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Synthesis and structure of $In(IO_3)_3$ and vibrational spectroscopy of $M(IO_3)_3$ ($M =$ Al, Ga, In)

Nhan Ngo[a], Katrina Kalachnikova[a], Zerihun Assefa[b,c], Richard G. Haire[c], Richard E. Sykora[a,c,*]

[a]Department of Chemistry, University of South Alabama, Mobile, AL 36688, USA
[b]Department of Chemistry, North Carolina A and T State University, Greensboro, NC 27411, USA
[c]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

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Abstract

The reaction of Al, Ga, or In metals and H_5IO_6 in aqueous media at 180 °C leads to the formation of $Al(IO_3)_3$, $Ga(IO_3)_3$, or $In(IO_3)_3$, respectively. Single-crystal X-ray diffraction experiments have shown $In(IO_3)_3$ contains the Te_4O_9-type structure, while both $Al(IO_3)_3$ and $Ga(IO_3)_3$ are known to exhibit the polar $Fe(IO_3)_3$-type structure. Crystallographic data for $In(IO_3)_3$, trigonal, space group $R\bar{3}$, $a = 9.7482(4)$ Å, $c = 14.1374(6)$ Å, $V = 1163.45(8)$ $Z = 6$, $R(F) = 1.38\%$ for 41 parameters with 644 reflections with $I > 2\sigma(I)$. All three iodate structures contain group 13 metal cations in a distorted octahedral coordination environment. $M(IO_3)_3$ ($M =$ Al, Ga) contain a three-dimensional network formed by the bridging of Al^{3+} or Ga^{3+} cations by iodate anions. With $In(IO_3)_3$, iodate anions bridge In^{3+} cations in two-dimensional layers. Both materials contain distorted octahedral holes in their structures formed by terminal oxygen atoms from the iodate anions. The Raman spectra have been collected for these metal iodates; $In(IO_3)_3$ was found to display a distinctively different vibrational profile than $Al(IO_3)_3$ or $Ga(IO_3)_3$. Hence, the Raman profile can be used as a rapid diagnostic tool to discern between the different structural motifs.

Keywords: Indium iodate; Aluminum iodate; Gallium iodate; Hydrothermal; Single crystal X-ray diffraction; Raman spectroscopy; Layered compound; Structure determination

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1. Introduction

Metal iodates have received significant attention because of their nonlinear-optical properties [1–11], and have been shown to exhibit piezoelectric, [4] pyroelectric [4–8], and second-harmonic generation properties [9–11]. Numerous reports have also focused on the aluminum iodate systems [12–25]. The chiral $Al(IO_3)_3 \cdot 2HIO_3 \cdot 6H_2O$ has been structurally characterized by both X-ray diffraction [12,13] and spectroscopic measurements [14,15] and its piezoelectric, elastic, and optical properties [16,17] have also been investigated. This material was found to exhibit a longitudinal piezoelectric effect ten times larger than α-quartz [17]. Upon heating to 340 °C, $Al(IO_3)_3 \cdot 2HIO_3 \cdot 6H_2O$ decomposes to the anhydrous $Al(IO_3)_3$ [13], which was just recently characterized structurally by single-crystal X-ray diffraction [18] and determined to be acentric. A mixed anion aluminum iodate, $Al(IO_3)_2(NO_3) \cdot 6H_2O$ has also been reported [15,19,20] and its structural characterization revealed the presence of the hydrated cations $Al[(H_2O)_6]^{3+}$ [19], which are also observed in $Al(IO_3)_3 \cdot 2HIO_3 \cdot 6H_2O$ [12,13] and $Al(IO_3)_3 \cdot 8H_2O$ [21,22]. Of these materials, only the anhydrous $Al(IO_3)_3$ contains iodate anions coordinated directly to the aluminum cations [18].

Very recently, the structure of $Ga(IO_3)_3$ was reported to be isostructural with $Al(IO_3)_3$ [26], but structural data for the iodate of indium has not been reported previously. We have recently begun to prepare single crystals of these

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*Corresponding author. Department of Chemistry, University of South Alabama, Room 223, The Chemistry Building, 307 University Boulevard, Mobile, AL 36688-0002, USA. Fax: +1 251 460 7359.

