Tin-based Chiral Perovskites with Second-order Nonlinear Optical Properties

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Abstract: Metal halide perovskites have attracted extensive attention as the most favorable candidate for nonlinear optical (NLO) effects, owing to their superior infrared transparency, flexible structures, and high laser-induced damage thresholds. Among the perovskite branches, the lead-based perovskites dominate in virtue of their fascinating optoelectronic properties. However, the ambient instability and toxicity of lead impede their practical applications. Herein, we report a new class of air-stable and lead-free zero-dimensional (0D) chiral perovskites manifesting efficient second-order NLO response. Interestingly, the tin-based perovskites demonstrate double-step reversible phase transitions with an acentric space group \( P2_1 \) at room temperature, while their racemic counterparts undergo a distinct one-step phase transition crystallizing in centric space group \( P2_1/c \). These findings reveal an executable approach to designing multifunctional lead-free perovskite-type switchable materials with SHG properties.

1. Introduction

Nonlinear optical (NLO) materials, displaying promising applications for laser frequency conversion, high-resolution photolithography,[1] and multiphoton microscopy,[2, 3] have become a rapidly growing field in modern materials. The NLO effects, dealing with the interactions between light (intense laser) and medium, are well-known fundamentals of light manipulation and photenergy conversion.[4] The second harmonic generation (SHG), an energy conserved process that
annihilation of two photons results in forming a new photon with twice the frequency, has become one of the most common and applied NLO effects in scientific and military fields since Franken et al. firstly discovered the optical second-harmonic phenomenon in 1961.\footnote{5} However, SHG response strictly requires the interacted medium with a non-centrosymmetric structure.\footnote{6–9} Therefore, the research of SHG-active materials has mainly focused on molecular materials with non-centrosymmetry.\footnote{10–12}

Organic-inorganic hybrid perovskites (OHPs), along with the excellent structural flexibility, easy accessibility, low-cost and outstanding optoelectrical properties, have been widely explored in the fields of solar cells,\footnote{13–15} photodetectors,\footnote{16, 17} light-emitting diodes\footnote{18–20} and field-effect transistors,\footnote{21, 22} and NLOs\footnote{23, 24}. Especially, chiral OHPs represent unique photoelectric characteristics\footnote{25–27} such as ferroelectricity,\footnote{28–30} circularly polarized photoluminescence (CPL)\footnote{31–33}, bulk photovoltaic effect (BPVE)\footnote{34} as well as spintronics.\footnote{35–37} More importantly, the introduction of chiral ligands will elicit the inherent structural non-symmetry directly. Thus, chiral perovskites were regarded as an ideal platform for supplying SHG response materials.\footnote{38–40} However, the toxicity and long-term air instability restrain widespread applications of perovskites containing Pb$^{2+}$, thus promotes the emergence of lead-free OHPs based on Sn$^{2+}$.\footnote{41–43} Unfortunately, the alternative Sn$^{2+}$ is easily oxidized in air. Therefore, Sn$^{4+}$-based perovskites, featuring stable and friend to the environment, are more suitable for future commercial NLO devices.

Herein, we employ the strategy\footnote{44} of introducing chiral organic amine (R-/S-MPEA) as a template for constructing chiral perovskite with intrinsic acentric structures required for second-order NLO effects. The achiral rac-MPEA is used as a comparison to verify the feasibility of this strategy. A series of novel Sn$^{4+}$-based chiral perovskites bis(methylphenethylamine) hexachloridostannate ([MPEA]$\text{SnBr}_6$) were successfully prepared, in which the isolated SnBr$_6^{2–}$ octahedrons are surrounded by MPEA$^+$ cations. These tin-based compounds formed zero-dimensional (0D) core-shell\footnote{45–47} structures by the self-assembled way. These as-synthesized Sn$^{4+}$-based 0D semiconductors represent remarkable air and humidity stability. Efficient SHG responses
with a comparably high polarization ratio are examined by utilizing the self-built optic experimental system. The high laser-induced damage threshold (LDT) also indicates brilliant optical stability. Notably, the chiral perovskites undergo double-step thermally induced structural reversible phase transitions, while their racemic compounds manifest a single structural phase transition. Such findings indicate a proper manner to design multifunctional perovskite-type semiconductors with second-order NLO activity.

