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Strong Kleinman-Forbidden Second Harmonic Generation in Chiral Sulfide: La_4InSbS_9

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Supporting Information

ABSTRACT: A new chiral sulfide family, Ln_4InSbS_9 (Ln = La, Pr, Nd), with its own structure type in space group $P4_12_12$ or its enantiomorph $P4_32_12$ has been synthesized by solid-state reaction. Remarkably, the La member shows the strongest Kleinman-forbidden second harmonic generation to date, with an intensity 1.5 times that of commercial $AgGaS_2$ at a laser wavelength of 2.05 μm, and exhibits type-I phase-matchable behavior. Density functional theory calculations and ab initio molecular dynamics simulations suggest that lattice vibrations may be responsible for the origin and magnitude of the strong SHG effect.

The prerequisite of a nonlinear optical (NLO) material is that it be crystallographically noncentrosymmetric (NCS). Out of the total 32 point groups, there are 20 NCS point groups, of which the chiral 422 and 622 ones should have null second harmonic generation (SHG) response under the restriction of Kleinman symmetry.[1] Nevertheless, as a result of dispersion, very small Kleinman-forbidden SHG coefficients are observed. For example, α-TeO_2 with 422 symmetry shows d_{14}(1.328 μm) $\approx$ 0.36 pm/V or d_{14}(1.064 μm) $\approx$ 0.61 pm/V,[2a−d,h] and $(K_3I)[SmB_{12}(GaS_4)_3]$ with 622 symmetry exhibits a powder SHG intensity 0.3 times that of potassium dihydrogen phosphate (KDP) at 1.94 μm.[2e] However, violation cases are also found in large-sized single crystals of α-SiO_2 (32 point group) and $LiIO_3$ (6 point group), for which the unexpected d_{14} values of 2.6×10^{-3} pm/V[2f] and 0.24 pm/V,[2g] respectively, have been observed. It has also been known that when the second harmonic frequency approaches that of the electronic exciton resonance ($2h\nu \approx E_g$), the small Kleinman-forbidden coefficient can become large.[2a,h−l] For example, α-TeO_2 shows a large Kleinman-forbidden d_{14} value of ~4.32 pm/V at 0.659 μm, which is 10 times larger than that at 1.328 μm, because the second harmonic wavelength (0.33 μm $\approx$ 3.76 eV) is very close to its optical band gap (3.75 eV).[2a,i,m]

The common strategy to predesign a NCS compound is to involve asymmetric building units in the crystal structure, such as d^0 transition-metal cations (Ti^{4+}, Nb^{5+}, W^{6+}, etc.) susceptible to second-order Jahn−Teller distortion or p cations with stereochemically active lone-pair electrons (Se^{4+}, Te^{4+}, As^{3+}, Sb^{3+}, etc).[3] We recently realized that in quaternary rare-earth metal/metal/antimony/chalcogenide systems, the SbQ_n polyhedron tends to adopt an asymmetric geometry, such as the dimeric teeter-totter Sb_2S_6 polyhedron in Ln_4GaSbS_9,[4a] the teeter-totter SbQ_4 (Q = S, Se) in $La_4FeSb_2Q_{10}$,[4b] and square-pyramidal SbS_5 in $Ln_2Mn_3Sb_4S_{12}$.[4c] More interestingly, the arrangement of such asymmetric units is crucially affected by the MQ_n polyhedron. For example, SbQ_n units are eventually arranged in a centrosymmetric structure when linked by FeS_4 or MnS_6[4b,c] but an NCS structure with a strong SHG effect when linked by Ga_2S_7.[4a]

In this communication, we report an unusual chiral quaternary sulfide showing the strongest Kleinman-forbidden NLO response to date. Density functional theory (DFT) calculations and ab initio molecular dynamics (MD) simulations suggest that lattice vibrations may be responsible for its origin and magnitude.

