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Macroscopic polarity control with alkali metal cation size and coordination environment in a series of tin iodates

Yeong Hun Kim, T. Thao Tran, P. Shiv Halasyamani, and Kang Min Ok

A series of stoichiometrically similar tin(IV) iodates, $\text{A}_2\text{Sn}(\text{IO}_3)_6$ (A = Li, Na, K, Rb, Cs) and $\text{Sn}^{4+}\text{Sn}^{6+}(\text{IO}_3)_6$ have been hydrothermally synthesized. X-ray diffraction was used to determine the crystal structures of the reported materials. All six materials reveal zero-dimensional molecular structures that consist of SnO$_6$ octahedra and IO$_3$ polyhedra. However, the size and coordination environment of cations significantly influence the macroscopic centricities of the materials. While Li$_2$Sn(IO$_3$)$_6$ and Na$_2$Sn(IO$_3$)$_6$ crystallize in the noncentrosymmetric (NCS) polar space group, $P6_3$, the K, Rb, Cs, and Sn phases crystallize in the centrosymmetric (CS) nonpolar space group, $R-3$. Infrared and UV-vis spectroscopies, thermal analyses, and local dipole moment calculations are reported. With the NCS polar materials, powder second-harmonic generation (SHG) properties, polarization, and piezoelectric measurements are also presented. The NCS properties are mainly attributable to the parallel alignment of the lone pairs in $\text{A}^{+}$ cations.

Introduction

Molecular materials have been of broad and current interest attributable to their wide ranges of important applications in photonics, information processing, data storage, and nanotechnology. Synthetic chemists have made continuous efforts to tune the characteristics of the materials by controlling the orientation and alignment of the molecules. Among many functional compounds, materials crystallizing in noncentrosymmetric (NCS) structures have drawn enormous attentions because of their technologically advanced properties, such as second-order nonlinear optical (NLO), piezoelectric, and multiferroic behaviors. Especially, polar materials exhibiting permanent dipole moments along a specifically defined direction are of great interest attributed to their two unique properties, i.e., pyroelectricity and ferroelectricity. Although the two interesting properties are found from polar materials, ferroelectricity is only observed when a switchable polarization exists within the crystal. In other words, a ferroelectric is a pyroelectric material that has a reversible polarization. Two successful approaches to develop superior performing polar materials are the crystallographically ordered $d^0$ transition metal oxyfluorides and oxides containing second-order Jahn-Teller (SOJT) distortive cations. With the former, changes in the bond network notably influence different crystal polarities. With the latter, incorporating locally polar polyhedra, such as octahedrally coordinated $d^0$ transition metal cations and lone pair cations, into an extended backbone plays an important role in creating a macroscopic polar structure. In addition, a number of NCS polar materials have been observed from $d^{10}$ transition metal cations revealing polar displacement as well as compounds composed of borate groups exhibiting unsymmetrical $\pi$-orbital systems. However, those local asymmetric building units frequently fall into line in an antiparallel manner and result in centrosymmetric (CS) nonpolar structures. Therefore, it is more important to understand key factors deciding the crystallographic centricity through close structural examinations. A series of alkali metal titanium iodate materials, $\text{A}_2\text{Ti}(\text{IO}_3)_6$ (A = Li, Na, K, Rb, Cs, Ag), with zero-dimensional structures have been recently reported, in which the size of alkali metal cations affect significantly the overall polarity of the materials. Other reported elements controlling the macroscopic polarity include the framework flexibility and the hydrogen bonding effect. Here we report hydrothermal syntheses and thorough characterizations of six new stoichiometrically similar molecular tin iodates, $\text{A}_2\text{Sn}(\text{IO}_3)_6$ (A = Li, Na, K, Rb, Cs) and $\text{Sn}^{4+}\text{Sn}^{6+}(\text{IO}_3)_6$. We will demonstrate how the cation size and coordination environment influence the polarity of the materials. With the polar iodates, Li$_2$Sn(IO$_3$)$_6$ and Na$_2$Sn(IO$_3$)$_6$, detailed NCS functional properties, such as second-harmonic generation (SHG), piezoelectricity, and polarization measurements will also be reported.
Experimental

