

Hydrothermal Synthesis and Crystal Structure of Polar and Nonpolar Compounds in Indium Iodate Family

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ABSTRACT: Using hydrothermal synthesis, a series of indium iodates α -K₃In(IO₃)₆ (**1**), β -K₃In(IO₃)₆ (**2**), In(OH)(IO₃)₂·H₂O (**3**), and In(IO₃)₃ (**4**) from zero-dimensional, one-dimensional, to two-dimensional have been prepared. Compound **1** crystallizes in an orthorhombic system with space group *Fdd2*, $a = 39.596(7)$ Å, $b = 8.2984(14)$ Å, $c = 11.258(2)$ Å, $V = 3699.1(11)$ Å³. Compounds **2**, **3**, and **4** are obtained in the same reaction reagents with different pH values. At a pH value of 0.5, compound **2** is formed, which crystallizes in a triclinic system with space group *P* $\bar{1}$, $a = 6.9441(14)$ Å, $b = 7.0685(14)$ Å, $c = 10.639(12)$ Å, $\alpha = 98.14(3)^\circ$, $\beta = 108.77(3)^\circ$, $\gamma = 102.72(3)^\circ$, $V = 469.4(20)$ Å³. The increase of pH value to 1.5 gives rise to compound **3**, which crystallizes in a triclinic system with space group *P* $\bar{1}$, $a = 6.7321(13)$ Å, $b = 7.5255(15)$ Å, $c = 7.6798(15)$ Å, $\alpha = 100.43(3)^\circ$, $\beta = 91.96(3)^\circ$, $\gamma = 106.64(3)^\circ$, $V = 365.09(12)$ Å³. When the pH value is further raised to 3, compound **4** is obtained in high yield (about 90% based on indium). The structure of compound **1** is made up of zero-dimensional units consisting of [In(IO₃)₆]³⁻ anions separated by K⁺ cations. The indium centers are ligated by six monodentate iodate anions, of which the terminal oxygen atoms form long ionic contacts with K⁺ cations. Distinctively, compound **1** crystallizes in the polar space group *Fdd2*. The polarity in the structure is imparted by the alignment of the stereochemically active lone pairs of electrons of the iodate anions along the *c*-axis. Second-harmonic generation of 532 nm light from a 1064 nm laser source yields a response approximately similar to that of KDP. The same reaction stoichiometric undergoes pH-mediated structural transformation leading to the formation of zero-dimensional compound **2**, one-dimensional compound **3**, and two-dimensional compound **4**. Compound **2** is also composed of [In(IO₃)₆]³⁻ anions separated by K⁺ cations but is nonpolar. Compound **3** displays a one-dimensional ribbon structure constructed from [InO₆] octahedra and [IO₃] pyramids and separated by water molecules. [InO₆] octahedra share corners to form a chain, of which two sides are decorated by [IO₃] pyramids by bridging the adjacent octahedra. Compound **4** is known to contain Te₄O₉-type structure, in which iodate anions bridge In³⁺ cations to form two-dimensional layers. The reaction conditions and thermal stabilities of these compounds are investigated.

Introduction

Materials containing units in asymmetric coordination environments are of current interest owing to their technologically important properties such as second-harmonic generation (SHG), piezoelectricity, ferroelectricity, and pyroelectricity. In addition to having asymmetrically coordinated units, materials exhibiting these properties must also be crystallographically noncentrosymmetric (NCS).¹ In a seminal paper by Kurtz and co-workers, it was established that the successful preparation of NCS materials was often dependent on the combination of three key structural features.² First, anions with a nonbonding, but stereochemically active, pair of electrons such as selenite^{3–5} or iodate^{6–10} have a tendency to align in the solid state to create polar structures. Second, transition metals have already been recognized as being susceptible to distortion from idealized octahedral symmetry. These distortions can be cooperative and lead to noncentrosymmetric (NCS) structures. Finally, large cations such as K⁺, Cs⁺, and Rb⁺ have a propensity for residing in sites where they form contacts with eight or more anions in an acentric environment. While there is no guarantee that the combination of these features will yield NCS structures, the tendency for this to be true is certainly apparent from extensive reviews of this area.¹ These ideas have been successfully applied in the syntheses of

