

A Journal of the Gesellschaft Deutscher Chemiker A DOCH International Edition Market Chemiker CDCh Chemiker Ch

Accepted Article

- Title: Chiral Hybrid Germanium(II) Halide with Strong Nonlinear Chiroptical Properties
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 2023, e202309600

Link to VoR: https://doi.org/10.1002/anie.202309600

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Chiral Hybrid Germanium(II) Halide with Strong Nonlinear Chiroptical Properties

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Abstract: Due to the pronounced anisotropic response to circularly polarized light, chiral hybrid organic-inorganic metal halides have been regarded as promising candidates for the application in nonlinear chiroptics, especially for the second-harmonic generation circular dichroism (SHG-CD) effect. However, designing novel leadfree chiral hybrid metal halides with large anisotropy factors and high laser-induced damage thresholds (LDT) of SHG-CD remains challenging. Herein, we develop the first chiral hybrid germanium halide, (R/S-NEA)₃Ge₂I₇·H₂O (R/S-NGI), and systematically investigated its linear and nonlinear chiroptical properties. S-NGI and R-NGI exhibit large anisotropy factors (g_{SHG-CD}) of 0.45 and 0.48, respectively, along with a high LDT of 3.08×10⁶ mJ/cm²; these anisotropy factors were the highest values among the reported leadfree chiral hybrid metal halides, together with a high LDT of 38.46 GW/cm². Moreover, the effective second-order nonlinear optical coefficient of S-NGI could reach up to 0.86 pm/V, which was 2.9 times higher than that of commercial Y-cut quartz. Our findings facilitate a new avenue toward lead-free chiral hybrid metal halides, and their implementation in nonlinear chiroptical applications.

Introduction

Chiral hybrid organic–inorganic metal halides possess intrinsic chirality and various unique properties, such as circular dichroism (CD), circularly polarized luminescence,^[1] the chirality-dependent

circular photogalvanic effect,^[2] the chiral-induced spin selectivity effect,^[3] and the chiral-phonon-activated spin Seebeck effect.^[4] Therefore, chiral hybrid metal halides have recently attracted wide attention due to their potential applications in various fields, such as circularly polarized photodetector, [1d, 2, 5] circularly polarized light sources,^[1a-c, 6] spin light-emitting diodes,^[7] spin filters,^[3a, 3b] ferroelectrics,^[8] and nonlinear optics.^[9] Since chiral hybrid metal halides simultaneously carry both CD and nonlinear optical (NLO) properties, they can exhibit optical activity in both linear and nonlinear optical processes, including second-harmonic generation circular dichroism (SHG-CD).^[10] However, only a few studies have focused on the SHG-CD of chiral hybrid metal halides. The first SHG-CD of chiral hybrid metal halides was reported on (R-MPEA)1.5PbBr3.5(DMSO)0.5 nanowires, with an effective second-order NLO coefficient of 0.68 pm/V.[10d] Subsequently, the SHG-CD of bulk chiral hybrid metal halide single crystals ((R/S)-3-aminopiperidine]Pbl₄) were investigated, exhibited an anisotropy factor (g_{SHG-CD}) of 0.21.^[10b] Moreover, considering the toxicity of lead, the development of lead-free chiral hybrid metal halide for nonlinear chiroptics is highly needed. In this aspect, copper- and bismuth-based chiral hybrid metal halides with g_{SHG-CD} of 0.41 and 0.26 were reported.^[10a, 10c] Since the upper limit of g_{SHG-CD} is 2, it is still a great challenge to design and synthesize eco-friendly chiral hybrid metal halides possessing both a large g_{SHG-CD} and SHG coefficient, together with a high laser-induced damage threshold (LDT).

