

Table 1. *X-ray Diffraction pattern of HgIn (−196°C)*

| <i>hkl</i> * | <i>hkl</i> † | <i>d</i> (Å) | | <i>I</i> | |
|--------------|--------------|--------------|-------|----------|-------|
| | | Obs. | Calc. | Obs. | Calc. |
| 111 | — | 4.375 | 4.386 | 3.4 | 6.4 |
| 100 | — | 3.090 | 3.011 | 2.4 | 7.8 |
| 110 | 100 | 2.804 | 2.799 | 298‡ | 100.0 |
| 211 | 110 | 2.243 | 2.253 | 54.2 | 54.2 |
| 222 | 111 | 2.176 | 2.193 | 14.0 | 16.8 |
| 221 | — | 2.006 | 2.004 | 3.0 | 3.0 |
| 110 | 110 | 1.786 | 1.786 | 25.6 | 26.7 |
| 210 | — | 1.656 | 1.654 | 2.4 | 3.0 |
| 322 | — | 1.599 | 1.606 | 3.3‡ | 1.4 |
| 111 | — | — | 1.536 | — | 1.2 |
| 200 | 111 | 1.505 | 1.505 | 17.0 | 15.4 |
| 333 | — | — | 1.462 | 1.2 | 1.0 |
| 332 | 211 | 1.448 | 1.452 | 11.4 | 13.7 |
| 220 | 200 | 1.400 | 1.399 | 20.0‡ | 12.1 |
| 321 | 210 | 1.384 | 1.385 | 20.0 | 23.4 |
| 311 | — | — | 1.333 | — | 0.8 |
| 433 | 221 | 1.201 | 1.211 | 5.7 | 7.7 |
| 331 | — | — | 1.194 | — | 0.6 |
| 210 | — | — | 1.164 | — | 1.0 |
| 211 | 210 | 1.150 | 1.151 | 14.0 | 13.4 |
| 432 | — | — | 1.131 | — | 1.0 |
| 422 | 220 | 1.124 | 1.127 | 5.7 | 6.3 |
| 443 | — | — | 1.116 | — | 0.5 |
| 310 | 211 | 1.099 | 1.101 | 14.2 | 12.0 |
| 444 | 222 | 1.098 | 1.096 | 5.1 | 6.0 |
| 320 | — | 1.070 | 1.068 | 6.0 | 8.8 |
| 211 | 211 | 1.031 | 1.031 | 4.0 | 5.3 |

* Rhombohedral, 2 atoms/cell (this work). Lines with $h+k+l$ odd are superstructure lines and cannot be indexed in terms of the rhombohedral cell with 1 atom/cell.

† Rhombohedral, 1 atom/cell (Mascarenhas, 1970).

‡ Intensity enhanced by texture.

(b) Texture effects common in quenched foils (Giessen, Morris & Grant, 1967) occur. After quenching, there was a strong (110) texture (closepacked planes); on annealing the foil at $\sim -40^\circ\text{C}$, there was a change to a pronounced (222) texture. Since unfortunately the textured (110) is also the plane of highest reflected intensity, the comparison of intensities for a quenched foil was carried out by matching $I(211)_{\text{obs}}$ and $I(211)_{\text{calc}}$.

As seen in Table 1, the superstructure lines cannot be indexed in terms of a smaller rhombohedral cell with 1 atom per cell and $a = 3.01_2 \text{ \AA}$, $\alpha = 72.7^\circ$. This cell corresponds to that of Mascarenhas (1970) who failed to observe these relatively weak lines. The correct rhombohedral cell is equivalent to a hexagonal cell with 6 atoms per cell and

$a = 3.57_2$, $c = 13.16_8$. The intensities of the order lines did not change appreciably over the temperature range -196°C to $> -56^\circ\text{C}$, which includes the temperature of -75°C (Mascarenhas, 1970). HgIn melts at -18°C .

The observed unit cell could alternately be of lower symmetry: $R3m$, with Hg in (a) $(x_1x_1x_1)$ with $x_1 \approx 0$ and In in $1(a)$: $(x_2x_2x_2)$ with $x_2 \approx 0.5$. Calculations with $x_2 < 0.5$ lead to progressively poorer intensity agreement for the weak lines; this confirms the high-symmetry structure assumed above.

The closest interatomic distances are:

$$d(\text{Hg-Hg}) = d(\text{In-In}) = 3.57_2 \text{ \AA}, \\ d(\text{Hg-In}) = 3.01_2 \text{ \AA}.$$

Thus, unlike (first nearest) neighbors in alternating layers are considerably closer than like (second-nearest) neighbors within each layer.