a number of NCS compounds including [(VO)₂(IO₃)₃O₂] (A = NH₄, Rb, Cs),¹¹ A(VO)₃(SeO₃)₂ (A = NH₄, K, Rb, Cs),¹² and AMoO₃(IO₃) (A = Rb, Cs).¹³ It is reported that the chiral Al(IO₃)₃·2HIO₃·6H₂O has been structurally characterized by both X-ray diffraction^{14,15} and spectroscopic measurements,^{16,17} and its piezoelectric, elastic, and optical properties^{18,19} have also been investigated. This material was found to exhibit a longitudinal piezoelectric effect 10 times larger than α -quartz. Recently, the framework of Ga(IO₃)₃²⁰ was reported to be isostructural with Al(IO₃)₃,²¹ and In(IO₃)₃²² was reported to possess Te₄O₉-type structure. Except these, no other iiiA elements' iodates have been reported up to now. Considering the coordination variety of iiiA elements, we have begun to apply those ideas established by Kurtz and co-workers to iiiA elements' iodates in order to design and synthesize some new NCS materials with potential properties. Using hydrothermal synthesis, a series of indium iodates: α -K₃In(IO₃)₆ (**1**), β -K₃In(IO₃)₆ (**2**), In(OH)(IO₃)₂·H₂O (**3**), and In(IO₃)₃ (**4**) from zero-dimensional, one-dimensional, to two-dimensional have been prepared. Compound **1** is NCS and has been characterized by SHG; compound **4** has already been reported,²² but we introduce it here in order to discuss the reaction conditions that influence the formation of the final products.

Experimental Procedures

Synthesis and Characterization. Compound **1** is synthesized from a mixture containing KIO₄(0.345 g, 1.5 mmol), In(NO₃)₃·20.5H₂O (0.38

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Table 1. Crystallographic Data for Compounds 1–4

	1	2	3	4
empirical formula	InI ₆ K ₃ O ₁₈	InI ₆ K ₃ O ₁₈	InI ₂ O ₈ H ₃	InI ₃ O ₉
weight	1281.52	1281.52	499.64	639.52
temperature (K)	293(2)	293(2)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
crystal system	orthorhombic	triclinic	triclinic	hexagonal
space group	<i>Fdd2</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>R</i> $\bar{3}$
<i>a</i> (Å)	39.596(7)	6.9441(14)	6.7321(13)	9.7701(14)
<i>b</i> (Å)	8.2984(14)	7.0685(14)	7.5255(15)	9.7701(14)
<i>c</i> (Å)	11.258(2)	10.639(2)	7.6798(15)	14.179(3)
α (deg)	90	98.14(3)	100.43(3)	90
β (deg)	90	108.77(3)	91.96(3)	90
γ (deg)	90	102.72(3)	106.64(3)	120
volume (Å ³)	3699.1(11)	469.37(20)	365.09(12)	1172.1(3)
<i>Z</i>	8	1	2	6
<i>D</i> _{calc} (g/m ³)	4.602	4.534	4.545	5.436
μ (mm ⁻¹)	12.056	11.877	11.697	14.903
<i>R</i> ₁ [<i>I</i> > 2(<i>I</i>)] ^a	0.0249	0.0435	0.0153	0.0259
<i>wR</i> ₂ [<i>I</i> > 2(<i>I</i>)] ^b	0.0518	0.0944	0.0371	0.0585

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

g, 1 mmol), 2,2'-bipy (0.085 g, 0.5 mmol), and 0.4 mL of HCl (38%) in the presence of water (5 mL) under hydrothermal conditions at 120 °C for 4 days. The pH value of this system is about 2.5. Block colorless crystals are collected in ca. 30% yield based on indium.

Compounds 2–4 are synthesized from a mixture containing KIO₄ (0.23 g, 1 mmol), In(NO₃)₃·20.5H₂O (0.38 g, 1 mmol), imidazole (0.068 g, 1 mmol) and 0.4 mL (for compound 2), 0.25 mL (for compound 3), 0.1 mL (for compound 4) of HCl (38%) in the presence of water (5 mL) under hydrothermal conditions at 100 °C for 7 days. It is noted that the pH value (0.5 for compound 2, 1.5 for compound 3, and 3 for compound 4) is the main factor affecting the formation of the products. Although imidazole is not incorporated into the products, it plays an important role in the formation of the final products in hydrothermal synthesis. However, only a small amount of In(IO₃)₃ is obtained without imidazole in the same condition whatever the pH value is. Compounds 2, 3, and 4 are isolated as platelet, needle, and block colorless crystals, respectively.

Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer. Inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300DV ICP instrument. Anal. Calcd for compound 1: K, 9.20; In, 9.02; Found: K, 9.15; In, 8.96. Anal. Calcd for compound 2: K, 9.23; In, 9.08; Found: K, 9.15; In, 8.96. Anal. Calcd for compound 3: In, 23.05; Found: In, 22.98. A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air at a heating rate of 20 °C/min. The diffuse-reflectance UV–vis spectrum for powder sample was obtained on a Perkin-Elmer Lambda 20 UV–vis spectrometer equipped with an integrating sphere, using BaSO₄ as the background material.

Structure Determination. Compound 1 was collected on a Siemens SMART CCD diffractometer with graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation at a temperature of 293 ± 2 K. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 30 s/frame. Data processing was accomplished with the SAINT processing program.²³

Compounds 2–4 were collected on a Rigaku RAXIS-RAPID single-crystal diffractometer equipped with a narrow-focus, 5.4-kW sealed-tube X-ray source (graphite-monochromated Mo K α radiation with $\lambda = 0.71073$ Å) at a temperature of 20 ± 2 °C. Data processing was accomplished with the PROCESS-AUTO processing program.

All the structures were solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares techniques against *F*² using the SHELXTL-97 crystallographic software package.²⁴ Details of the final refinement are given in Table 1.

Results and Discussion

Structure. An ORTEP drawing of the asymmetric unit of compound 1 is shown in Figure 1a, which crystallizes in an orthorhombic space group *Fdd2* with unit cell content of 15 non-hydrogen atoms. There are one indium atom, three iodine atoms, nine oxygen atoms, and two potassium atoms in an asymmetric