Syntheses

Li₂CO₃ (Hayashi, 98.0%), Na₂CO₃ (Hayashi, 99.5%), K₂CO₃ (Jin Chemical, 99.5%), Rb₂CO₃ (Alfa Aesar, 99.8%), Cs₂CO₃ (Aldrich, 99.0%), SnCl₂ (Alfa Aesar, 98%), and HIO₃ (Alfa Aesar, 99.0%) were used as received. Single crystals of the reported compounds have been obtained through hydrothermal reactions. For Li₂Sn(IO₃)₆, 0.185 g (2.50 × 10⁻³ mol) of Li₂CO₃, 0.119 g (6.25 × 10⁻⁴ mol) of SnCl₂, 5.940 g (3.38 × 10⁻² mol) of HIO₃, and 10 mL of deionized water were combined. For Na₂Sn(IO₃)₆, 0.265 g (2.50 × 10⁻³ mol) of Na₂CO₃, 0.119 g (6.25 × 10⁻⁴ mol) of SnCl₂, 5.940 g (3.38 × 10⁻² mol) of HIO₃, and 10 mL of deionized water were combined. For K₂Sn(IO₃)₆, 0.173 g (1.25 × 10⁻³ mol) of K₂CO₃, 0.119 g (6.25 × 10⁻⁴ mol) of SnCl₂, 1.320 g (7.50 × 10⁻² mol) of HIO₃, and 5 mL of deionized water were combined. For Rb₂Sn(IO₃)₆, 0.289 g (1.25 × 10⁻³ mol) of Rb₂CO₃, 0.119 g (6.25 × 10⁻⁴ mol) of SnCl₂, 1.100 g (6.25 × 10⁻³ mol) of HIO₃, and 7.5 mL of deionized water were combined. For Cs₂Sn(IO₃)₆, 0.407 g (1.25 × 10⁻³ mol) of Cs₂CO₃, 0.237 g (1.25 × 10⁻³ mol) of SnCl₂, 1.650 g (9.38 × 10⁻³ mol) of HIO₃, and 7.5 mL of deionized water were combined. For Sn₂⁺Sn⁴⁺(IO₃)₆, 0.053 g (5.00 × 10⁻⁴ mol) of Na₂CO₃, 0.017 g (1.25 × 10⁻⁴ mol) of SnO, 1.056 g (6.00 × 10⁻³ mol) of HIO₃, and 2 mL of deionized water were combined. The respective mixtures were transferred into 23 mL Teflon-lined stainless steel autoclaves. After sealing, the autoclaves were gradually heated to 230 °C for 4 days, before being cooled to room temperature at a rate of 6 °C h⁻¹. After cooling, the autoclaves were opened and the products were recovered by filtration and washed with water. Colorless crystals of Li₂Sn(IO₃)₆, Na₂Sn(IO₃)₆, K₂Sn(IO₃)₆, Rb₂Sn(IO₃)₆, and Cs₂Sn(IO₃)₆ were obtained in 54%, 46%, 78%, 72%, and 85% yields, respectively, based on SnCl₂. Although several attempts have been made, we were not able to synthesize a pure phase of Sn²⁺Sn⁴⁺(IO₃)₆. A few colorless cube crystals of Sn²⁺Sn⁴⁺(IO₃)₆ were manually extracted from black plates crystals of SnO for single crystal X-ray diffraction. Thus, with Sn²⁺Sn⁴⁺(IO₃)₆, only the crystal structure will be given here. Powder X-ray diffraction patterns on the bulk samples for other five compounds revealed that the synthesized materials are pure and in very good agreements with the generated patterns from the single-crystal data (see the ESI).

