

ment SO_3 est relié à trois octaèdres MnO_6 . Alors que chaque cation Mn^{2+} est environné par trois atomes d'oxygène de trois groupements SO_3 différents et trois atomes d'oxygène de trois molécules d'eau différentes, pour $\text{CoPO}_3 \cdot 3\text{H}_2\text{O}$ l'environnement des deux types d'ions Co^{2+} est assuré soit par deux atomes d'oxygène et quatre molécules d'eau pour $\text{Co}(1)$, soit par quatre atomes d'oxygène et deux molécules d'eau pour $\text{Co}(2)$. Notons cependant que la géométrie de ces deux octaèdres de cobalt est tout à fait équivalente.

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Acta Cryst. (1987). C43, 613–616

Ca_8In_3 , a Structure Related to the BiF_3 Type

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(Received 14 July 1986; accepted 3 November 1986)

Abstract. $M_r = 665.1$, triclinic, $aP22$, $P1$, $a = 9.606$ (2), $b = 9.717$ (2), $c = 9.782$ (2) Å, $\alpha = 69.65$ (2), $\beta = 78.85$ (2), $\gamma = 60.34$ (1)°, $V = 743.7$ (3) Å³, $Z = 2$, $D_x = 2.97$ Mg m⁻³, $\text{Mo K}\alpha$, $\lambda = 0.7107$ Å, $\mu = 7.13$ mm⁻¹, $F(000) = 614$, room temperature, $R = 0.027$ for 2789 reflections with $F_o > 3\sigma(F_o)$. The Ca_8In_3 structure is derived by distortion of the face-centered cubic BiF_3 type (also called AlFe_3 or BiLi_3 type). It can be described as a three-layered structure along the a axis, the atoms being located at $x \simeq 0$, $x \simeq \frac{1}{3}$ and $x \simeq \frac{2}{3}$. Three different coordination polyhedra are found around the In atoms: distorted cubicosahedra (ten-vertex polyhedra) for In(1), In(2), In(4) and In(6), cubes for In(3) and icosahedra for In(5). Distorted cubicosahedra centered by In at $x \simeq 0$ and $x \simeq \frac{1}{3}$ are alternately joined by an edge and by a face and form parallel rows; cubes and icosahedra centered by In at $x \simeq \frac{2}{3}$ are joined by an edge and also form parallel rows.

Introduction. In the Ca–In system (Bruzzzone & Ruggiero, 1964) three phases exist, all with congruent melting points: CaIn_2 (CaIn_2 type), CaIn (CsCl type) and Ca_3In . The powder pattern of this last phase was indexed on the basis of a face-centered cubic cell with $a = 7.860$ Å, but the possible isotypism with the BiF_3 type, having a similar symmetry and lattice constant, was considered as dubious by the authors, owing to the

poor agreement between observed and calculated intensities.

The structure determination of this phase, the composition of which was found to be Ca_8In_3 , is the aim of the present work, and forms part of a systematic study on the crystal chemistry of compounds formed by the alkaline earths with Group IIIb elements.

Experimental. Sample of nominal composition Ca_3In prepared from Ca (99.9 wt%, Fluka, Switzerland) and In (99.999 wt%, Koch-Light, England) by melting in sealed Fe crucible and slowly cooling. Polyhedral single crystal $0.04 \times 0.08 \times 0.13$ mm, Enraf–Nonius CAD-4 automatic diffractometer with graphite monochromator, ω – θ scan mode; lattice constants determined by least squares over 25 diffractometer-measured reflections in the range $25 < \theta < 27.5^\circ$; semiempirical absorption correction by azimuthal scan data of five top reflections, ratio between max. and min. transmission factors 1.84; max. value of $(\sin\theta)/\lambda$ 0.65 Å⁻¹, with $-12 \leq h, k, l \leq 12$; intensity variation of the check reflections 0.5%; 6808 measured reflections, 3404 independent with $R_{\text{int}} = 0.019$, 615 unobserved with $F_o < 3\sigma(F_o)$, 2789 used in the refinement. Structure model given by direct methods refined only to an R value of 0.33 in $P\bar{1}$; structure resolution in $P1$ by direct methods and difference Fourier synthesis; definition of origin by fixing the atomic coordinates of In(1) at 0,0,0.

