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# Hydrothermal Investigation of the Systems $In_2O_3$-$H_2O$-$Na_2O$ and $In_2O_3$-$D_2O$-$Na_2O$. The Crystal Structure of Rhombohedral $In_2O_3$ and of $In(OH)_3$

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Cubic indium oxide, a new rhombohedral modification of indium oxide, indium trihydroxide, indium oxide hydroxide, and the corresponding deuterated compounds have been prepared by hydrothermal methods.

Rhombohedral indium oxide, $In_2O_3$, has a corundum structure. The space group is $R\bar{3}c$ with $a = 5.49$ Å and $c = 14.52$Å. The cell contains six formula units. Indium atoms are octahedrally coordinated with six oxygen atoms. Atomic coordinates, temperature factors and other relevant crystallographic data obtained from X-ray and neutron diffraction investigations are reported.

Indium trihydroxide, $In(OH)_3$, is cubic. The space group is $Im3$ with $a = 7.97_9$ Å. The cell contains eight formula units. Each indium atom is octahedrally coordinated with six oxygen atoms, and each oxygen atom is coordinated with two indium atoms. Atomic coordinates, temperature factors, and other crystallographic data are reported. A neutron diffraction investigation of indium trideuteroxide, $In(OD)_3$, shows a statistical distribution of the deuterium atoms in the structure. The deuterium atoms are equally distributed between two sets of coordinates with a half atom at each position.

## I. HYDROTHERMAL INVESTIGATION

In the system $In_2O_3$—$H_2O$ the compounds $In(OH)_3$, InOOH, and cubic $In_2O_3$ have been prepared by hydrothermal methods, and the formation ranges of the compounds have been studied by Roy and Shafer.[1] In a previous investigation,[2] these formation ranges were confirmed. A more detailed in-

vestigation has now shown that $In_2O_3$ can be prepared in a cubic and in a rhombohedral modification by using hydrothermal methods and alkaline solutions in a temperature and pressure range within the previously reported formation range of indium oxide hydroxide. This formation range was chosen with the intention of preparing samples of InOOH and InOOD.

## Experimental

*Chemistry.* Hydrothermal experiments were performed in pressure bombs lined with pure silver or pure gold. The balanced pressure technique was used. The experimental conditions used for the system $In_2O_3-H_2O-Na_2O$ are given in Table 1. Freshly precipitated indium trihydroxide was used in most of the experiments. Table 2 gives the experi-

Table 1. Experimental conditions for hydrothermal preparations in the system $In_2O_3$ - $H_2O$ - $Na_2O$.

| Exp. No. | Max.temp. °C | Pressure atm | Time h | NaOH M | Initial condition | Result |
|---|---|---|---|---|---|---|
| 1 | 185 | 50 | 112 | 15 | $In(OH)_3$ [a] | $In(OH)_3$ |
| 2 | 240 | 33 | 48 | 0 | " | $In(OH)_3$ |
| 3 | 275 | 75 | 24 | 0.1 | " | $In(OH)_3$ |
| 4 | 275 | 75 | 24 | 0.6 | " | $In(OH)_3$ |
| 5 | 275 | 70 | 26 | 1.0 | " | $In(OH)_3$ and InOOH |
| 6 | 307 | 94 | 173 | 0.55 | " | c-$In_2O_3$ |
| 7 | 315 | 104 | 126 | 0.55 | " | c-$In_2O_3$ |
| 8 | 325 | 150 | 24 | 0.1 | " | InOOH |
| 9 | 325 | 140 | 29 | 0.3 | " | InOOH |
| 10 | 325 | 120 | 27 | 0.6 | " | InOOH |
| 11 | 325 | 120 | 24 | 1.0 | " | InOOH |
| 12 | 330 | 127 | 24 | 0.05 | " | InOOH |
| 13 | 337 | 138 | 186 | 0.28 | " | InOOH |
| 14 | 360 | 190 | 18 | 0.05 | " | InOOH |
| 15 | 375 | 230 | 40 | 0.05 | " | c-$In_2O_3$ |
| 16 | 375 | 257 | 24 | 0.1 | " | InOOH and rh-$In_2O_3$ |
| 17 | 375 | 270 | 24 | 0.1 | " | InOOH and rh-$In_2O_3$ |
| 18 | 375 | 170 | 25 | 0.3 | " | InOOH, c-$In_2O_3$ and rh-$In_2O_3$ |
| 19 | 375 | 260 | 27 | 0.3 | " | InOOH and rh-$In_2O_3$ |
| 20 | 375 | 250 | 26 | 0.3 | " | InOOH and rh-$In_2O_3$ |
| 21 | 375 | 260 | 26 | 0.6 | " | InOOH |
| 22 | 375 | 240 | 27 | 1.0 | " | InOOH and c-$In_2O_3$ |
| 23 | 380 | 800 | 66 | 0 | " | InOOH |
| 24 | 380 | 245 | 96 | 0.08 | " | InOOH |
| 25 | 380 | 250 | 96 | 0.08 | " | InOOH |
| 26 | 380 | 450 | 127 | 1.0 | " | c-$In_2O_3$ |
| 27 | 385 | 275 | 48 | 0.1 | " | InOOH |
| 28 | 390 | 250 | 19 | 0 | In | InOOH and c-$In_2O_3$ |
| 29 | 390 | 250 | 24 | 0.1 | " | InOOH and c-$In_2O_3$ |
| 30 | 390 | 500 | 60 | 0.1 | " | InOOH |
| 31 | 410 | 650 | 72 | 0.18 | $In(OH)_3$ [a] | InOOH |
| 32 | 450 | 175 | 17 | 3.3 | " | c-$In_2O_3$ |
| 33 | 500 | 800 | 52 | 0.8 | " | c-$In_2O_3$ |
| 34 | 230 | 200 | 26 | 0 | $In(OH)_3$ [b] | $In(OH)_3$ |
| 35 | 270 | 330 | 33 | 0 | " | InOOH and c-$In_2O_3$ |
| 36 | 330 | 750 | 29 | 0 | " | c-$In_2O_3$ |