E-mail address: rsykora@jaguar1.usouthal.edu (R.E. Sykora).

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elements' iodates, and investigated their structures using both X-ray diffraction and Raman vibrational techniques. Herein, we report the hydrothermal syntheses and Raman vibrational profiles of the group 13 iodates, $M(IO_3)_3$ ($M = $ Al, Ga, In). In addition, the structure of $In(IO_3)_3$ was determined using single crystal X-ray diffraction and it is reported here.

2. Experimental

2.1. Materials and methods

Materials for the syntheses were Al (foil, 99+%, Alfa-Aesar), Ga (ingot, 99.99%, Alfa-Aesar), In (ingot, 99.99%, Alfa-Aesar), and H_5IO_6 (98%, Alfa-Aesar). All materials were used as received. The reactions given below produced the highest yields and best quality of the respective compounds.

2.2. Synthesis of $M(IO_3)_3$ ($M = $ Al, Ga, In)

Synthesis of $In(IO_3)_3$ involved combining In (4.88 mg, 0.0425 mmol) and H_5IO_6 (32.11 mg, 0.1409 mmol) in a quartz reaction vessel. After the addition of 0.3 mL of water, the reaction vessel was sealed and heated in a box furnace to 180 °C, where the reaction proceeded under autogenously generated pressure. After 70 h, the furnace was cooled at 10 °C/h to 100 °C, turned off, and allowed to cool to 20 °C. The reaction produced colorless, single crystals of $In(IO_3)_3$ as the sole crystalline product. The syntheses of $Al(IO_3)_3$ and $Ga(IO_3)_3$ were carried out in a similar manner, except that Al (2.16 mg, 0.0801 mmol) and H_5IO_6 (51.45 mg, 0.2257 mmol), or Ga (3.07 mg, 0.0440 mmol) and H_5IO_6 (30.32 mg, 0.1330 mmol) were used for the syntheses. The products of the reactions were colorless, single crystals of $Al(IO_3)_3$ and $Ga(IO_3)_3$. The reactions listed above produced the metal iodates with nearly quantitative yields.

2.3. Crystallographic studies

Crystals of $Al(IO_3)_3$, $Ga(IO_3)_3$, and $In(IO_3)_3$ (dimensions of $0.240 \times 0.028 \times 0.028$ mm, $0.027 \times 0.036 \times 0.032$ mm, and $0.160 \times 0.160 \times 0.058$ mm, respectively) were selected and mounted on quartz fibers with epoxy and aligned on a Bruker SMART APEX CCD X-ray diffractometer with a digital camera. Unit cell determinations on $Al(IO_3)_3$ and $Ga(IO_3)_3$ confirmed the reported structures for these materials [18,26]. For $In(IO_3)_3$, intensity measurements were performed using graphite monochromated, Mo $K\alpha$ radiation from a sealed tube using a monocapillary collimator. The intensities and positions of reflections of a sphere were collected by a combination of 3 sets of exposure frames. Each set had a different ϕ angle for the crystal, and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time per frame of 20 s for the crystal of $In(IO_3)_3$.

Determination of the integrated intensities and the global cell refinement were performed with the Bruker SAINT (v 6.02) software package using a narrow-frame, integration algorithm. A face-indexed absorption correction was applied with the program XPREP [27], followed by a semi-empirical absorption correction using SADABS [28]. SADABS is routinely used to make incident beam and decay corrections on area-detector X-ray diffraction data [29]. The program suite SHELXTL (v 5.1) was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL) [27]. The final refinement for $In(IO_3)_3$ included anisotropic displacement parameters for all atoms and a secondary extinction parameter. Selected crystallographic details are listed in Table 1 and the final positional parameters are located in Table 2. Further details of the crystal structure investigation for $In(IO_3)_3$ may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-416802.

2.4. Raman spectroscopy

Raman spectroscopy was performed using an argon-ion laser (Coherent, model 306) and a double-meter spectrometer (Jobin-Yvon Ramanor model HG.2S). The resolution of the monochromator at 514.5 nm is 0.5 cm^{-1}. The monochromator is interfaced with a personal computer; scanning and data collections are controlled by LabSpec (version 3.04) software. Signal detection was acquired with a water-cooled photo-multiplier tube (Hamamatsu R636).