The structure of HgIn is a superstructure based on the $A10$ -Hg type in the same way in which the structure of CuPt is a superstructure based on the $A1$ -Cu type; both structures differ from the parent types by small changes of the rhombohedral angle occurring upon ordering on alternate close-packed planes. Crystal-chemically, phases of the $A1$, $A6$, or $A10$ types and their superstructures would be expected for Hg-In phases; the prevalence of the $A1$ type and its distortion variants in stable or metastable B metal alloys with ~ 2.3 to > 3 valence electrons per atom has been demonstrated (Giessen, 1969). Indeed, metastable Hg-In phases show further, complex distortions of the α -Hg type.

The authors acknowledge financial support by the Army Research Office, Durham, Contract 31-124-G1127.

References

- DUWEZ, P. (1966). *Prog. Solid State Chem.* **3**, 377.
 ELLIOT, R. P. (1965). *Constitution of Binary Alloys, First Supplement*, p. 531. New York: McGraw-Hill.
 GIESSEN, B. C. (1969). *Advanc. X-ray Analysis*, **12**, 23.
 GIESSEN, B. C., MORRIS, M. & GRANT, N. J. (1967). *Trans. Met. Soc. AIME*, **239**, 883.
 GIESSEN, B. C. & WILLENS, R. (1969). *Phase Diagrams*, Vol. III, Edited by A. M. ALPER, p. 103. New York: Academic Press.
 MASCARENHAS, Y. P. (1970). *J. Appl. Cryst.* **3**, 294.
 SMITHELLS, C. J. (1967). *Metals Reference Book*, 4th ed., Vol. 1, p. 205. New York: Plenum Press.

Acta Cryst. (1972). **B28**, 321

Lattice parameters and space groups of the acetates of IVb group elements. By B. KAMENAR and M. BRUVO, *Laboratory of General and Inorganic Chemistry, Faculty of Science, The University, P. O. Box 153, Zagreb, Yugoslavia*

(Received 9 June 1971)

Lattice parameters and space groups of the acetates of IVb group elements are recorded. Crystals of tin(IV) acetate are isostructural with lead(IV) acetate.

The crystals of silicon(IV) acetate, germanium(IV) acetate, tin(IV) acetate and lead(IV) acetate were prepared by the methods described in the literature of Brauer (1960). Since these acetates are very sensitive to moisture, the crystals

were sealed in capillary tubes in a dry-box under nitrogen. Crystal data as determined from oscillation and Weissenberg photographs are listed in Table 1. The densities were determined pycnometrically. The systematic absences of the

Table 1. *Crystal data*

| | <i>a</i> | <i>b</i> | <i>c</i> | β | Space group | <i>Z</i> | D_m^* (g.cm ⁻³) | D_x (g.cm ⁻³) |
|---------------------------------------|---------------|----------------|----------------|--------------|----------------------------------|----------|----------------------------------|--------------------------------|
| Si(OOCOCH ₃) ₄ | 7.42 ± 0.02 Å | — | 11.34 ± 0.02 Å | — | <i>P</i> 4 ₂ <i>c</i> | 2 | 1.40 | 1.34 |
| Ge(OOCOCH ₃) ₄ | 7.36 ± 0.02 | 15.45 ± 0.03 Å | 45.77 ± 0.05 | — | <i>Pna</i> 2 ₁ | 16 | 1.43 | 1.51 |
| Sn(OOCOCH ₃) ₄ | 12.93 ± 0.02 | 26.62 ± 0.04 | 7.86 ± 0.02 | 105.3 ± 0.2° | <i>P</i> 2 ₁ | 8 | 1.77 | 1.80 |
| Pb(OOCOCH ₃) ₄ | 13.01 ± 0.02 | 26.59 ± 0.04 | 7.86 ± 0.02 | 105.6 ± 0.2° | <i>P</i> 2 ₁ | 8 | 2.23 | 2.24 |

* The D_m values are not accurate owing to the extremely high sensitivity of these compounds to moisture and the subsequent hydrolysis.

reflexions $0k0$ for k odd indicated $P2_1$ or $P2_1/m$ as the possible space groups for tin(IV) acetate and lead(IV) acetate. The final choice of $P2_1$ was ratified by usual statistical tests (Howells, Phillips & Rogers, 1950) and moment tests (Foster & Hargreaves, 1963).

Very close values of unit-cell parameters and the same space-group extinctions for tin(IV) acetate and lead(IV) acetate indicate isomorphism of their crystal structures.