a) prepared by precipitation with sodium hydroxide solutions.
b) prepared by precipitation with ammonium hydroxide solutions.
c-$In_2O_3$: cubic modification, rh-$In_2O_3$: rhombohedral modification.

Table 2. Experimental conditions for hydrothermal preparations in the system $In_2O_3$ - $D_2O$ - $Na_2O$.

| Exp. No. | Max.temp. °C | Pressure atm | Time h | NaOD M | Initial condition | Result |
|---|---|---|---|---|---|---|
| 1 | 180 | 40 | 25 | 0 | $In(OD)_3$ | $In(OD)_3$ |
| 2 | 190 | 50 | 36 | 0 | " | $In(OD)_3$ |
| 3 | 210 | 18 | 36 | 0.05 | " | $In(OD)_3$ |
| 4 | 350 | 170 | 72 | | In and $Na_2O_2$ | c-$In_2O_3$ trace of InOOD |
| 5 | 360 | 250 | 5 | 0.06 | $In(OD)_3$ | rh-$In_2O_3$ |
| 6 | 360 | 400 | 36 | 1.2 | rh-$In_2O_3$ | InOOD |
| 7 | 330 | 720 | 24 | 0.1 | $In(OD)_3$ | c-$In_2O_3$ |
| 8 | 380 | 320 | 110 | 0.1 | $In(OD)_3$ | InOOD and rh-$In_2O_3$ |
| 9 | 380 | 240 | 218 | 0.1 | $In(OD)_3$ | rh-$In_2O_3$ and c-$In_2O_3$ |
| 10 | 390 | 435 | 93 | 0 | $In(OD)_3$ | rh-$In_2O_3$ |

Table 3. Guinier powder data for rhombohedral $In_2O_3$.

Unit cell parameters a = 5.49 Å, c = 14.52 Å, using $CuK\alpha_1$ = 1.54051 Å and $a_{NaCl}$ = 5.6389 Å.

| h k l | $10^5 \sin^2\theta_{obs}$ | $10^5 \sin^2\theta_{calc}$ | $I_o$ |
|---|---|---|---|
| 0 1 2 | 3751 | 3750 | 50 |
| 1 0 4 | 7128 | 7127 | 100 |
| 1 1 0 | 7862 | 7873 | 90 |
| 0 0 6 | 10139 | 10131 | 10 |
| 1 1 3 | 10439 | 10406 | 20 |
| 2 0 2 | 11667 | 11623 | 10 |
| 0 2 4 | 15057 | 15000 | 70 |
| 1 1 6 | 18030 | 18003 | 60 |
| 1 2 2 | 19551 | 19496 | 10 |
| 0 1 8 | 20675 | 20634 | 30 |
| 2 1 4 | 22888 | 22873 | 60 |
| 3 0 0 | 23646 | 23620 | 50 |
| 2 0 8 | 28532 | 28507 | 10 |
| 1 0 10 | 30751 | 30764 | 20 |
| 2 2 0 | 31472 | 31493 | 20 |
| 3 0 6 | 33742 | 33750 | 10 |

mental conditions used for the system $In_2O_3-D_2O-Na_2O$. Freshly precipitated $In(OD)_3$ was treated with NaOD solutions in 99.7 % $D_2O$. NaOD solutions were obtained by dissolving Na in $D_2O$. All manipulations with compounds containing deuterium were performed in a glove box under dry nitrogen.

