

## Crystal Structure and Crystal Chemistry of a New Sulfide $\text{In}_{6.6}\text{Ca}_{3.1}\text{S}_{13}$ \*

G. CHAPUIS AND A. NIGGLI

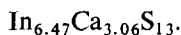
*Swiss Federal Institute of Technology, Department of Crystallography and Petrography, Zürich, Switzerland.*

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The compound  $\text{In}_{6.6}\text{Ca}_{3.1}\text{S}_{13}$  has been obtained by chemical transport reactions with iodine in the gas phase. The quantitative composition of  $\text{In}_{6.6}\text{Ca}_{3.1}\text{S}_{13}$  was determined by the electron microprobe method and confirmed by the structure analysis. This new phase is not similar to the compound  $\text{In}_2\text{CaS}_4$  as described by Hahn and Klingler (1). Its space group is  $C2/m$ ; the lattice parameters are  $a = 37.6$ ,  $b = 3.84$ ,  $c = 13.7$  Å and  $\beta = 91.65^\circ$ . There are four formula units in the cell. The structure consists of a sulfur framework forming cubic close packing only in certain domains. All In atoms occupy octahedral voids, whereas Ca atoms are surrounded by nine S atoms. The refinement of the structure showed that two In positions are partially substituted by Ca and that one of the Ca positions is only partially occupied.

### Introduction

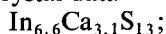
The compound  $\text{In}_{6.6}\text{Ca}_{3.1}\text{S}_{13}$  which was synthesized by R. Nitsche (2) has yellow needle-like crystals with a diameter of about .001 mm. The quantitative electron microprobe analysis (ARL-EMX) gave the following composition (within an error of 2% and with 1S3 atoms in the asymmetric unit, as shown later by the structure analysis):



A compound of similar composition has been synthesized earlier by Hahn and Klingler (1) with the stoichiometric formula  $\text{In}_2\text{CaS}_4$ . From a powder diffractogram, they postulated a normal spinel structure with the parameter  $a = 10.77$  Å. On the other hand, Flahaut et al. (3) observed the existence of a partial solid solution in the system  $\text{In}_2\text{S}_3$ - $\text{In}_2\text{CaS}_4$ . However, it is surprising to find in these structures the Ca atoms in tetrahedral voids, though Hahn and Klingler rejected the hypothesis of an inverse spinel structure where the Ca atoms, larger than In atoms, would occupy octahedral voids.

### Experimental

#### Crystal data



Formula weight = 1298.9;

habit: long prismatic  $b$ ;

\* This work is a part of the Ph.D. thesis of G. Chapuis.

$a = 37.630(10)$ ,  $b = 3.8358(9)$ ,  
 $c = 13.7129(29)$ ,  $\beta = 91.65^\circ(1)$ ,  
 $V = 1979.5(1.4)$  Å<sup>3</sup>;  $Z = 4$ ,  $D_x = 4.34$ ;  
 $\lambda_{\text{CuK}\alpha} = 1.54178$  Å;  
 Systematic absences:  $(hkl) h + k = 2n$ ;  
 Space group  $C2/m$ ;  
 $\mu = 789$  cm<sup>-1</sup>;  
 Crystal size.  $.090 \times .015 \times .005$  mm.

The intensities of  $\text{In}_{6.6}\text{Ca}_{3.1}\text{S}_{13}$  have been measured on a four-circle Picker automatic X-ray diffractometer. All reflexions within the values of  $2\theta = 1.5^\circ$  and  $100^\circ$  have been obtained by the  $\theta$ - $2\theta$  scan method (scan length:  $2\theta = 1.80^\circ$  and corrected for higher values of  $2\theta$ ). The background has been measured on both sides of each reflection. A total of 4325 observations have been measured by a scintillation counter (.0025 mm Ni-filter in the reflected beam). After data reduction (Lorentz and polarization factors, no absorption correction), 1191 independent reflections resulted, 220 of which having an intensity  $< 3\sigma(I)$ . To each reflection the weight  $w(F) = 1/\sigma^2(F) = (2F/\sigma_c)^2$  has been assigned, where  $\sigma_c$  = standard deviation of the observation (Poisson).

