A Polar and Chiral Indium Telluride Featuring Supertetrahedral T2 Clusters and Nonlinear Optical Second Harmonic Generation

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Extended chalcogenide frameworks exhibit an impressive structural diversity that gives rise to interesting properties such as porosity, fast ion conductivity, ion-exchange, photoconductivity, and photocatalytic behaviors.[1−8] Low synthesis temperatures favor this diversity. Among the chalcogenides, tellurides are the most challenging to synthesize because of the low reactivity of tellurium and environmental instability of tellurides. Several synthetic methodologies are known to produce tellurides. The most commonly used are high temperature fusion of the elements followed by solvent extraction of alloy phases,[9,10] molten salt flux synthesis,[11−13] the treatment of binary alloys with potassium (or other alkali metals),[14] electrochemical synthetic methods,[15] chemical transport reactions, and solvothermal techniques.[16,17]

Metal Zintl anions[18,19] ($Ge_9^{4−}$, $Sn_9^{4−}$, $Pb_9^{4−}$, $Bi_4^{5−}$, $Sb_4^{5−}$, etc.) are known to be strong reducing agents, which can activate tellurium. We anticipate that new structures might be realized if such Zintl anions or intermetallic phases were employed as starting materials to prepare metal tellurides under solvothermal conditions. Reactions at room temperature between $Sn_9^{4−}$ and Te were reported by Fässler et al.;[20] however, the solvothermal chemistry of Zintl phases and tellurium is little explored.

We report here that the intermetallic Zintl phase of nominal composition "KIn_2"[21] reacts with Te to produce $\{[In(en)_3][In_5Te_9(en)_2]\cdot0.5en\}_n$ (**1**) (*en* = ethylenediamine), a layered chiral compound with truncated adamantane In_4Te_9 clusters. Unlike the well-known sulfide- or selenide-based open frameworks that usually contain adamantane building units, the heretofore reported tellurides feature no such units.

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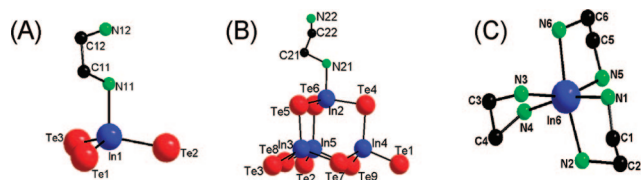
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Figure 1. Ball and stick model of three different units in compound **1**. (A) $[InTe_3(en)]^{3-}$ T1 tetrahedron; (B) adamantane $[In_4Te_9(en)]^{6-}$ T2 cluster; (C) the countercation $\Delta^{M\Delta\Delta\Delta}-[In(en)_3]^{3+}$. The range of N−In distances and N−In−N angles are 2.31−2.39 Å and 76.2 − 164.7°, respectively.

To the best of our knowledge, this is first report of a telluride-based framework constructed from adamantane clusters.

The polar character of **1** is the result of the $[In_5Te_9(en)_2]^{3-}$ layers. The chirality arises from both these layers and the presence of the chiral coordination complexes of $\Delta^{M\delta\lambda\lambda}-[In(en)_3]^{3+}$. Compound **1** exhibits strong nonlinear optical second harmonic generation response that arises from the polar character and the high polarizability of indium and tellurium atoms.

To prepare crystals of $\{[In(en)_3][In_5Te_9(en)_2] \cdot 0.5en\}_n$, we mixed 204 mg (1.6 mmol) of Te, 108 mg (0.40 mmol) of nominal "KIn₂", and 4.0 mL of dry *en* (distilled from sodium) in a 23 mL Teflon-lined stainless steel autoclave in a dry box. This mixture was stirred for 10 min, and the vessel was sealed and heated at 190 °C for 10 days. The autoclave was subsequently allowed to cool to room temperature. Orange air-stable hexagonal crystals (compound **1**) were collected and the corresponding yield was 40% (based on "KIn₂"). The crystal structure[22] of compound **1** was determined from single-crystal X-ray diffraction data collected at 100 K on a STOE II X-ray diffractometer. The existence of *en* molecules was confirmed by IR spectroscopy (see Figure S1 in the Supporting Information) and quantification was made through thermogravimetric analysis (TGA, see Figure S2 in the Supporting Information). The calculated atomic In/Te ratio from the single-crystal structure analysis is in agreement with energy-dispersive X-ray spectroscopy analysis (EDS, see Figure S3 in the Supporting Information).[23]