Table 1
Crystallographic data for $In(IO_3)_3$

Compound	$In(IO_3)_3$
Formula mass (amu)	639.52
Color and habit	Colorless, hexagonal plate
Crystal system	Trigonal
Space group	$R\bar{3}$ (No. 148)
a (Å)	9.7482(4)
c (Å)	14.1374(6)
V (Å^3)	1163.45(8)
Z	6
T (K)	173
λ (Å)	0.71073
$2\theta_{max}$ (°)	56.56
ρ_{calcd} (g cm^{-3})	5.477
μ(Mo $K\alpha$) (cm^{-1})	150.13
Reflections collected	3842
Independent reflections	644 [R(int) = 0.0223]
Data/restraints/parameters	644/0/41
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$[a]	0.0138
$Rw(F_o^2)$[b]	0.0341

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = \left[\sum\left[w(F_o^2 - F_c^2)^2\right] \Big/ \sum wF_o^4\right]^{1/2}$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $In(IO_3)_3$

Atom	Site	x	y	z	U_{eq} (Å^2)[a]
In(1)	6c	0	0	0.1765 (1)	0.007 (1)
I(1)	18f	−0.0041 (1)	0.2951 (1)	0.4189 (1)	0.008 (1)
O(1)	18f	−0.1345 (3)	0.3764 (3)	0.4247 (2)	0.012 (1)
O(2)	18f	0.1768 (3)	0.4818 (3)	0.3946 (2)	0.010 (1)
O(3)	18f	0.0273 (3)	0.2749 (3)	0.5431 (2)	0.016 (1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3. Results and discussion

3.1. Syntheses

The reaction of Al, Ga, or In metal with periodic acid in aqueous media at 180 °C leads to the formation of $Al(IO_3)_3$, $Ga(IO_3)_3$, or $In(IO_3)_3$ single crystals. These reactions utilize the strong oxidizing ability of periodate to oxidize these main group metals with the simultaneous reduction of periodate to iodate. It is likely that some water is also oxidized, as an excess of oxidizing equivalents are supplied by the reduction of periodate when the metal: H_5IO_6 stoichiometric ratio is 1:3. The reduction of periodate under hydrothermal conditions has been employed successfully to produce a number of metal iodates [30,31]. The previous syntheses of $Al(IO_3)_3$ and $Ga(IO_3)_3$ were also performed by hydrothermal reactions; the reaction of $Al(NO_3)_3 \cdot 9H_2O$ with H_5IO_6 [18] and the reaction of Ga_2O_3 and H_5IO_6 in an aqueous HNO_3 solution [26] produce $Al(IO_3)_3$ and $Ga(IO_3)_3$.

3.2. Structure of $In(IO_3)_3$

$In(IO_3)_3$ crystallizes in space group $R\bar{3}$ with the Te_4O_9-type structure [32]. This structure type has also been previously reported for $Sc(IO_3)_3$ [30]. The indium ion resides on the site of three-fold symmetry in the structure, (0, 0, z), and its environment consists of six iodate groups bound in a monodentate fashion as shown in Fig. 1. The coordination environment for In is only slightly distorted from an ideal octahedron and the observed In–O bond lengths are 2.138(2) and 2.157(2) Å. These distances are only slightly longer that the Sc–O distances observed in $Sc(IO_3)_3$, 2.084(3) and 2.110(3) Å [30], consistent with the slightly smaller ionic radius of six-coordinate Sc^{3+} (0.745 Å) relative to six-coordinate In^{3+} (0.800 Å) [33]. There is one crystallographically unique iodate group found in the structure. It contains three I–O bonds with distances of 1.805(2), 1.809(2), and 1.825(2) Å, in addition to a lone-pair of electrons, and therefore the iodate anion's site symmetry is C_1. In addition to these three short I–O bond distances, a fourth I–O interaction of 2.557(2) Å is found resulting in an IO_{3+1} group. The presence of the IO_{3+1} moiety has been observed in other iodate structures [9]; it is also present in $Sc(IO_3)_3$, where the long I–O interaction was reported to have a distance of 2.56 Å [30]. In the structure of Te_4O_9, TeO_4 groups containing four similar Te–O bond lengths (from 1.9 to 2.1 Å) are present [32]. In $In(IO_3)_3$, as also in $Sc(IO_3)_3$, the main deviation from the Te_4O_9 structure is the bond lengthening of one I–O bond resulting in the IO_{3+1} groups. A more comprehensive listing of bond lengths and angles for $In(IO_3)_3$ can be found in Table 3. The bond valence sums calculated for the In and I cations in $In(IO_3)_3$ are 3.09 and 4.97 [34], respectively, consistent with the assignment of In(III) and I(V).

