# Polymorphism of In<sub>5</sub>S<sub>5</sub>Cl – X-ray and HRTEM-Investigations Vera Nickel,<sup>[a]</sup> Hans-Jörg Deiseroth,<sup>\*[a]</sup> Lorenz Kienle,<sup>\*[b]</sup> Viola Duppel,<sup>[c]</sup> and Christof Reiner<sup>[a]</sup>

Dedicated to Professor Arndt Simon on the Occasion of His 70th Birthday

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Abstract. In<sub>5</sub>S<sub>5</sub>Cl belongs to the group of mixed valence indium compounds with indium occurring simultaneously in three oxidation states  $(In_5S_5Cl = In^+(In_2)^{4+}2In^{3+}5S^{2-}C\Gamma)$ . It was shown in an earlier work that  $In_5S_5Cl$  obtained from InCl<sub>3</sub>, indium and sulfur at 550 °C, crystallises in a monoclinic structure type in contrast to the orthorhombic bromide,  $In_5S_5Br$ . The main difference of both structure types is an ordered mutual exchange of  $In^+$  and  $(In_2)^{4+}$  in specific crystallographic positions. This exchange is possible due to the almost identical coordination pattern of both ions. A closer inspection of the real structure

#### Introduction

The group 13 element indium forms a great variety of stable mixed valence halides and chalcogenides. Beside the group specific oxidation numbers +I and +III of the isolated atoms, indium forms cationic clusters of different type with specific average oxidation numbers of the constituting atoms. The most common cluster is an  $[In_2]^{4+}$  dumbbell, which occurs in several binary and ternary solids, e.g. in InS [1] or in KInBr<sub>3</sub> [2]. Further examples are chainlike  $[In_3]^{5+}$ - (In<sub>4</sub>Se<sub>3</sub>, [3]),  $[In_5]^{7+}$  and  $[In_6]^{8+}$ -units (both in In<sub>11</sub>Mo<sub>40</sub>O<sub>62</sub>, [4]), or the tetrahedral  $[In_5]^{7+}$  ion, which is observed in Na<sub>23</sub>In<sub>5</sub>O<sub>15</sub> [5]. All these clusters can be well understood by simple two centre two electron bonds of the constituting atoms. Some of these clusters occur together with In<sup>+</sup> or In<sup>3+</sup> or simultaneously with both species in the above mentioned mixed valence compounds. A typical example is  $In_6S_7$  (=  $In^+(In_2)^{4+}3In^{3+}7S^{2-}$ ) with indium in three different oxidation

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of monoclinic In<sub>5</sub>S<sub>5</sub>Cl by High Resolution Transmission Microscopy (HRTEM) already showed the presence of small orthorhombic domains in the real structure of this compound. Now we also obtained macroscopic quantities of orthorhombic In<sub>5</sub>S<sub>5</sub>Cl by the reaction of InCl<sub>3</sub>, indium and sulfur at reaction temperatures below 500 °C (*Pmn*2<sub>1</sub>, *a* = 3.907(1) Å, *b* = 9.021(2) Å, *c* = 14.866(3) Å, *Z* = 2). The new polymorph is analysed by X-ray single crystal and X-ray powder diffraction and HRTEM investigations.