The compounds Ln_4InSbS_9 (Ln = La, Pr, Nd) crystallize in space group $P4_12_12$ or its enantiomorph $P4_32_12$ [Table S1 in the Supporting Information (SI)] and are characterized by unusual $[In_2Sb_2S_{11}^{10-}]_\infty$ infinite helical chains propagating along the c direction and separated by isolated Ln^{3+} cations and discrete S^{2-} anions. These chains are further packed around the 4_1 helical axes (Figure 1a). Such chains are built from dimeric teeter-totter Sb_2S_6 polyhedra and dual-apex-shared In_2S_7 tetrahedra (Figure 1b); they are reminiscent of the chains in Ln_4GaSbS_9[4a] but differ in that Sb_2S_6 and In_2S_7 are arranged around a 2-fold screw axis, which means that neighboring dimers are oriented in opposite directions (Figure 1c), whereas the neighboring Sb_2S_6 or Ga_2S_7 in Ln_4GaSbS_9 are arranged in-phase (Figure S5 in the SI).

The SbS_4 polyhedron is remarkably distorted as a consequence of the stereochemically active lone-pair electrons of Sb^{3+}, with Sb−S bond distances of 2.44−2.91 Å that are comparable to those found in Ln_4GaSbS_9 (2.45−2.84 Å),[4a] $La_4FeSb_2Q_{10}$ (2.46−2.92 Å),[4b] and $La_7Sb_9S_{24}$ (2.43−3.00 Å).[5] The InS_4 tetrahedron is less distorted, with In−S distances of 2.45−2.49 Å and S−In−S angles ranging from 104 to 111°. These are comparable to those in $CuInS_2$.[6] La^{3+} cations and isolated S^{2-} anions (sulfur atoms S7, S8, S9, and S10) occur between the infinite helical chains. Thus, the formula can be written as $(La^{3+})_8([In_2Sb_2S_{11}]^{10-})(S^{2-})_7$. The cationic La1 and La2 exhibit normal LaS_6 trigonal-prismatic coordination, and La3 and La4 are found in LaS_7 monocapped trigonal prisms with La−S lengths varying from 2.84 to 3.45 Å, comparable to those in γ-La_2S_3,[7] α-La_2S_3,[8] $La_7Sb_9S_{24}$,[5] and $La_4FeSb_2S_{10}$.[4b]

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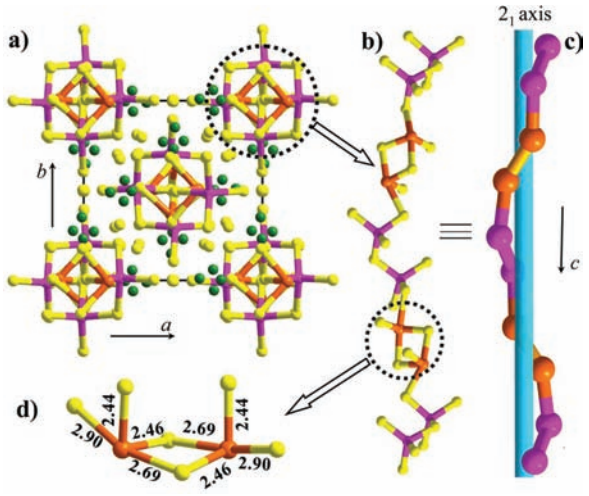

Figure 1. (a) View of La_4InSbS_9 along (001). (b) Helical $[In_2Sb_2S_{11}^{10-}]_\infty$ chains along the *c* direction. (c) Helical configuration of the chains. S atoms have been omitted for clarity, and the 2_1 screw axis is visualized as a thick blue line. (d) Local coordination of the dimeric teeter-totter Sb_2S_6 polyhedra. Green, La; pink, In; orange, Sb; yellow, S.

