2* of the orthorhombic system, and is constructed by the NCS chromophores of the tetragonal pyramid (BiS_5) and tetrahedron (InS_4), and charge-compensating Ba^{2+} ion [61]. The Bi^{3+} ion is coordinated by five S^{2-} ions, and the bond lengths of Bi--S vary from 2.582(5) to 2.959(4) Å, featuring the irregular tetragonal pyramid (BiS_5). In the tetrahedron (InS_4), the In^{3+} ion is coordinated by four S atoms in the tetrahedral arrangement with bond lengths ranging from 2.447(6) to 2.578(6) Å. The edge-shared BiS_5 tetragonal pyramids with parallel arrangements are formed into a chain, and the corner-shared InS_4 tetrahedrons are also formed into a chain. These two chains are further interconnected with each other through sharing corner to form the whole $_1^\infty[BiInS_5]^{4-}$ anionic chain. The NCS chromophores of (BiS_5) and (InS_4) develop into a compound keeping in NCS structure, as shown in Figure 1.3a. Compound Ba_2BiGaS_5 was prepared by a solid-state reaction method from stoichiometric amounts of BaS, Bi, Ga, and S. It crystallizes in CS space group *Pnma* of the orthorhombic system, and is constructed by the NCS chromophores of the tetragonal pyramid (BiS_5) and tetrahedron (GaS_4), and charge-compensating Ba^{2+} ion [61]. The coordinate environments of chromophores (BiS_5) and (GaS_4) in the CS crystal Ba_2BiGaS_5 are the same as those in the NCS crystal Ba_2BiInS_5. In the CS crystal Ba_2BiGaS_5, however, the edge-shared BiS_5 tetragonal pyramids with anti-parallel arrangements are formed into a chain, and the tetrahedron GaS_4 is connected with the tetragonal pyramid BiS_5 by the sharing corner and the tetrahedrons are the alternate arrangements along the chain constructing by the BiS_5. Furthermore, they form an infinite one-dimensional (1D) $_1^\infty[BiGaS_5]^{4-}$ anionic chain. The developments of the NCS chromophores appear in the alienated process and obtain the CS crystal Ba_2BiGaS_5, as shown in Figure 1.3b. It is a very interesting that the different crystal symmetries between the CS Ba_2BiGaS_5 and NCS Ba_2BiInS_5 are obtained from the same coordinate structure of NCS chromophores of tetrahedron (GaS_4/InS_4) and tetragonal pyramid (BiS_5). We check the configurations of these two crystals in details. A small size GaS_4 is connected with the neighboring BiS_5 through edge-sharing. This situation leads to a *trans* arrangement along the $_1^\infty[BiGaS_5]^{4-}$ chain with the apexes of BiS_5 pyramids reversed up and down alternately, and results in the CS nonpolar structure of compound Ba_2BiGaS_5. A large size InS_4 is connected with the neighboring BiS_5 through corner-sharing and it results in *cis* arrangement along the $_1^\infty[BiInS_5]^{4-}$ anionic chain with the parallel apexes of BiS_5 pyramids, and obtains the NCS polar structure of Ba_2BiInS_5.

(a)

(b)
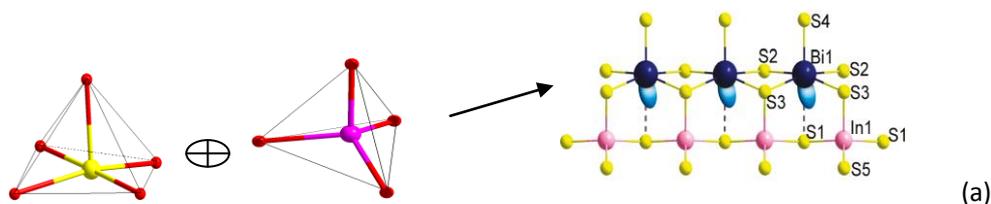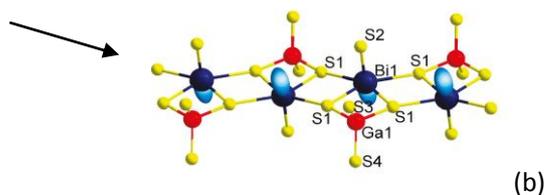
Figure 1.3. The skeleton frame of NCS chromophore developments (no shown Ba^{2+} ions), (a) normal process of growth from chromophores (BiS_5) and (InS_4) into material Ba_2BiInS_5; (b) alienated process of growth from chromophores (BiS_5) and (GaS_4) into material Ba_2BiGaS_5.

NCS materials of $SnGa_4Q_7$ (Q = S, Se) and $Ba_8Sn_4S_{15}$ with Sn-Q covalent interactions