Single-crystal X-ray diffraction

The crystal structures of the reported materials were determined by a standard crystallographic method. A colorless rod (0.018 × 0.020 × 0.073 mm³) for Li₂Sn(IO₃)₆, a colorless rod (0.020 × 0.020 × 0.100 mm³) for Na₂Sn(IO₃)₆, a colorless cube (0.036 × 0.038 × 0.038 mm³) for K₂Sn(IO₃)₆, a colorless cube (0.030 × 0.031 × 0.031 mm³) for Rb₂Sn(IO₃)₆, a colorless cube (0.031 × 0.031 × 0.032 mm³) for Cs₂Sn(IO₃)₆, and a colorless cube (0.031 × 0.031 × 0.032 mm³) for Sn²⁺Sn⁴⁺(IO₃)₆ were used for single crystal X-ray diffraction analyses. Diffraction data were collected at room temperature using a Bruker SMART BEEZE diffractometer equipped with a 1K CCD area detector using graphite monochromated Mo Kα radiation. A narrow-frame method was used with an exposure time of 10 s/frame, and scan widths of 0.3° in omega to collect a hemisphere of data. The maximum correction applied to the intensities was < 1%. The data were integrated using the SAINT program, with the intensities corrected for polarization, Lorentz factor, air absorption, and absorption attributed to the variation in the path length through the detector faceplate. The data were solved with SHELXS-97 and refined using SHELXL-97. All calculations were performed using the WinGX-98 crystallographic software package. Crystallographic data and selected bond distances for the reported materials are summarized in Tables 1 and 2, respectively.

<table>
<thead>
<tr>
<th>Table 1 Crystallographic data for A₂Sn(IO₃)₆ (A = Li, Na, K, Rb, Cs) and Sn²⁺Sn⁴⁺(IO₃)₆</th>
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<tbody>
<tr>
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<td>z/Å</td>
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<tr>
<td>R(F²)</td>
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<tr>
<td>R₁(F²)</td>
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<td>Flack parameter</td>
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¹R(F) = ∑|Fₒ| - |F(calc)| / ∑|Fₒ|.

²R₁(F²) = [Σw(F² - F(calc)²)² / Σw(F(calc)²)]¹/².
Table 2 Selected bond distances (Å) for \( A_2Sn(IO_3)_6 \) (\( A = Li, Na, K, Rb, Cs \)) and \( Sn^{2+}(IO_3)^{-6} \)

<table>
<thead>
<tr>
<th>bond</th>
<th>Li(_2)Sn(IO(_3))(_6)</th>
<th>Na(_2)Sn(IO(_3))(_6)</th>
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<tr>
<td>Sn(1)–O(1) ( \times 3 )</td>
<td>2.070(19)</td>
<td>2.10(3)</td>
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<tr>
<td>Sn(1)–O(1) ( \times 3 )</td>
<td>2.115(18)</td>
<td>2.14(3)</td>
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<tr>
<td>I(1)–O(1)</td>
<td>1.875(19)</td>
<td>1.87(3)</td>
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<tr>
<td>I(1)–O(2)</td>
<td>1.798(16)</td>
<td>1.77(3)</td>
</tr>
<tr>
<td>I(1)–O(3)</td>
<td>1.791(17)</td>
<td>1.80(2)</td>
</tr>
<tr>
<td>A(1)–O(2) ( \times 3 )</td>
<td>2.11(3)</td>
<td>2.28(2)</td>
</tr>
<tr>
<td>A(1)–O(3) ( \times 3 )</td>
<td>2.25(3)</td>
<td>2.42(3)</td>
</tr>
</tbody>
</table>

Powder X-ray diffraction (PXRD)

PXRD data were obtained using a Bruker D8-Advance diffractometer (Cu K\( \alpha \) radiation). The diffraction data were collected at room temperature with 40 kV and 40 mA. The ground samples were mounted on sample holders and scanned in the 20 range 5–70° with a step size of 0.02° and a step time of 0.2 s.

Infrared (IR) spectroscopy

IR spectra were obtained on a Thermo Scientific Nicolet 6700 FT-IR spectrometer in the spectral range 400–4000 cm\(^{-1}\). The samples were embedded in KBr matrices for the measurements.

UV-vis spectroscopy

UV-vis diffuse reflectance spectra were obtained on a Varian Cary 500 scan UV-vis-NIR spectrophotometer equipped with a double-beam photomultiplier tube in the range of 200–1500 nm at room temperature.