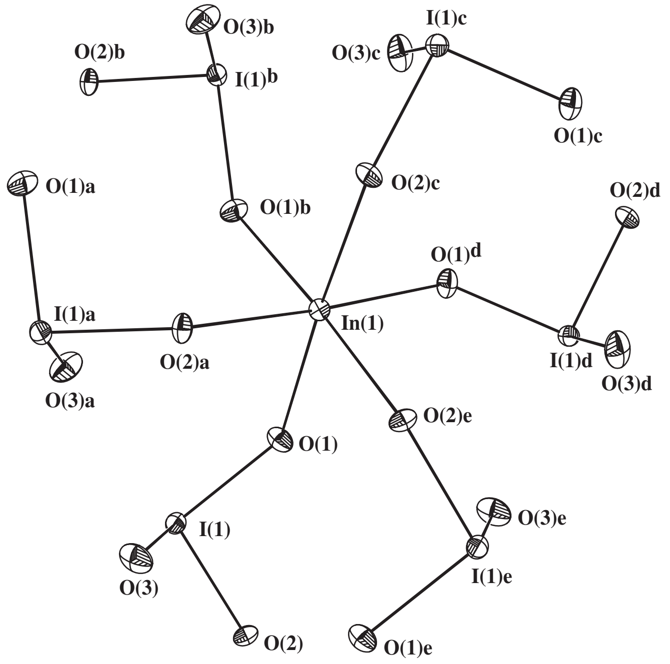

Fig. 1. A representation of the building unit in $In(IO_3)_3$. (50% probability ellipsoids are shown.) Operations used to generate symmetry equivalent atoms: (a) $x-y-\frac{1}{3}, x-\frac{2}{3}, \frac{1}{3}-z$; (b) $y-x, -x, z$; (c) $y-\frac{1}{3}, \frac{1}{3}-x+y, \frac{1}{3}-z$; (d) $-y, x-y, z$ and (e) $\frac{2}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z$.

The iodate anions are formally bidentate, coordinating in a monodentate fashion to two indium cations. As seen in Fig. 2, two iodate anions bridge between two equivalent indium cations; therefore each indium cation is only bridged by iodate to three neighboring indium positions. This leads to the two-dimensional layers (Fig. 3), found in the crystallographic ab plane in $In(IO_3)_3$, as opposed to the three-dimensional network structure found for $Al(IO_3)_3$ and $Ga(IO_3)_3$. The layers contain distorted octahedral holes formed by the terminal oxygen atoms on the iodate anions as also previously observed for $Sc(IO_3)_3$ [30].

In the anhydrous iodates of aluminum and gallium [18,26], the metal cations are coordinated in a monodentate fashion by six symmetry-equivalent iodate anions, giving rise to distorted, octahedral MO_6 polyhedra. This metal coordination is similar to that found in $In(IO_3)_3$, although the reported Al–O (1.894 and 1.922 Å) [18] and Ga–O (1.960 and 1.980 Å) [26] bond distances are shorter than the observed In–O bond distances found in $In(IO_3)_3$, consistent with the trend for the ionic radii of the trivalent cations of these elements [33]. As in $In(IO_3)_3$, the iodate anions in $M(IO_3)_3$ ($M = $ Al, Ga) are formally bidentate and bridge two gallium atoms in the structure; each iodate also contains one terminal oxygen. A major difference is that in the structures of $Al(IO_3)_3$ and $Ga(IO_3)_3$ each metal position is bridged by iodate anions to six additional metal sites. This results in a three-dimensional structure as shown in Fig. 3b. The major difference between the $In(IO_3)_3$ and the $M(IO_3)_3$ ($M = $ Al, Ga) structures is illustrated by Fig. 3; Fig. 3a illustrates the two-dimensional layers of $In(IO_3)_3$, while Fig. 3b shows a view of the three-dimensional structure of $Al(IO_3)_3$ and $Ga(IO_3)_3$ as viewed along the *a*-axis.