states [6, 7]. In such compounds the indium species can be easily distinguished because of their specific coordination and characteristic distances to anions of their first coordination sphere. According to the classification of Robin and Day [8], all these solids belong to group I mixed valence compounds. A peculiar case with respect to this classification is the title compound In<sub>5</sub>S<sub>5</sub>Cl which contains three different cationic indium species and two different anionic ones:  $In_5S_5Cl$  (=  $In^+(In_2)^{4+}2In^{3+}5S^{2-}Cl^-$ ). In spite of apparent structural differences between  $In^+$  and  $(In_2)^{4+}$ (In<sup>+</sup>: spherical ion,  $r \approx 140$  pm [9], (In<sub>2</sub>)<sup>4+</sup>: dumbbell shaped ion with covalent In–In bonding ( $d_{\text{In–In}} \cong 270 \text{ pm}$  [9]) both ions surprisingly have a more or less similar coordination of nine nonmetal atoms forming a tricapped trigonal prism. Because of this peculiar geometrical situation, one can expect both ions to be able to interchange their places at least in the sense of a partial disorder. We could show in an earlier work [10] that this is actually possible. A complementary interchange of  $In^+$  and  $(In_2)^{4+}$  on specific positions resulting in two different ordered structure types was found for monoclinic  $In_5Ch_5Cl$  (Ch = S, Se) "Cl-type" and for orthorhombic  $In_5Ch_5Br$  (Ch = S, Se) "Br-type". Tlln<sub>4</sub>Se<sub>5</sub>Br (with In<sup>+</sup> completely substituted by Tl<sup>+</sup>), was the first example to break this initially assumed "systematic" because it crystallises in the monoclinic "Cl-type" [11]. In<sub>5</sub>S<sub>5</sub>Cl presented in this paper is the first dimorphic example of this series of solids that forms two polymorphs (monoclinic "Cl type" and orthorhombic "Br-type") depending on the synthesis conditions.

# **Results and Discussion**

#### General Remarks

As mentioned above, the compounds  $MIn_4Ch_5X (M = Tl, In, Ch = S, Se, X = Cl, Br)$  of which  $TlIn_4S_5Br$  could not yet



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been obtained can be described in the mixed valence notation  $MIn_4Ch_5X = M^+(In_2)^{4+}2In^{3+}5Ch^{2-}X^-$ . The hitherto known compounds crystallise either in the monoclinic "Cl-type" or in the orthorhombic "Br-type". Neglecting the type of non-metals (chalcogen or halogen) the first coordination spheres of the different In/Tl-species are similar in both structure types: octahedral for In<sup>3+</sup> and tricapped trigonal prismatic for  $(In_2)^{4+}$  and  $M^+$ . The octahedra form two-dimensional units of cis- and trans-edge sharing double-octahedra chains extending parallel to the shortest axis of the respective structure type (*b* for the monoclinic, *a* for the orthorhombic type) (Figure 1).



**Figure 1.** Projection of the monoclinic (above) and orthorhombic (below, left)  $In_5S_5X$  (X = Cl, Br) structure type with emphasis on the tricapped trigonal prismatic coordination of  $In^+$  and  $(In_2)^{4+}$  (below right, in projection dark gray or light gray triangles). In the monoclinic type the double octahedra (medium gray) are surrounded either by 4  $In^+$  and 2 ( $In_2$ )<sup>4+</sup>-dumbbells or by 2  $In^+$  and 4 ( $In_2$ )<sup>4+</sup>-dumbbells ("4,2" or "2,4"-arrangement). In the orthorhombic type all double octahedra are surrounded by 3  $In^+$  and 3 ( $In_2$ )<sup>4+</sup>-dumbbells ("3,3"-arrangement).

Both structure types can be easily distinguished in structure projections along the short axis focusing on the local pattern formed by the  $In(Ch/X)_6$ -octahedra and the surrounding trigonal prisms as outlined in detail in [10] and summarised in Figure 1. In an earlier work we could show by HRTEM investiga-

tions that the real structure of orthorhombic  $In_5S_5Br$  on an atomic scale is nearly free of chemical defects, whereas the *monoclinic*  $In_5S_5Cl$  exhibits *multiple twinning*, an *intergrowth* with  $In_6S_7$  in nanodimensions and thin, in rare cases more expanded *lamellar intergrowth* of *orthorhombic*  $In_5S_5Cl$  [10], which was not yet known as macroscopic phase at that time. Earlier experiments to enhance the size of the orthorhombic domains in  $In_5S_5Cl$  by annealing "monoclinic"  $In_5S_5Cl$  at different temperatures failed. In the course of a series of further synthesis experiments in the system indium/sulfur/chlorine at lower temperatures we now obtained surprisingly orthorhombic  $In_5S_5Cl$  in macroscopic quantities.