Thermogravimetric analysis (TGA)

TGA was performed on a Setaram LABSYS TG-DTA thermogravimetric analyser. The samples were contained in alumina crucibles and heated to 1000 °C at a rate of 10 °C min\(^{-1}\) under flowing argon.

Scanning electron microscope (SEM)/energy-dispersive analysis by X-ray (EDAX)

SEM/EDAX analyses were conducted by Hitachi S-3400N/10000 energy EX-250 instruments. EDAX for \( A_2Sn(IO_3)_6 \) (\( A = Li, Na, K, Rb, Cs \)) reveal A:Sn:I ratios of approximately N/A:1.0:5.6, 1.9:1.0:5.9, 1.8:1.0:6.2, 1.7:1.0:6.2, and 2.0:1.0:5.8, respectively.

Powder second-harmonic generation (SHG) measurements

Powder SHG measurements on polar NCS compounds, Li\(_2\)Sn(IO\(_3\))\(_6\) and Na\(_2\)Sn(IO\(_3\))\(_6\) were performed on a modified Kurtz NLO system\(^{41}\) using 1064 nm radiation using a DAWA Q-switched Nd:YAG laser operating at 20 Hz. SHG efficiencies for polycrystalline samples have been known to depend on particle size; thus, powder samples were graded into distinct ranges of particle size. To compare suitably with known SHG materials, crystalline \( \alpha \)-SiO\(_2\) and LiNbO\(_3\) were also sieved into the same particle size ranges. Samples with particle size range of 45–63 µm were used to compare SHG efficiencies.

Polycrystalline samples with different particle size ranges were placed in individual capillary tubes. The frequency-doubled SHG light, 532 nm green, was gathered and detected by a photomultiplier tube (PMT, Hamamatsu). A narrow-pass interference filter (532 nm) was attached to the PMT to detect only the SHG light. To monitor the SHG signal, a digital oscilloscope (Tektronix TDS1032) was connected. A detailed description of the equipment and the methodology has been published.\(^{42}\)

Piezoelectric measurements

Converse piezoelectric measurements were performed using a Radiant Technologies RT66A piezoelectric test system with a TREK (model 609E–6) high-voltage amplifier, Precision Materials Analyzer, Precision High-Voltage Interface, and MTI 2000 Fotonic Sensor. NCS Na\(_2\)Sn(IO\(_3\))\(_6\) was pressed into a 12 mm diameter and ~0.8 mm thick pellet and sintered at 300 °C for 6 h. A conducting paste was applied on both sides of the pellet surfaces for electrodes. A maximum voltage of 500 V was applied to the sample.

Polarization measurements

The polarization measurements were carried out on a Radiant Technologies RT66A ferroelectric test system with a TREK high-voltage amplifier between room temperature and 200 °C in a Delta 9023 environmental test chamber. The unclamped pyroelectric coefficient, \( dP/dT \), was determined by measuring the polarization \( (P) \) as a function of temperature \( (T) \). A detailed statement of the methodology used has been reported.\(^{42}\) The same pellet of Na\(_2\)Sn(IO\(_3\))\(_6\) used for piezoelectric measurements was utilized for polarization measurements. To determine the ferroelectric behaviour, polarization measurements were done at room temperature under a static electric field of 15.0 kV/cm at frequencies ranging 100–1000 Hz. For the pyroelectric measurements, the polarization was measured statically from room temperature to 200 °C in 20 °C increments, with an electric field of 15.0 kV/cm. The temperature was allowed to stabilize before the polarization was measured.
Results and discussion

Crystal structures

All six stoichiometrically similar tin iodates exhibit zero-dimensional structures that are composed of SnO$_6$ octahedra and IO$_3$ groups (see Fig. 1).