Over the past years, diverse metal cations such as Sn²⁺, Cu²⁺, Mn²⁺, Ag⁺, Bi³⁺, Sb³⁺ and In³⁺ have introduced to construct environmentally friendly chiral hybrid metal halides.^[9c, 10c, 11] However, a chiral hybrid germanium(II) halide perovskitederivative has not been reported until now. Achiral germanium halides (such as CsGel₃, CH₃NH₃Gel₃, CH(NH₂)₂GeBr₃ and (n-C₄H₉)₂GeBr₄) have attracted significant interest due to their application in nonlinear optics and ferroelectrics.^[12] However, due to thier intrinsic achiral nature, these germanium halides do not possess any chiroptical response, such as SHG-CD. Therefore, we believed that chiral germanium halides could be an excellent platform to achieve both high $g_{\rm SHG-CD}$ and a large second-order NLO coefficient. In this work, chiral germanium iodide perovskitederivatives, (R-NEA)₃Ge₂I₇·H₂O (R-NGI) and (S-NEA)₃Ge₂I₇·H₂O (S-NGI) together with their racemic counterpart ((rac-NEA)Gel₃, rac-NGI) were synthesized by introducing the chiral cations, Rand S-1-naphthalen-1-ylethanammonium (R/S-NEA+).[13] To the best of our knowledge, this is the first report of a chiral hybrid germanium halide. Both R- and S-NGI crystallized into the P21 Sohncke space group, and exhibited a strong SHG response under excitation from 800 to 960 nm. The second-order NLO coefficient of S-NGI reached 0.86 pm/V, which was 2.9 times higher than that of the commercial crystal Y-cut quartz. Moreover, a high g_{SHG-CD} of 0.48 was achieved for *R*-NGI, which was the largest value among the lead-free chiral hybrid metal halides. Our work facilitates a new avenue toward lead-free chiral hybrid metal halides and their application in nonlinear chiroptics.

Results and Discussion

The chiral hybrid germanium halide was synthesized through a cooling-induced crystallization method as illustrated in Figure 1a. The detailed synthetic process for crystal growth is described in the experimental section. The morphology of the as-grown crystal is a thin plate (as shown in Figure 1c) with size of 4 mm. Single crystal X-ray diffraction (SCXRD) was used to determine the crystal structure. Both R- and S-NGI crystallized into the P21 Sohncke space group and exhibited almost identical unit cell parameters, while rac-NGI crystallizes into the Pbca centrosymmetric space group (as summarized in Table S1). As shown in Figure 1d and Figure S1, one-dimensional Ge₂I₇³⁻ chains were formed through the face-shared Gel₆⁴⁻ octahedral, which indicated the 1D structure of R/S/rac-NGI. There are two types of Ge-I bonds, shorter Ge-I bonds with bond lengths between 2.78 Å and 2.84 Å, and longer Ge-I bonds with bond lengths between 3.27 Å and 3.45 Å in R/S-NGI (as shown in Figure S2-S3). To investigate the influence of the chiral cations and the lone pair effect of Ge2+ on the distortion of inorganic skeleton,[14] the bond length distortion index (D) and bond angle variance $(\sigma^2)^{[15]}$ were calculated based on Equations 1 and 2:

$$D = \frac{1}{6} \sum_{i=1}^{6} \frac{|d_i - d_0|}{d_0}$$
(1)
$$T^2 = \frac{1}{6} \sum_{i=1}^{12} (\theta_i - 90)^2$$
(2)

where
$$d_i$$
 is the individual Ge-I bond length, d_0 is the mean Ge-
bond length, θ_i represents the angle of the I-Ge-I bond.^[15b] As

shown in Table S2, *R*-NGI and S-NGI exhibit much larger distortion index (0.0324 and 0.0384) and bond angle variance

(36.52 and 35.84 deg²) than that of *rac*-NGI (0.0160 and 32.41 deg²). Therefore, the distortion of the chiral germanium halide is much larger than that of the racemic counterpart, which is possibly caused by the lone pair electrons of Ge²⁺ and chirality transfer by the chiral cations.^[12b]



Figure 1. The synthesis, morphology and crystalline structures of chiral hybrid germanium halide. (a) The synthetic process of chiral hybrid germanium halide. (b) The chemical structures of *R*/*S*-NEA. (c) The photograph of *R*/*S*-NGI single crystal (scale bar is 3 mm). (d) The crystalline structure of the *R*/*S*-NGI.

XPS measurement was further conducted to determin the valency of Ge in the crystal. As shown in Figure 2a, a peak located at 1219.5 eV (Ge $2p_{3/2}$) was observed, which agreed with the binding energy of Gel₂.^[16] Therefore, the valence of Ge in *R/S*-NGI was 2+. Subsequently, the energy dispersive spectroscopy (EDS) mapping was carried out to verify the composition and elemental distribution in the chiral hybrid germanium halide. As shown in Figure 2b and S4, the EDS mapping of the S-NGI and *rac*-NGI crystal showed the coexistence of C, N, Ge and I, and all elements exhibited a uniform distribution as expected.