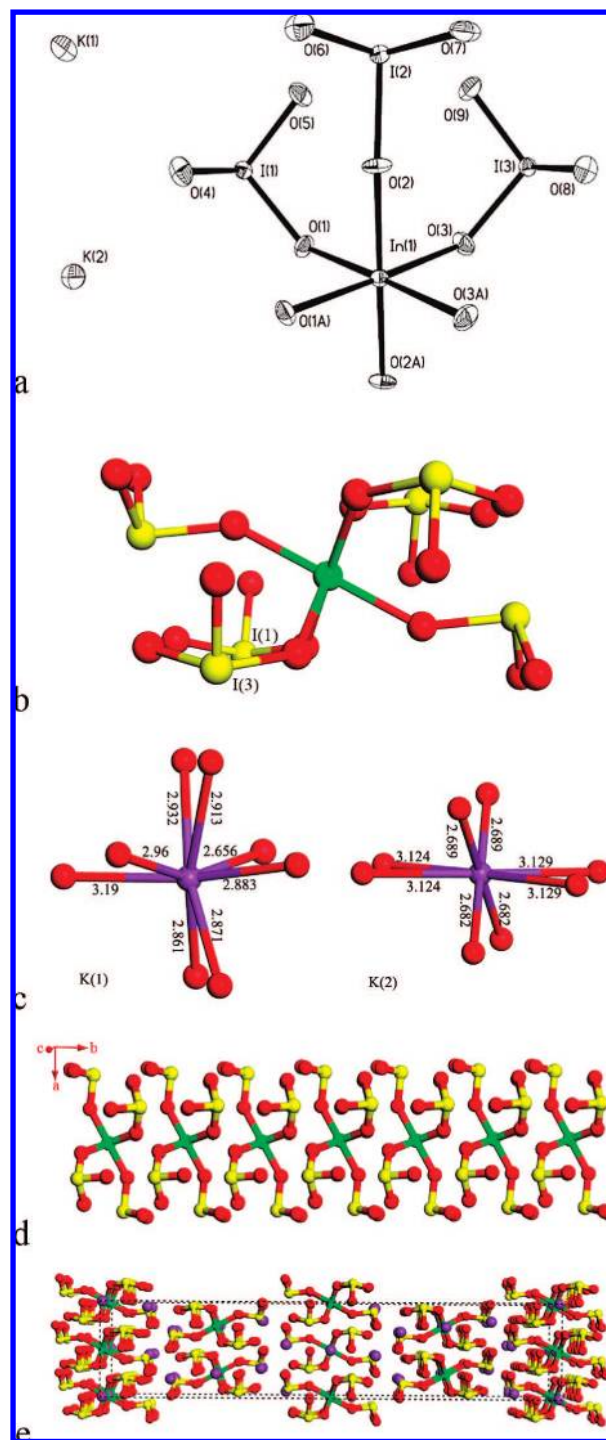


Figure 1. (a) Asymmetric unit of compound 1. (b) The crystallographically unique I(1) and I(3) iodate units in the [In(IO₃)₆]³⁻ anion are aligned (c) The environments around the K⁺ cations. (d) Iodate groups display alignment along the polar *b*-axis. (e) A packing diagram for compound 1 projected along the *c*-axis. The following colors correspond to these atoms: indium, green; iodine, yellow; oxygen, red; potassium, purple.

unit. The indium site in an asymmetric unit exhibits a distorted octahedral geometry with [InO₆]. The iodine sites show [IO₃] pyramidal geometry, in which iodine and oxygens are all at the vertical positions. Structure determination indicates that compound K₃In(IO₃)₆ is made up of zero-dimensional units consisting of [In(IO₃)₆]³⁻ anions and separated by K⁺ cations. In connectivity terms, each In³⁺ cation is bonded to six oxygen atoms in an

octahedral environment with In–O bond ($2 \times \text{In}(1)\text{--O}(1)$ 2.174 Å, $2 \times \text{In}(1)\text{--O}(2)$ 2.107 Å, $2 \times \text{In}(1)\text{--O}(3)$ 2.188 Å). All six oxygen atoms linked to In^{3+} cations are further connected to I^{5+} cations, which are bonded to three oxygen atoms in pyramidal geometry. I–O distances within the iodate anions can be roughly correlated with their binding mode. The I–O distances observed where one of the oxygen atoms is involved in bonding to the indium atom are slightly longer than the terminal ones. In the iodate anions containing I(1), the terminal I–O distances are 1.802 and 1.799 Å, whereas the bridging oxo atom has a bond distance of 1.846 Å. The same pattern is observed for I(2) and I(3) with terminal distances of 1.797 and 1.802 Å and bridging distance of 1.839 Å for I(2), and terminal distances of 1.808 and 1.800 Å and bridging distance of 1.856 Å for I(3), respectively.

The most important feature of compound **1** is that it crystallizes in the polar space group $Fdd2$. Like the reported polarity metal iodates, such as $\text{Na}_2[\text{UO}_2(\text{IO}_3)_4(\text{H}_2\text{O})]$,²⁵ $\text{A}[(\text{VO}_2)(\text{IO}_3)_3\text{O}_2]$ ($A = \text{NH}_4, \text{Rb}, \text{Cs}$),¹¹ and $\text{NpO}_2(\text{IO}_3)$,²⁶ the iodate anions are all aligned so that the lone-pair of electrons is directed along a single crystallographic axis. Similar alignment is also observed in the structure of compound **1**. The crystallographically unique I(1) and I(3) iodate units in the $[\text{In}(\text{IO}_3)_6]^{3-}$ anion are aligned along the b -axis, as is shown in Figure 1b. Owing to translational symmetry, all of the $[\text{In}(\text{IO}_3)_6]^{3-}$ anions are therefore aligned in the same manner in the overall structure with the slight difference that some anions are aligned along the positive b -axis and some are aligned along the negative b -axis due to the vertical symmetry, which is shown in Figure 1d.

The environments around the K^+ cations must also contribute to the acentricity of the overall structure of compound **1**. There are two crystallographically unique K^+ cations in this structure. K(1) and K(2) each forms eight contacts ranging from 2.65 to 3.19 Å with surrounding oxygen atoms to yield an approximately distorted dodecahedral environment, as is shown in Figure 1c. The environments around the K^+ cations are also consistent with a polar structure. A packing diagram for compound **1** is shown in Figure 1e.