Compounds $SnGa_4S_7$ and $SnGa_4Se_7$ were prepared from reactants of Sn, Ga, and S/Se by a solid-state reaction method at high temperature, respectively. Both compounds are crystallize in NCS space group *Pc* of the monoclinic system, the remarkable configurations of three dimension frameworks are formed by the tetranuclear secondary basic structure unit Ga_4Q_{11} which is constructed by four GaQ_4 tetrahedrons, and the SnQ_4 tetragonal pyramid locating in the cavities [63]. In other words, the NCS crystals $SnGa_4Q_7$ (Q = S, Se) are constructed by NCS chromophores of tetrahedron (GaQ_4) and tetragonal pyramid (SnQ_4), as plotted in Figure 1.4. The Sn atom is bonded to four Q atoms at two short and two long distances, forming the SnQ_4 tetragonal pyramid, and the Sn−S bond distances range from 2.654 to 2.992 Å in the $SnGa_4S_7$ and the Sn-Se bonds vary from 2.773 to 3.111 Å in the $SnGa_4Se_7$. All Ga sites are coordinated by four Q atoms to form the tetrahedrons GaQ_4. The Ga−S bond lengths range from 2.214 to 2.337 Å in the $SnGa_4S_7$ and the Ga-Se bonds vary from 2.346 to 2.463 Å in the $SnGa_4Se_7$. The atomic covalent radius of S, Se, and Sn are individually 1.05(3), 1.20(4), and 1.39 (4) Å [64], and here, the bond lengths of Sn-S and Sn-Se are little larger than the sum of covalent radius due to the crowd coordination environments of SnG_4 (G = S, Se). The calculated ELF (electron localization function) plot shows that there is a charge distribution along the bond axis of Sn-Se (Figure 1.5a). This finding indicates the Sn−Se covalence interactions.
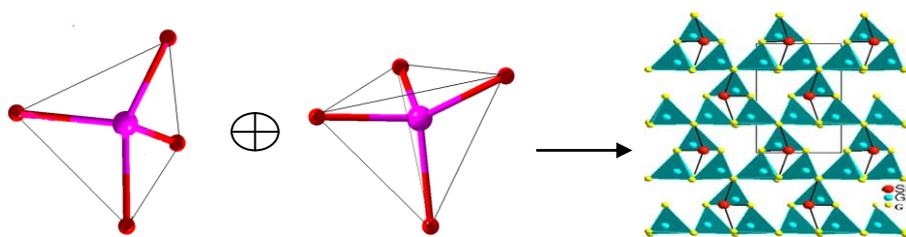
Figure 1.4. The skeleton frame of NCS chromophore developments of normal process from (SnS_4/Se_4) and (GaS_4/Se_4) into NCS materials of $SnGa_4Q_7$ (Q = S, Se).

(a)   (b)
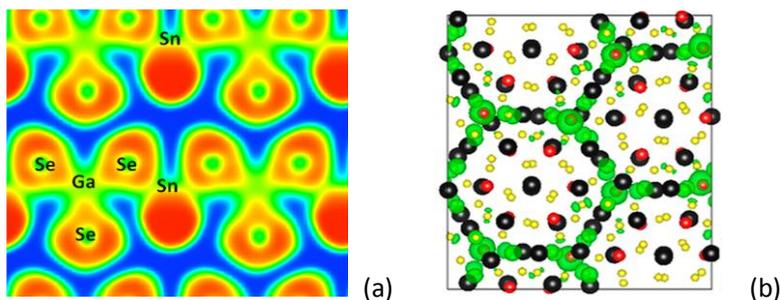
Figure 1.5. (a) The electron localization function map of $SnGa_4Se_7$ at (001) plane cutting through the Sn and Ga atoms and the electron localization function value ranging from 0 (blue) to 1 (red); (b) the charge distributions of the occupied bands nearby the Fermi level for $Ba_8Sn_4S_{15}$ (black, Ba; red, Sn; yellow, S).

Compound $Ba_8Sn_4S_{15}$was prepared from a stoichiometric mixture of the $BaS/SnS/SnS_2$ by a solid-state reaction method at high temperature, and it crystallizes in the NCS space group *Pca2₁* of orthorhombic system [65]. The $Ba_8Sn_4S_{15}$ crystal is constructed by the NCS chromophores of tetrahedrons (SnS_4) and pyramids (SnS_3) with Ba^{2+} cations inserting between them for charge balance. Figure 1.6 gives the skeleton frame of chromophore developments of normal process from NCS chromophores (SnS_3) and (SnS_4). In the tetrahedrons SnS_4, the Sn−S distances range from 2.3373 to 2.4124 Å, and the calculated BVS of Sn is 4.20 or 4.09 which is close to oxidation state +4; in the SnS_3 pyramids, the Sn-S bond lengths range from 2.5336 to 2.6817 Å, and the calculated BVS of Sn is 1.93 which is close to oxidation state +2 [65]. At the right of figure 1.6, the secondary basic structure unit of $Ba_8Sn_4S_{15}$ is regarded as a coin-like structure, which forms the two-dimensional (2D) honeycomb structure by alternate arrangement in parallel. The skeleton of the honeycomb (coin-like configuration) is formed by 6 SnS_3 pyramidal units and 18 Ba atoms in the ordered arrangement on the edge and isolated nine SnS_4 tetrahedral units and eight Ba atoms fill in the cells of the honeycomb. The charge distributions near the Fermi level are main contributions from SnS_3 pyramidal units, shown in figure 1.5b. This finding also indicates the Sn-S covalent interaction in SnS_3.
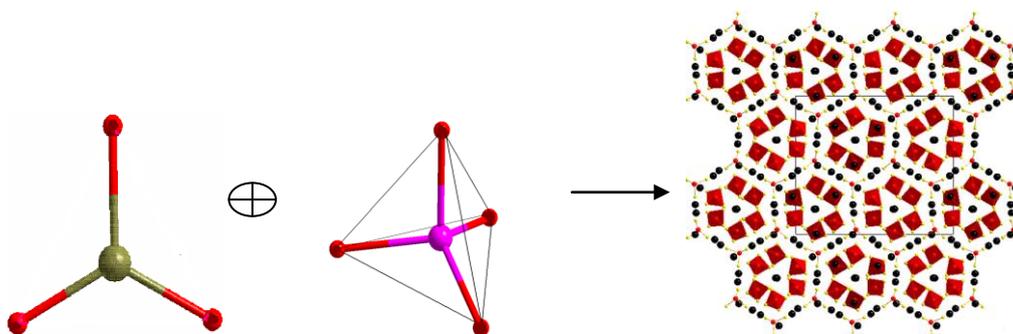
Figure 1.6. The skeleton frame of NCS chromophore developments of normal process from chromophores (SnS_3) and (SnS_4) into NCS material of $Ba_8Sn_4S_{15}$