Figure 2. (a) High-resolution XPS spectra of Ge $2p_{3/2}$ in the S-NGI crystal. (b) SEM image and corresponding EDS mapping of the S-NGI crystal. (c, d) Calculated electronic band structures (left panel) and partial DOS (right panel) of S-NGI (c) and *R*-NGI (d).

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Figure 3. Linear optical properties of R/S/rac-NGI. (a) UV–visible diffuse reflectance spectra of R/S/rac-NGI. (b) Tauc plots of R/S/rac-NGI. (c) CD spectra of R/S/rac-NGI. (d) Calculated gabs spectra of R/S/rac-NGI.

To further understand the electronic properties of *R/S/rac*-NGI, their electronic band structures and density of states (DOS) were calculated based on density functional theory (DFT). As shown in Figure 2c-d, *R/S/rac*-NGI exhibited direct bandgap features with the valence band maximum (VBM) and conduction band minimum (CBM) located at same K point. The partial DOS (Figure S5) and isosurface plot of the wave functions of VBM and CBM (Figure S6) indicated that the CBM of *R/S/rac*-NGI was mainly composed by the chiral cations, while the VBM was mainly composed of Ge 4s and I 5*p* orbitals. Therefore, the electronic transition occurred from the inorganic framework to chiral organic cations after photoexcitation.

The linear optical property of these chiral hybrid germanium halides was initially investigated by UV–visible diffuse reflectance spectroscopy. As shown in Figure 3a, a strong absorption peak located at 392 nm was observed for *R*/S-NGI, while it was at 411 nm for *rac*-NGI. The band gaps of *R*/S-NGI (2.75 eV) is slightly larger than that of *rac*-NGI (2.69 eV, as shown in Figure 3b), which should be attributed to the decreasing of orbital overlap of [Gel₆]



Figure 4. NLO property of *S*-NGI. (a) Schematic of the home-built micro-area NLO characterization system. (b) The SHG intensity of the S-NGI crystal pumped at various wavelengths. (c) Comparison of the SHG signals of *S*-NGI, *rac*-NGI and commercial Y-cut quartz under the same experimental conditions. (d) Polar SHG intensity plots of the *S*-NGI crystal as a function of the rotation angle of the linear polarizer. The dots are the experimental data, and the solid line is the theoretical fitting with the $cos^4\theta$ function.^[17] (e) SHG intensity as a function of the rotation angle of the $\lambda/4$ plate. The excitation and detection wavelengths are 880 and 440 nm, respectively. (f) Polar SHG intensity plots of the *S*-NGI crystal as a function of polarization angle.

unit through introducing the chiral cations.^[18] The stability of *R*/*S*-NGI was also tested by measuring the time-dependent absorption spectra. As shown in Figure S8, the absorption spectra did not change after exposure to air for 1 hour. The CD spectra were also measured to quantify the optical activity of *R*/*S*/*rac*-NGI. As depicted in Figure 3c, CD signals with opposite signs at 392 nm for *R*/*S*-NGI are observed, which was consistent with the

absorption peak. In addition, no CD signal was observed for *rac*-NGI, as expected. Therefore, the chirality was successfully transferred from the chiral cations to the inorganic skeleton of *R/S*-NGI. The CD asymmetry factors (g_{abs}) were 3.75×10^{-4} and -3.96×10^{-4} at 392 nm for *R*- and *S*-NGI, respectively, which is much lower than that of the 2D chiral lead halides (Table S4).^[19] To investigate the origin of this, the transition probability for the left-

handed circularly polarized (LCP) and right-handed circularly polarized (RCP) light absorption is calculated (as shown in Figure S9). The transition probability difference between LCP and RCP

light is only 0.014 and -0.019 Dybe² for *R*-NGI and *S*-NGI at B point, respectively, thus the $g_{\rm abs}$ of chiral germanium halide is much lower than that of chiral lead halide.^[20]