Compound **1** crystallizes in the hexagonal space group $P6_1$.[22] It features layers of $[In_5Te_9(en)_2]^{3-}$ in a new structural motif. The net is formed by linking adamantane $[In_4Te_9(en)]^{6-}$ clusters with In^{3+} centers. The linking indium atoms (T1) and clusters (T2) are shown in structures A and B in Figure 1. Tetrahedral In clusters (T1) and the adamantane-shaped T2 clusters are the first and second members in a series of supertetrahedral homologous series of clusters (the T*n* series).[5a] The chemical formula for the discrete T1
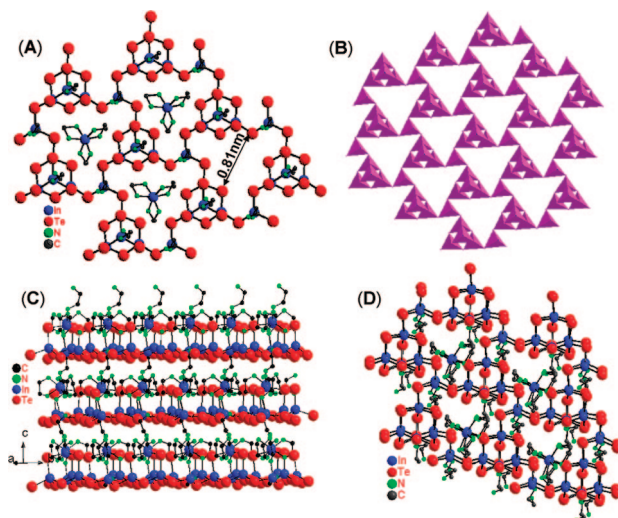
(22) Single-crystal X-ray diffraction data were collected at 100 K using a STOE imaging-plate diffraction system (IPSD-2) with graphite-monochromatized Mo Kα radiation. A numerical absorption correction was applied using the X-RED program set. Direct methods and full-matrix least-squares refinements against F^2 were performed with SHELXTL package. Crystal data for $\{[In(en)_3][In_5Te_9(en)_2].0.5en\}_n(1)$: Hexagonal $P6_1$, $Z = 6$, $a = b = 11.6147(2)$ Å, $c = 51.9135(15)$ Å, $\gamma = 120°$, $V = 6064.9(2)$ Å³, $2\theta_{max}$ (Mo Kα) = 46.58°, $D_{calcd} = 3.512$ g/cm³, $\mu = 9.750$ mm⁻¹, total reflections = 3777, unique reflections $[F_o^2 > 2\sigma (F_o^2)] = 3399$, parameters = 217, GOF = 1.169, R1 = 7.72% and wR2 = 17.35% for $I > 2\sigma(I)$. Because of the disorder of the free *en* molecules, it was impossible to locate them in the final structural refinement and this accounts for the relatively high R1 value.
(23) EDS analysis: the calculated ratio for In and Te is 2:3 and the result from EDS is 39.65:60.28.

Figure 2. (A) View of a single $[In_5Te_9(en)_2]^{3-}$ layer of compound **1**; (B) polyhedral representation of a single layer (organic group and cation complexes are omitted for clarity); (C) side view of three layers ($\Delta^{M\delta\lambda\lambda}-[In(en)_3]^{3+}$ complexes sit in pockets associated with the windows within the layer); (D) stacking of two layers viewed down the *c*-axis. Blue, In; red, Te; black, C; green, N.

tetrahedron and T2 clusters are $[InTe_3(en)]^{3-}$ and $[In_4Te_9(en)]^{6-}$, respectively. These, however, differ from the conventional T1 and T2 in that one of the Te atoms has been replaced by a monodentate *en* ligand. The *en* ligand serves as a terminal group and does not allow further connectivity of the framework. Of the nine telluride atoms, three are terminal (Te1, Te2, and Te3). The terminal Te atoms then coordinate to In1 which acts a linking ion between adjacent T2 clusters (Figure 1a). The replacement of the fourth telluride ion with a neutral *en* molecule to occupy one coordination site of indium in both T1 tetrahedron and T2 clusters, causes a structural distortion as seen in the relevant Te−In−Te bond angles (see the Supporting Information cif file). Normally, the distances of In−Te in the *en*-coordinated indium sites of T1 and T2 are slightly shorter than that in en-free In/Te anions[7c,13a,24] and range from 2.722(1) to 2.744(1) Å. The Te−In−Te bond angles are between 98.24(2) and 118.87(3)° and the N−In−Te bond angles are between 98.67(12) and 114.89(3)°.