### Structure Solution and Refinement

During the process of structure solution, the different programs of the X-ray system (4) have been used. The Wilson plot of normalized

structure factors  $E$  indicated centrosymmetry. With 108  $E$  values  $>1.5$  the structure has been solved by direct methods. The  $E$  map revealed all the In positions whereas the Ca and S positions appeared in a second Fourier map. A least-squares refinement with isotropic temperature factors has been applied by minimizing the function  $\sum w||F_o|-|F_c||^2$  with a block diagonal matrix, each block containing all the parameters of the same atom and one block for the scale factor. For the In, Ca and S atoms, the atomic scattering factors given by Cromer and Mann (5) have been used. At this stage of refinement, a difference Fourier synthesis called for the introduction of population parameters for two In [In(6) and In(8)] and one Ca [Ca(1)] positions. Considering the volume of the coordination polyhedra around the In atoms, a partial substitution of the two In positions by Ca had to be postulated. This is due to the fact that the Ca atoms partly occupy the nearest In(6) and In(8) positions as well (Fig.1 and 2). A further refine-

ment with the population parameters and anisotropic temperature factors calculated with

$$q(h_1, h_2, h_3) = \exp[-2\pi^2 \cdot \sum_{i,j} U^{ij} h_i h_j a_i^* a_j^*],$$

gave a final  $R = \sum ||F_o|-|F_c|| / \sum |F_o| = 0.051$ . With the values of the population parameters the formula In<sub>6.59</sub>Ca<sub>3.10</sub>S<sub>13</sub> was obtained, in agreement with the microprobe analysis, within an error of 2%.

## Results

Table I shows the final fractional coordinates and thermal parameters. Because every atom occupies the special equipoints  $i$  ( $xoz, \dots$ ), the  $y$  coordinate is omitted. All the values of  $U^{22}$  are too large: the model tries to compensate the absorption effect in the direction  $b$  of the prism by increasing the thermal vibrations of the atoms in this direction, without influencing the positional parameters.

TABLE I  
FRACTIONAL COORDINATE;  $x, z$  ( $y = o$ ) AND ANISOTROPIC THERMAL COEFFICIENTS  
 $\exp[-2\pi^2 \cdot \sum_{i,j} U^{ij} h_i h_j a_i^* a_j^*]$ .

	$x$	$z$	$U^{11}$	$U^{22}$	$U^{33}$	$U^{13}$
In(1)	0	0	.0048(20)	.0175(19)	.0056(18)	-.0009(14)
In(2)	0	.5000	.0009(20)	.0236(21)	.0140(20)	.0008(15)
In(3)	.1066(1)	.9701(3)	.0092(14)	.0221(15)	.0053(13)	-.0062(10)
In(4)	.2670(1)	.4365(3)	.0034(14)	.0210(15)	.0092(13)	.0026(9)
In(5)	.4126(1)	.5034(3)	.0021(14)	.0213(14)	.0081(13)	-.0001(9)
In(6)	.2470(2)	.6311(4)	.0072(20)	.0237(20)	.0110(19)	-.0033(15)
In(7)	.2821(1)	.0868(3)	.0055(14)	.0268(15)	.0134(14)	-.0007(10)
In(8)	.4588(1)	.2067(4)	.0042(17)	.0195(16)	.0085(15)	-.0008(12)
Ca(1)	.3520(5)	.2693(13)	.0081(38)	.0379(23)	.0044(25)	-.0023(20)
Ca(2)	.4331(4)	.7742(10)	.0054(22)	.0191(21)	.0181(21)	-.0045(16)
Ca(3)	.3293(3)	.8390(10)	.0059(22)	.0249(23)	.0165(20)	-.0013(15)
S(1)	.1263(4)	.5803(11)	.0073(52)	.0054(45)	.0026(45)	-.0025(36)
S(2)	.2105(4)	.3003(12)	.0003(49)	.0201(52)	.0104(40)	.0006(36)
S(3)	.3674(4)	.6429(12)	.0048(52)	.0198(51)	.0067(48)	-.0008(37)
S(4)	.4673(5)	.3975(12)	.0050(45)	.0180(48)	.0036(37)	.0035(30)
S(5)	.2903(5)	.4655(13)	.0072(58)	.0235(55)	.0270(63)	-.0128(43)
S(6)	.2063(5)	.7840(12)	.0077(55)	.0238(55)	.0056(50)	.0010(39)
S(7)	.3505(5)	.0549(13)	.0033(53)	.0153(51)	.0174(50)	.0011(38)
S(8)	.1135(4)	.1494(12)	.0048(59)	.0120(50)	.0015(47)	-.0023(39)
S(9)	.0883(5)	.7920(12)	.0005(52)	.0239(52)	.0239(54)	.0012(36)
S(10)	.0545(4)	.3940(12)	.0004(58)	.0115(61)	.0043(41)	.0000(37)
S(11)	.0075(5)	.1824(12)	.0044(56)	.0062(48)	.0023(36)	-.0012(36)
S(12)	.4509(4)	.0111(12)	.0022(50)	.0163(50)	.0089(51)	-.0005(36)
S(13)	.2165(5)	.0547(12)	.0003(51)	.0200(53)	.0070(47)	-.0009(36)