2. Results and Discussion

2.1. Crystal structures of the perovskites

Chiral \((R-/S\text{-MPEA})_2\text{SnBr}_6\) and racemic \((\text{rac\text{-MPEA}})_2\text{SnBr}_6\) were crystallized from the concentrated hydrobromic acid mixed solution containing a stoichiometric amount of \(\text{SnCl}_2\cdot2\text{H}_2\text{O}\) and the corresponding \(R-/S-/\text{rac\text{-MPEA}}\text{Br}\) salts at room temperature (the details process is shown in the Experimental Section). The well-matched powder X-ray diffraction (PXRD) patterns verified the phase purity of the three as-synthesized crystals (Supporting Information, Figure S1). In addition, all the three compounds crystallize in a monoclinic system exhibiting a similar lattice constant (Supporting Information, Table S1). Crystal structures of the chiral perovskites contain two amine cations and one \(\text{SnBr}_6^{2-}\) anion in their asymmetric units (Supporting Information, Figure S2a). The pair of enantiomers both adopts chiral space group \(P2_1\). As shown in Figure 1a and 1b, there is a mirror symmetry relationship between the two corresponding enantiomorphic structures. Expectedly, the racemic compound yields centrosymmetric space group \(P2_1/c\) belonging to the \(2/m\) crystallographic point group. The asymmetric unit consists of only one independent MPEA\(^+\) cation and half \(\text{SnBr}_6^{2-}\) anion (Supporting Information, Figure S2b). The comparison views of unit cells are shown in Figure S2c and 2d, as well as Figure S2e and 2f.

Considering the similar 0D tin halide perovskite structures of all three compounds at the molecular level\(^{[45-47]}\) we take \((R\text{-MPEA})_2\text{SnBr}_6\) as an example described in detail. The inorganic octahedrons are independent of each other in our 0D perovskites, while they are connected by corner-sharing/edge-sharing/face-sharing in the 3D/2D/1D perovskites. As shown in Figure 1c,
individual inorganic SnBr$_6^{2-}$ octahedral anions are isolated from each other, and periodically embedded in the organic MPEA$^+$ cations. There are no interactions between the optically active Sn$^{4+}$ halide species, and it should be mainly due to the distance between two Sn$^{4+}$ centers being more than 1 nm. The ideal 0D core-shell structure is more clearly shown in the space-filled model (Figure 1d), in which the inorganic halide anions are surrounded by organic amine cations. This ideal host-guest system gives rise the material to show inherent properties of isolated SnBr$_6^{2-}$ moieties.

![Figure 1. Packing patterns of crystal structures of (a) (R-MPEA)$_2$SnBr$_6$ and (b) (S-MPEA)$_2$SnBr$_6$ along the b-axis, showing the relationship of mirror symmetry. H atoms are invisible for the sake of clarity. Single crystal structure of 0D organic-inorganic hybrids, taking (R-MPEA)$_2$SnBr$_6$ as an example. (c) View of one isolated SnBr$_6^{2-}$ octahedron surrounded by MPEA$^+$ cations and separated from each other. The turquoise dashed lines represent C–H···Br bonding interactions between the MPEA$^+$ cations and inorganic halide anion. (d) The space-filling model indicates an individual SnBr$_6^{2-}$ covered by organic MPEA$^+$ cations.