#### X-ray Powder Investigations of Monoclinic and Orthorhombic In<sub>5</sub>S<sub>5</sub>Cl Samples

Monoclinic  $In_5S_5Cl$  can be obtained from mixtures of  $InCl_3$ , indium and sulfur with the total composition  $In_5S_5Cl$  which are annealed *above* 500 °C (e.g. 550 °C). The product consists of extremely thin (1–15 µm) orange-red transparent needles with a length up to some mm. Scanning electron images show that these needles typically are bundles of several crystals with intergrowth along the needle axis [010]. X-ray powder patterns of such samples in comparison to calculated patterns based on single crystal data show a good agreement concerning the positions of the reflection angles. Strong differences of intensities [10] are due to texture effects, which result from a preferred orientation of the needles on a flatbed holder or in a capillary. A careful inspection of the resulting powder diagrams gives no evidence for the presence of additional orthorhombic  $In_5S_5Cl$ .

From mixtures of InCl<sub>3</sub>, indium and sulfur with the total composition In<sub>5</sub>S<sub>5</sub>Cl, which are annealed below 500 °C the new orthorhombic modification of In<sub>5</sub>S<sub>5</sub>Cl is formed. Orthorhombic In<sub>5</sub>S<sub>5</sub>Cl can already be detected by powder X-ray diffraction in samples which were annealed at 300 °C only. The visible formation of needles, however, becomes more pronounced with increasing temperature. At a higher magnification and with a certain experience the needles of orthorhombic In<sub>5</sub>S<sub>5</sub>Cl can even be distinguished from the monoclinic ones. The orthorhombic ones show a more regular shape and less intergrowth along the needle axis. X-ray powder patterns exhibit only minor texture effects. Measured and calculated patterns agree almost completely (Figure 2 a). In particular no reflections of the monoclinic modification of In<sub>5</sub>S<sub>5</sub>Cl are present (Figure 2 b). Samples of orthorhombic In<sub>5</sub>S<sub>5</sub>Cl, which are annealed at 550 °C show new reflections of the monoclinic polymorph already within one day. After five days the transition is complete. We assume that the sample recrystallises under participation of a gas phase reaction including molecular species like In<sub>2</sub>Ch and InX. An alternative interdiffusion of  $(In_2)^{4+}$  and  $In^+$  ions in the bulk seems to be unlikely. It is *not* possible to transform monoclinic In<sub>5</sub>S<sub>5</sub>Cl back to the orthorhombic polymorph by annealing the monoclinic phase *below* 500 °C. This behaviour was checked at several temperatures in the range of 300-500 °C and with different annealing times (up to 4 weeks). The volumes of the two polymorphs, which



result from the refinements of X-ray powder patterns, show only minor differences (Table 1). In differential thermal analyses both polymorphs exhibit a thermal effect in the same temperature range (590 °C for orthorhombic and 605 °C for monoclinic  $In_5S_5Cl$ ).



**Figure 2. (a)** Section of a measured X-ray powder pattern of orthorhombic  $In_5S_5Cl$  (above) in comparison to a calculated one (below, calculated from single crystal data). **(b)** Sections of a measured X-ray powder pattern of orthorhombic  $In_5S_5Cl$  (above) in comparison to a calculated one of monoclinic  $In_5S_5Cl$  (below, calculated from single crystal data) [10].

Table 1. Comparison of the lattice constants for the monoclinic and orthorhombic polymorphs of  $In_5S_5Cl$  obtained from powder data with internal standard (Si).

	Lattice constants /Å; /°; /Å <sup>3</sup>	Space group
In <sub>5</sub> S <sub>5</sub> Cl	a = 8.944(2) b = 3.9111(8) c = 14.985(4) $\beta = 93.60(3)$ V = 523.1(2)	P2 <sub>1</sub> /m
In <sub>5</sub> S <sub>5</sub> Cl	a = 3.9031(1) b = 9.010(3) c = 14.836(5) V = 521.7(2)	Pmn2 <sub>1</sub>

Powder investigations of samples, which are quenched from temperatures slightly above these thermal effects, prove that these temperatures represent in both cases the decomposition of the solids.