## Discussion

The present hydrothermal investigation shows that the formation ranges of oxides, oxide hydroxides and trihydroxides in the systems $In_2O_3-H_2O-Na_2O$ and $In_2O_3-D_2O-Na_2O$ are as expected different from the formation ranges in the system $In_2O_3-H_2O$.[1] Cubic indium oxide has been prepared at temperatures as low as 307°C, and a new rhombohedral modification of indium oxide has been prepared. Figs. 1, 2, and 3 show some of the experimental results. It is assumed that indium oxide hydroxide and rhombohedral indium oxide are metastable phases. From the experimental results available it is difficult to draw any conclusions as to how the parameters, temperature, pressure and NaOH concentration, should be chosen in order to avoid the formation of cubic indium oxide in the temperature range 245—435°C; this is the previously reported temperature range for the formation of InOOH.[1]

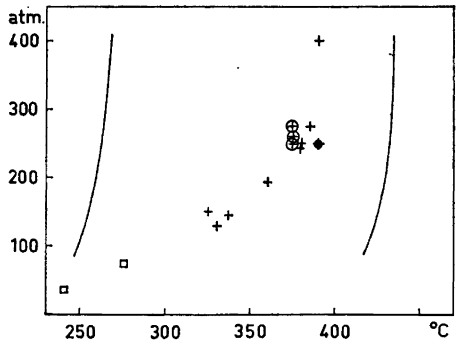


*Fig. 1.* Formation of compounds in the system $In_2O_3-H_2O-Na_2O$. Maximum concentration of sodium hydroxide in the hydrothermal solvent is 0.1 M. The compounds obtained have the following signatures: indium trihydroxide: square; indium oxide hydroxide: cross; cubic indium oxide: filled circle; rhombohedral indium oxide: open circle. The curve to the left indicates the boundary between the formation ranges of indium trihydroxide and indium oxide hydroxide, and the curve to the right that between the formation ranges of indium oxide hydroxide and cubic indium oxide, as reported in Ref. 1.

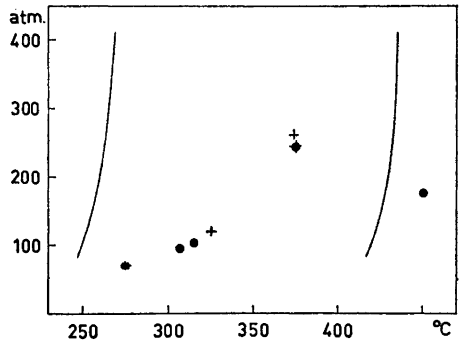


*Fig. 2.* Formation of compounds in the system $In_2O_3-H_2O-Na_2O$. Concentration range of the hydrothermal solvent is 0.6—1.0 M sodium hydroxide. Rhombohedral indium oxide was not obtained in this concentration range. Cubic indium oxide was obtained in the indium oxide hydroxide formation range reported in Ref. 1.

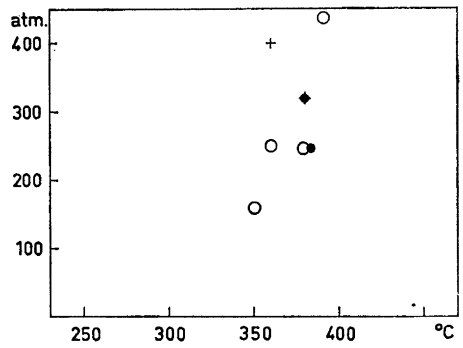


*Fig. 3.* Formation of compounds in the system $In_2O_3-D_2O-Na_2O$. Maximum concentration of NaOD in the hydrothermal solvent is 0.1 M. The compounds InOOD: cross, cubic indium oxide: filled circle, and rhombohedral indium oxide: open circle, were obtained.

## II. STRUCTURE OF RHOMBOHEDRAL $In_2O_3$

A three-dimensional single-crystal X-ray analysis of the new rhombohedral modification of indium oxide was undertaken in order to compare the structure with that of cubic indium oxide.[3]

### Experimental

*Chemistry.* Rhombohedral $In_2O_3$ (from expt. No. 10, Table 2) was analysed by EDTA titration.[4] (Found: In 82.6. Calc. for $In_2O_3$: In 82.7). Heating of rhombohedral $In_2O_3$ for 3 h at 995°C gave no loss in weight; treatment for 3 h at 1205°C resulted in a weight loss of 1.1 %. Differential thermal analysis was carried out with a Du Pont 900 Differential Thermal Analyzer using a heating rate of 20°C/min. Up to 500°C no phase transformation was observed.