2.2. Reversible phase transition properties

The thermogravimetric analysis (TGA, powder samples) curves of the three compounds show their decomposition temperature at up to ~547 K (Figure S3). Thermal analysis of three compounds via differential scanning calorimetry (DSC) reveals that (R-MPEA)$_2$SnBr$_6$ and (S-MPEA)$_2$SnBr$_6$ undergo two reversible phases transitions, while their racemic counterpart exhibits only one-step
phase transition before decomposition. The DSC curve of \((R\text{-MPEA})_2\text{SnBr}_6\) shows two distinct endothermic peaks at \(T_1 = 404\ \text{K}\) and \(T_2 = 447\ \text{K}\) in the heating run, and two conspicuous exothermic peaks at 359 K and 437 K in the cooling process (Figure 2a). The wide thermal hysteresis of 45 K/10 K reveals the feature of first-order phase transition. Similarly, the DSC curve of the enantiomer \((S\text{-MPEA})_2\text{SnBr}_6\) also exhibits two pairs of reversible peaks, of which the endothermic peaks are at \(T_1 = 398\ \text{K}\) and \(T_2 = 449\ \text{K}\) in the heating process, and two exothermic peaks are at 348 K and 438 K in the cooling mode (Figure 2c). But there is a negligible difference (about 6 K) between the pair of as-grown enantiomers at their first phase transition points. In addition, as shown in Figure S4a, the reversible phase transition points \((T_2 = 445\ \text{K}, \text{heating} / 403\ \text{K}, \text{cooling})\) of racemic compound are very close to the second phase transition points of the pair of enantiomers. The sharp peaks and extremely wide thermal hysteresis at 42 K usually assign to the first-order feature. The molar heat capacity \(C_P\) traces further confirm the first-order transition at \(T_1\) and \(T_2\) (Figure S5). The enthalpy change \(\Delta H\) and entropy change \(\Delta S\) of three compounds are calculated and listed in Table S3. The calculated large \(N\) (microscopic state change) values obtained by Boltzmann equation \(\Delta S = R\ln(N)\) in the heating process indicate the phase transitions of all the three compounds belong to order-disorder types. For simplicity, the phase below \(T_1\) is labeled as room-temperature phase (RTP), the phase between \(T_1\) and \(T_2\) as intermediate temperature phase (ITP), and the phase above \(T_2\) as high-temperature phase (HTP). The phase transition points of \((R\text{-MPEA})_2\text{SnBr}_6\) and \((S\text{-MPEA})_2\text{SnBr}_6\) under intermediate temperature are beyond the capability of our heating device, therefore, the crystal data of the phase cannot be collected.

To further confirm the reversible phase transitions, we carried out variable-temperature PXRD at selected temperatures. The PXRD patterns of \((R\text{-MPEA})_2\text{SnBr}_6\) are shown in Figure 2b. There appear two new diffraction peaks at 12.56° and 25.39° at 403 K (ITP), compared with the PXRD curves at 300 K (RTP). We mark them with pentagonal stars and diamonds, respectively. Continually heating up to 448 K, three new peaks at 12.92°, 17.73°, and 22.29° occur, and two splitting peaks at 20.26° and 20.58° disappear. Meanwhile, the two peaks at 15.63° and 15.84°
merge into a single peak. Predictably, the variable-temperature PXRD of (S-MPEA)$_2$SnBr$_6$ shows almost the same behaviors as its enantiomer (Figure 2d). It is worth noting that the crystal lattice expands, and the interplanar crystal spacing becomes broader with the increase of temperature from 300 K to 448/452 K, which causes the blue shift of the XRD peaks of (R-MPEA)$_2$SnBr$_6$ and (S-MPEA)$_2$SnBr$_6$. However, as depicted in Figure S4b, the PXRD patterns of compound (rac-MPEA)$_2$SnBr$_6$ reveal simply a single-step transition. At 355 K (HTP), seven diffraction peaks at 20.00º, 20.40º, 20.61º, 24.07º, 26.78º, 30.45º, and 33.55º disappear, and three peaks at 7.93º, 12.57º and 25.18º move to lower angle, corresponding to RTP. Generally, the large number reduction of diffraction peaks uncovers a structure transition to higher symmetry. Additionally, the PXRD patterns of the three compounds after cooling back to room temperature (300 K) agree well with the original patterns recorded at 300 K. These results fully prove that both chiral materials have two reversible structural phase transitions, while the racemic compound has only one reversible phase transition.
2.3. Air stability

The phase stability of materials in the ambient atmosphere is of great concern for further device applications. Hence, to investigate our perovskites’ phase stability, the milled sample powders were stored in plastic sample tubes and exposed to the air and sunlight for different periods. Subsequently, PXRD data of (R-MPEA)$_2$SnBr$_6$ were collected after 7, 30, and 180 days, respectively. As shown in Figure S6a, the three experimental curves are nearly the same and match well with the calculated ones, implying the phase-stability of (R-MPEA)$_2$SnBr$_6$ in ambient air.