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Photophysics Simulations and Micro-Mechanisms of Infrared NLO Materials

Physical properties

The optical conversion efficiency is the most important standard to evaluate optical property of NLO materials. While we select a NLO crystal as frequency conversion devices with a certain laser wavelength, the first option is to require high conversion efficiency. For simplicity of representation, we only consider the SHG process of NLO response. The SHG conversion efficiency is defined as $\eta = I_{2\omega}/I_\omega$, which is a rate of SHG and incident light intensities. The SHG intensity $I_{2\omega}$ can be written in terms of the intensity of the incident field according to the couple wave theory, and the expression is written as following [66a]:

$$I_{2\omega} = \frac{32 d_{eff}^2 \omega^2 I_\omega^2}{n_\omega^2 n_{2\omega} \varepsilon_0 c^2} L^2 \frac{\sin^2(\Delta k L/2)}{(\Delta k L/2)^2} \quad (1).$$

In the MKS system, we can write the conversion efficiency as

$$\eta = C \bullet FOM \bullet I_\omega L^2 \lambda_\omega^{-2} \bullet PMF , \quad (2);$$

in which the *PMF* is phase mismatch factor, which includes entirely the effect of wave vector, the constant $C = 128\pi^2 \varepsilon_0^{-1}$, the $FOM = d_{eff}^2 (n_\omega^{-2} n_{2\omega}^{-1})$ is defined as a figure of merit. Here, the relative of $\omega = 2\pi c/\lambda$ is employed from formula (1) to (2). In accordance with formula (2), to maximize the SHG efficiency it is essential that the condition of perfect phase matching is satisfied, i.e. $\Delta k \to 0$ and $PMF = 1$, otherwise, it is a dramatic decrease in the SHG efficiency. Under the condition of $PMF = \sin^2(\Delta k L/2) \bullet (\Delta k L/2)^{-2}$ perfect phase matching, the SHG efficiency can be improved by using higher radiation intensity I_ω and shorter radiation wavelength λ_ω, longer interaction length L, and greater figure of merit *FOM*. The powder SHG conversion efficient of a new material can be determined by comparisons with standard material in terms of the measurements of SHG intensity *vs* particle size [63,68].

FOM is determined by the SHG coefficient *d* and refractive index *n* of material, and they can be simulated or calculated by the energy band theory combining with sum-over-states method [67] or classical anharmonic oscillator model [66b]. The bulk SHG coefficient, d_{eff}, can be estimated by the comparisons between the incident optical intensities of the sample and known material [68]. The optical parameters *d* and *n* are related to the space structure, charge distribution and transition energy of crystal material. The *FOM* is a primary index for screening of different NLO materials.

Radiation intensity I_ω is dependence on the incident optical power *P* at the fundamental frequency and the cross-sectional area *A*, and it is in accordance with the relation of $I_\omega = P/A$. Accordingly, to obtain the strongest radiation intensity, there must have the largest possible power *P* and the smallest possible area *A* if the threshold of the NLO crystal is not a limiting factor. In fact, this situation is not possible, and the threshold is dependent on optical gap of material. The latter can be obtained by the calculation of band structures or the measurement of UV−vis diffuse

reflectance spectra [69].

Additionally, the SHG efficiency can be improved if there has a large ratio L/λ_ω. To obtain a large ratio L/λ_ω, it requires light pass the journey of crystal as long as possible or a large size of crystal and provide a shorter incident wavelength. For a thick crystal (a large L), the maximum ratio L/λ_ω for a given wavelength λ_ω is limited by thermal conductivity of material (low thermal conduction will lead to the heat accumulation and the crystal burst within a large size of crystal). For a thin crystal (very small L), to obtain a large ratio L/λ_ω requires radiation wavelength as short as possible. It is limiting by the given wavelength of radiation source and the anti-damage ability of material. Accordingly, we require a width window of light transparence in NLO materials. This fact allows to have a wide coverage of the tunable incident wavelength.

The NLO crystal with high quality laser frequency conversion must meet the conditions of strong radiation intensity I_ω, short radiation wavelength λ_ω, long interaction length L, and great figure of merit FOM, which associates with high conversion efficient. Additionally, NLO crystals require: (1) the stability of physical and chemical properties, high hardness, anti-moisture; (2) a good optics uniformity of large size crystal; (3) easy processing and low price for crystal, etc. In fact, it is very few that the NLO crystal is in full compliance with the terms mentioned above. We only select the NLO crystal that meets the most basic conditions according to the application requirement. For example, we require a high conversion efficient, a large *FOM*, width infrared transparence including two windows of atmosphere (about 4 and 16 μm), and large threshold for infrared NLO crystals.