Detailed structural investigations of the acetates of silicon, tin and lead are in progress, but we do not intend to proceed with the crystal structure analysis of germanium(IV) acetate because of its large unit cell and the diffuse reflexions at room temperature.

We thank Professor D. Grdenić for suggesting the problem and the Republic Foundation for Scientific Research, Zagreb, for financial support.

References

- BRAUER, G. (1960). *Handbuch der Präparativen Anorganischen Chemie*, Band 1, pp. 622, 644, 664, 681. Stuttgart: Ferdinand Enke Verlag.
- FOSTER, F. & HARGREAVES, A. (1963). *Acta Cryst.* **16**, 1133.
- HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.

Acta Cryst. (1972). **B28**, 322

Dehydration and transformation phases of scholzite $\text{CaZn}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. By REINHARD CZAYA, *Mineralogisch-Petrographisches Institut und Museum der Universität Kiel, 2300 Kiel, Olshausenstrasse 40-60, Deutschland (BRD)*

(Received 17 June 1971)

Dehydration and transformation processes in scholzite from Australia have been investigated using high-temperature microscopy, thermo-gravimetric analysis, differential thermal analysis, infrared spectroscopy and single-crystal and high-temperature X-ray powder diffraction methods. The two H_2O molecules present in scholzite leave the substance without destruction of the initial single crystals at two temperatures, 188 and 402°C. The crystal structure of the monohydrate is closely related to the structure of scholzite, as deduced from single-crystal photographs, whereas the anhydride develops as a mixture of different phases (α , β and γ). Above 900°C the β -phase with hexagonal indexing ($a_0 = 5.18$, $c_0 = 7.67$ Å) alone is found. From the structural aspects of scholzite and geometrical considerations supported by high-temperature X-ray powder data an ordered trigonal double sheet $[\text{Zn}_2\text{P}_2\text{O}_8]^{2-}$ in the β -phase is proposed.

Crystals of scholzite from Australia were investigated. The crystal data are as follows: $a_0 = 17.19_1$, $b_0 = 22.52_4$, $c_0 = 6.37_1$ Å, space group $Pmcm$, $Pcm2_1$ or $P2cm$, $Z = 4$, $D_{exp} = 3.05 \pm 0.01$ g.cm⁻³. The melting point of the anhydride is $1031 \pm 2^\circ\text{C}$. Scholzite has an orthorhombic subcell with $A = a$, $B = b/3$ and $C = c/2$ (Taxer, 1970). The chemical analysis is: CaO 15.7%, ZnO 37.2%, P_2O_5 37.9%, H_2O 8.6%, and the crystals show changes in light transmission observed under the microscope at approximately 200 and 400°C. No further changes are found up to the melting point.

Differential thermal analysis (DTA) measurements indicate dehydration in two steps at 188 ± 1 and $402 \pm 1^\circ\text{C}$. Weight losses found by thermo-gravimetric analysis (TGA) measurements are 4.32% at 188°C and 4.29% at 402°C. The total weight loss of 8.61% can be attributed to the removal of two H_2O molecules (theoretical value: 8.58%). Infrared measurements (KBr method) reveal two water absorption bands at 3350 cm^{-1} and 3420 cm^{-1} ($3.0\mu\text{m}$ and $2.9\mu\text{m}$) for Scholzite. The monohydrate only shows the band at 3420 cm^{-1} ($2.9\mu\text{m}$) with one half of the integral

intensity of the broad composite band found in scholzite. Single crystal X-ray photographs of the monohydrate are identical with those of scholzite but show a quadrupling of the c axis. The formation of the monohydrate is topotactic and irreversible. The anhydride also develops within the initial scholzite single crystal, as is shown in a textured X-ray photograph, and is not single-phased. At approximately 900°C the single β -phase develops from the mixture as can be seen from high-temperature powder diffraction. The β -phase can be indexed with hexagonal axes $a_0 = 5.13$, $c_0 = 7.67$ Å.

Corresponding cells have been found in the synthetic isostructural compounds $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ (Takeuchi & Donnay, 1959) and $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$ (Takeuchi, 1958; Sorrell, 1958). Both structures are characterized by a $[\text{Al}_2\text{Si}_2\text{O}_8]^{2-}$ double-sheet which is trigonal for $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ and the low-temperature form of $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$, whereas high-temperature form of $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$ is hexagonal. For synthetic β - $\text{CaZn}_2(\text{PO}_4)_2$ the hexagonal cell with $a = 5.13$, $c = 7.67$ Å was found by Kreidler & Hummel (1966). X-ray powder