

## On the Existence of Crystalline $\text{In}_2\text{O}$

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The preparation of crystalline  $\text{In}_2\text{O}$  has been reported by Thiel and Luckmann,<sup>1</sup> Klemm and Vogel<sup>2</sup> and by Gastinger.<sup>3</sup> Brauer<sup>4</sup> gives a preparation procedure for  $\text{In}_2\text{O}$  based on the results reported in Refs. 1 and 2. Thiel and Luckmann<sup>1</sup> reduced  $\text{In}_2\text{O}_3$  with hydrogen at 400°C and sublimed the residue at 750°C at a pressure of  $10^{-3}$ – $10^{-4}$  mm Hg. The reaction product was

Table 1.

Exp. No.	$\text{In}_2\text{O}_3$ sample	Reduction h	Reduction °C	Sublimation h	Sublimation °C	mm Hg	Product formed
1	I	3	410	5	650	$5 \times 10^{-5}$	In, trace of $\text{In}_2\text{O}_3$
2	II	5	425	6	700	$2 \times 10^{-5}$	In and $\text{In}_2\text{O}_3$
3	II	10	400	5	640	$3 \times 10^{-4}$	In
4	II	12	385	7	490	$1 \times 10^{-5}$	product did not sublime
5	III	2	400	5	650	$5 \times 10^{-5}$	In and $\text{In}_2\text{O}_3$

Table 2.

$\text{In}_2\text{O}_3$ <i>d</i> obs (Å)	<i>j</i>	In <i>d</i> obs (Å)	<i>j</i>	Sample from No. 2 Table 1 <i>d</i> obs (Å)	Powder pattern of “ $\text{In}_2\text{O}$ ” from Ref. 2 <i>d</i> (Å)
4.15	m				
2.92	vs			2.93	2.9
		2.72	vs	2.72	2.7
2.69	vw				
2.52	vs			2.53	2.5
		2.46	m	2.46	
2.38	m				
		2.28	s	2.28	2.3
2.25	w				
2.15	m				
2.06	w				
1.98	m				2.0
1.84	w				
1.78	vs			1.79	1.8
1.72	w				
		1.67	m	1.68	1.7
1.64	m				
		1.62	m	1.62	1.6
1.59	w				
1.55	m				
1.52	s			1.53	1.5
1.48	m				
		1.46	m	1.46	1.45
1.45	m				
		1.39	m	1.39	1.4
		1.36	w	1.36	1.35
vw	very weak	m	medium	vs	very strong
w	weak	s	strong		

identified by chemical analysis as  $\text{In}_2\text{O}$  and by an unpublished X-ray powder pattern. Klemm and Vogel<sup>2</sup> used the same method and identified the reaction product as  $\text{In}_2\text{O}$  by chemical analysis. An X-ray powder pattern of  $\text{In}_2\text{O}$  and of  $\text{In}_2\text{O}_3$  obtained with a Debye-Scherrer camera is represented diagrammatically. The intensities of the reflections are given as the height of the lines in the diagram and the positions of the reflections are given in the line diagram at the appropriate scattering angles. Gastinger<sup>3</sup> reported that indium can be oxidised to  $\text{In}_2\text{O}$  by  $\text{CO}_2$  at  $850^\circ\text{C}$  and 10 torr. The compound formed was not characterised by its X-ray powder pattern. By an electron diffraction study of  $\text{In}_2\text{O}$  vapour obtained from the reaction of indium oxide ( $\text{In}_2\text{O}_3$ ) with indium metal, Rambidi and Tolmachev<sup>5</sup> found an In—O distance of  $2.02 \pm 0.01 \text{ \AA}$  and an In—O—In angle of  $150^\circ \pm 10^\circ$ .  $\text{In}_2\text{O}$  was also observed in the gas phase by Burns, De Maria, Drowart and Inghram.<sup>6</sup>

In order to characterise crystalline  $\text{In}_2\text{O}$  more thoroughly, preparations were tried by the method reported by Brauer.<sup>4</sup> Three different samples of cubic  $\text{In}_2\text{O}_3$  were used. One sample (I) was prepared from freshly precipitated indium trihydroxide by heating at  $360^\circ\text{C}$  for 60 h. A Guinier powder pattern of (I) proved that it was microcrystalline  $\text{In}_2\text{O}_3$ . The second sample (II) was prepared by treating freshly precipitated indium trihydroxide with a 0.1 m NaOH solution in a pressure bomb at  $373^\circ\text{C}$  and 230 atm. for 40 h. A Guinier powder pattern of (II) had sharp lines all characteristic of  $\text{In}_2\text{O}_3$ . The third sample (III) was prepared from (II) by ignition at  $1100^\circ\text{C}$  for 60 h. A Guinier powder pattern showed that (III) was still  $\text{In}_2\text{O}_3$ .

The samples (I, II, III) were reduced with hydrogen at  $380\text{--}425^\circ\text{C}$ . The reduced samples were shown by Guinier powder patterns to be mixtures of In and  $\text{In}_2\text{O}_3$ . These mixtures were sublimed at  $650^\circ\text{C}$  at a pressure of  $10^{-4}\text{--}10^{-5}$  mm Hg, and the sublimed products were characterised by Guinier powder patterns. Five independent reductions and sublimations were performed. All products formed by the sublimation were proved by the Guinier powder pattern to be In or mixtures of cubic  $\text{In}_2\text{O}_3$  and In. The experimental conditions are given in Table 1. Table 2 gives the powder pattern of the product formed in experiment No. 2 (see Table 1). All the lines in the powder pattern belong to the patterns of indium and cubic indium oxide, ( $\text{In}_2\text{O}_3$ ).

The powder patterns of indium and indium oxide were obtained with the same Guinier camera as that used for the reaction products from the reductions. The patterns agreed well with the previously reported powder patterns for indium (ASTM 5-0642) and indium oxide (ASTM 6-0416). For comparison, the powder pattern of  $\text{In}_2\text{O}$  reported by Klemm and Vogel<sup>2</sup> has been calculated from the line diagram. This pattern is probably also a combination of the powder patterns of indium and indium oxide. To our knowledge an unambiguous proof for the existence of crystalline  $\text{In}_2\text{O}$  has not yet been given.

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## The High-Temperature Phases $\text{Ni}_{3\pm x}\text{Se}_2$ and $\text{Ni}_6\text{Se}_5$

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In the nickel-selenium system a phase  $\text{In}_2\text{O}_3$  with rhombohedral (pseudocubic) structure and no appreciable range of homogeneity exists.<sup>1-3</sup> According to our high temperature X-ray study the rhombohedral deformation persists up to  $600^\circ\text{C}$ . Above this temperature transformation to a face-centered cubic structure takes place. In contrast to the rhombohedral phase, the high-temperature phase has a broad range of homogeneity, as indicated by the large variation in lattice constants with composi-