# X-ray Single Crystal Investigation and Comparison of the Polymorphs

For a single crystal measurement, a small red transparent needle of orthorhombic  $In_5S_5Cl$  was selected from a heterogeneous sample, which was annealed at 550 °C for only one day (see above). The crystal was measured with a STOE IPDS I. The analysis of the collected data with the programs RECIPE and SPACE [12] showed the presence of three domains, which were intergrown unsystematically. With the program TWIN [12], overlapping reflections were rejected and the data of the major domain were used for the structure solution and refinement. A summary of the data collection, refinement details and atomic positions is given in Table 2 and Table 3.

Table 2. Summary of data collection and refinement details for orthorhombic  $\rm In_5S_5Cl.$ 

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Empirical formula Formula weight /g·mol <sup>-1</sup>	In <sub>5</sub> S <sub>5</sub> Cl 769.85
Space group	$Pmn2_1$
Formula units per unit cell	Z = 2
Crystal shape	dark red needle
Crystal dimension /mm	$0.1 \times 0.02 \times 0.01$
lattice constants /Å	
	a = 3.907(1)
	b = 9.021(2)
	c = 14.866(3)
Volume /Å <sup>3</sup>	V = 524.0(2)
Density (calcd.) /g·cm <sup>-3</sup>	$\rho = 4.880$
Absorption coefficient /mm <sup>-1</sup>	$\mu = 12.019$
F(000)	684
Diffractometer	STOE-IPDS (Graphite monochroma-
	tor)
Wavelength /Å	0.71073 (Mo-K <sub>α</sub> )
Temperature /K	T = 293
Measured $\theta$ range /°	2.64–29.22
Index ranges	$-5 \le h \le 4$
	$-12 \le k \le 12$
	$-20 \le l \le 20$
Measured reflections	1560
Independent reflections	1380
Completeness to $\theta$ /%	96.6
R <sub>int.</sub>	0.0652
Data/Restraints/Parameter	1560 / 1 / 70
<i>R</i> values $(I \ge 2\sigma(I))$	$R_1 = 0.0335, wR_2 = 0.0719$
R values (all data)	$R_1 = 0.0421, wR_2 = 0.0749$
Weighting Scheme*	A = 0.0458 B = 0
GooF	0.976
Difference Fourier residuals /	$\rho_{\text{max.}} = 1.782;  \rho_{\text{min.}} = -1.222$
e·Å <sup>-3</sup>	
$w = 1/[\sigma^2(F_0^2) + (AP)^2 + BP].$	$P = (F_0^2) + 2F_c^2)/3$
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In contrast to monoclinic  $In_5S_5Cl$ , the structure refinement of orthorhombic  $In_5S_5Cl$  does not show any significant anomalies. This is somewhat surprising because  $In_5S_5Cl$  is the first dimorphic example thus exhibiting ideal requirements for a nanoscale intergrowth of both modifications. In order to ensure this observation and to derive information about the homoge-

**Table 3.** Atomic coordinates, equivalent isotropic displacement parameters  $U_{\text{eq}} / \text{Å}^2$  and occupancy for orthorhombic In<sub>5</sub>S<sub>5</sub>Cl, all atoms in Wyckoff position 2*a*.

Atom	x	У	Z	$U_{ m eq}$ /Å $^2$	sof
In1	0	0.8876(1)	0.40427(6)	0.0119(2)	1
In2	1/2	0.5990(1)	0.52420(6)	0.0120(2)	1
In3	1/2	0.1880(1)	0.30337(7)	0.0161(2)	1
In4	1/2	0.48008(9)	0.25427(6)	0.0115(2)	1
In5	1/2	0.8579(2)	0.11078(8)	0.0283(4)	0.951(6)
S1	1/2	0.7001(3)	0.3615(2)	0.0084(6)	1
S2	1/2	0.4290(3)	0.6604(2)	0.0104(6)	1
S3	0	0.7674(3)	0.5658(2)	0.0096(6)	1
S4	1/2	0.0642(4)	0.4556(2)	0.0119(6)	1
S5	0	0.0296(3)	0.2518(2)	0.0113(5)	1
Cl	0	0.4096(3)	0.4593(2)	0.0153(6)	1

neity on a nanoscale, HRTEM investigations were carried out (see below).