Based on similar structures to (R-MPEA)$_2$SnBr$_6$, compounds (S-MPEA)$_2$SnBr$_6$ and (rac-MPEA)$_2$SnBr$_6$ possess the same outstanding air-stability (Supporting Information, Figure S6b, and Figure S6c). Additionally, photoluminescence (PL) emission spectra of (R-MPEA)$_2$SnBr$_6$ show little change after storage for different times, also indicate the well-stable properties of our materials.
(Figure S6d, Supporting Information). All these results demonstrate the promising potential applications of these three compounds.

2.4. Linear optical properties

To investigate the linear optical and chiroptical properties of the chiral compounds, we firstly prepared thin films of \((R\text{-MPEA})_2\text{SnBr}_6\) and \((S\text{-MPEA})_2\text{SnBr}_6\), respectively (see details in Experimental Section). The PXRD patterns of these films agree well with the simulated ones, confirming the structural consistency of single crystals after being in the thin films (Figure S9). The UV–vis absorption spectra of \((R\text{-MPEA})_2\text{SnBr}_6\) and \((S\text{-MPEA})_2\text{SnBr}_6\) thin films show similar features with an absorption peak at around 336 nm (Figure 3a). Figure 3c shows the corresponding circular dichroism (CD) spectra with strong CD response (at 268 and 352 nm) but opposite signs for the two chiral thin films. The CD spectra of chiral organic ligands \(R/\text{-S-MPEA}\) were measured at 226 and 257 nm in our previous work\(^{[40]}\). Comparatively, the CD signs of the prepared chiral materials originate from the Cotton effects near the exciton absorbance and bandgap region.

We also measured the diffusive reflectance spectrum (DRS) and PL emission spectra of the three compounds and simultaneously observed these compounds displaying almost identical behaviors. Figure S7a exhibits direct bandgap semiconductor characteristics as shown in the same type of 0D inorganic tin(IV) halide perovskites\(^{[48]}\). The optical bandgaps of these three compounds are around 2.68 eV (Figure S7, inset and Figure S8, Supporting Information). However, they present not expectedly strong PL emission peaks at 470 nm with 260 nm short wave ultraviolet excitation (Figure S7b).
2.5. Second-order NLO properties

The introduced chiral amine group successfully breaks the intrinsic centrosymmetry of typical halide perovskite materials. Due to our bulk perovskites crystalize in the chiral space group (P2₁), the bulk effect SHG response is typically analyzed, compared to surface effect[49]. We performed SHG measurement to prove second-order NLO effects of our chiral perovskites at room temperature and used the Y-cut quartz plate (5 × 5 × 0.5 mm³) as the reference. Firstly, taking (R-MPEA)₂SnBr₆ crystal as an example, the DRS reveals that its absorption band edge is ~450 nm (Figure S7a). This result indicates that (R-MPEA)₂SnBr₆ should be suitable for SHG measurements with a femtosecond pulsed laser (wavelength tunable from 690 nm to 1040 nm) in a reflection acquisition mode.