3.3. Raman spectroscopy

Raman spectra have been reported previously for a number of crystalline iodates [35–44]. Although the isolated IO_3^- ion has a C_{3v} ($3m$) point group, the site symmetry in crystalline solids is usually reduced to C_{2v}, C_s, or C_1, and the Raman profiles are affected as a consequence. Cumulated data indicate that iodate salts with low IO_3^- site symmetry ($< C_{3v}$) display a strong symmetric I–O stretching mode (ν_1) and two asymmetric modes ν_{3a} and ν_{3b} [45].

Table 3
Bond distances (Å) and angles (deg) for $In(IO_3)_3$

Bond distances (Å)			
In(1)–O(1) × 3	2.138 (2)	I(1)–O(1)	1.805 (2)
In(1)–O(2) × 3	2.157 (2)	I(1)–O(2)	1.825 (2)
		I(1)–O(3)	1.809 (2)
Angles (deg)			
O(1)–In(1)–O(1)b	91.40 (9)	O(1)–I(1)–O(2)	96.42 (11)
O(1)–In(1)–O(2)a	93.85 (9)	O(1)–I(1)–O(3)	101.44 (11)
O(1)–In(1)–O(2)c	89.74 (9)	O(2)–I(1)–O(3)	99.18 (11)
O(2)a–In(1)–O(2)c	84.92 (9)		

(a) $x-y-\frac{1}{3}$, $x-\frac{2}{3}$, $\frac{1}{3}-z$; (b) $y-x$, $-x$, z; (c) $\frac{2}{3}-x$, $\frac{1}{3}-y$, $\frac{1}{3}-z$.

The Raman profile of these three group 13 iodates, $Al(IO_3)_3$, $Ga(IO_3)_3$, and $In(IO_3)_3$, are compared in Figs. 4 and 5. Fig. 4 covers the IO_3^- stretching region, while Fig. 5 covers the bending and lattice mode vibrational regions. Owing to their structural similarities, the Al- and Ga-iodates show almost identical spectral profiles, as seen in Figs. 4 a and b. Both structures are hexagonal, crystallizing in the chiral space group of $P6_3$. In contrast, $In(IO_3)_3$ crystallizes in a trigonal system with the space group of $R\bar{3}$. The change in structural features results in drastically different Raman profiles for the two classes of compounds, which is particularly evident in the IO_3^- stretching region shown in Fig. 4. Detailed group theoretical analyses of the two structural systems were conducted to pursue their differences.

In $Al(IO_3)_3$ and $Ga(IO_3)_3$, which crystallize in the C_6^6 ($P6_3$) space group [18,26], the metal atoms in the unit cell occupy 2*b* Wyckoff sites. Hence, both the Al and Ga atoms have a C_3 site symmetry with an imposed three-fold symmetry. All of the atoms in the iodate anions reside on general positions, and occupy 6*c* Wyckoff sites. Hence, when compared with the pyramidal C_{3v} ($3\,m$) symmetry for an isolated IO_3^- ion, the iodate ions of these compounds have a lower C_1 site symmetry.

The 26 atoms in the unit cell ($Z = 2$) consist of a total of 78 fundamental modes represented by $13A+13B+13E_1+13E_2$. Three of these modes ($A+E_1$) are acoustic, and are involved in propagation of sound waves in the