Phase matching requirement

Figure 2.1a shows a plot of the SHG intensity *vs*. particle size for $SnGa_4G_7$ powders (G = S, Se), and the $AgGaS_2$ powder was prepared with the same size ranges as the reference [63]. The SHG intensities of these powders are essentially proportional to particle sizes, which indicate that they are the type-I phase-matching materials [70]. The Type-I phase matching represents that the polarizations of both two input beans at ω frequencies are parallel to each other, and the polarization of output bean at 2ω is orthogonal to input beans. In accordance with formula (2), phase-matching requirement is essential to maximize the SHG efficiency. Furthermore, we can derive the relative SHG conversion efficiencies $\eta^S/\eta^R = (I^S_{2\omega}/I_\omega)/(I^R_{2\omega}/I_\omega)$ from the relative SHG intensities $I^S_{2\omega}/I^R_{2\omega}$ between sample and reference. From figure 2.1a, we can find that the SHG intensities of $SnGa_4S_7$ and $SnGa_4Se_7$ are about 1.3 and 3.8 times than that of the benchmark $AgGaS_2$ at the particle size of 150−210 μm, respectively. These findings indicate that the conversion efficiencies of $SnGa_4G_7$ (G = S, Se) are 1.3 and 3.8 times larger than that of those of $AgGaS_2$, separately, under the same experimental conditions and devices. Figure 2.1b gives the plots of the SHG intensity of particle-size dependence for $Ba_8Sn_5S_{15}$ powders. It shows the important feature of the particle-size in figure 2.1b, and it is a peak of the intensity when the particle size is close to 95 μm. An intensity is approximately linear increasing with particle size

while the particle size is less than 95 μm, and it is an inverse relation between intensity and size while the particle size is larger than 95 μm. Similar features of the particle-size dependence are exhibited by powders of quartz (α-SiO_2) as illustrated in the inset of figure 2.1b, which indicates that $Ba_8Sn_4S_{15}$ and α-SiO_2 are not phase-matching materials on the basis of SHG measurements in powders[70]. By the comparisons of the intensity localized at the peak between $Ba_8Sn_4S_{15}$ and α-SiO_2, we can derive that the SHG intensity and SHG conversion efficient of $Ba_8Sn_4S_{15}$ are separately about 250 times than those of α-SiO_2, and we also can find that the SHG intensity and SHG conversion efficient are separately about 10 times than those of $AgGaS_2$ at the particle size of 25−45 μm from figure 2.1b.
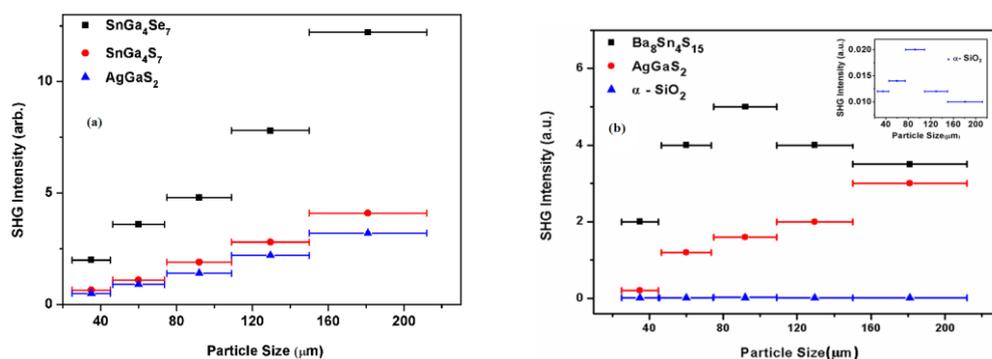
Figure 2.1. The SHG intensity *vs.* particle size of powders (a) $SnGa_4G_7$ (G = S, Se) and $AgGS_2$; (b) $Ba_8Sn_4S_{15}$, α-SiO_2 (inset panel), and $AgGaS_2$.

Figure of merit and nonlinear optical coefficient

In accordance with formula (1), the SHG intensity $I_{2\omega}$ is direct proportion to the NLO coefficient d^2_{eff} and is inverse proportion to refractive indexes ($n^2_\omega n_{2\omega}$). And, both the refractive index and NLO coefficient are inverse relations with the band gaps. The figure of merit (*FOM)* is a balance indication of contradiction contributions between the refractive index and NLO coefficient, and well describes the quality of material-self. The *FOM* relative value between the sample and reference can be derived from the plots of SHG intensity vs. particle size, furthermore, the NLO coefficient of sample can be estimated from $d^S_{eff} \approx (I^S_{2\omega}/I^R_{2\omega})^{1/2}d^R_{eff}$ from the *FOM* relative value when omitting the differences of refractive n between the sample and reference. The *FOM*s of $SnGa_4G_7$ (G = S, Se) are about 1.3 and 3.8 times than that of $AgGaS_2$, and their SHG coefficients d_{eff} are estimated to be 15.85 and 27.10 pm/V, respectively, with $AgGaS_2$ (d^R_{eff} = 13.9 pm/V [71]) as a reference in figure 2.1a [63]. The theoretical values of the SHG coefficient d are also obtained by using the velocity-gauge formula derived by Sipe et al.[67]. The space groups of $SnGa_4G_7$ (G = S, Se) crystals belong to class m, and there are ten nonvanishing tensors (d_{11}, d_{12}, d_{13}, d_{15}, d_{24}, d_{26}, d_{31}, d_{32}, d_{33}, and d_{35}) of second-order susceptibility. Judging from Kleinman's symmetry, only six independent tensor components (d_{11}, d_{12}, d_{13}, d_{15}, d_{24}, and d_{33}) are taken into account in the calculations, and the calculated values are listed in Table 1. The largest and smallest components (d_{33} and d_{12}) are calculated to be 37.51 and -1.77 pm/V for $SnGa_4Se_7$, and to be 15.70

and -2.39 pm/V for SnGa$_4$S$_7$ at a wavelength of 2.05 μm, respectively. The largest components of calculations are the same order of magnitude as the experimental estimation for SnGa$_4$G$_7$ (G = S, Se).