Anisotropic refinement to 197 parameters based on F^2 's, $R = 0.027$, $wR = 0.048$, $S = 0.36$, $w = 1/[\sigma^2(F_o) + 0.01008F_o^2]$, max. shift to e.s.d. 0.6, max. and min. heights in final difference Fourier synthesis 1.1 and $-0.9 \text{ e } \text{Å}^{-3}$; empirical secondary-extinction correction based on $F_c' = F_c(1 - 0.0016 \times 10^{-4} F_c^2/\sin\theta)$. Since changing the sign of the positional parameters gave no improvement in the final R value, the original configuration was retained. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); programs used: *MULTAN80* (Main *et al.*, 1980) and *SHELX76* (Sheldrick, 1976).

Atomic coordinates and thermal parameters are given in Table 1;* interatomic distances involving the In atoms are given in Table 2.

Discussion. The structure of Ca₈In₃ can be derived by distortion of the face-centered cubic BiF₃ type (also called AlFe₃ or BiLi₃ type) reported by Villars & Calvert (1985). The In atoms are practically in the Bi positions, while the Ca atoms are more or less displaced from the positions occupied by F. The displacement allows a smaller number of Ca atoms to be arranged in the lattice giving rise to a different stoichiometry. The indices of nearly all of the strongest reflections can be transformed to indices of a hypothetical face-centered cubic cell with lattice constant $a \simeq 7.9 \text{ Å}$ and volume equal to two-thirds of the volume of the triclinic cell, using, for example, the transformation matrix:

$$\begin{pmatrix} -\frac{2}{3} & -\frac{1}{6} & \frac{1}{2} \\ \frac{2}{3} & -\frac{5}{6} & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{pmatrix}$$

Thus, the planes (21 $\bar{1}$), (1 $\bar{1}$ 1) and (122) which are almost perfectly perpendicular with a mean interplanar spacing of 3.95 Å correspond to the (200) planes of the hypothetical cubic cell. This hypothetical cubic cell is the same as reported by Bruzzone & Ruggiero (1964).

The structure of Ca₈In₃ is built up of three layers stacked in the *a* direction, the atoms being located at $x \simeq 0$, $x \simeq \frac{1}{3}$ and $x \simeq \frac{2}{3}$. A better description is obtained in terms of coordination polyhedra of the In atoms, the vertices of which are occupied only by Ca atoms.

Around In(1), In(2), In(4) and In(6) a ten-vertex polyhedron is found which can be considered a distorted cubicosahedron, with a greater distortion for In(1) and In(4). This polyhedron, consisting of one half of a cube and one half of an icosahedron in the more regular shape, has two symmetry planes and two

rectangular faces. It is present in numerous intermetallic compounds, for example, in MnAl₆ around Mn, in WAl₄ around one of the two W positions, and in W₅Si₃ around one of the two Si atoms, as pointed out by Kripyakevich (1977). In the literature different names have been proposed for this polyhedron by authors who recognized its presence in ionic, metallorganic or intermetallic compounds ['bicapped dodecahedron' by Bandurkin & Dzhurinskii (1973), 'decatetrahedron' by Robertson (1977), 'cubicosahedron' by Bruzzone & Merlo (1982)]. Lacking an unequivocal denomination, we prefer to use the term 'cubicosahedron' to emphasize its particular shape. However, this polyhedron can become more or less distorted, such that the rectangular faces are no longer planar, and in this case it represents the final result of a progressive transformation of a tricapped trigonal prism when the central atom approaches a lateral face which is now capped by two atoms instead of one. Moreover, the triangular bases of the prism can often no longer be parallel. The cubicosahedron in both regular and distorted forms is also found in several binary intermetallic phases formed by Ga (Fornasini & Pani, 1986).

As can be seen in Fig. 1, the distorted cubicosahedra, centered at $x \simeq 0$ by In(1) and In(6) and alternately joined by an edge and by a face, form unconnected rows parallel to [01 $\bar{1}$]. The same situation is found for the polyhedra centered at $x \simeq \frac{1}{3}$ by In(4) and In(2), which are very similar to those of In(1) and In(6) respectively and form analogous rows (Fig. 2). At $x \simeq \frac{2}{3}$ a nearly perfect cube surrounds the In(3) atom, the only atom maintaining the same coordination as Bi in the BiF₃ type. The other atom, In(5), is surrounded by an icosahedron with two Ca atoms further away. The In—Ca distances involving In(3) are on average the shortest ones, whilst those involving In(5) are the longest ones. These cubes and icosahedra joined by an edge alternate giving unconnected rows along the [01 $\bar{1}$] direction, as shown in Fig. 3. Interestingly enough, similar rows of cubes and icosahedra centered by Ga atoms are found also in the structure of the phase Ho₆Co₂Ga reported by Parthé & Chabot (1984).