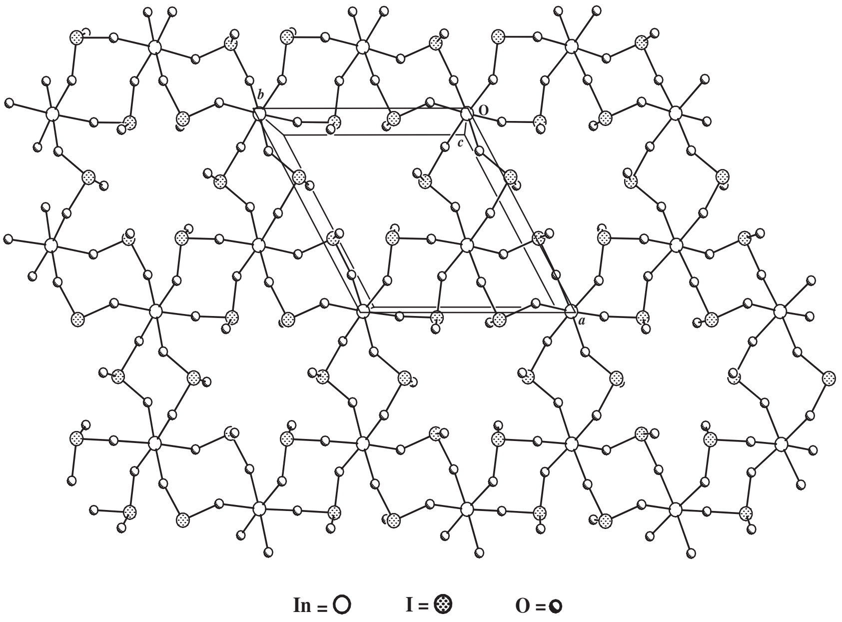

Fig. 2. A ball and stick plot of a two-dimensional layer found in the *ab* plane of $In(IO_3)_3$.

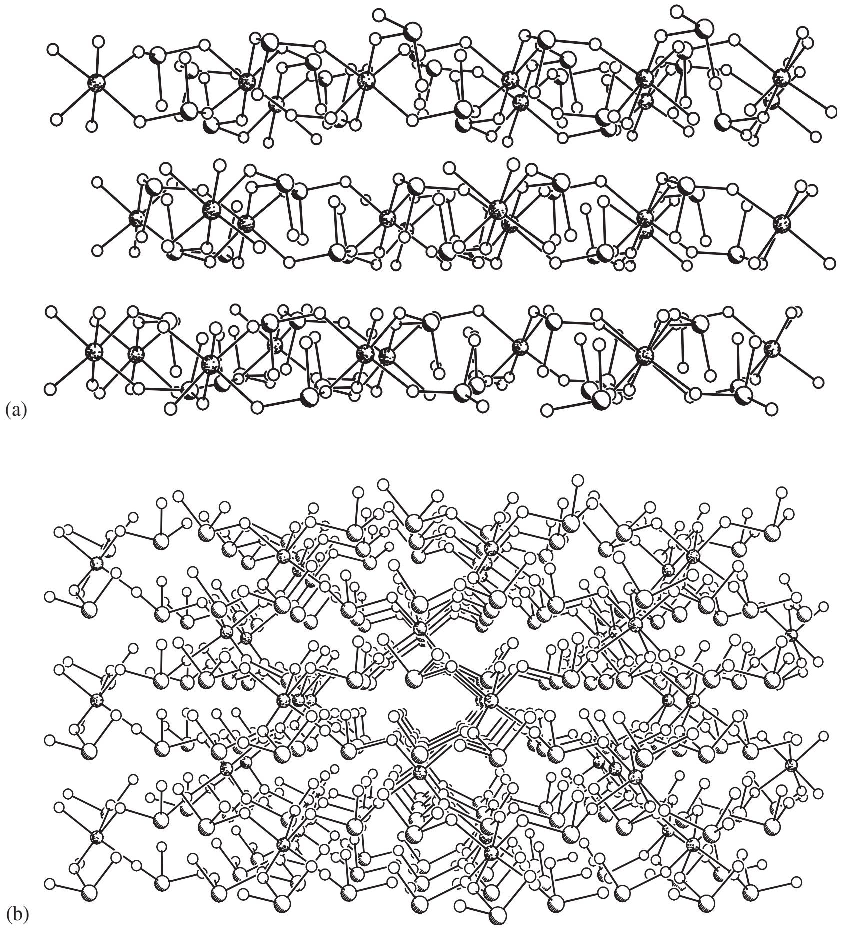

Fig. 3. (a) A ball and stick plot of the two-dimensional layers of $In(IO_3)_3$ as viewed parallel to the crystallographic *ab* plane. (b) A ball and stick plot of the three-dimensional structure of $Ga(IO_3)_3$ as viewed down the crystallographic *a*-axis.