![Fig. 1 Ball-and-stick models for (a) NCS polar Na$_2$Sn(IO$_3$)$_6$ and (b) CS nonpolar K$_2$Sn(IO$_3$)$_6$ in the ab-plane.](Image)

As seen in Fig.1, the large molecular groups of SnO$_6$ and IO$_3$ polyhedra are kept apart by alkali metal or Sn$^{2+}$ cations. Thus, the reported materials share a general connectivity term of $[\text{SnO}_6]$-$6[\text{IO}_3]$ with charge balance retained by two alkali metal cations or a Sn$^{2+}$ cation. Interestingly, however, while Li$_2$Sn(IO$_3$)$_6$ and Na$_2$Sn(IO$_3$)$_6$ crystallize in NCS polar space group, $P6_3$ (No. 173), A$_2$Sn(IO$_3$)$_6$ (A = K, Rb, Cs) and Sn$^{2+}$Sn$^{4+}$(IO$_3$)$_6$ crystallize in CS nonpolar space group, $R-3$ (No. 148). The Sn$^{4+}$ cations in NCS Li$_2$Sn(IO$_3$)$_6$ and Na$_2$Sn(IO$_3$)$_6$ reveal $C_T$-type distortions and result in three short and three long Sn–O bonds. Here the Sn$^{4+}$ cation is disordered over two sites with 50% occupancy on each site, which makes the materials effectively 0-dimensional molecular structures. Similar disordered structures have been observed from polar titanium iodates. The observed Sn–O bond lengths for Li$_2$Sn(IO$_3$)$_6$ and Na$_2$Sn(IO$_3$)$_6$ are 2.070(19)–2.115(18) Å and 2.10(3)–2.14(3) Å, respectively. The I$^{4+}$ cations in Li$_2$Sn(IO$_3$)$_6$ and Na$_2$Sn(IO$_3$)$_6$ are in asymmetric trigonal pyramidal environment attributed to their stereoeactive lone pairs. The I–O bond distances for Li$_2$Sn(IO$_3$)$_6$ and Na$_2$Sn(IO$_3$)$_6$ range from 1.791(17) to 1.875(19) Å and from 1.77(3) to 1.873(3) Å, respectively. The Li$^+$ and Na$^+$ cations are in pseudo-octahedral coordination moieties with six oxygen ligands with bond lengths in the range 2.11(3)–2.42(3) Å. With CS A$_2$Sn(IO$_3$)$_6$ (A = K, Rb, Cs) and Sn$^{2+}$Sn$^{4+}$(IO$_3$)$_6$, the Sn$^{4+}$ cations are in the center of their normal octahedra with one unique Sn–O bond lengths of approximately 2.04 Å. Similar to those of Li$_2$Sn(IO$_3$)$_6$ and Na$_2$Sn(IO$_3$)$_6$, each I$^{4+}$ cation in CS A$_2$Sn(IO$_3$)$_6$ and Sn$^{2+}$Sn$^{4+}$(IO$_3$)$_6$ is linked to three oxygen atoms in a trigonal pyramidal environment with the I–O bond lengths in the approximate range 1.78(3)–1.87 Å (see Table 2). The K$^+$, Rb$^+$, Cs$^+$, and Sn$^{2+}$ in CS tin iodates are in ninefold coordination environments with contact distances in the range 2.827(6)–3.149(2) Å. Similar coordination moieties for the CS tin iodates strongly indicate that the materials are isostructural to each other and the lone pair on Sn$^{2+}$ is not stereoeactive but inert. Similar inertness of the lone pair cations have been observed previously in other materials. Bond valence sum calculations$^{35, 46}$ for the alkali-metal cations, Sn$^{2+}$, Sn$^{4+}$, and I$^{4+}$ on the reported tin iodates resulted in values of 0.90–1.26, 2.05, 3.70–4.15, and 4.93–5.03, respectively.

As can be seen in Fig. 2, all of the lone pairs on the iodates are aligned in a parallel manner in Li$_2$Sn(IO$_3$)$_6$ and Na$_2$Sn(IO$_3$)$_6$, in which a produced macroscopic dipole moment makes the materials crystallographic polar. However, in A$_2$Sn(IO$_3$)$_6$ (A = K, Rb, Cs) and Sn$^{2+}$Sn$^{4+}$(IO$_3$)$_6$, the lone pairs on iodate polyhedra positioned trans to each other are oriented in opposite directions (see Fig. 3), which results in a complete cancellation of the polarization generated from the local dipole moments. Thus, the materials crystallize in the CS nonpolar space group.