*X-Ray technique.* The powder pattern of rhombohedral $In_2O_3$ was obtained with a Guinier-de Wolff camera. Purified NaCl was used as internal standard. The pattern could be indexed on a hexagonal cell with $a = 5.49$ Å, $c = 14.52$ Å (Table 3). Intensities of the lines in the powder pattern were determined visually.

The powder pattern of the sample treated at 995°C showed some lines from the cubic polymorph of $In_2O_3$. The powder pattern of the sample treated at 1205°C showed a complete transformation of rhombohedral $In_2O_3$ to the cubic modification.

A single crystal of dimensions 0.02 mm × 0.02 mm × 0.02 mm was investigated by Weissenberg methods. The crystal was from expt. No. 10, Table 2. Integrated Weissenberg photographs were taken of *hk*0, *hk*2, *hk*4, and *hk*6, using multiple film technique, with Ni-filtered Cu$K\alpha$-radiation. The rotation axis was 001, in terms of the hexagonal setting. 22 independent intensities were measured photometrically.

*Neutron technique.* Neutron diffraction powder patterns were obtained with a neutron diffractometer at the Swedish Research Council's Laboratory, Studsvik, using 1.07 Å neutrons. The samples were kept in a parallel-sided aluminium box, with specimen thickness of 3 mm (sample from experiment No. 5, Table 2). The intensities were obtained from the recorded powder patterns by measuring the areas under the peaks with a planimeter. The intensities were corrected for the contributions from the aluminium (111) and (200) reflections from the container. Four consecutive powder patterns were recorded and the intensities used in the structure calculation were obtained as averages of the measurements. Peaks with a height above the background less than half of the intensity of the background were not used in the calculations.

## Crystal data and structure determination

The new indium oxide modification is rhombohedral with space group $R\bar{3}c$, (No. 167). With hexagonal setting, the axes are $a = 5.49$ Å, $c = 14.52$ Å. Density calc. (for six formula units in the unit cell): 7.3 g/cm³. Density determined pycnometrically: $6.4 \pm 1.0$ g/cm³. Cu$K\alpha$-radiation absorption coefficient $\mu = 1482$ cm$^{-1}$.

Table 4 gives atomic coordinates and temperature factors with their standard deviations. Table 5 gives interatomic distances.

*Table 4.* Atomic coordinates and temperature factors.

| Rhombohedral $In_2O_3$. Weissenberg data, 22 reflections, $R = 4.3$ %. | | | | | | | |
|---|---|---|---|---|---|---|---|
| Atom | $x$ | $\sigma x$ | $y$ | $z$ | $\sigma z$ | $B$(Å²) | $\sigma B$(Å²) |
| In | 0 | | 0 | 0.166 | 0.001 | 0.38 | 0.07 |
| O | 0.30 | 0.01 | 0 | 0.25 | | 2.3 | 1.3 |
| Rhombohedral $In_2O_3$. Neutron data, 11 peaks, $R = 11.0$ %. Powder. | | | | | | | |
| Atom | $x$ | $\sigma x$ | $y$ | $z$ | | $B$(Å²) | |
| In | 0 | | 0 | 0.166 | | 0.38 | |
| O | 0.31 | 0.005 | 0 | 0.25 | | 2.3 | |

*Table 5.* Bond angles and interatomic distances with standard deviations, determined from X-ray and neutron data. Rhombohedral $In_2O_3$.

| Angles about In (degrees) | $v$ | $\sigma v$ |
|---|---|---|
| $O_1$—In—$O_2$ | 93.8 | 1.3 |
| $O_2$—In—$O_6$ | 90.8 | 1.6 |
| $O_2$—In—$O_4$ | 86.0 | 1.3 |
| Distances within coordination polyhedra (Å) | | |
| | $l$ | $\sigma l$ |
| In—$O_1$ | 2.27 | 0.05 |
| In—$O_6$ | 2.07 | 0.05 |
| $O_1$—$O_2$ | 3.31 | 0.05 |
| $O_2$—$O_6$ | 3.09 | 0.05 |
| $O_4$—$O_6$ | 2.90 | 0.07 |
| $O_2$—$O_4$ | 2.96 | 0.04 |

The powder pattern of rhombohedral $In_2O_3$ is very similar to that of $Cr_2O_3$ reported in the ASTM index. This led to the assumption that the new $In_2O_3$ polymorph probably had a corundum structure. The Weissenberg photographs agreed with the space group $R\bar{3}c$. In the ideal corundum structure the metal atoms are in special positions (0,0,0.1667) and the oxygen atoms

are in special positions (0.3333,0,0.25), using hexagonal setting. In a structure factor calculation these coordinates gave a conventional $R$-value of 5.2 %.