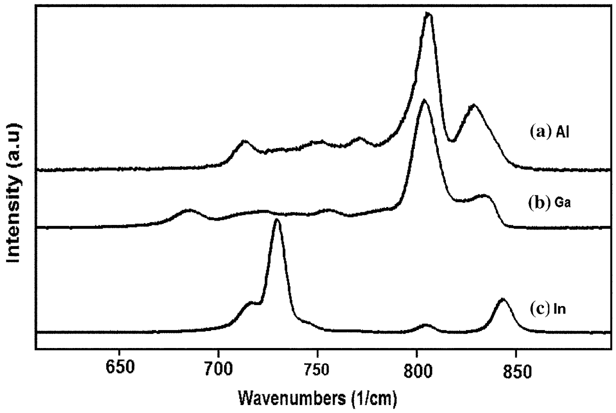

Fig. 4. Raman spectrum of: (a) $Al(IO_3)_3$; (b) $Ga(IO_3)_3$ and (c) $In(IO_3)_3$ crystals covering the IO_3^- stretching region. The spectra were collected at room temperature.

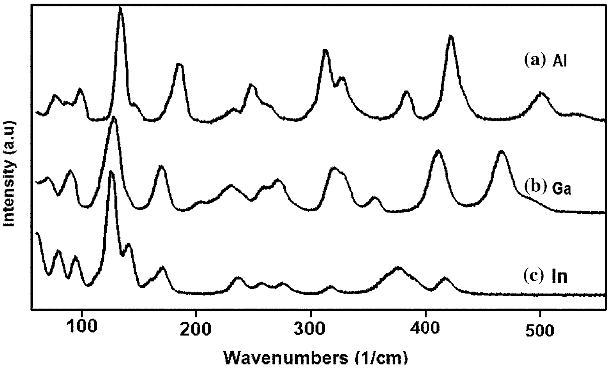

Fig. 5. Raman spectrum of: (a) $Al(IO_3)_3$; (b) $Ga(IO_3)_3$ and (c) $In(IO_3)_3$ crystals covering the low-frequency bending and crystal lattice vibrational regions. The spectra were collected at room temperature.

crystal. The remaining 75 modes contribute to the normal modes of allowable vibrations. Site group analysis [46] conducted for the crystals indicates that the iodate anions in the unit cell have internal vibrational contributions of

$$\Gamma_{\text{internal iodate modes}} = 6A + 6B + 6E_1 + 6E_2.$$

Among these modes only the A, E_1, and E_2 modes are Raman active. Since the E_1 and E_2 modes are degenerate, 18 Raman bands are expected for this system.

In the stretching mode region, covering 600–900 cm^{-1}, the most intense band for the $Al(IO_3)_3$ compound is observed at 806 cm^{-1}. In addition, a relatively strong band is observed at $829\,\mathrm{cm}^{-1}$ with an undefined broad shoulder at $837\,\mathrm{cm}^{-1}$. Weaker broad bands are also evident at 770, 750, and $712\,\mathrm{cm}^{-1}$. In the bending mode ($300–550\,\mathrm{cm}^{-1}$) region, five well-defined bands are observed at 500, 422, 383, 327, and $313\,\mathrm{cm}^{-1}$. A broad shoulder is also evident at $534\,\mathrm{cm}^{-1}$. Therefore, of the eighteen Raman bands predicted for the internal vibrational motions, a total of 13 were observed for $\mathrm{Al(IO_3)_3}$, experimentally. As Figs. 4 and 5 show, a very similar vibrational profile is observed for $\mathrm{Ga(IO_3)_3}$ as compared to $\mathrm{Al(IO_3)_3}$, where only a small shift in the Raman bands are present.

Group theory also indicates that the lattice mode vibrations for the crystals of $\mathrm{Al(IO_3)_3}$ and $\mathrm{Ga(IO_3)_3}$ consist of the following contributions:

$$\Gamma_{\text{external (lattice) modes}} = 6A + 7B + 6E_1 + 7E_2.$$

Of these modes, only the $6A + 6E_1 + 7E_2$ lattice vibrational contributions are Raman active.

Following previous suggestions, the Raman bands observed at frequencies $<300\,\mathrm{cm}^{-1}$ are assigned here to external vibration (lattice mode) contributions. The Raman spectra of the two compounds were collected down to $60\,\mathrm{cm}^{-1}$ covering most of the lattice vibrational region. The spectrum of $\mathrm{Al(IO_3)_3}$ in the $60–300\,\mathrm{cm}^{-1}$ region shows a total of 9 well defined Raman bands at 264, 247, 232, 185, 147, 134, 99, 88, and $77\,\mathrm{cm}^{-1}$. Except for a slight shift in energies, $\mathrm{Ga(IO_3)_3}$ provides a similar profile for this region.