An ORTEP drawing of the asymmetric unit of compound **2** is similar to that of compound **1** with the difference that compound **2** crystallizes in a triclinic system with space group $P\bar{1}$. The indium site in an asymmetric unit exhibits an octahedral geometry with $[\text{InO}_6]$. Iodine sites show $[\text{IO}_3]$ pyramidal geometry. Structure determination indicates that compound **2** is also made up of zero-dimensional units consisting of $[\text{In}(\text{IO}_3)_6]^{3-}$ anions and separated by K^+ cations (see Figure 2a). Each In^{3+} cation is bonded to six oxygen atoms in an distorted octahedral environment with In–O bond ($2 \times \text{In}(1)\text{--O}(1)$ 2.215 Å, $2 \times \text{In}(1)\text{--O}(2)$ 2.152 Å, $2 \times \text{In}(1)\text{--O}(3)$ 2.127 Å). All six oxygen atoms linked to In^{3+} cation are further connected to I^{5+} cations, which are bonded to three oxygen atoms in pyramidal environment. I–O distances within the iodate anions can be roughly correlated with their binding mode ranging from 1.794 to 1.852 Å. Iodate has two terminal oxo groups and shares one oxygen atom with $[\text{InO}_6]$ octahedra. It is observed that the I–O bond lengths for oxygen atoms bound to $[\text{InO}_6]$ octahedra are longer than those of the terminal oxo groups. K(1) and K(2) each forms eight contacts ranging from 2.66 to 3.13 Å with surrounding oxygen atoms to yield an approximately distorted dodecahedral environment, as is shown in Figure 1b.

It is noteworthy that the structural building unit of compound **2** is mostly the same as that of compound **1**, but compound **2** crystallizes in the centrosymmetric space group $P\bar{1}$. This precludes any possibility of net alignment of either the iodate anions or the distortion of the K^+ cations. So compound **2** is nonpolar. A packing diagram for compound **2** is shown in Figure 2b.

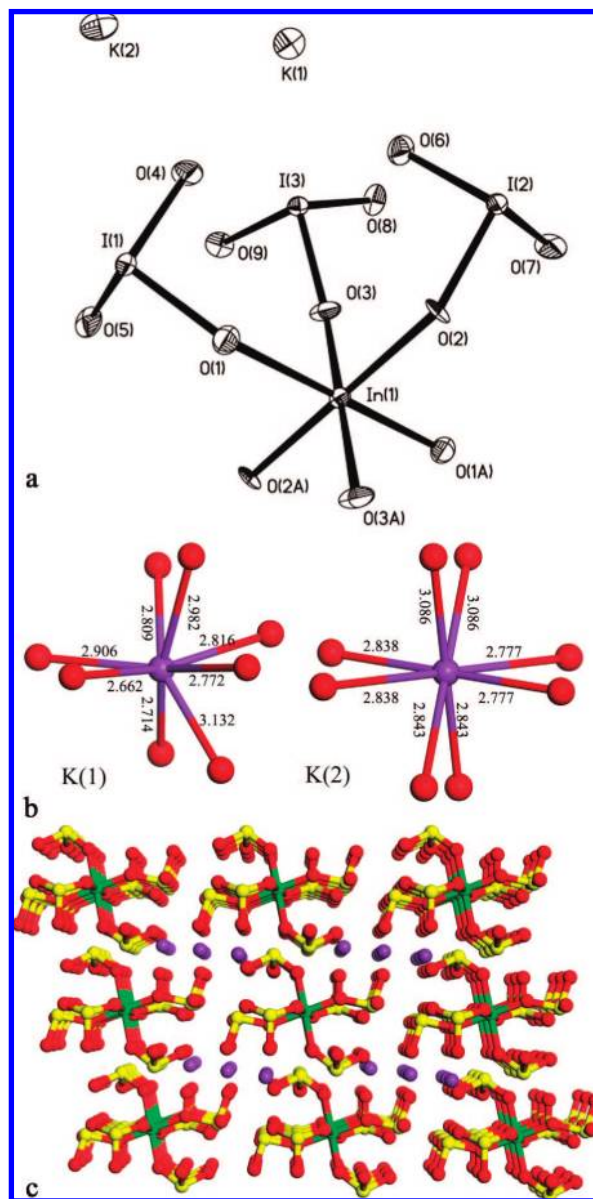


Figure 2. (a) Asymmetric unit of compound **2**. (b) The environments around the K^+ cations. (c) A packing diagram for compound **2** projected along the a -axis. The following colors correspond to these atoms: indium, green; iodine, yellow; oxygen, red; potassium, purple.