![Fig. 2 Ball-and-stick representation of Na$_2$Sn(IO$_3$)$_6$ in the ac-plane.](Image)
IR spectroscopy

The reported tin iodate compounds reveal Sn–O and I–O vibrations in the IR spectra. The Sn–O vibrations are found at ca. 660–663 cm\(^{-1}\). The I–O stretching and bending are also observed around 709–824 and 426–497 cm\(^{-1}\), respectively. The assignments are consistent with those previous published.\(^{47-49}\) The IR spectra are given in the ESI.

UV-vis diffuse reflectance spectroscopy

UV-vis diffuse reflectance spectra were obtained for the reported tin iodates. Absorption (\(K/S\)) data were calculated from the Kubelka-Munk function:\(^{50,51}\)

\[
F(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S}
\]

in which \(S\) is the scattering, \(K\) is the absorption, and \(R\) is the reflectance. In the \(K/S\) vs. \(E\) plots, extrapolating the linear part of the rising curve to zero yielded the onset of absorption at 3.9, 4.0, 4.0, 4.1, and 4.1 eV for \(\text{Li}_2\text{Sn}(\text{IO}_3)_6\), \(\text{Na}_2\text{Sn}(\text{IO}_3)_6\), \(\text{K}_2\text{Sn}(\text{IO}_3)_6\), \(\text{Rb}_2\text{Sn}(\text{IO}_3)_6\), and \(\text{Cs}_2\text{Sn}(\text{IO}_3)_6\), respectively (see the ESI). The band gaps for the reported compounds are attributed to the interaction of the Sn–O and I–O bonds and the distortions arising from \(\text{IO}_3\) groups.

Thermogravimetric analysis (TGA)

The thermal behaviors of the reported materials were investigated using TGA. TGA measurements showed that the materials decompose above 400 \(^\circ\)C. Powder XRD for the thermally decomposed products revealed SnO\(_2\) and alkali metal tin oxides. The TGA diagrams are found in the ESI.

Noncentrosymmetric (NCS) properties

\(\text{Li}_2\text{Sn}(\text{IO}_3)_6\) and \(\text{Na}_2\text{Sn}(\text{IO}_3)_6\) crystallize in the NCS polar space group, \(P6_1\); thus, their SHG properties have been investigated. The SHG efficiencies of the NCS tin iodates are very strong; both \(\text{Li}_2\text{Sn}(\text{IO}_3)_6\) and \(\text{Na}_2\text{Sn}(\text{IO}_3)_6\) exhibit SHG efficiencies of \(~400\) times that of \(\alpha\)-\(\text{SiO}_2\), which compares well to \(\text{BaTiO}_3\) \((400\) times that of \(\alpha\)-\(\text{SiO}_2\)).\(^{41}\) The SHG efficiencies for alkali metal titanium iodates, \(\text{Li}_2\text{Ti}(\text{IO}_3)_6\) and \(\text{Na}_2\text{Ti}(\text{IO}_3)_6\), are \(~500\) and \(~400\) times that of \(\alpha\)-\(\text{SiO}_2\), respectively.\(^{28,29}\) The larger SHG efficiency of \(\text{Li}_2\text{Ti}(\text{IO}_3)_6\) compared to that of \(\text{Li}_2\text{Sn}(\text{IO}_3)_6\) may be attributed to the constructive addition of polarizations from both TiO\(_6\) and IO\(_3\) polyhedra. Overall, the similar efficiencies strongly indicate that the SHG for the iodates are mainly attributable to the alignment of the dipole moments in the IO\(_3\) groups (see Fig. 2 and dipole moment calculations section). In addition, we were able to determine the type I phase-matching capabilities for the NCS polar materials by sieving them into various particle sizes and measuring the SHG as a function of particle size. As seen in Fig. 4, both \(\text{Li}_2\text{Sn}(\text{IO}_3)_6\) and \(\text{Na}_2\text{Sn}(\text{IO}_3)_6\) are phase-matchable and can be classified as the class A category of SHG materials, as defined by Kurtz and Perry.\(^{41}\)