As mentioned above, the crystallographically independent indium atoms have the same type of coordination in both polymorphs (Figure 1). The average and individual In-Ch/X distances are reasonable and show good internal and external agreement (Table 3, Table 4). Nevertheless, a significant difference in the first coordination sphere is observed for In5 (In<sup>+</sup>). In the monoclinic phase the first coordination sphere of In5 consists of six sulfur and three chlorine atoms whereas in the orthorhombic polymorph In5 has eight sulfur atoms and one chlorine atom. All other indium atoms have the same S/Cl ratio in their coordination sphere. The slight underoccupancy for In5 (In<sup>+</sup>) is a feature of all solids containing In<sup>+</sup>. It is most likely due to an interchange of a small fraction of In<sup>+</sup> and (In<sub>2</sub>)<sup>4+</sup>. The Madelung Parts of Lattice Energy (MAPLE, [13, 14]) for mono-

Table 4. Comparison of selected distances /Å for monoclinic [10] and orthorhombic  $\rm In_5S_5Cl.$ 

In <sub>5</sub> S <sub>5</sub> Cl, monoclinic		$In_5S_5C$	In <sub>5</sub> S <sub>5</sub> Cl, orthorhombic		
In1-	S5	2.57(1)	In1-	S5	2.603(3)
	S2(2x)	2.620(7)		S4(2x)	2.634(2)
	S1	2.61(1)		S3	2.634(3)
	S1(2x)	2.653(7)		S1(2x)	2.661(2)
	Ø	2.621		Ø	2.638
In2-	S3	2.54(1)	In2-	S3(2x)	2.551(2)
	S4(2x)	2.544(7)		S2	2.540(3)
	S4	2.59(1)		S1	2.585(3)
	Cl(2x)	2.776(7)		Cl(2x)	2.769(2)
	Ø	2.628		Ø	2.628
In3–	S2	2.50(1)	In3–	S4	2.524(3)
	S5(2x)	2.57(1)		S5(2x)	2.539(2)
	Ø	2.547		Ø	2.534
In4–	S3(2x)	2.517(7)	In4–	S2(2x)	2.537(2)
	S1	2.54(1)		S1	2.546(3)
	Ø	2.527		Ø	2.540
In4–	In3	2.723(4)	In4–	In3	2.734(1)
In5–	Cl(2x)	3.187(9)	In5–	S4(2x)	3.103(3)
	S5(2x)	3.206(9)		S5(2x)	3.257(3)
	S4	3.28(1)		Cl	3.301(3)
	Cl	3.34(1)		S2(2x)	3.326(3)
	S3(2x)	3.398(9)		S3	3.446(3)
	S1	3.93(1)		S1	3.990(3)
	Ø	3.348		Ø	3.345

Table 5. MAPLE values for monoclinic [10] and orthorhombic  $\mathrm{In}_{s}\mathrm{S}_{s}\mathrm{Cl}.$ 

	MAPLE /kcal·mol <sup>-1</sup> monoclinic	MAPLE /kcal·mol <sup>-1</sup> orthorhombic
In1 (In <sup>3+</sup> )	-873,53	-911,63
$\ln 2$ ( $\ln^{3+}$ )	-831,28	-808,78
$In3 (In^{2+})$	-328,12	-337,65
In4 $(In^{2+})$	-341,63	-318,64
$In5 (In^+)$	-149,57	-159,44
S1	-442,47	-463,59
S2	-473,40	-413,13
S3	-395,47	-443,57
S4	-461,87	-378,02
S5	-386,62	-368,18
Cl1	-78,44	-124,13
Σ	-4762,4	-4726,76