Naturally, La_4InSbS_9 is diamagnetic. Pr_4InSbS_9 obeys the Curie–Weiss law over the entire experimental temperature region, whereas Nd_4InSbS_9 deviates from it below 40 K (Figure S6). Their Curie constants and Weiss temperature are 6.54 and 7.25 emu K/mol and −21.67 and −22.74 K, respectively. The experimental effective magnetic moments are 7.23 and 7.61 μ_B, respectively, which are comparable to the calculated values, 7.16 and 7.24 μ_B.[9]

The optical band gaps for the La, Pr, and Nd members were estimated to be 2.07, 2.09, and 2.12 eV, respectively, (Figure 2b and Figure S7), which are comparable to that of commercial $AgGaS_2$ (2.62 eV),[10] implying that La_4InSbS_9 may have a suitable laser damage threshold for NLO applications. Several Nd^{3+} characteristic f–f transition absorptions between 1.3 and 2.1 eV were observed for Nd_4InSbS_9, similar to those for $NaNdGa_4Se_8$.[11] The diffuse-reflectance and IR spectroscopy studies indicated that powdered La_4InSbS_9 exhibits wide transparency comparable to that of powdered $AgGaS_2$ [1.0–25 μm (Figure 2c) vs 0.6–25 μm (Figure S8)]. These data distinguish La_4InSbS_9 as a potential candidate for NLO materials in the mid- and far-IR regions.

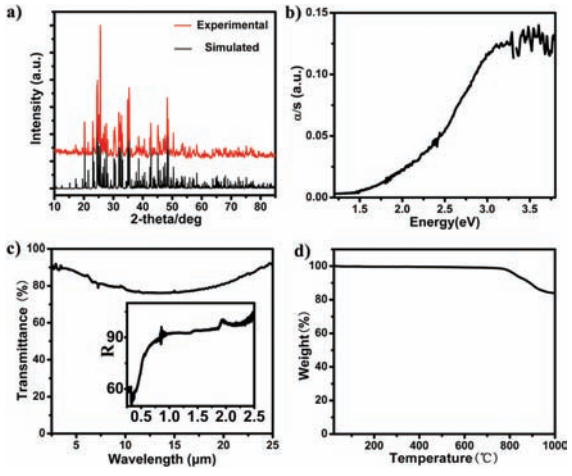

Figure 2. (a) Experimental and simulated X-ray diffraction patterns, (b) UV/vis/NIR diffuse reflectance spectrum, (c) IR and (inset) UV/vis/NIR transmittance curves, and (d) thermogravimetric analysis curve for La_4InSbS_9.

The electronic structures of La_4InSbS_9 were investigated using DFT (Figure S9). The valence band (VB) maximum and conduction band (CB) minimum are located at different *k* points indicating an indirect band gap of 2.23 eV, which is close to the experimental value. As the total and partial density of states (DOS) (Figure S10) indicate, the top of the VB is dominated by S 3p states, whereas the bottom of the CB is primarily derived from La 5d states mixed with some Sb 5p and In 5s states. Thus, the band gap absorption is likely to be the result of electronic transitions from S 3p to La 5d states.

Remarkably, La_4InSbS_9 displays an SHG intensity 1.5 times that of commercial $AgGaS_2$ in an IR laser at 2.05 μm (Figure 3). Moreover, the SHG intensities increase with the particle size and are saturated at a maximum value, indicating type-I phase-matchable behavior. No obvious SHG signals were observed for the Pr and Nd members, possibly because of their much poorer crystallinity.

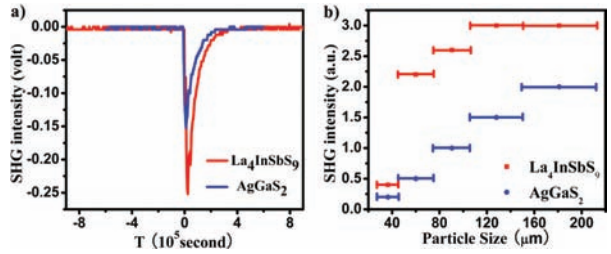

Figure 3. (a) Oscilloscope traces of the SHG signals of La_4InSbS_9 and $AgGaS_2$ at the same particle size of 150–210 μm. (b) Particle-size dependence of the SHG intensity for La_4InSbS_9 and $AgGaS_2$.