In the X-ray structure determinations coordinates and temperature factors were refined by the method of Bhuiya and Stanley.[5] The atomic scattering factors used in the refinement were from Vol. III of *International Tables for X-ray Crystallography*. The interpolation formula of Bassi [6] was applied. The program used was written by Danielsen.[7] Table 6 is a list of observed and calculated structure factors for rhombohedral $In_2O_3$.

Table 6. X-ray structure factors rhombohedral $In_2O_3$.

| h k l | Fo | Fc |
|---|---|---|
| 3 0 0 | 1365 | 1287 |
| 6 0 0 | 738 | 723 |
| 1 1 0 | 1219 | 1277 |
| 2 2 0 | 1005 | 997 |
| 3 3 0 | 781 | 840 |
| 1 4 0 | 866 | 856 |
| 2 0 2 | 585 | -601 |
| 0 1 2 | 856 | -801 |
| 1 0 4 | 677 | -715 |
| 0 2 4 | 653 | -701 |
| 2 1 4 | 615 | -614 |
| 1 3 4 | 541 | -491 |
| 4 0 4 | 445 | -443 |
| 3 2 4 | 491 | -487 |
| 0 5 4 | 465 | -438 |
| 2 4 4 | 384 | -402 |
| 4 1 4 | 344 | -396 |
| 3 0 6 | 947 | 924 |
| 1 1 6 | 1248 | 1309 |
| 2 2 6 | 1101 | 1017 |
| 3 3 6 | 727 | 719 |
| 1 4 6 | 830 | 850 |

Table 7. Observed and calculated neutron intensities for rhombohedral $In_2O_3$, hexagonal setting.

| $2\theta_c$ | h k l | $I_o$ | | $I_c$ |
|---|---|---|---|---|
| 15.5° | 0 1 2 | 168 | | 238 |
| 21.4° | 1 0 4 | 39 | | 33 |
| 25.5° | 0 0 6 | | 71 | |
| 25.9° | 1 1 3 | 1166 | 1137 | 1213 |
| 27.4° | 2 0 2 | | 5 | |
| 31.2° | 0 2 4 | 99 | | 91 |
| 34.2° | 1 1 6 | 674 | 838 | 852 |
| 35.7° | 1 2 2 | | 14 | |
| 36.8° | 0 1 8 | 11 | | 8 |
| 38.8° | 2 1 4 | 779 | 74 | 708 |
| 39.5° | 3 0 0 | | 634 | |
| 41.0° | 1 2 5 | 40 | | 26 |
| 43.5° | 2 0 8 | 40 | | 37 |
| 45.2° | 1 1 9 | | 291 | |
| 45.3° | 1 0 10 | 348 | 35 | 346 |
| 45.9° | 2 2 0 | | 1 | |
| 46.4° | 2 1 7 | | 19 | |
| 47.4° | 3 0 6 | | 42 | |
| 47.8° | 2 2 3 | 359 | 217 | 348 |
| 48.1° | 1 3 1 | | 9 | |
| 48.7° | 3 1 2 | | 80 | |

Table 8. Observed and calculated neutron intensities for $In(OD)_3$.

| $2\theta_c$ | h k l | $I_o$ | | $I_c$ |
|---|---|---|---|---|
| 18.9° | 2 1 1 | 19 | | 18 |
| 24.5° | 3 1 0 | 214 | 43 | 212 |
| 24.5° | 1 3 0 | | 169 | |
| 26.9° | 2 2 2 | 14 | | 18 |
| 29.1° | 2 3 1 | 24 | 15 | 16 |
| 29.1° | 3 2 1 | | 1 | |
| 31.2° | 4 0 0 | 31 | | 30 |
| 34.9° | 2 4 0 | 25 | 12 | 29 |
| 34.9° | 4 2 0 | | 17 | |
| 40.0° | 5 1 0 | | 5 | |
| 40.0° | 1 5 0 | 19 | 3 | 20 |
| 40.0° | 1 4 3 | | 8 | |
| 40.0° | 4 1 3 | | 4 | |
| 43.1° | 5 2 1 | 11 | 7 | 8 |
| 43.1° | 5 1 2 | | 1 | |
| 46.1° | 5 0 3 | 48 | 18 | 47 |
| 46.1° | 0 5 3 | | 29 | |
| 47.5° | 6 0 0 | 23 | 24 | 25 |
| 47.5° | 4 4 2 | | 1 | |

In the calculation of the neutron structure factors for rhombohedral indium oxide only the $x$ coordinate of the oxygen atom was varied. The atomic scattering amplitudes for indium [8] and oxygen [9] were 0.39 and 0.577 (cm $\times$ $10^{-12}$), respectively. The program used was the same as that employed for the X-ray data.[7] From the calculated structure factors the intensities ($I = j \cdot F^2/\sin^2\theta$) were obtained. The best agreement between observed and calculated neutron intensities was obtained with the coordinates given in Table 4. The calculated intensities corresponding to this set of coordinates are given in Table 7.