clinic and orthorhombic  $In_5S_5Cl$  favours the monoclinic phase over the new orthorhombic one ( $\Delta \approx 0.8$  %, Table 5). The partial MAPLE values of the octahedrally coordinated  $In^{3+}$  ions (In1 and In2) are more balanced for the monoclinic compound. The small value for  $Cl^-$  in the monoclinic phase is remarkable. In both structure types three of five crystallographically independent chalcogen atoms have significant higher values than two others. For the evaluation of this calculation one should consider, that only the orthorhombic structure type does *not* show chemical defects (see below).

#### HRTEM Investigations of Orthorhombic In<sub>5</sub>S<sub>5</sub>Cl

The crystal structure of the chemically homogeneous samples was examined by electron diffraction techniques. All analysed selected areas (about 50) show Bragg intensities, which can be indexed assuming the orthorhombic structure type. Particularly for zone axis [100], which correlates with the [010] orientation of the monoclinic structure, exactly rectangular patterns were recorded. This contrasts to monoclinic In<sub>5</sub>S<sub>5</sub>Cl, which exhibits significant deviations from rectangularity and orthorhombic symmetry. Diffuse scattering, particularly diffuse streaks 00l indicating lamellar intergrowth phenomena, was not observed. Strongly excited but kinematically forbidden reflections directed our attention to structural deviations from the orthorhombic model with space group  $Pmn2_1$ . A careful comparison of different electron diffraction techniques led to the conclusion that such violations (which are not observed in the X-ray experiments) are produced by multiple scattering effects. The intensity of the kinematically forbidden reflections is strongly minimised when the crystal was tilted from the precise zone axis orientation or when precession electron diffraction was applied. In this case, an average of many tilted patterns is recovered by moving the electron beam on a precession cone [15]. One example is presented in Figure 3 for a thick crystal along [110]. The serial reflection condition (00l with l = 2n) is strongly violated in the SAED pattern, which was performed with a fixed electron beam (a), cf. arrows. These intensities are strongly reduced when switching to the precession mode (c). Moreover, the expected differences in reflection intensity are more pronounced in the PED pattern and approximate well the simulated pattern of b).



**Figure 3.** a) SAED pattern, b) simulated PED pattern (precession angle 3°, thickness: 20 nm), c) PED pattern. All zone axis [110].

The absence of stripes in brightfield contrast, the HRTEM micrographs and the corresponding Fourier transforms proof that lamellar structures based on chemical or polymorphic intergrowth and twinning as described for the sample annealed at 550 °C [10] were limited to exceptional cases. The single layers are imaged edge-on in all zone axes orientations [uv0], e.g. [100]. As specified above, only one type of layer is present for the orthorhombic structure type and adjacent layers appear shifted and inversed when projected along [100]. Consequently, the characteristic contrasts representing the layers are shifted and inversed as well cf. Figure 4. The cut-out in a) left shows the contrast simulation for a single layer ( $\Delta f = -40$  nm) based on the model from X-ray analysis. On the right four of these cut-outs are combined by applying a shift and an inversion like for the consecutive layers in the orthorhombic structure. The experimental micrograph (Figure 4b) clearly shows the arrangement of the layers and the good correlation to the inserted simulation proofs the 3,3-arrangement of the single layers. A convincing agreement of simulated and experimental micrographs is also found when varying the focus, e.g. when selecting strong underfocus conditions, cf. Figure 4 c.