The *FOM* of Ba$_8$Sn$_4$S$_{15}$ is 250 times than that of α-SiO$_2$ and the SHG coefficient d_{eff} is estimated to be 6.39 pm/V in the intensity of localized at the peak (i.e. particle size of 95 μm) with α-SiO$_2$ (d^R_{eff} = 0.30 pm/V [72]) as a reference in figure 2.1b [65]. Additionally, the *FOM* of Ba$_8$Sn$_4$S$_{15}$ is 1.12 times than that of AgGaS$_2$ and the SHG coefficient d_{eff} is estimated to be 14.71 pm/V in the intensity at particle size of 180 μm with AgGaS$_2$ (d^R_{eff} = 13.9 pm/V [71]) as a reference in figure 2.1b [65]. The space group of Ba$_8$Sn$_4$S$_{15}$ belongs to class mm2, and there are five nonvanishing tensors (d_{15}, d_{24}, d_{31}, d_{32}, and d_{33}) of second-order susceptibility. Under the restriction of Kleinman's symmetry, only three independent SHG tensor components (d_{31}, d_{32}, and d_{33}) are considered. The calculated frequency-dependent SHG coefficients d_{31}, d_{32}, and d_{33} are plotted in figure 2.2 based on classical anharmonic oscillator model[65, 66b]. It is found from figure 2.2 that the theoretical values of d_{31}, d_{32}, and d_{33} are about 23.97, 21.97, and 23.92 pm/V at a wavelength of 2.05 μm (0.60 eV), respectively. Noted here, the theoretical SHG coefficients d_{ij} only come from the electronic contributions, no including the contributions from lattice vibrations; and the measured SHG coefficients d_{ij} of powder depend on the particle size. Accordingly, the estimated value of d_{eff} based on the experimental measurement must come from the saturate particle size, i.e. SHG intensity is independent with the variation of particle size.

Table 1. Theoretical SHG coefficients d_{ij} (pm/V) at a wavelength 2.05 μm.

Compounds	d_{11}	d_{12}	d_{13}	d_{15}	d_{24}	d_{33}
SnGa$_4$S$_7$	−6.82	−2.39	−3.54	9.12	−10.19	15.70
SnGa$_4$Se$_7$	−4.82	-1.77	−5.54	18.84	−13.80	37.51
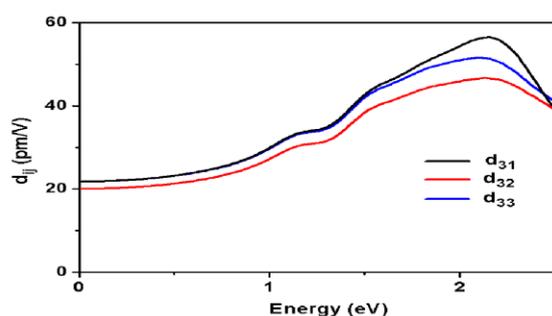
Figure 2.2. The calculated frequency-dependent second harmonic generation tensor components for Ba$_8$Sn$_4$S$_{15}$.

Laser induced damage thresholds

The damage threshold of material is also an important evaluation condition for a good quality NLO material. The damage threshold value is related to the parameters I_ω and λ_ω written in formula (1). The materials with higher damage threshold can ~~allows to~~ be illuminated by high

intensity of laser, and this material will has a large SHG conversion efficiency. It was reported that the laser damage probability depends on the fluency [73-75]. It was given that the fluence or energy density (J/cm^2) ~~is relation~~ relates with the electric field (E$^2_0$) and incident wavelength λ [73]. Here, a single pulse laser induced damage threshold (LIDT) is employed to evaluate the powder damage threshold [76]. The same particle size of samples $SnGa_4G_7$ (G = S, Se), $Ba_8Sn_4S_{15}$ and reference $AgGaS_2$ were packaged into the disks with a diameter of 8 mm. The optical microscope was used to observe the changes of the compounds when high-power 1064 nm laser radiation passed with a pulse width τ_p of 8 ns. The power of the laser beam was measured by a Nova II sensor, and the damage spot was measured using a Vernier caliper. Then the recorded laser power and the measured area of the damage spot were used to derive the LIDT values of the samples $SnGa_4G_7$ (G = S, Se), $Ba_8Sn_4S_{15}$ and reference $AgGaS_2$, respectively [63,65]. The results of powder LIDTs using single pulse measurement for these samples and reference are summarized in Table 2. The values in brackets are corresponding to particle size rage (25--45 μm) of $Ba_8Sn_4S_{15}$ and $AgGaS_2$, and the other values are corresponding to particle size (150–210 μm) of $SnGa_4S_7$, $SnGaSe_7$ and $AgGaS_2$ at Table 2. The comparisons between the sample and reference would be made under the same experimental conditions. Accordingly, we find that the LIDT of $Ba_8Sn_4S_{15}$ (122.1 MW/cm^2) is about 26 times than that of $AgGaS_2$ (4.6 MW/cm^2), and the LIDTs of $SnGa_4S_7$ (165.1 MW/cm^2) and $SnGa_4Se_7$ (40.0 MW/cm^2) are about 19 and 4.6 times that of $AgGaS_2$ (8.6 MW/cm2), respectively. The high LIDTs imply that these materials are promising for high-power NLO application in the IR region.