Figure 5. Intensity and polarization dependent SHG feature of S-NGI. (a) SHG spectra of S-NGI under various excitation powers. (b) Logarithmic diagrams of the power-dependent SHG intensity. The solid line is the linear fitting with a slope of 1.9. The SHG intensity drops when the incident power is higher than 38.46 GW/cm², indicating the laser damage threshold. The excitation and detection wavelengths are 880 and 440 nm, respectively. (c) SHG intensity as a function of the rotation angle of the *A*/4 plate measured under different incident light intensities at 880 nm. (d) Polar SHG intensity plots of *S*-NGI under different incident light intensities at 880 nm. (e) g_{SHG-CD} and SHG intensity as a function of the incident light intensities. (f) Comparison of d_{eff} and g_{SHG-CD} in the literature and this work.

Next, we investigated the SHG characteristics of these chiral hybrid germanium halides. All samples for SHG measurement were prepared under N₂ atmosphere and measured using air-free holders. As shown in Figure 4, Figure S10-S11, *R/S*-NGI exhibit an evident SHG signal under a wide excitation wavelength from 800 to 960 nm. To evaluate the second-order NLO coefficient (d_{eff}) of *R/S*-NGI, a commercial Y-cut quartz with a d_{eff} of 0.3 pm/V was used as the reference. The NLO coefficient is estimated according to Equation 3^[10a]:

$$\frac{d_{\text{eff}(R/S-\text{NGI})}}{d_{\text{eff}(\text{ref})}} \approx \frac{L_{(R/S-\text{NGI})}}{L_{(ref)}} \frac{P_{in(ref)}}{P_{(R/S-\text{NGI})}} \sqrt{\frac{I_{\text{out}(R/S-\text{NGI})}}{I_{\text{out}(ref)}}}$$
(3)

where the superscripts "*R*/*S*-NGI" and "ref" refer to the samples and Y-cut quartz, d_{eff} are the effective second-order NLO coefficient, *L* is the effective crystal thickness, P_{in} represents the incident light intensity, and I_{out} represents the output intensity of SHG. During the SHG measurement, the same laser conditions, such as the same laser beam, power density and wavelength were used for both *R*/*S*-NGI and Y-cut quartz. The thicknesses of *R*-NGI and S-NGI for SHG measurement were 82.16 and 57.4 µm (as shown in Figure S12), respectively, which are similar with that of the Y-cut quartz (50 µm). The calculated d_{eff} is 0.65 pm/V for *R*-NGI and is 0.86 pm/V for *S*-NGI, which was approximately 2.9 times larger than that of Y-cut quartz. Notably, these value were larger than those of most noncentrosymmetric hybrid metal halides, such as (*R*-NEA)CuCl₄ (0.4×Y-cut quartz),^[10c] [(*R*/*S*)-3aminopiperidine]PbI₄ (2.1×KDP, d_{eff} of KDP is 0.4 pm/V),^[10b] (BA)₂(EA)₂Pb₃I₁₀ (0.4×KDP)^[21] and (2-FBA)₂PbCI₄ (0.9×KDP)^[22]. We also measured the SHG response of *rac*-NGI, and a negligible SHG signal was detected owing to the intrinsic achiral nature. To thoroughly understand the nonlinear optical properties of these chiral hybrid germanium halides, linear polarization-dependent SHG was measured. The polarization sensitive signal followed a dipole profile which was consistent with the $cos^4\theta$ function for both *R*-NGI and *S*-NGI (Figure 4d and Figure S11d). The maximum SHG signal occurred at 0° and 180°, which should correspond to the optical axis of the crystal. The polarization ratio, defined as $\rho = (I_{max} - I_{min})/(I_{max} + I_{min})$, which is 0.46 for *R*-NGI and 0.55 for *S*-NGI, respectively.