## **Experimental Section**

#### Synthesis

The synthesis of the polymorphs of  $In_5S_5Cl$  was carried out from sulfur (Chempur, pieces, 99,999 %), indium (Chempur, shots, 99,9999 %) and  $InCl_3$  (Heraeus, powder, 99,999 %) in stoichiometric amounts (ratio 14:15:1) or from the powdered binary starting materials InS (prereacted from In and S),  $In_2S_3$  (Alfa, powder, 99,999 %) and InCl<sub>3</sub> in the ratio 2:1:1. The respective starting materials were weighed in an argon



**Figure 4.** a) Cut-out of a simulated micrograph based on orthorhombic In<sub>5</sub>S<sub>5</sub>Cl and composite image, see text; b) and c) experimental micrographs and inserted simulations with  $\Delta f = -40$  nm and  $\Delta f = -85$  nm, respectively (t = 3.9 nm). All zone axis [100], the images of a) were scaled by 300 % with respect to b) and c).

filled glove box and transferred into evacuated dry quartz glass ampoules (d = 12 mm, l = 60-80 mm). The samples were heated to the final temperature and annealed for several days or weeks.

For temperatures above 723 K, fine needle-shaped crystals of monoclinic  $In_5S_5Cl$  were observed. The crystals were dark red and not markedly air sensitive. For temperatures between 573 K and 723 K, the resulting red brown powder consisted of microcrystalline orthorhombic  $In_5S_5Cl$ . Below an annealing temperature of 573 K, no  $In_5S_5Cl$  was formed. The annealing of a homogenised orthorhombic microcrystalline phase for one day at 723 K led to a partial transformation to the

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monoclinic phase. Simultaneously monoclinic and orthorhombic needle shaped crystals suitable for single crystal analyses were formed.

#### X-ray Powder Investigations

X-ray powder measurements were carried out on a SIEMENS D5000 diffractometer (transmission mode) with Ge-monochromatised Cu- $K_{\alpha 1}$ radiation. To verify the lattice constants of the two modifications of In<sub>5</sub>S<sub>5</sub>Cl, X-ray powder diagrams were measured with an internal standard (silicon).

## X-ray Single Crystal Investigation

For X-ray structure determination of orthorhombic In<sub>5</sub>S<sub>5</sub>Cl, a needleshaped crystal with appropriate size was separated from the bulk, fixed with grease on top of a glass capillary and mounted on a STOE IPDS I imaging plate diffraction system using graphite monochromatised Mo- $K_{\alpha}$  radiation. Data analysis and evaluation were performed with the STOE IPDS program package [12]. The programs RECIPE [12] and SPACE [12] were used to analyse the reciprocal space. For structure solution SHELXS97 [16] was used. The structure was refined as an inversion twin using SHELXL97 [17].

A summary of crystal and experimental data as well as structure refinement details for orthorhombic In<sub>5</sub>S<sub>5</sub>Cl is reported in Table 2–Table 4. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-421050, the name of the author(s) and citation of the paper.

# Thermal Analysis

Differential thermal analysis was carried out with a LINSEIS L-62 instrument. Carefully ground samples (sealed in evacuated quartz glass capillaries) were heated to a final temperature of 1073 K with heating/ cooling rates of 5 K·min<sup>-1</sup>. Orthorhombic In<sub>5</sub>S<sub>5</sub>Cl shows two endothermic effects upon the heating cycle, one at 856 K, and a second broader one at 966 K. After heating up the sample to 860 K followed by rapid cooling (fast lifting of the DTA oven, estimated cooling rate 573 K·min<sup>-1</sup>), the resulting powder diagrams showed the presence of In<sub>6</sub>S<sub>7</sub> as a decomposition product and reflections of orthorhombic In<sub>5</sub>S<sub>5</sub>Cl.

## **HRTEM** Investigation

All specimens were placed on copper grids, which were fixed in a side entry, double tilt holder with the tilting limited to a maximum of  $\pm 25^{\circ}$ in two directions. High resolution transmission electron microscopy (HRTEM), precession electron diffraction (PED) and selected area electron diffraction (SAED) were performed with a Philips CM30ST (300 kV, LaB<sub>6</sub> cathode). The EMS program package [18] was applied for the simulation of HRTEM micrographs and electron diffraction patterns. EDX (energy dispersive X-ray spectroscopy) was performed in the scanning- and nanoprobe mode of CM30ST with a Si/Li-EDX detector (Noran, Vantage System).

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