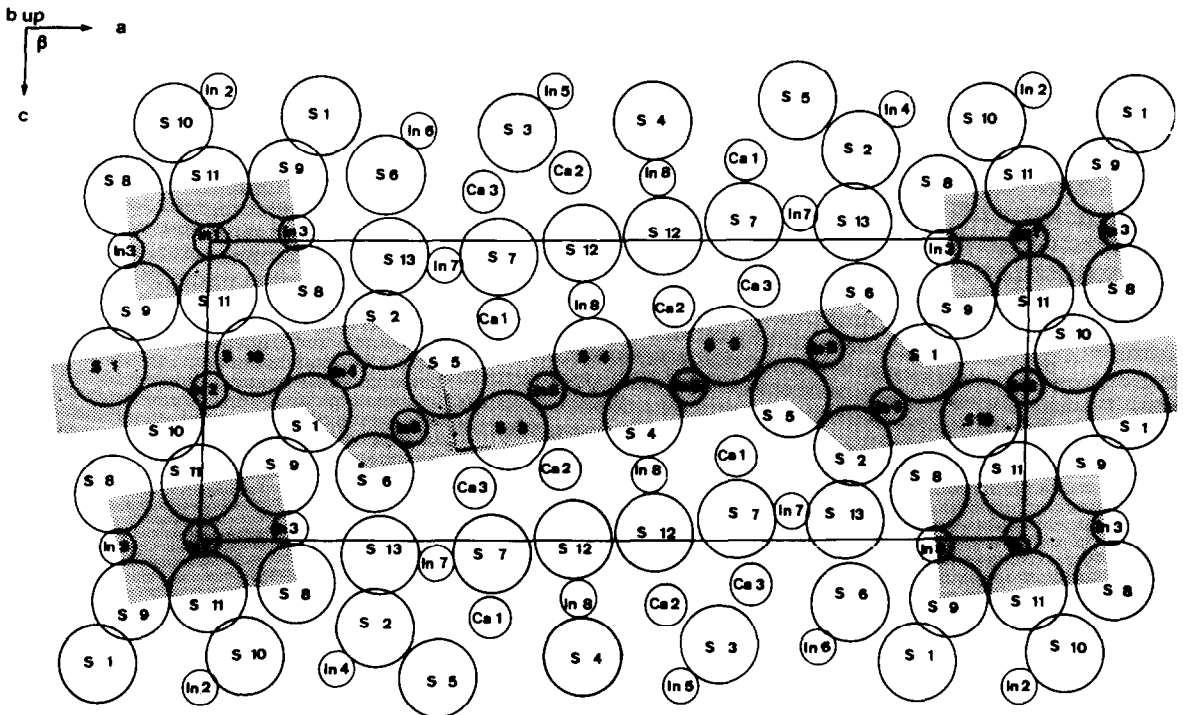


FIG. 1. Layer  $y = 0$  of the structure. The domains with sulfur close packing are shaded and the limits have arbitrarily been laid through the centers of S atoms. The prismatic domains in  $(0y0)$  are symmetrically repeated in  $(\frac{1}{2}y0)$ .