As the Ca—Ca distances are spread over a large range (3.47–4.39 Å), the calcium environments are somewhat irregular. The atoms from Ca(1) to Ca(10) have four In neighbors forming a nearly regular tetrahedron and nine Ca neighbors, with three kinds of polyhedra: one around Ca(1) and Ca(8), another around Ca(2), Ca(5), Ca(6), Ca(7), Ca(9) and Ca(10), and another around Ca(3) and Ca(4). The Ca(11), Ca(12), Ca(15) and Ca(16) atoms are surrounded by three In and ten Ca atoms with two types of coordination, one for Ca(11) and Ca(15), and the other for Ca(12) and Ca(16). Finally, Ca(13) and Ca(14) are coordinated to four In and eleven Ca atoms.

As already observed for the compound Ca₂₈Ga₁₁ (Fornasini & Pani, 1986), the more electronegative

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43571 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atoms in Ca_8In_3 present several different coordinations, a fact which seems responsible for the complexity of the structure and the low symmetry, very unusual for an intermetallic phase.

Table 1. Atomic coordinates and thermal parameters for Ca_8In_3

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j, \text{ E.s.d.'s are given in parentheses.}$$

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{eq}}(\text{\AA}^2)$ |
|--------|------------|------------|------------|-------------------------------|
| Ca(1) | 0.0151 (6) | 0.8888 (7) | 0.3915 (5) | 0.018 (2) |
| Ca(2) | 0.9629 (6) | 0.1614 (6) | 0.6090 (5) | 0.017 (2) |
| Ca(3) | 0.9947 (6) | 0.3612 (7) | 0.8507 (5) | 0.017 (2) |
| Ca(4) | 0.3348 (7) | 0.9586 (6) | 0.1515 (5) | 0.019 (2) |
| Ca(5) | 0.6445 (6) | 0.0636 (7) | 0.8521 (5) | 0.020 (2) |
| Ca(6) | 0.3650 (7) | 0.1621 (7) | 0.3890 (5) | 0.021 (2) |
| Ca(7) | 0.7090 (7) | 0.7810 (7) | 0.6119 (6) | 0.021 (2) |
| Ca(8) | 0.3161 (6) | 0.4317 (7) | 0.6067 (5) | 0.018 (2) |
| Ca(9) | 0.6210 (6) | 0.5374 (7) | 0.3924 (5) | 0.017 (2) |
| Ca(10) | 0.6877 (7) | 0.2602 (7) | 0.1477 (5) | 0.018 (2) |
| Ca(11) | 0.9968 (6) | 0.3706 (6) | 0.2028 (5) | 0.024 (2) |
| Ca(12) | 0.5455 (7) | 0.5062 (7) | 0.7997 (6) | 0.027 (2) |
| Ca(13) | 0.0602 (6) | 0.7246 (6) | 0.8309 (6) | 0.019 (2) |
| Ca(14) | 0.2670 (6) | 0.6030 (7) | 0.1708 (6) | 0.026 (2) |
| Ca(15) | 0.3307 (6) | 0.9498 (7) | 0.7986 (6) | 0.027 (2) |
| Ca(16) | 0.7882 (7) | 0.8127 (7) | 0.2004 (6) | 0.024 (2) |
| In(1) | 0.0† | 0.0† | 0.0† | 0.0155 (5) |
| In(2) | 0.3287 (2) | 0.8214 (2) | 0.5293 (3) | 0.0171 (7) |
| In(3) | 0.6645 (3) | 0.1638 (3) | 0.4980 (3) | 0.0154 (3) |
| In(4) | 0.3299 (1) | 0.3243 (1) | 0.0003 (1) | 0.0173 (6) |
| In(5) | 0.6691 (3) | 0.6614 (3) | 0.9990 (3) | 0.0170 (3) |
| In(6) | 0.0005 (2) | 0.5019 (2) | 0.4750 (2) | 0.0147 (7) |

† Arbitrarily fixed.