The arrangement of the In−Te network creates windows within the layers defined by 18-membered rings formed by nine tetrahedral indium sites (Figure 2B). The size of these windows are ~0.81 nm (with van der Waals radii taken into account). The total charge of each window is −3 and is balanced by octahedral $\Delta^{M\delta\lambda\lambda}- [In(en)_3]^{3+}$ complexes (Figure 1C), which occupy the middle of each window (structures A and D in Figure 2). The layers are stacked along the *c*-axis with an eclipsed fashion so that the T2 clusters and windows are in registry (structures C and D in Figure 2). The distance between adjacent layers of $[In_5Te_9(en)_2]^{3-}$ is ~5.0 Å, which is filled by one-half of each metal complex ($\Delta^{M\delta\lambda\lambda}- [In(en)_3]^{3+}$, the other half-is in plane), terminal *en* molecules, and disordered free *en* molecules.

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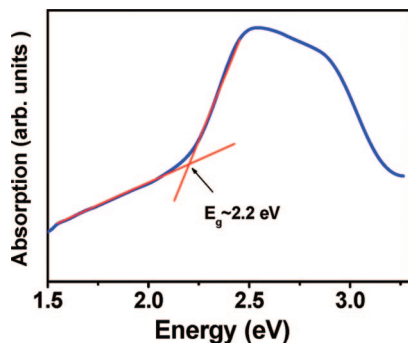
Figure 3. UV−vis absorbance of a single crystal of compound **1**.

Figure 4. (A) SHG comparison between compound **1** and AgGaSe$_2$; (B) dependence of SHG intensity on the particle size of compound **1**.

Li et al. reported an interesting layered chalcogenide $\{[Zn(en)_3][In_{16}(Te_2)_4(Te_3)Te_{22}]\}_n$,[7b] designated as **2**, which also contains metal complexes as a structure-directing agent and so-called T2 clusters as building blocks. The "T2 clusters" in this compound, however, do not have adamantine shapes and are different from those observed in **1**. There are several differences between these two structures: (a) **1** contains alternating T1 tetrahedron and T2 clusters while compound **2** is built from pseudo T2 clusters; (b) the dangling groups in the clusters of **1** are neutral *en* molecules, whereas in **2**, the pseudo T2 clusters have terminal Te^{2-} anions; and (c) the layer connectivity is different.

The solid-state UV−vis absorption of a single crystal of **1** revealed an absorption edge at ∼2.2 eV, consistent with its orange color (Figure 3). The thermogravimetric analysis (TGA) shows that there are two stages of weight loss: the first is a small weight loss of 1.30% starting at 322 K and it is attributed to free *en* (calcd, 1.38%). The second stage of weight loss (13.40%) starting at 520 K is from the loss of all coordinated amines (calcd, 13.84%; see Figure S2 in the Supporting Information). After TGA, the X-ray powder diffraction indicated that the main phase of the residue was In$_2$Te$_3$ (see Figure S4 in the Supporting Information).

The second harmonic generation (SHG) response of this noncentrosymmetric material was measured at room temperature with a modified Kurtz powder technique.[25] The SHG intensit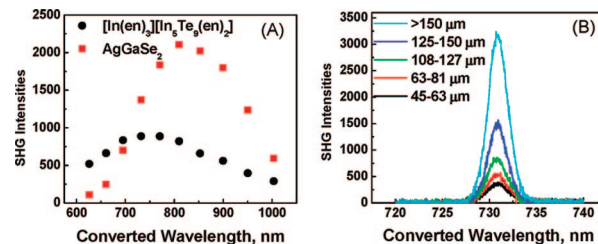ies were measured on polycrystalline samples in the range of 1200−2000 nm using an optical parametric amplifier driven by the 355 nm output of a YAG laser. Compound **1** displayed relatively high SHG intensities, which is approximately half-that of AgGaSe$_2$ (a commercial NLO material, Figure 4A).[26] The SHG intensity of $\{[In(en)_3][In_5Te_9(en)_2]\cdot0.5en\}_n$ (**1**) increases with the increasing particle size, indicating type I phase-matchablility (Figure 4B).[25]

In conclusion, the intermetallic Zintl phase with nominal "KIn$_2$" composition is a novel starting material to activate tellurium under solvothermal conditions. The hybrid framework of $\{[In(en)_3][In_5Te_9(en)_2]\cdot0.5en\}_n$ (**1**) is based on the truncated adamantane clusters of $[In_4Te_9(en)]^{6-}$ and represents a rare example of chiral and polar material containing supertetrahedral building blocks. The polar compound has good second harmonic generation response with type I phase-matchability. We anticipate that using Zintl phases as reactive starting materials will offer additional opportunities to prepare novel crystalline chalcogenides.

Supporting Information Available: IR spectra, EDS analysis, and TGA graph (PDF); X-ray crystallographic files in CIF format for the structure determination of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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