The structure may be described by considering the sulfur packing. As shown in Fig. 1, three different domains exist, two of which are cubic close packings of sulfur atoms differently orientated and shaded in Fig. 1. (The ccp. notion is to be understood in the architectural sense; in fact, the physical sulfur density in the nonshaded domain is even slightly higher.) All In atoms are found in the octahedral voids of the three domains. Table III gives the interatomic distances In-S. On the other hand, Ca atoms are located in the third domain in the center of a trigonal prism formed by S atoms;

in the plane of the Ca, perpendicular to the prism axis, there is another group of three S resulting in a 9-coordination of Ca atoms (Fig. 2). However one of the Ca-S distances is significantly longer than the others (Table II).

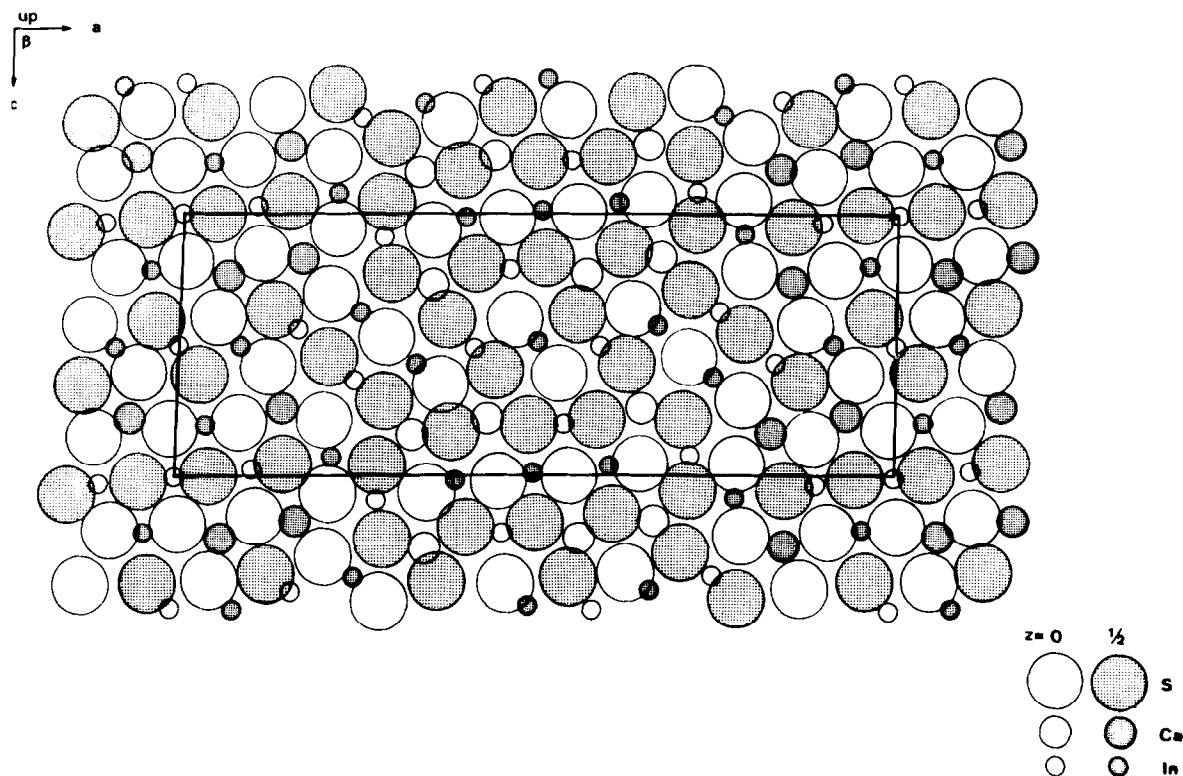
### Discussion

The chemical composition looks rather unusual taking into account the obvious primary assumption of 1S2 per asymmetric unit, corresponding to a close packing. A thirteenth S atom which showed up in Fourier maps was confirmed

TABLE II  
INTERATOMIC DISTANCES Ca-S (Å)<sup>a</sup>

	Prism			Coplanar distances		
Ca(1)	[1] 2.925(12)	[6] 2.985(12)	[9] 3.091(13)	[7] 2.934(16)	[5] 3.598(17)	[4] 4.643(18)
Ca(2)	[8] 2.826(12)	[10] 3.037(13)	[11] 2.999(13)	[3] 3.001(17)	[12] 3.300(16)	[4] 4.467(17)
Ca(3)	[2] 3.064(13)	[8] 2.877(12)	[13] 2.980(13)	[3] 3.100(16)	[7] 3.037(16)	[6] 4.663(17)

<sup>a</sup> The numbers given in brackets characterize the S atoms.