As shown in Figure 3a, compound **3** crystallizes in a triclinic space group $P\bar{1}$ with unit cell content of 12 non-hydrogen atoms. There are two indium atoms, two iodine atoms, seven oxygen atoms, and one water molecule in an asymmetric unit. Of the two indium sites, In(1) and In(2) both exhibit octahedral geometry with $[\text{InO}_6]$, which are defined by four oxygen donors from iodates ($2 \times \text{In}(1)\text{--O}(2)$ 2.140 Å, $2 \times \text{In}(1)\text{--O}(3)$ 2.201 Å and $2 \times \text{In}(2)\text{--O}(4)$ 2.159 Å, $2 \times \text{In}(2)\text{--O}(5)$ 2.146 Å) and two bridged oxygen atoms from OH groups ($2 \times \text{In}(1)\text{--O}(1)$ 2.101 Å and $2 \times \text{In}(2)\text{--O}(1)$ 2.122 Å). The axial oxygen atom corners are shared by neighboring octahedra to form $\cdots\text{OH}\text{--}\text{In}\text{--}\text{OH}\text{--}\text{In}\text{--}\cdots$ chains with In–OH–In angles of 180° . Such coordination environment is familiar in a metal-oxide organic framework.^{27,28} Iodine sites all take the form of $[\text{IO}_3]$ pyramidal geometry, which have one terminal oxo group and share two oxygen atoms with $[\text{InO}_6]$ octahedra. The bond distances range from 1.776 to 1.834 Å and I–O–I angles range from 97.14 to 102.31° . It is also observed that the I–O bond lengths for

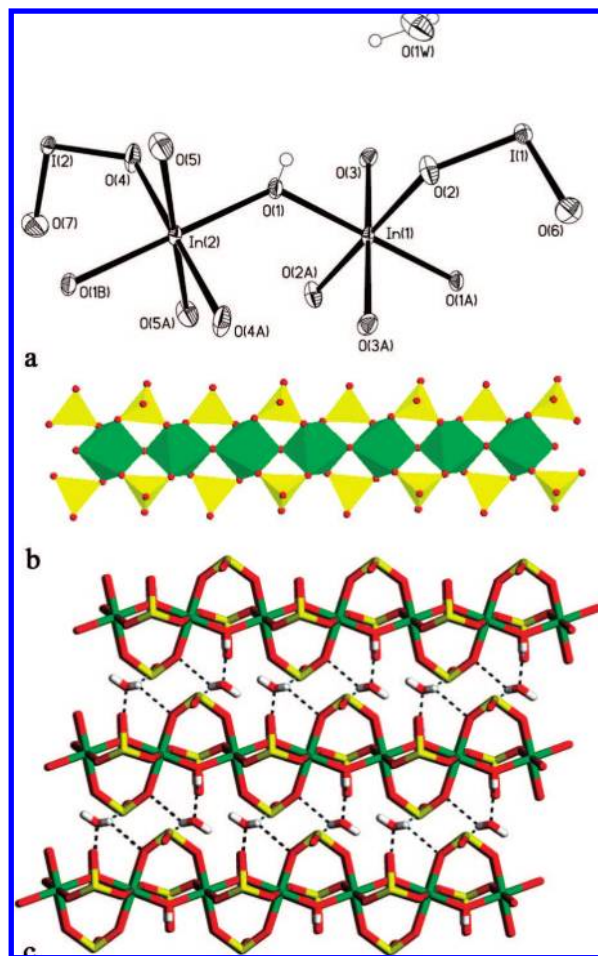


Figure 3. (a) Asymmetric unit of compound 3. (b) View of the one-dimensional ribbon in compound 3. (c) The packing of one-dimensional chains projected along the *a*-axis. The following colors correspond to these atoms: indium, green; iodine, yellow; oxygen, red.

oxygen atoms bound to [InO₆] octahedron are longer than those of the terminal oxo groups.

Structure determination indicates that compound 3 possesses a one-dimensional ribbon structure. As can be seen from Figure 3b, [InO₆] octahedra share corners with each other to form a chain, of which two sides are bridged by iodates to form a one-dimensional ribbon structure. Further, the adjacent ribbons are connected by water molecules via hydrogen bonds with the OH...O distances ranging from 2.00 to 2.63 Å, which perform a certain function on stabilizing the structure, leading to a pseudo two-dimensional layered structure (see Figure 3c).