At first sight, this nonzero SHG response of La_4InSbS_9 is very surprising. As it crystallizes in space group $P4_12_12$, which belongs to the 422 point group, the space-group symmetry requires two nonvanishing tensors of second-order susceptibilities to follow the equation $d_{14} = -d_{25}$. On the other hand, under the restriction of Kleinman symmetry,[1] d_{14} must be equal to d_{25} (i.e., $d_{14} = d_{25}$). Consequently, both d_{14} and d_{25} must be equal to zero. Therefore, any material crystallizing in the 422 point group is forbidden from exhibiting an SHG response by Kleinman symmetry. Since Kleinman symmetry is based on the assumption that the medium is dispersionless, the presence of dispersion can damage its validity, leading to a very weak SHG response. For instance, α-TeO_2 exhibits a small d_{14} of ∼ 0.36 pm/V at 1.328 μm.[2a,h] Electronic exciton resonance, which would be expected only when the second harmonic frequency is close to an absorption band gap of the material, can significantly enhance the SHG effect,[12] leading to strong violations of Kleinman symmetry.[2a,h−l] For instance, α-TeO_2[2a,i] displays a large d_{14} value of 4.32 pm/V at 0.659 μm, for which the second harmonic wavelength is 0.33 μm (∼3.76 eV), which is very close to its optical band gap (3.75 eV).[2m] However, this cannot explain the very large SHG coefficient of the title compound La_4InSbS_9 under our measurement conditions (roughly estimated to be 20 pm/V, which is 5 times that of α-TeO_2). In this case, the second harmonic wavelength is ∼1.00 μm (∼1.2 eV), which differs significantly from the optical band gap (2.07 eV). Therefore, the electronic resonance

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would not be expected. As a further confirmation of this, we first calculated the second-order NLO susceptibility coefficients of La_4InSbS_9 using the length-gauge formalism derived by Aversa and Sipe, and null static SHG coefficients were then obtained to satisfy the Kleinman relations in the zero-frequency limit[13] (for details, see the SI). Consequently, the second-order NLO coefficients of some possible configurations of La_4InSbS_9 were calculated. These configurations were obtained via ab initio MD simulations at 300 K using the Nosé algorithm (for details, see the SI). The structure simulation length was 10 ps with a time step of 1 fs. After 7 ps, 11 typical configurations were chosen. The calculation results are summarized in Table S4. Nine of the 11 configurations had NLO coefficients close to 15 pm/V, which roughly agrees with the experimental observation: 1.5 times that of $AgGaS_2$ [i.e., d_{36}(10.6 μm) = 13 pm/V).[14] These results strongly suggest that thermal vibrations of the lattice induce structure configurational variations that may be responsible for the strong SHG effect of La_4InSbS_9.

Meanwhile, La_4InSbS_9 exhibits excellent thermal stability and shows no obvious weight loss up to 765 °C (Figure 2d and Figure S11). The 16% weight loss above 765 °C corresponds to the decomposition and the volatilization of Sb_2S_3 (mp 550 °C) and is close to the calculated value of 15.7% (for details, see the SI)

In summary, three quaternary chiral chalcogenides with their own structure type, $Ln_4InSbS_9 \equiv (Ln^{3+})_8([In_2Sb_2S_{11}]^{10-})(S^{2-})_7$ (Ln = La, Pr, Nd) have been reported. The major structure motif is $[In_2Sb_2S_{11}{}^{10-}]_\infty$ infinite helical chains propagating along the c direction that are well-separated by Ln^{3+} cations and discrete S^{2-} anions. Remarkably, the La member shows the strongest Kleinman-forbidden SHG effects to date, with an intensity 1.5 times that of the commercial IR NLO material $AgGaS_2$ under type-I phase-matching conditions at a laser wavelength of 2.05 μm. Meanwhile, the powdered La member exhibits a band gap of 2.07 eV, high transparency (1.00−25.00 μm), and excellent thermal stability up to 765 °C. These primary data indicate that La_4InSbS_9 is a potential candidate for IR NLO applications. The theoretical studies suggest that the origin and magnitude of the strong SHG response may originate from thermal vibrations of the lattice.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF), experimental and theoretical methods, and additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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