Table 2. Interatomic distances (\AA) in Ca_8In_3 involving the In atoms up to 4.6 \AA .

E.s.d.'s are less than 0.01 \AA .

| | | | |
|--------------|------|--------------|------|
| In(1)–Ca(3) | 3.28 | In(2)–Ca(1) | 3.21 |
| –Ca(10) | 3.29 | –Ca(9) | 3.28 |
| –Ca(15) | 3.30 | –Ca(6) | 3.28 |
| –Ca(16) | 3.31 | –Ca(15) | 3.29 |
| –Ca(13) | 3.38 | –Ca(12) | 3.30 |
| –Ca(14) | 3.41 | –Ca(4) | 3.46 |
| –Ca(4) | 3.58 | –Ca(2) | 3.62 |
| –Ca(2) | 3.61 | –Ca(8) | 3.65 |
| –Ca(1) | 3.61 | –Ca(7) | 3.69 |
| –Ca(5) | 3.65 | –Ca(13) | 3.71 |
| In(3)–Ca(10) | 3.22 | In(4)–Ca(12) | 3.30 |
| –Ca(9) | 3.24 | –Ca(5) | 3.31 |
| –Ca(2) | 3.24 | –Ca(4) | 3.32 |
| –Ca(5) | 3.25 | –Ca(11) | 3.33 |
| –Ca(6) | 3.26 | –Ca(14) | 3.41 |
| –Ca(7) | 3.31 | –Ca(13) | 3.43 |
| –Ca(8) | 3.32 | –Ca(6) | 3.59 |
| –Ca(1) | 3.35 | –Ca(3) | 3.60 |
| In(5)–Ca(11) | 3.40 | –Ca(8) | 3.63 |
| –Ca(15) | 3.45 | –Ca(10) | 3.67 |
| –Ca(16) | 3.45 | In(6)–Ca(8) | 3.19 |
| –Ca(12) | 3.49 | –Ca(7) | 3.25 |
| –Ca(3) | 3.54 | –Ca(2) | 3.28 |
| –Ca(7) | 3.56 | –Ca(16) | 3.30 |
| –Ca(5) | 3.56 | –Ca(11) | 3.34 |
| –Ca(10) | 3.58 | –Ca(3) | 3.45 |
| –Ca(4) | 3.58 | –Ca(1) | 3.63 |
| –Ca(9) | 3.62 | –Ca(6) | 3.64 |
| –Ca(13) | 4.05 | –Ca(9) | 3.71 |
| –Ca(14) | 4.13 | –Ca(14) | 3.73 |

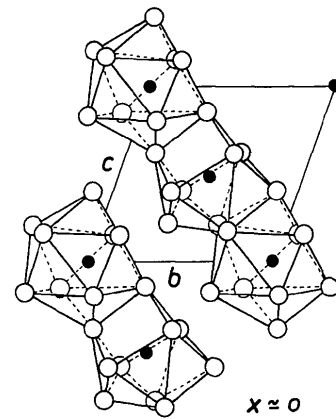


Fig. 1. Coordination polyhedra (distorted cubicosahedra) around In(1) and In(6). The atoms are projected on the (100) plane and the unit-cell contour is drawn at $x = 0$.

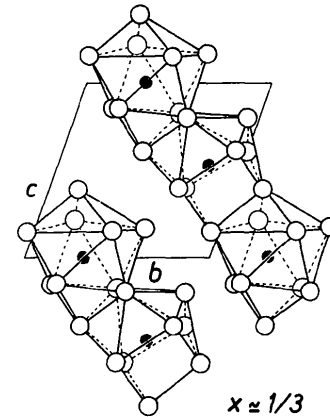


Fig. 2. Coordination polyhedra (distorted cubicosahedra) around In(2) and In(4). The atoms are projected on the (100) plane and the unit-cell contour is drawn at $x = \frac{1}{3}$.