It is known that In(IO₃)₃ possesses Te₄O₉-type structure.²⁹ The indium ion resides on the site of 3-fold symmetry in the structure and its environment consists of six iodate groups bound in a monodentate fashion. The iodate anions are formally bidentate, coordinating to two indium cations. As seen in Figure 4, two iodate anions bridge between two equivalent indium cations, so each indium cation is only bridged by iodate to three neighboring indium positions, leading to two-dimensional layers.

Compounds 1 and 2 are both made up of zero-dimensional units consisting of [In(IO₃)₆]³⁻ anions separated by K⁺ cations. The obvious difference in the structure of 1–2 is the orientation of the C_{3v} iodate anions, or more specifically, the alignment of the stereochemically active lone pair of electrons on the iodine atoms. Compound 1 crystallizes in the polar space group *Fdd*2, which is in the crystal class *mm*2. Therefore, the polarity in the

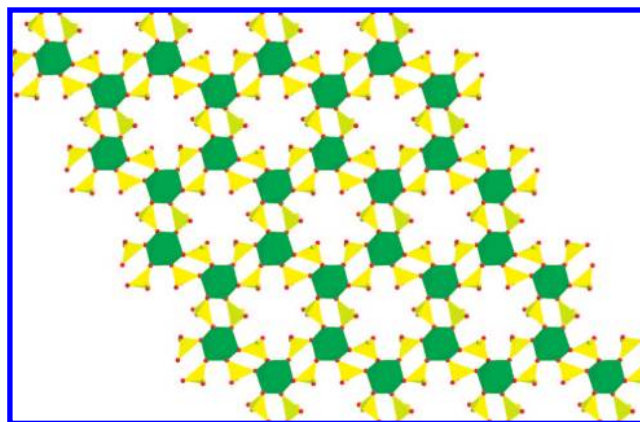


Figure 4. View of the two-dimensional layer in compound 4. The following colors correspond to these atoms: indium, green; iodine, yellow; oxygen, red.

structures should be along the *b*-axis. Examinations of the crystal structure show that the iodate groups do indeed display alignment along the polar *b*-axis. The crystallographically unique I(1) and I(3) iodate units in the [In(IO₃)₆]³⁻ anion are aligned along the *b*-axis, as is shown in Figure 1b. Owing to translational symmetry, all of the [In(IO₃)₆]³⁻ anions are therefore aligned in the same manner in the overall structure, as illustrated in Figure 1d. Compound 2 possesses the same structural building unit [In(IO₃)₆]³⁻ anion, but crystallizes in the centrosymmetric space group *P* $\bar{1}$, whose origin is at $\bar{1}$. This precludes any possibility of net alignment of either the iodate anions or the distortion of the K⁺ cations. So compound 2 is nonpolar. As to compounds 2–4, building blocks [InO₆] octahedra and [IO₃] pyramids exhibit a distinct arrangement, leading to the phenomenon that the framework of these three compounds display zero-dimensional, one-dimensional, to two-dimensional structure, respectively. The environment of indium atom in compounds 2 and 4 consists of six iodate groups bound in a monodentate fashion. In compound 2, iodates do not connect to any other indium atoms, while in compound 4 each of two iodates bridges another equivalent indium atom. Therefore, compound 2 displays zero-dimensional units, whereas compound 4 presents a two-dimensional layered structure. In compound 3, the environment of the indium atom consists of four iodate groups bound in a monodentate fashion in the basal plane and two apical oxygen ions connected with other indium cations. The iodate groups just bridge the adjacent [InO₆] octahedra on the same chain. So compound 3 exhibits a one-dimensional ribbon structure. Compounds 2–4 have been prepared by a hydrothermal method with the same reagents. The reason why they exhibit such different structural dimensionality lies in the pH-mediated structural transformation. Compounds 2, 3, and 4 are obtained with pH values of 0.5, 1.5, and 3, respectively. With the decrease in pH value, the dimensionality of the framework decreases from 2-D, 1-D, to 0-D. This is mainly because with the increase in the concentration of [H]⁺, the activity of terminal oxygen atoms decreases. They are much more easily protonated than coordinated so that the charge of the host net changes from neutral to negative, which may instruct our experiment to introduce some other cations, even organamines, to the framework.