Converse piezoelectric measurements on bulk \(\text{Na}_2\text{Sn}(\text{IO}_3)_6\) revealed a \(d_{33}\) charge constant of 29.2 pm/V (see the ESI). The value compares well to that for other iodates, \(i.e.,\) \(\text{KIO}_3\) \((d_{33} = 39\) pm/V) and \(\text{Na}_2\text{Ti}(\text{IO}_3)_6\) \((d_{33} = 60\) pm/V).\(^{29,52}\) Ferroelectric and pyroelectric measurements for \(\text{Na}_2\text{Sn}(\text{IO}_3)_6\) were also performed. Although the material is polar, \(\text{Na}_2\text{Sn}(\text{IO}_3)_6\) is not ferroelectric as can be seen in the ferroelectric measurements (see the ESI). Polarization measurements using 15 kV/cm indicated an induced maximum polarization of only 0.07 \(\mu\)C/cm\(^2\). In order to be ferroelectric, the dipole moment needs to be reversible. In \(\text{Na}_2\text{Sn}(\text{IO}_3)_6\), the distortion associated with
Sn$^{4+}$ is negligible, as we will discuss more in detail later (see dipole moment calculations section). With I$^+$ in the IO$_3$ polyhedron in an extended solid-state structure, the macroscopic polarization cannot be switched in the presence of an external electric field, because polarization reversal for the lone pair cation is extremely unfavorable. The energetically very unfavorable polarization reversal of the IO$_3$ polyhedron has been demonstrated before through calculations. Although Na$_2$Sn(IO$_3$)$_6$ is not ferroelectric, the compound is pyroelectric. Thus, the pyroelectric coefficient for Na$_2$Sn(IO$_3$)$_6$ has been determined by measuring the polarization between room temperature and 200 °C, with an external electric field of 15.0 kV/cm. The obtained pyroelectric coefficients is approximately 0.5 $\mu$C m$^{-2}$ K$^{-1}$, which is similar to that of sodium titanium iodate, Na$_2$Ti(IO$_3$)$_6$ (0.8 $\mu$C m$^{-2}$ K$^{-1}$).\textsuperscript{29}

### Dipole moment calculations

The reported stoichiometrically similar compounds contain asymmetric polyhedra, i.e., IO$_3$ groups attributed to the lone pairs. Thus, the asymmetric environment of the IO$_3$ polyhedron has been quantified through local dipole moment calculations using the method described before.\textsuperscript{8, 9, 53} The distortion of SnO$_6$ octahedra has been also calculated for comparison. We found that the local dipole moments for IO$_3$ and SnO$_6$ groups in A$_2$Sn(IO$_3$)$_6$ (A = Li, Na, K, Rb, Cs) are calculated to be about 13.1–13.9 and 0–0.4 D (Debyes), respectively, which are very similar values to those of previously reported iodate materials.\textsuperscript{28, 29, 49} As we described earlier, while the polarization arising from the distortion of SnO$_6$ octahedra is negligible, the polarization associated with IO$_3$ polyhedra is significant. Thus, the functional properties for NCS polar materials are attributed to a net moment originated from the alignment of IO$_3$ groups. The local dipole moments for the IO$_3$ and SnO$_6$ groups are summarized in Table 3.

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<th>Compound</th>
<th>Species</th>
<th>Dipole moment (D)</th>
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<td>Li$_2$Sn(IO$_3$)$_6$</td>
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<td>Sn(1)O$_6$</td>
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<td>Cs$_2$Sn(IO$_3$)$_6$</td>
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### NCS polar vs. CS nonpolar structures