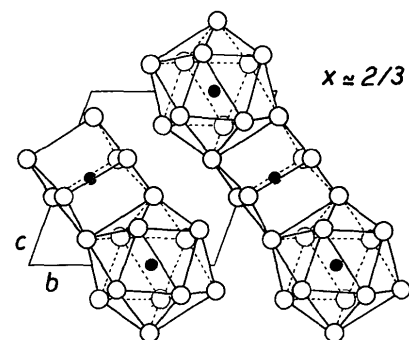


Fig. 3. Coordination polyhedra (cubes and icosahedra) around In(3) and In(5). The atoms are projected on the (100) plane and the unit-cell contour is drawn at $x = \frac{2}{3}$.

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Acta Cryst. (1987). **C43**, 616–618

Structure du Molybdophosphate d'Yttrium et Sodium Na₂Y(MoO₄)(PO₄)

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Abstract. $M_r = 389.79$, monoclinic, $C2/c$, $a = 13.928$ (11), $b = 18.016$ (10), $c = 6.847$ (6) Å, $\beta = 119.62$ (6)°, $V = 1494$ (4) Å³, $Z = 8$, $D_m = 3.44$ (5), $D_x = 3.467$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 9.75$ mm⁻¹, $F(000) = 1456$, $T = 293$ K, final $R = 0.041$ for 2158 independent reflexions with $I > 3\sigma(I)$. The three-dimensional framework is made up of chains of edge-sharing YO₈ polyhedra linked by isolated MoO₄ and PO₄ tetrahedra. This framework leaves voids in which the Na atoms are inserted. The Na atoms are sixfold coordinated if distances less than 3.0 Å are considered.

Introduction. Les luminophores à base de terres rares sont des matériaux soit stoechiométriques: NdP₅O₁₄ (Weber, Damen, Danielmeyer & Tofield, 1973) soit constitués d'un réseau-hôte dopé par des ions actifs tels que le YAG: Y₃Al₅O₁₂:Nd³⁺ (Danielmeyer, Blätte & Balmer, 1973).

La présence dans ces matériaux, de groupements tétraédriques isolés (phosphates, vanadates) peut être un facteur favorable à la réalisation de luminophores performants par exemple Na₃La(PO₄)₂:Ce,Tb (Parent, Fava, Salmon, Le Flem & Hagenmuller, 1980).

Dans le système Na₂MoO₄-YPO₄ nous avons mis en évidence une nouvelle phase Na₂Y(MoO₄)(PO₄) offrant un réseau-hôte aux ions actifs. La connaissance de la structure cristalline de cette phase est nécessaire à une étude ultérieure de ses propriétés luminescentes.

Des monocristaux ont été préparés par action d'un mélange stoechiométrique de (NH₄)₂HPO₄ et Y₂O₃ sur un excès de Na₂MoO₄ utilisé comme flux. Après un premier traitement de 15 h à 673 K, le mélange est porté dans un creuset de platine pendant 4 h à 1023 K puis refroidi jusqu'à la température ambiante à la vitesse de 10 K h⁻¹.

Partie expérimentale. Parallélépipède (0,07 × 0,13 × 0,26 mm). D_m par picnométrie, diffractomètre Philips PW 1100. Monochromateur: graphite. Paramètres cristallins affinés à partir de 25 réflexions ($17 < 2\theta < 25^\circ$). Domaine de mesure: 3–45° (θ), type de balayage: ω , domaine de balayage: (1,20 + 0,20 tan θ)°, vitesse de balayage: 0,03° s⁻¹. Trois réflexions de référence: $\bar{2}21$, 421 et $28\bar{2}$, variation négligeable. Nombre de réflexions mesurées: 4681 ($h - 24 \rightarrow 24$, $k - 35 \rightarrow 35$, $l 0 \rightarrow 11$). 2363 réflexions indépendantes, $R_{\text{int}} = 0,042$. Les intensités sont corrigées de Lorentz-polarisation et de l'absorption après indexation des faces, facteurs de transmission: 0,2226–0,6130. 205 réflexions ont été éliminées correspondant à $I < 3\sigma(I)$. La structure a été résolue en exploitant la fonction de Patterson et les synthèses de Fourier. L'affinement sur F (matrice complète), utilisant les facteurs thermiques anisotropes, a conduit à $R = 0,041$, $wR = 0,049$, $S = 5,417$. Un schéma de pondération unitaire a été utilisé. $(\Delta/\sigma)_{\text{max}} = 0,00$, $\Delta\rho_{\text{max}} = 1,37$ e Å⁻³. Facteurs de diffusion atomique et valeurs de