Table 2. Results of powder LIDT measurements for compounds

Compound	damage energy (mJ)	spot diameter (mm)	damage threshold (MW/cm^2)
$SnGa_4S_7$	49.83	3.1	165.1
$SnGa_4Se_7$	34.00	5.2	40.0
$Ba_8Sn_4S_{15}$	55.37	3.8	122.1
$AgGaS_2$	12.13 (10.05)	6.7 (8.3)	8.6 (4.6)

Micro mechanism of NLO response for infrared materials

Band structures and density of states

The structures of energy bands are used to determine the optical gap and transparent zone, and the transport properties of material. The densities of states near to Fermi level are employed to determine the atomic or group charge distribution, and to analyze the process of charge transfers and the electronic origin of NLO response. The calculated band structures along the special k-point in the first Brillouin zone (BZ) and the partial density of states (PDOS) and total density of states (TDOS) are plotted in Figure 2.3 for Ba_2BiInS_5 compound [61]. It is found from Figure 2.3a that the valence band maximum (VBM) is located at the middle of the Γ--S line, while the

conduction band minimum (CBM) is located at the Γ point, indicating an indirect band gap of 1.61 eV for Ba_2BiInS_5 compound. It is found from figure 2.3b that the highest occupied states ranging from -4.0 to 0.0 eV (Fermi level) mainly contain S-3p states with small mixtures of Bi-6s6p and In-5s5p states; the lowest unoccupied states from 1.6 eV to 4.5 eV strongly involve unoccupied Bi-6p states and less unoccupied In-5s5p states. Thus, the charge transfers from occupied S-3p states to unoccupied Bi-6p states and to the hybridized In-5s5p states are believed to make main contributions to the optical absorption. We can see from PDOS that the dominant contribution to Bi-6s state is found at the lower energy range of -8.0 to -9.4 eV, and that the indirect mixing between Bi-6s and Bi-6p states is mediated by hybridization with S-3p states at the top of valence band for Ba_2BiInS_5 compound. Although the hybridized states of Bi-6s with S-3p close to the Fermi level account for only a small fraction of the total Bi-6s states, they play an important and crucial role in the formation of the Bi-6s stereochemically active lone-pair electron. These results show that the formation of the Bi^{3+} $6s^2$ lone pair has dependence on the S^{2-} anion, and this dependence on the electronic states of the anion is evidence of the stereochemically active lone pair. It can be also found another evidence of the stereochemically active lone-pair electron based on partial electron density (PED) of 2.4 [61]. The PEDs of the states from -2.5 to 0.0 eV (Fermi level) were calculated for Ba_2BiInS_5 compound, and plotted in Figure 2.4. Two dimensional electron density slices containing Bi and S atoms are shown through the (001) plane. An almost spherical electron distribution can be seen around the S atoms, and an asymmetric density distribution is clearly present around each Bi atom which directs away from their nearest-neighboring S atom. This finding indicates that there are the stereochemically active Bi^{3+} lone pairs. The stereochemically active Bi^{3+} lone pairs manifest in parallel local dipole alignment fashions and the cooperative effects of all local dipoles lead to the enhancement of macroscopic dipole moments. This is micro origin leading to a large SHG response of Ba_2BiInS_5 compound. Figure 2.5 gives the plots of the calculated band structures and densities of states of the $Ba_7Sn_5S_{15}$ [62]. It is found from Figure 2.5a that this compound is an indirect band-gap material with a gap of 2.14 eV. From Figure 2.5b, we find that the band just above the Fermi level is predominately derived from Sn-5p states in group $[Sn_2S_3]^{2-}$, and is also small contributions from Sn-5s and S-3p states in group $[SnS_4]^{4-}$. However, the band just below the Fermi level is mostly composed of S-3p states in $[Sn_2S_3]^{2-}$ and $[SnS_4]^{4-}$ groups, respectively. Accordingly, the charge transfers across the band-gap edge originate from the (Sn_2S_3) and (SnS_4) polyhedrons, respectively.

(a)   **(b)**
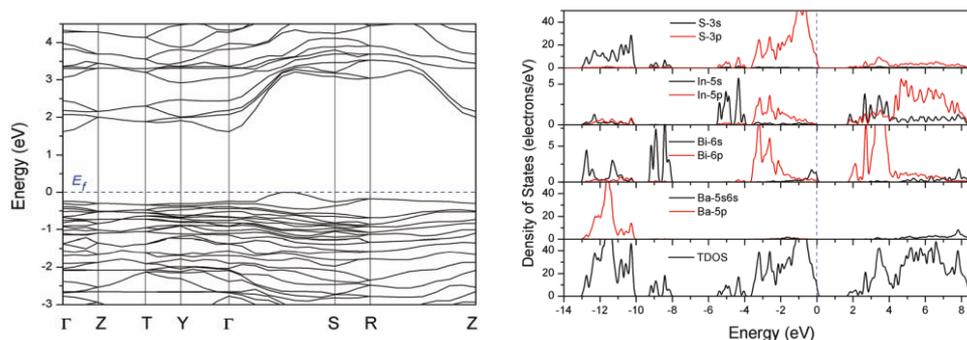
Figure 2.3. (a) The band structures and (b) total and partial density of states for Ba_2BiInS_5 using the norm-conserving pseudopotential method. The Fermi level is set at 0.0 eV.
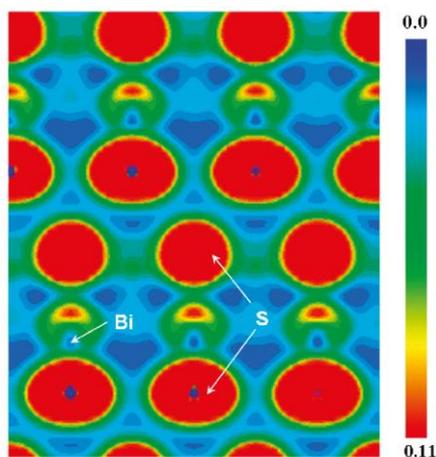
Figure 2.4. The partial electron density maps for compound Ba_2BiInS_5 , and the electron density is represented from blue (0.0 e/Å^3) to red (0.11 e/Å^3). The above DFT calculations were performed by using the PAW potential method.