FIG. 2. Projection of the structure along the *b* axis.

clearly by a difference synthesis. In order to maintain the electroneutrality of the system, some sites of electropositive elements have to be (statistically) unoccupied.

The kind of coordination around Ca atoms is not new. Some authors (6–9) have described different oxides with the same Ca coordination though the S and O packings in these structures

are different. Table IV gives a synopsis of these compounds. In order to compare oxides and sulfides, the mean values of the distances of the cations to the nine chalcogenides has been normalized to 1. If the distances Ca–O and Ca–S for eight atoms of the coordination polyhedron (6 on the vertices of the trigonal prism and 2 in the coplanar triangle) are similar, this is not the

TABLE III  
INTERATOMIC DISTANCES In–S (Å)<sup>a</sup>

In(1)	[11] 2.507(13)	[11] 2.507(13)	[12] 2.670(9)	[12] 2.670(9)	[12] 2.670(9)	[12] 2.670(9)
In(2)	[4] 2.660(8)	[4] 2.660(8)	[4] 2.660(8)	[4] 2.660(8)	[10] 2.552(13)	[10] 2.552(13)
In(3)	[7] 2.538(9)	[7] 2.538(9)	[8] 2.467(13)	[9] 2.521(3)	[12] 2.910(10)	[12] 2.910(10)
In(4)	[1] 2.540(10)	[2] 2.507(13)	[3] 2.546(9)	[3] 2.546(9)	[5] 2.820(10)	[5] 2.820(10)
In(5)	[1] 2.649(9)	[1] 2.649(9)	[3] 2.583(13)	[4] 2.542(13)	[10] 2.664(9)	[10] 2.664(9)
In(6)	[2] 2.654(10)	[2] 2.654(10)	[5] 2.701(10)	[5] 2.842(13)	[5] 2.701(10)	[6] 2.633(13)
In(7)	[6] 2.635(8)	[6] 2.635(8)	[7] 2.616(14)	[13] 2.731(9)	[13] 2.501(14)	[13] 2.731(9)
In(8)	[4] 2.629(13)	[9] 2.610(9)	[9] 2.610(9)	[11] 2.681(10)	[11] 2.681(10)	[12] 2.699(13)

<sup>a</sup> The last three columns gives the distances in the plane of the Ca atoms perpendicular to the trigonal prism axis. The numbers given in brackets characterize the S atoms.

TABLE IV

Ca-S AND Ca-O DISTANCES FOR DIFFERENT CHALCOGENIDES. THE MEAN DISTANCE FOR EACH COORDINATION FIGURE HAS BEEN NORMALIZED TO 1

Structures	Prism		Coplanar triangle			
$\text{In}_{6.6}\text{Ca}_{3.1}\text{S}_{13}$	90	.92	.95	.90	1.11	1.43
	89	.94	.95	.94	1.03	1.40
$\text{V}_2\text{CaO}_4(7)$	90	.94	.96	.95	.97	1.46
$\text{Ti}_2\text{CaO}_4(7)$	.93	.96	1.02	.96	1.02	1.25
$\text{Ti}_2\text{CaO}_4(6)$	.90	.96	.96	1.07	1.07	1.23
$\text{Fe}_2\text{CaO}_4(8)$	.90	.95	.97	.99	1.01	1.37
$\text{Sc}_2\text{CaO}_4(9)$	93	.93	.95	.99	1.01	1.37

case for the ninth distance. This phenomenon is particularly important in the sulfide structure of  $\text{In}_{6.6}\text{Ca}_{3.1}\text{S}_{13}$ .

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