## Discussion

The crystallographic investigation demonstrated that rhombohedral $In_2O_3$ has a corundum structure with indium atoms octahedrally coordinated with oxygen atoms. The indium and oxygen coordinates are close to the values derived from a consideration of the ideal corundum structure. The agreement between observed and calculated X-ray structure factors is as good as can be

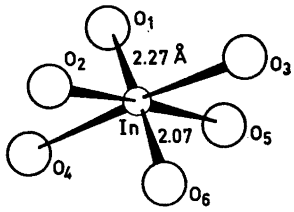


*Fig. 4.* Coordination polyhedron in rhombohedral indium oxide.

expected with photographic data, and the oxygen coordinate obtained from the neutron diffraction patterns is in agreement with the result obtained from the X-ray investigation. However, the In—O distances are not determined with very high precision because of the limited amount of data. The rather short In—O distance of 2.07 Å with a standard deviation of 0.05 Å is not significantly different from the shortest In—O distance of 2.13 ± 0.01 Å in the cubic $In_2O_3$ modification, and the In—O distance of 2.27 Å with a standard deviation of 0.05 Å is not significantly different from the longest In—O distance of 2.23 ± 0.01 Å in the cubic modification of $In_2O_3$.[3] Fig. 4 shows the slightly distorted octahedron in rhombohedral indium oxide. The packing of the atoms in the rhombohedral modification is, however, clearly closer than the packing of the atoms in the cubic modification, since the densities are 7.30 g/cm³ and 7.12 g/cm³, respectively. The rhombohedral modification is assumed to be a high pressure modification of indium oxide. The high pressure modifications of the C-type rare earth oxide structure are the B- and A-type rare earth oxide structures.[10] Although indium follows the rare earth metals in forming a cubic oxide, $In_2O_3$, the formation of the rhombohedral modification shows that the $In^{3+}$ ion also has additional similarities with ions of smaller ionic radii, *e.g.* $Cr^{3+}$. This similarity between indium and chromium is further demonstrated by the isostructural character of indium oxide hydroxide [2] and the orthorhombic modification of chromium oxide hydroxide.[11]

## III. STRUCTURE OF $In(OH)_3$

Schubert and Seitz [12] claimed from Debye-Scherrer photographs that indium trihydroxide, $In(OH)_3$, was isostructural with scandium trihydroxide, but no quantitative data for the structure have been reported. It was therefore decided to reinvestigate the crystal structure of indium trihydroxide.

### Experimental

*Chemistry.* Indium trihydroxide (from expt. No. 1, Table 1) and indium trideuteroxide (from experiment No. 3, Table 2) were analysed by EDTA titration.[4] (Found: In 69.3. Calc. for $In(OH)_3$: In 69.2. Found: In 68.3. Calc. for $In(OD)_3$: In 68.0). Thermogravimetric analysis of $In(OH)_3$ in the temperature range 25—500°C showed a weight loss corresponding to the formation of $In_2O_3$. (Found: Weight loss 15.4. Calc. for $In(OH)_3$: Weight loss 16.3). The compound formed was found by X-ray powder analysis to be cubic $In_2O_3$. The weight loss commenced at 258°C and ceased at 315°C. Differential thermal analysis of $In(OH)_3$ was obtained with a heating rate of 40°C/min, and a transformation was observed in the temperature range 310—330°C. Using a heating rate of 5°C/min the transformation was observed at 300°C.

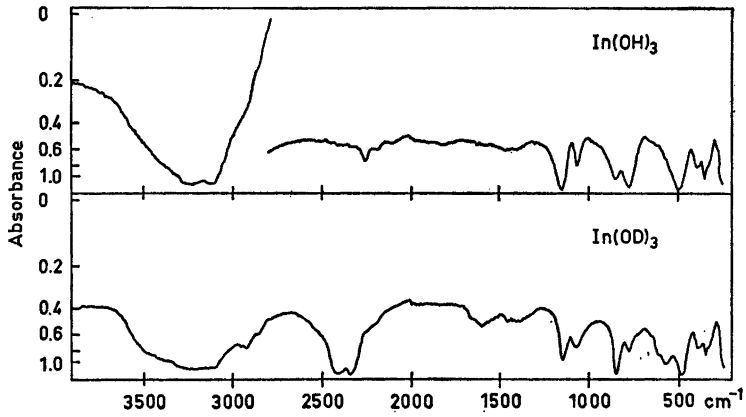


*Fig. 5.* Infra-red spectra of indium trihydroxide and of indium trideuteroxide.