We utilized a home-built set-up equipped with a confocal laser scanning microscope to probe the NLO properties of (R-MPEA)₂SnBr₆ (see details in the Experimental Section). The scanned mapping image of the SHG signal clearly shows the outline of this compound and suggests the second-order NLO activity of this chiral material (Figure 4a). The wavelength-dependent SHG spectra demonstrate that this chiral compound represents a sharp SHG signal band when the excitation wavelength tunes between 800 nm and 1020 nm at 20-nm steps with the pumping power maintained at 20 mW (Figure 4b).
wavelength of the excitation light, of which position depends on the frequency of the fundamental laser beam. The apparent up-conversion behavior switching near-infrared (NIR) light to the visible demonstrates that the band emission is an NLO process. Further, the effective second-order nonlinearity value ($d_{eff}^p$) of (R-MPEA)$_2$SnBr$_6$ crystal was estimated to be $\sim$0.33 pm V$^{-1}$ with a linearly polarized pump wavelength at 980 nm by comparison with the plate of Y-cut quartz (see details in Supporting Information). This value is about 18 times $\alpha$-SiO$_2$[50] and slightly lower than the chiral 2D perovskite analog.[40, 51] The power dependence (Figure 4c) suggests a quadratic dependence for SHG intensity on laser power and reveals the two-photo nature of this NLO process. It is worth noting that the SHG intensity does not decrease until the pump power is higher than $\sim$420 mW (840 nm). Therefore, we estimate the LDT of as-tested chiral perovskite to be $\sim$1.34 $\times$ 10$^5$ W cm$^{-2}$, supposing the excited laser spot of $\sim$20 $\mu$m in diameter. This result reveals that the optical stability is much higher than that of perovskite-type NLO materials.[52]

The polarization dependence tests were conducted by rotating the $\lambda/2$ plate to generate linearly polarized light with different directions, in which p-polarized (parallel to the plane of incidence) input polarization at 0º angle and fixed linear-polarized output polarization. The polarization plots (Figure 4d) accorded well with $\cos^4 \theta$ function,[40] demonstrate the anisotropy of materials with P2$_1$ space group[50,53] (see details in Supporting Information). The polarization ratio defined as $\rho = (I_{max} - I_{min})/(I_{max} + I_{min})$ is $\sim$0.83 for a linearly polarized analyzer and suggests a comparably high sensitivity of SHG to the crystal symmetry.
Figure 4. NLO responses of the (R-MPEA)$_2$SnBr$_6$ crystal. (a) Scanned mapping image by detecting SHG signals. Scanned area: 500 × 500 μm$^2$. (b) The wavelength dependence plots excited at different wavelengths. (c) The power dependence spectra of SHG signals, the curve shows their quadratic fit. (d) The polarization dependence spectra with selected excitation wavelength, the curves represent the cos$^4$θ fit for SHG.

3. Conclusion

In summary, we successfully designed and manufactured three chiral lead-free perovskites involving (R-MPEA)$_2$SnBr$_6$, (S-MPEA)$_2$SnBr$_6$, and (rac-MPEA)$_2$SnBr$_6$ via the readily solution-processed strategy. All three compounds represent excellent air stability over usual 3D/2D/1D analogs. Single-crystal XRD confirms the absolute configuration of these three 0D mononuclear molecules, which demonstrate perfect host-guest engineering. We purposely constructed chiral perovskites employing incorporating chiral amine into hybrid perovskites. The well-defined chiral compounds not only exhibit brilliant chiroptical effects (obviously opposite CD signs in the range
of 250–500 nm) but efficient second-order NLO response with high LDT. The racemic compounds possess inherent structural centrosymmetry without expected effects. Furthermore, the R-/S-perovskite enantiomers both reveal the multi-stage reversible phase transitions while the corresponding raceme displays the single-stage phase transitions. This work offers a feasible strategy for targeted design intrinsic non-centrosymmetric perovskites NLO materials with potential commercial application value.

4. Experimental Section

Materials: The following chemicals were commercially available unless otherwise indicated. R-(+)-β-methylphenethylamine (R-MPEA) (98%), S-(−)-β-methylphenethylamine (S-MPEA) (98%), and (±)-β-methylphenethylamine (rac-MPEA) (98%) were purchased from Heins Opde Technology Ltd. (Tianjin, China). 48% aqueous hydrobromide acid solution, SnCl₂·2H₂O, (98.0%), and N,N-dimethylformamide (DMF, 99.7%) were purchased from Sigma-Aldrich (Shanghai, China).

