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

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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

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