(a)   (b)
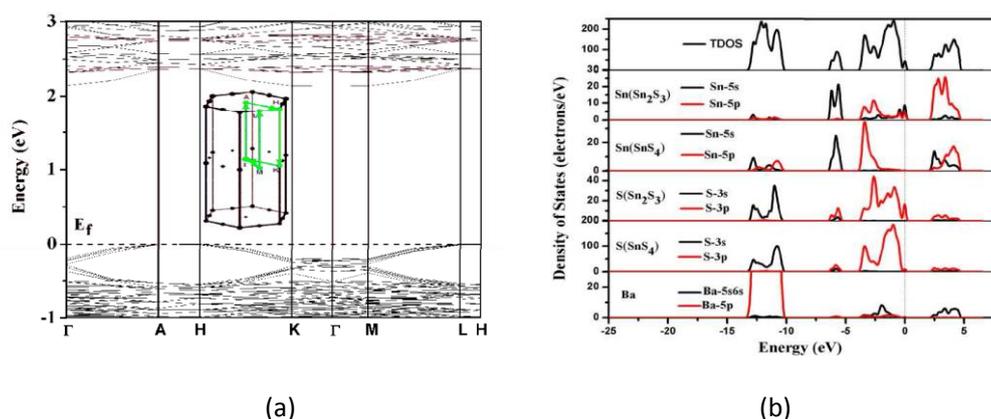
Figure 2.5. (a) The band structures and (b) density of states for $Ba_7Sn_5S_{15}$ compound

Local dipole moment

The local dipole moments of $[Sn_2S_3]^{2-}$ and $[SnS_4]^{4-}$ is 2.1287, 0.9547 Debye, respectively in $Ba_7Sn_5S_{15}$ compound based on the electronic structural calculations of isolate groups [62]. These results show that the polarization is much larger for the isolate trigonal-bipyramidal $[Sn_2S_3]^{2-}$ than for the isolate tetrahedral $[SnS_4]^{4-}$ in $Ba_7Sn_5S_{15}$ material. Accordingly, we consider that the group (Sn_2S_4) makes a most of contribution to the NLO response of $Ba_7Sn_5S_{15}$ material. Figure 2.6a gives the top view of the electron density contour surface for isolate $[Sn_2S_3]^{2-}$, and it indicates the charge transfers from S^{2-} to Sn^{2+} ions. Figure 2.6b gives the plots of group $[Sn_2S_3]^{2-}$ arrangements in the $Ba_7Sn_5S_{15}$ crystal, and it is found ~~finds~~ that the dipole origination of $[Sn_2S_3]^{2-}$ along the z direction is parallel to each other. The polarity superposition of the $[Sn_2S_3]^{2-}$ groups will strengthen the crystal polarity and lead to a large SHG response of a crystal material $Ba_7Sn_5S_{15}$.

Table 3 lists the local dipole moments of the $[SnS_3]^{4-}$ and $[SnS_4]^{4-}$ anionic groups within $Ba_8Sn_4S_{15}$ compound based on the calculations of *ab* initio method with the Gaussian03 package [65]. The obtained results show that the polarization of the isolate pyramidal $[SnS_3]^{4-}$ is much larger than that of the isolate tetrahedral $[SnS_4]^{4-}$. The average dipole moments of the $[SnS_4]^{4-}$ and total dipole moments of 6 $[SnS_4]^{4-}$ groups in the unit cell are 1.8305 and 10.9832 Debye, respectively, and the average dipole moments of $[SnS_3]^{4-}$ and total dipole moments of 2 $[SnS_3]^{4-}$ anions are 11.7229 and 23.4459 Debye, respectively in the unit cell of $Ba_8Sn_4S_{15}$ compound. A large dipole moment of $[SnS_3]^{4-}$ anion is attributed to its pyramidal geometry, which has the lone pair electrons of stereochemical activity. Thus, the $[SnS_3]^{4-}$ anions can make more contribution than the $[SnS_4]^{4-}$ anions to the NLO response of $Ba_8Sn_4S_{15}$.