We further investigated the SHG-CD property of *R*/S-NGI. During the measurement, the excitation laser was switched between left- and right-handed polarization (LCP and RCP) by rotating the $\lambda/4$ plate. As shown in Figure 4e-4f and Figure S11b-S11c, the SHG intensity was changed following the rotation of the $\lambda/4$ plate. In particular, the SHG signal of the *R*-NGI crystal under RCP light excitation was much larger than that under LCP light excitation, and the opposite trend was obtained for S-NGI. Then, to quantify the SHG-CD effect of these chiral hybrid germanium halides, the anisotropy factor (g_{SHG-CD}) was calculated based on Equation 4:

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$$g_{\text{SHG-CD}} = \frac{2(I_{\text{LCP}} - I_{\text{RCP}})}{(I_{\text{LCP}} + I_{\text{RCP}})}$$

(4)

where I_{LCP} and I_{RCP} represent the SHG intensities under LCP

and RCP light excitation, respectively. The calculated g_{SHG-CD} values under 880 nm excitation is around 0.48 for R-NGI and 0.45 for S-NGI, respectively, larger than those of other lead-free chiral hybrid metal halides (Table S3). The high anisotropy factor demonstrated that chirality was successfully transferred to the germanium halide, which could be directly used to distinguish LCP and RCP light. The g_{SHG-CD} is much larger than g_{CD} , which is consistent with the previous reports.^[10a-d] The irrelevant $g_{\text{SHG-CD}}$ and g_{CD} could be explained by the different physical process of SHG and CD. The CD is the absorption difference between LCP and RCP light which involves electronic transitions between the ground state and excited state. However, SHG is a parametric process involving virtual states instead of electronic transition (as shown in Figure S13), corresponding to the destruction of two fundamental photons followed by the generation of one second harmonic photon.[23]

We further investigated the dependence of the SHG intensity on the power of the excitation laser (Figure 5a). As shown in Figure 5b, the SHG intensity showed a quadratic dependence on the power of the pump laser, consistent with the two-photon nature of the SHG process. Furthermore, the SHG intensity dropped when the excitation power was larger than 38.46 GW/cm², which can be consider as the laser damage threshold (LDT) of S-NGI. The dependence of the SHG and SHG-CD properties on the excitation power was also investigated. As depicted in Figure 5c-e and Figure S11i, with increasing laser intensity, the SHG intensity also increased, while the g_{SHG-CD} value initially increased and then decreased for both R-NGI and S-NGI. Therefore, the chiral hybrid germanium halides exhibited not only large g_{SHG-CD} but also a high second-order NLO coefficient and LDT (as shown in Figure 5f and Figure S14); thus, they are promising platform for the investigation of the nonlinear chiroptical effect. Notably, the g_{SHG-CD} value of chiral germanium halide was larger than those of other chiral metal halides (Figure S15). Moreover, different from the circularly polarized light detectors working in the visible region, the chiral germanium halide exhibited strong polarization sensitivity in the near-infrared region.

Conclusion

The first chiral hybrid germanium halides (R-NGI and S-NGI) were designed and synthesized through the cooling-induced crystallization method. These chiral hybrid germanium halides nonlinear chiroptical exhibited strong effects under photoexcitation from 800 nm to 960 nm, and the effective secondorder NLO coefficient could reach up to 0.86 pm/V, which was approximately 2.9 times larger than that of the commercial Y-cut quartz. Most importantly, the g_{SHG-CD} of 0.48 was attained for R-NGI, which is the highest value of the lead-free chiral hybrid metal halides. The chiral hybrid germanium halide not only possessed large effective second-order NLO coefficient but also a high LDT (38.46 GW/cm²). Our work is an excellent addition to the lead-free chiral hybrid metal halide family along with its implication in nonlinear chiroptical systems.

Acknowledgements

H.W. and J.L. contributed equally to this work. The authors gratefully acknowledge the financial support from the NSFC (Grant Number: 52103218, 92256202, 12261131500, 62174079) of China, the Fundamental Research Funds for the Central Universities, Nankai University (Grant Number: 023-63233038), the Natural Science Foundation of Guangdong Province (2022A1515011246), the Opening Project of State Key Laboratory of Polymer Materials Engineering (Sichuan University) (Grant No. sklpme2021-05-02) and the 111 Project (B18030). All the theoretical calculations were performed on National Supercomputer Center in Guangzhou.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: chirality • germanium • second-harmonic generation • nonlinear chiroptics • perovskites

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The first chiral germanium halide is synthesized, which exhibits strong nonlinear chiroptical property. The second-harmonic generation circular dichroism of the chiral germanium halide can reach 0.48, which is the highest value among lead-free chiral metal halides. Moreover, a large effective second-order nonlinear optical coefficient of 0.86 pm/V and a high laser-induced damage threshold of 3.08×10^6 mJ/cm² are also obtained.