Supplementary Information

New materials for infrared non linear optics. Syntheses, structural characterisations, second harmonic generation and optical transparency of M(IO₃)₃ metallic iodates.

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Table S1 Selected interatomic distances (Å) (with e.s.d) and bond angles (°) (with e.s.d) for α-In(IO₃)₃ and β-In(IO₃)₃.

<table>
<thead>
<tr>
<th></th>
<th>α-In(IO₃)₃</th>
<th>β-In(IO₃)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-O₁</td>
<td>2.136(4) x3</td>
<td>2.156(3) x3</td>
</tr>
<tr>
<td>In-O₁₃</td>
<td>2.139(5) x3</td>
<td>2.141(3) x3</td>
</tr>
<tr>
<td>I-O₁</td>
<td>1.827(4)</td>
<td>1.825(3)</td>
</tr>
<tr>
<td>I-O₂</td>
<td>1.778(5)</td>
<td>1.803(4)</td>
</tr>
<tr>
<td>I-O₃</td>
<td>1.833(5)</td>
<td>1.798(3)</td>
</tr>
<tr>
<td>I-O₁⁺</td>
<td>3.014(5)</td>
<td>2.567(4)</td>
</tr>
<tr>
<td>I-O₂ᵐ</td>
<td>2.696(5)</td>
<td>3.024(4)</td>
</tr>
<tr>
<td>I-O₃ᵐ</td>
<td>2.915(5)</td>
<td>3.115(4)</td>
</tr>
<tr>
<td>O₁-In-O₁Ⅱ</td>
<td>88.7(2)</td>
<td>84.9(1)</td>
</tr>
<tr>
<td>O₁-In-O₁Ⅲ</td>
<td>84.5(2)</td>
<td>89.8(1)</td>
</tr>
<tr>
<td>O₁-In-O₁Ⅳ</td>
<td>96.1(2)</td>
<td>174.7(1)</td>
</tr>
<tr>
<td>O₁-In-O₂Ⅲ</td>
<td>171.6(2)</td>
<td>94.0(1)</td>
</tr>
<tr>
<td>O₁-In-O₂Ⅳ</td>
<td>91.3(2)</td>
<td>91.2(1)</td>
</tr>
<tr>
<td>O₂-In-O₂Ⅲ</td>
<td>97.9(2)</td>
<td>99.7(2)</td>
</tr>
<tr>
<td>O₂-In-O₂Ⅳ</td>
<td>95.1(2)</td>
<td>101.4(2)</td>
</tr>
<tr>
<td>O₂-In-O₃</td>
<td>100.6(2)</td>
<td>96.5(2)</td>
</tr>
</tbody>
</table>
| Symmetry card for α-In(IO₃)₃: ¹(1-x, 1-y, z+1/2); ¹¹ (1-x+y, 1-x, z); ¹ii (y, -x+y, z+1/2); ¹iv (x-y+1, x, z+1/2); ²iv (x-y, x, z+1/2).
| Symmetry card for β-In(IO₃)₃: ¹(1/3-x, 2/3-y, 5/3-z); ¹¹ (y-2/3, -x+y-1/3, 5/3-z); ¹ii (x-y+1/3, x-1/3, 5/3-z); ¹iv (-x+y, -x, z); ²iv (y+1/3, 2/3-x+y, 5/3-z); ²iv (2/3-x, 1/3-y, 4/3-z).|

Phase transition of α-In(IO₃)₃ in β-In(IO₃)₃

In order to determine the transition temperature, temperature dependent X-ray powder diffraction experiments have been performed. X-ray powder diffraction patterns of α-In(IO₃)₃ and β-In(IO₃)₃ are presented in Fig. S1. The evolution of the powder patterns has been followed on the most intense peaks in the range 26° to 43° (Fig. S2). This experiment shows the transformation of α-In(IO₃)₃ to β-In(IO₃)₃ at around 365°C. The phase transition is not reversible.
Fig. S1 X-ray diffraction powder patterns of $\alpha$-In(IO$_3$)$_3$ (bottom) and $\beta$-In(IO$_3$)$_3$ (top) recorded at $\lambda$(Fe$\alpha_1$) = 1.93604 Å. The insert shows the powder patterns of the most intense peaks in the range 26° to 43°.

Fig. S2 Temperature dependent powder diffraction patterns of $\alpha$-In(IO$_3$)$_3$ ($\theta$ range 26° to 43°). Arrows indicate the apparition of peaks of the $\beta$-In(IO$_3$)$_3$ phase.
**DSC analyses:** DSC analyses for compounds $\alpha$-In(IO$_3$)$_3$, $\beta$-In(IO$_3$)$_3$ and Ga(IO$_3$)$_3$ were carried out on a NETZSCH ATD-DSC 404S apparatus and ran in the range 25-600°C, in argon flow at 5°C/min heating rate (Fig. 10).

For $\alpha$-In(IO$_3$)$_3$, the DSC curve shows decomposition at 535°C which corresponds to the formation of indium oxide In$_2$O$_3$ (JCPDS file no. 71-2194). However, $\alpha$-In(IO$_3$)$_3$ undergoes a phase transition at about 365°C which isn’t observed on the DSC curve. The DSC curve of $\beta$-In(IO$_3$)$_3$ shows the same thermal behaviour as $\alpha$-In(IO$_3$)$_3$. So, for clarity, it was not represented in Fig. 10.

For Ga(IO$_3$)$_3$, it reveals decomposition at around 525°C. The composition of the residue was determined by X-ray powder diffraction and identified as being the gallium oxide $\gamma$-Ga$_2$O$_3$ (JCPDS file no. 20-0426).

![DSC curves](image)

**Fig. S3** DSC curves of Ga(IO$_3$)$_3$ (black line) and $\alpha$-In(IO$_3$)$_3$ (dotted line).