Compounds Preparation: The precursors R-/S-/rac-MPEABr were synthesized by reference to our previous work. The 2:1 molar ratio of obtained precursors and SnCl₂·2H₂O dissolved in hydrobromide acid solution. Then, the mixed solution was left open and stand in a shaking-free place. The corresponding single crystals grew by solvent slow evaporation. After 24 hours, colorless plate-like crystals were obtained. All experiments are conducted in the air. The target compounds were filtrated and dried for further study.

Thin Films Preparation: The resulting perovskite crystals (109 mg) dissolved in DMF (0.125 mL, molar concentration 1 M) in advance. Quartz (circular, diameter: 10 mm) and glass (square, width: 20 mm) substrates were washed by successively using concentrated sulfuric acid, deionized water, and isopropanol in a sonicator for 30 min. Thin films on glass substrates, used for PXRD measurements, were prepared by spin coating 100 µL of the corresponding solution onto substrates at a spin rate of 2500 rpm for 30 s, followed by thermal annealing at 70 ºC for 10 min. Thin films on quartz substrates, used for UV–vis absorption and CD measurements, were prepared by spin

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coating 10 µL of this solution on the clean surface of substrates at the spin rate of 1500 rpm for 30 s, subsequently annealing at 70 °C for 10 min to remove the residue DMF solvent.

**Single Crystal and Powder X-ray Diffraction:** Single-crystal XRD data of (R-MPEA)$_2$SnBr$_6$, (S-MPEA)$_2$SnBr$_6$, and (rac-MPEA)$_2$SnBr$_6$ were collected with Cu Ka radiation (λ = 1.5418 Å) at 100 K on a SuperNova diffractometer. The final crystal structures were resolved by direct methods, the SHELXL programs, and full-matrix least-squares on $F^2$ with Olex2$^{[54]}$ software. PXRD measurements were performed on a MiniFlex600 powder X-ray diffractometer with Cu Ka radiation (λ = 1.5418 Å) at a scanning rate of 5° min$^{-1}$ from 3° to 40°.

**Linear Optical Measurements:** For powder absorption, the prepared products were ground by a mortar and pestle. UV–vis DRS spectra were performed in a Hitachi U-4100 spectrophotometer using BaSO$_4$ as the 100% reflectance standard. The measurements were conducted in the wavelength range of 230–800 nm at room temperature. For thin film samples, UV–vis absorption spectra were collected in a SHIMADZU UV-3600 spectrophotometer, operating in the 190–900 nm region. Quartz substrates were used as 100% transmittance standard. PL emission spectra were obtained in a Hitachi F-2500 spectrophotometer with an ultraviolet excitation wavelength of 260 nm. CD measurements were recorded with a MOS-450 spectrophotometer in the transmission mode. The CD spectra were recorded in the 500–190 nm region and with 1 nm resolution.

**Thermal Measurements:** TGA measurements were conducted using Thermo Plus EVO 2 with a heating rate of 10 K min$^{-1}$ from 300 K to 800 K under Ar atmosphere.

DSC measurements were conducted before decomposition using METTLER TOLEDO DSC1 with a temperature range from 300 K to 470 K under N$_2$ atmosphere with a scanning rate of 10 K min$^{-1}$.

**NLO Measurements:** The NLO properties of chiral perovskites were investigated with a home-built set-up$^{[8]}$ with a femtosecond laser pump (Mai Tai HP, 100 fs, 80 MHz, 690–1040 nm). The measurements were conducted under a reflection geometry at a 45° angle of both incidence and detection.
Supporting Information

Supporting Information is available from the Wiley Online Library or the author.

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Lead-free chiral perovskite-type semiconductors have been constructed, demonstrating efficient second-order nonlinear optical response as well as multi-step phase transition properties. The remarkable air-stability, environmental friendliness, and high laser-damaged thresholds enable them as potential candidates for future commercialized nonlinear optical device applications.

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