(a) (b)
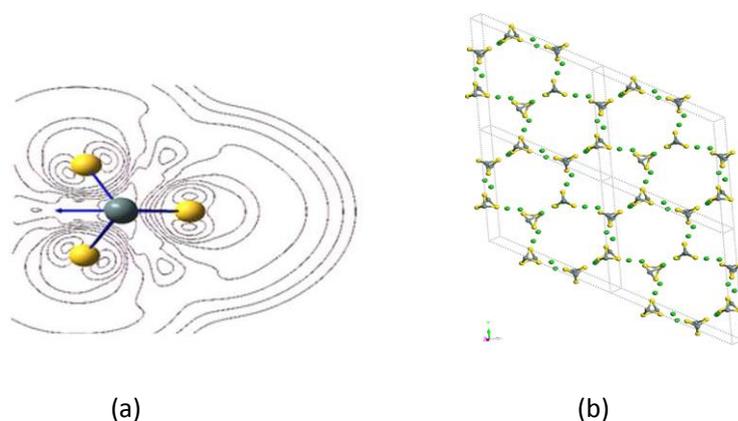
Figure 2.6. (a) The top view of electron density contour surface and the dipole moment for isolate $[Sn_2S_3]^{2-}$. (b) The arrangement of $[Sn_2S_3]^{2-}$ in a 2x2 unit cell for the $Ba_7Sn_5S_{15}$ crystal, the $[SnS_4]^{2-}$ group was not shown for clarity. Atom color: S: yellow, Sn: gray, Ba:green.

Table 3. Calculative Dipole Moment of $[SnS_4]^{4-}$ and $[SnS_3]^{4-}$ Anions

Anion group	dipole moment (Debye)
$[Sn(1)S_4]^{4-}$	1.2359
$[Sn(2)S_4]^{4-}$	3.0696
$[Sn(3)S_4]^{4-}$	1.8126
$[Sn(4)S_4]^{4-}$	1.5062
$[Sn(5)S_4]^{4-}$	2.0640
$[Sn(6)S_4]^{4-}$	1.2949
$[Sn(7)S_3]^{4-}$	11.8679
$[Sn(8)S_3]^{4-}$	11.5780

Summary and Prospect

We describe the optimization of NCS chromophore of materials, and present a way of designing syntheses of inorganic NCS compounds based on the normal processes of development of NCS chromophores. We introduce the alienation process of NCS chromophore development while the NCS compound is not formed by NCS chromophore. We illustrate these concepts by taking actual examples. The NCS chromophores of (SnS_4) and (Sn_2S_3) were normal development

to obtain the NCS crystal of $Ba_7Sn_5S_{15}$. The NCS chromophores of (BiS_5) and (InS_4) were development into a compound of Ba_2BiInS_5 keeping in NCS structure. The NCS crystals $SnGa_4Q_7$ (Q = S, Se) were obtained by NCS chromophores of (GaQ_4) and (SnQ_4). On the contrary, the CS compound of $Ba_6Sn_7S_{20}$ was obtained because the developments of NCS chromophores of the (SnS_4) and (SnS_5) alienate from the normal process of growth. We give more examples of NCS chromophore developments which are normal or alienable process of chromophore growth in this paper. Here, we only describe the inorganic NCS chalcogenides which are constructed by two chromophores. And they are constructed by three or multiple NCS chromophores which would be obtained basis on the present method.

For NCS compounds, we investigate their NLO properties of micro-crystals (powders) and electronic origin of NLO response in views of the calculations and simulations. The SHG intensity, laser-induced damage threshold, and infrared transparency were measured. Furthermore, the relative conversion efficiency and figure of merit are derived based on SHG intensity measurements. The calculated charge distributions and local dipole are employed to evaluate the micromechanism of NCS materials. It is found that the NCS materials of $SnGa_4Q_7$ (Q = S, Se) appear with large conversion efficiencies, high damage threshold and wide transparencies in the mid-infrared region. And, the study of micro-mechanism elucidate that the stereochemically active lone-pair electrons of Sn^{2+} can significantly improve the polarity of the $[SnQ_4]$ chromophore. Large NLO responses of them originate from the covalent interactions of Sn−Q and the cooperative effects of polarities between the $[SnQ_4]$ and $[GaQ_4]$ chromophores. It is also found that the $Ba_7Sn_5S_{15}$ material is type-I phase-matchablility, and that the SHG conversion efficiency and figure of merit are about twice of that of $AgGaS_2$ at the saturated particle size (particle size of 150−212 μm). The $Ba_8Sn_4S_{15}$ is not phase-matching material. The SHG intensity and conversion efficient of $Ba_8Sn_4S_{15}$ are separately about 250 times than those of α-SiO_2, and the SHG intensity and conversion efficient are separately about 10 times than those of $AgGaS_2$ at the particle size of 25−45 μm.

~~On the basis of considering~~ Based upon the requirements of high quality NLO crystals, we believe that the NLO crystals of $SnGa_4Q_7$ (Q = S, Se) are in full compliance with the mentioned requirements and they are good candidates to be applied in laser frequency conversion of mid-infrared zone. In the future, the key work is to grow the single crystals with size of larger than 10 mm at one hand, and on the other hand, ~~the work is seeks~~ we try to prepare the transparent film with NLO response.

Notes and References

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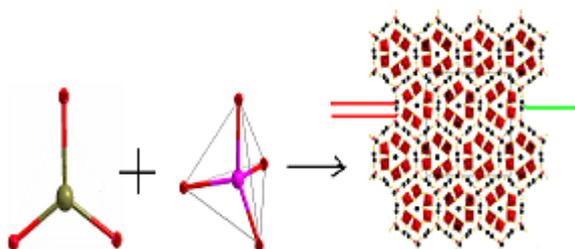
Text:

The designs of NCS compounds based on normal development of NCS chromophore is presented and the NLO properties are investigated.

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