The infra-red spectra of $In(OH)_3$ and $In(OD)_3$ have been obtained over the frequency range 400 to 4000 $cm^{-1}$ on a Perkin-Elmer Model 521 spectrophotometer. The pellet technique was used with mixtures of 4 mg of sample and 200 mg of CsI. The infra-red spectra are shown in Fig. 5.

*X-Ray technique.* A single crystal of $In(OH)_3$ from experiment No. 1, Table 1, with dimensions 0.1 mm × 0.1 mm × 0.1 mm was investigated by precession methods. Integrated precession photographs were taken using Zr-filtered Mo$K\alpha$-radiation of (*h*0*l*), (*hk*0), (*hk*1), (*hk*2) and (*hk*3). 48 independent reflections were measured photometrically.

Another single crystal from the same preparation of $In(OH)_3$ with dimensions 0.08 mm × 0.08 mm × 0.08 mm was investigated by Weissenberg methods. Integrated Weissenberg photographs were taken of (*hk*0), (*hk*2) and (*hk*4), using the multiple film technique, with Zr-filtered Mo$K\alpha$-radiation. 134 independent reflections were measured photometrically.

The intensities were corrected for the usual Lorentz-polarisation factors; no absorption corrections were applied.

A powder pattern of $In(OH)_3$ was obtained with a Guinier camera using Cu$K\alpha_1$ radiation. Germanium was used as internal standard, $a_{Ge} = 5.6576$ Å. The unit cell parameter was determined from the powder pattern.

*Neutron technique.* Four neutron diffraction powder patterns were obtained with the same diffractometer as used for rhombohedral indium oxide. The specimen thickness of the parallel-sided aluminium box was 6 mm. The intensities were obtained from the patterns in the same way as for rhombohedral indium oxide. Table 8 gives a list of observed intensities.

## Crystal data and structure determination

$In(OH)_3$ is cubic with space group *Im*3 (No. 204). The unit cell contains eight formula units. $a = 7.97_9$ Å. Density calc. (for eight formula units in the cell): 4.33 g/$cm^3$. Absorption coefficient $\mu = 89$ $cm^{-1}$ for Mo$K\alpha$-radiation.

Table 9 gives atomic coordinates and temperature factors with their standard deviations and Table 10 gives interatomic distances.

In the refinement of the structure, the atomic scattering curves used for indium and oxygen were calculated by the method of Forsyth and Wells.[13] The program used was written by Danielsen.[7]

*Table 9.* Atomic coordinates and temperature factors.

$In(OH)_3$. Precession data, 48 reflections, $R = 5.3$ %, Crystal 1.

| Atom | $x$ | $y$ | $\sigma y$ | $z$ | $\sigma z$ | $B$(Å²) | $\sigma B$(Å²) |
|---|---|---|---|---|---|---|---|
| In | 0.25 | 0.25 | | 0.25 | | 0.28 | 0.03 |
| O | 0 | 0.326 | 0.003 | 0.169 | 0.003 | 0.9 | 0.4 |

$In(OH)_3$. Weissenberg data, 134 reflections, $R = 7.4$ %, Crystal 2.

| Atom | $x$ | $y$ | $\sigma y$ | $z$ | $\sigma z$ | $B$ (Å²) | $\sigma B$ (Å²) |
|---|---|---|---|---|---|---|---|
| In | 0.25 | 0.25 | | 0.25 | | 0.38 | 0.02 |
| O | 0 | 0.323 | 0.004 | 0.176 | 0.004 | 1.1 | 0.3 |

$In(OD)_3$. Neutron data, 10 peaks, $R = 7.7$ %. Powder.

| Atom | $x$ | $y$ | $\sigma y$ | $z$ | $\sigma z$ | $B$ (Å²) |
|---|---|---|---|---|---|---|
| In | 0.25 | 0.25 | | 0.25 | | 0.38 |
| O | 0 | 0.323 | | 0.176 | | 1.1 |
| $\frac{1}{2}$D | 0 | 0.446 | 0.007 | 0.177 | 0.007 | 1.1 |
| $\frac{1}{2}$D | 0 | 0.303 | 0.007 | 0.055 | 0.007 | 1.1 |

*Table 10.* Bond angles and interatomic distances with standard deviations, determined from X-ray and neutron data. $In(OH)_3$.