$\mathrm{In(IO_3)_3}$ crystallizes in space group C_{3i}^2 ($R\bar{3}$); the In atoms occupy a $6c$ Wykoff position and therefore contains a site symmetry of C_i. However, the atoms comprising the iodate anions occupy general positions with site symmetries of C_1. Site group analysis conducted for this system indicates that the iodate anions in the unit cell have internal vibrational contributions of

$$\Gamma_{\text{internal iodate modes}} = 6A_\mathrm{g} + 6A_\mathrm{u} + 6E_\mathrm{g} + 6E_\mathrm{u},$$

where only the A_g and E_g, modes are Raman active. Hence, a total of only 12 Raman bands corresponding to internal stretching and bending modes are expected for the $\mathrm{In(IO_3)_3}$ system. The Raman spectra shown in Figs. 4c and 5c, collected at room temperature, show a combined total of 10 bands for the stretching ($600–900\,\mathrm{cm}^{-1}$; Fig. 4c) and bending ($300–550\,\mathrm{cm}^{-1}$; Fig. 5c) regions. The most intense band in the stretching region is observed at $729\,\mathrm{cm}^{-1}$. This profile is in sharp contrast to that observed in the $\mathrm{Al(IO_3)_3}$ and $\mathrm{Ga(IO_3)_3}$ systems, where the most intense bands were located at higher energies ($>800\,\mathrm{cm}^{-1}$). Hence, the Raman profile can be used as a rapid diagnostic tool to discern the different structural motifs of these compounds.

Other Raman peaks in the $\mathrm{In(IO_3)_3}$ system include a relatively strong band at $843\,\mathrm{cm}^{-1}$ in addition to weaker bands and/or shoulders at 804, 745, and $714\,\mathrm{cm}^{-1}$. In the $300–550\,\mathrm{cm}^{-1}$ bending mode region, several Raman bands are observed at 417, 377, and $317\,\mathrm{cm}^{-1}$ with the band at $377\,\mathrm{cm}^{-1}$ having undefined broad shoulders at $\sim$360 and $\sim$$390\,\mathrm{cm}^{-1}$.

Group theoretical analysis for the lattice modes of the crystal indicates contributions of

$$\Gamma_{\text{external (lattice) modes}} = 6A_\mathrm{g} + 8A_\mathrm{u} + 6E_\mathrm{g} + 8E_\mathrm{u},$$

where only the A_g and E_g modes are Raman active, thus indicating a total of 12 bands expected from crystal lattice vibrations. The Raman profile shown in Fig. 5c clearly indicates the presence of at least 9 bands in the lattice mode region of $60–300\,\mathrm{cm}^{-1}$. These bands are observed at 277, 257, 237, 171, 159, 141, 126, 95, and $79\,\mathrm{cm}^{-1}$.

4. Conclusion

$\mathrm{Al(IO_3)_3}$, $\mathrm{Ga(IO_3)_3}$, and $\mathrm{In(IO_3)_3}$ have been prepared by reacting the appropriate group 13 metal with $\mathrm{H_5IO_6}$ in aqueous media at 180 °C. Single-crystal X-ray diffraction has shown that $\mathrm{In(IO_3)_3}$ contains the $\mathrm{Te_4O_9}$-type structure in contrast to the $\mathrm{Fe(IO_3)_3}$-type structure observed previously for $\mathrm{Al(IO_3)_3}$ and $\mathrm{Ga(IO_3)_3}$. The difference is presumably due to the increased size of In^{3+} as compared to Ga^{3+} and Al^{3+}. Raman spectra have been collected for all three metal iodates and although $\mathrm{Al(IO_3)_3}$ and $\mathrm{Ga(IO_3)_3}$ show similar profiles due to their isostructural nature, $\mathrm{In(IO_3)_3}$ has been found to display a distinctively different vibrational profile. Therefore, Raman spectroscopy can be used as a rapid diagnostic tool to discern the different structural motifs of these two structure types.

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