Although all six stoichiometrically similar materials, A$_2$Sn(IO$_3$)$_6$ (A = Li, Na, K, Rb, Cs) and Sn$^{4+}$Sn$^{2+}$(IO$_3$)$_6$, share a molecular structure consisting of SnO$_6$ octahedra and IO$_3$ polyhedra, an interesting change in macroscopic polarity occurs from the NCS polar structure for the compounds containing smaller cations, Li$^+$ and Na$^+$, to the CS nonpolar structure for those with larger cations, K$^+$, Rb$^+$, Cs$^+$, and Sn$^{4+}$. With Li$_2$Sn(IO$_3$)$_6$ and Na$_2$Sn(IO$_3$)$_6$, the alkali metal cations, Li$^+$ and Na$^+$ are in six-coordinate pseudo-octahedral coordination environment attributed to their smaller cation size. To maintain this octahedral coordination mode around the Li$^+$ and Na$^+$ cations, the IO$_3$ groups should be aligned in a parallel manner around the Sn$^{4+}$ cation, which subsequently results in a NCS polar structure (see Fig. 5a). It should be noted, however, that this parallel alignment in the crowded environment is only possible when the ionic radii of the cations are small. Whereas, the cations, K$^+$, Rb$^+$, Cs$^+$, and Sn$^{4+}$ in CS nonpolar structures maintain nine-coordinate environments with oxide ligands attributable to the larger ionic radii (see Fig. 5b). As seen in Fig. 5b, the larger A$^+$ cations can have nine oxide contacts by rotating the IO$_3$ polyhedra with respect to the Sn$^{4+}$ cation. Thus, the local dipole moments for IO$_3$ polyhedra point in opposite directions equally and render the material CS nonpolar. Similar cation size effect on the coordination environments and macroscopic centricity has been observed before.\textsuperscript{29, 54, 55}

![Fig. 5 Ball-and-stick representations for (a) NCS Na$_2$Sn(IO$_3$)$_6$ and (b) CS K$_2$Sn(IO$_3$)$_6$, with the alkali metal coordination environments emphasized. Note the IO$_3$ groups in Na$_2$Sn(IO$_3$)$_6$ are aligned in a parallel manner attributed to the six-coordinate Na$^+$ cation, whereas the IO$_3$ polyhedra in K$_2$Sn(IO$_3$)$_6$ rotate with respect to Sn$^{4+}$ due to nine-coordinate K$^+$ cation.](image)
Conclusions

Six new tin iodates, $A_2$Sn(IO₃)₆ (A = Li, Na, K, Rb, Cs) and Sn²⁺Sn⁴⁺(IO₃)₆, have been synthesized hydrothermally and their structures were determined through single crystal X-ray diffraction. All six stoichiometrically similar tin iodates exhibit molecular structures that are composed of SnO₆ octahedra and IO₃ groups. While the compounds containing smaller cations, Li⁺ and Na⁺, are NCS polar, those with the larger cations, K⁺, Rb⁺, Cs⁺, and Sn²⁺, are CS nonpolar. The smaller alkali metal cations, Li⁺ and Na⁺, are in six-coordinate pseudo-octahedral coordination moieties and contact with oxide ligands on six different IO₃ groups. The compact interactions demand the lone pairs in IO₃ groups to align in a parallel manner and let Li₂Sn(IO₃)₆ and Na₂Sn(IO₃)₆ crystallize in the NCS polar space group. The larger cations, K⁺, Rb⁺, Cs⁺, and Sn²⁺, interact with oxide ligands on IO₃ and SnO₆ groups in nine-coordinate environments. To maintain these contacts, the IO₃ polyhedra should rotate with respect to the SnO₆ octahedron, in which the rotation aligns the polarizations from the IO₃ groups in opposite directions. Thus, all tin iodates with larger cations, K₂Sn(IO₃)₆, Rb₂Sn(IO₃)₆, Cs₂Sn(IO₃)₆, and Sn²⁺Sn⁴⁺(IO₃)₆ crystallize in the CS nonpolar space group. The NCS functional properties such as SHG, piezoelectricity, and pyroelectricity are attributable to the parallel alignment of the lone pairs on the $I^{5+}$ cations.

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Notes and references

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1Electronic Supplementary Information (ESI) available: X-ray crystallographic file in CIF format, calculated and observed X-ray diffraction patterns, TGA diagrams, IR spectra, UV-vis diffuse reflectance spectra, piezoelectric, polarization, and pyroelectric measurements data. CCDC 1041408-1041413. For ESI and crystallographic data in CIF or other electronic form see DOI: 10.1039/b000000c/

37. SAINT, Program for Area Detector Absorption Correction; version 4.05; Siemens Analytical X-ray Instruments: Madison, WI, USA, 1995.