Characterization. In the absence of an external physical property measurement that confirms acentricity, it can be haphazard to refine a structure in a noncentrosymmetric setting. While we were unable to solve compound 1 in a centrosymmetric space group, it is still possible that its space group is

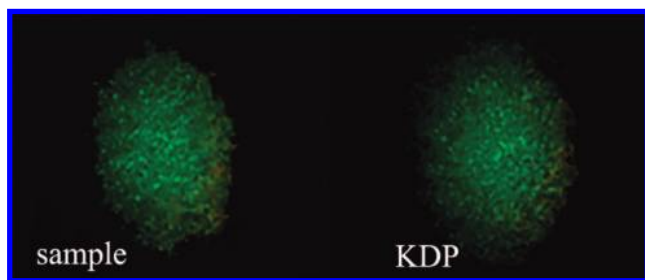


Figure 5. The NLO signals of compound **1** (a) and KDP (b).

incorrect. SHG measurement allows for confirmation of our space group assignment and provides an evaluation of the potential usefulness of these compounds in device applications. The NLO efficiency of compound **1** was evaluated by the Kurtz and Perry powder test.³⁰ The fundamental beam was emitted by a Q-switched, mode-locked Nd³⁺:YAG laser operating at 1.06 μm and generating pulses of 25 ps duration and of 10 mJ energy. The NLO efficiency was estimated by visual comparison with the signals of compound **1** and KDP sample having the same average granulometry. As shown in Figure 5, the intensity of SHG light generated by compound **1** was as good as that generated by KDP. The large response of compound **1** is not only due to the polarity of the space group and the alignment of the lone pairs on the iodate anions but also due to the large degree of polarization of the environments of K⁺ cations.

The transparency of potential NLO materials in regions of interest is of critical concern since minimal absorbance of the source and SHG light reduces laser damage to the crystal and improves efficiency. Furthermore, the electronic spectra of the compound provide fundamental information on the nature of conduction in the extended structure. A UV–vis diffuse reflectance spectrum was collected from crystalline sample that was ground into fine powders. The spectrum of **1** from 800 to 200 nm (see Supporting Information) shows that **1** is essentially transparent to approximately 2.6 eV. Plots of absorbance squared versus energy and the square root of absorbance versus energy both show nearly linear dependence. Therefore, it is unclear whether this compound has direct or indirect band gap. Extrapolation of absorbance squared versus energy to absorbance = 0 provides an approximate band gap of 2.9 eV.

Thermal analyses for compounds **1** and **3** were performed in air from 40 to 800 °C (see Supporting Information). TG curve for **1** indicates that it is stable up to ca. 300 °C; from 300 to 610 °C, three steps of weight loss should correspond to the slow condensation of the [IO₃] group into I₂O₅ and the volatilization of iodine groups (weight loss: exptl 59.46%, calcd 59.9%). The initial weight loss for compound **3** in the temperature range 180–210 °C is due to the removal of water molecules (weight loss: exptl 7.2%, calcd 8.15%). Over the range 400–580 °C, the weight loss should correspond to the condensation of the [IO₃] group into I₂O₅ and the sublimation of iodine (weight loss: exptl 50.83%, calcd 51.5%).

Conclusion

In this study, a series of indium iodates $\alpha\text{-K}_3\text{In}(\text{IO}_3)_6$ (**1**), $\beta\text{-K}_3\text{In}(\text{IO}_3)_6$ (**2**), $\text{In}(\text{OH})(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ (**3**), and $\text{In}(\text{IO}_3)_3$ (**4**) have been prepared by a hydrothermal method. Compounds **1** and **2** both consist of $[\text{In}(\text{IO}_3)_6]^{3-}$ anions separated by K⁺ cations, but exhibit polar and nonpolar respectively due to the different alignment of the stereochemically active lone pair of electrons on the iodine atoms, which demonstrated well the concepts

established by Kurtz and co-workers. Subtle changes in reaction stoichiometry allow for the isolation of compounds **2**, **3**, and **4** displaying zero-dimensional, one-dimensional, to two-dimensional structures respectively. The above researches are affluent in the iiiA elements' iodates family and prove that iodate is a flexible ligand for preparing compounds with unprecedented structures. We are currently carrying out the substitution of potassium cations for some other alkali metals in similar hydrothermal systems and intend to synthesize some new NCS materials.

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Supporting Information Available: X-ray crystallographic files (CIF) and other data for **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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