| Angles about In (degrees) | $v$ | $\sigma v$ |
|---|---|---|
| $O_1-In-O_2$ | 93.9 | 0.7 |
| $O_1-In-O_5$ | 86.1 | 0.7 |
| Angles about $O_1$ (degrees) | | |
| $In-O_1-\frac{1}{2}D_1$ | 105 | 2 |
| $In-O_1-\frac{1}{2}D_2$ | 103 | 2 |

Distances within coordination polyhedra (Å)

| | $l$ | $\sigma l$ |
|---|---|---|
| $In-O_5$ | 2.171 | 0.008 |
| $O_1-O_2$ | 3.173 | 0.026 |
| $O_1-O_5$ | 2.964 | 0.026 |
| $O_1-\frac{1}{2}D_1$ | 0.98 | 0.06 |
| $O_1-\frac{1}{2}D_2$ | 0.98 | 0.06 |

Distances between coordination polyhedra (Å)

| | | |
|---|---|---|
| $O_1-O_7$ | 2.744 | 0.029 |
| $O_7-O_8$ | 2.798 | 0.029 |

The intensity data from the two $In(OH)_3$ crystals were treated separately. The agreement between calculated and observed structure factors is good for both sets of data. The coordinates of the oxygen atoms do not deviate

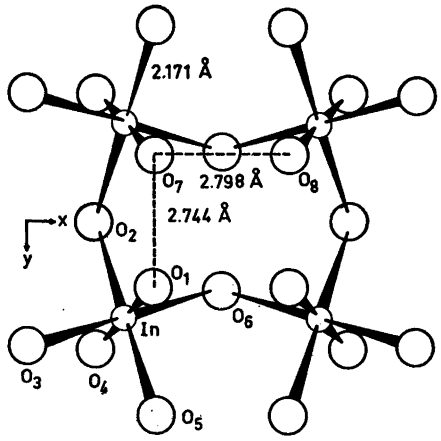


*Fig. 6.* Projection in the [001] direction of four of the eight octahedra in the unit cell of indium trihydroxide.

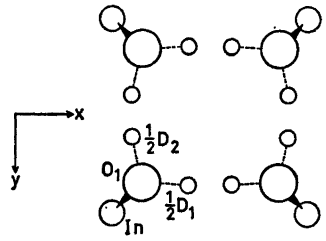


*Fig. 7.* Positions of oxygen and deuterium atoms in the $xy0$-plane and of indium atoms in the $xy1/4$-plane of $In(OD)_3$.

significantly from one measurement to the other. A table of observed and calculated structure factors for $In(OH)_3$ is not printed to save space. One of the authors (A.N.C) can supply copies of this table on request.

The position of the deuterium atom in the indium trideuteroxide structure was determined by an iterative procedure. Assuming the deuterium atom to be in the special position $(0,y,z)$ and the O—D distance to be 1 Å, the coordinates (0,0.445,0.190) and (0,0.315,0.052) give the usual coordination of the oxygen atoms, with an In—O—D angle of 100.5°. However, this packing of the deuterium atoms is only possible when the assumption is made that the deuterium atoms are equally distributed between two sets of coordinates. To limit the number of parameters to be varied in the structure factor calculation only the positional parameters of the deuterium atoms were varied. The temperature factor for the deuterium atom was chosen as 1.1. The best agreement between observed and calculated neutron intensities was obtained with the coordinates given in Table 9 and the intensities calculated from this set of coordinates are given in Table 8. In the structure factor calculation the atomic scattering amplitude for deuterium [9] was 0.65 (cm $\times$ $10^{-12}$), the scattering amplitudes for indium and oxygen were the same as those used for rhombohedral indium oxide.

## Discussion

The present investigation confirms that indium trihydroxide has the structure reported by Schubert and Seitz.[12] The In—O distance of 2.171 Å is comparable with the In—O distances of 2.15 Å and 2.20 Å found in indium oxide hydroxide.[2] Fig. 6 is a projection of the $In(OH)_3$ structure in the [001] direction. The structure has $In(OH)_6$ octahedra. Each $OH^-$ ion is coordinated

with two $In^{3+}$ ions to form infinite In—O—In chains. The In—O—In angle in the chains is 133.7° with a standard deviation of 0.7°. The O—O distances of 2.744 Å and 2.798 Å, with a standard deviation of 0.029 Å, are probably significantly different. These two distances are interpreted as being dependent upon hydrogen bond formation; this should correspond to two hydroxyl absorption bands in the infra-red spectra of indium trihydroxide. For both $In(OH)_3$ and $In(OD)_3$ the absorption band at 3200 $cm^{-1}$ and 2400 $cm^{-1}$ are observed as doublets (Fig. 5). The neutron diffraction investigation shows that the hydrogen atoms are statistically distributed in the structure. Fig. 7 shows the positions of oxygen and deuterium atoms in the $xy$-plane.

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