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Hydrothermal Preparation of Hydroxy Stannates

The Crystal Structure of $MnSn(OH)_6$

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The hydroxy stannates, $MeSn(OH)_6$, of calcium, manganese, iron, cobalt, and zinc were prepared in hydrothermal recrystallisation. The crystal structure of $MnSn(OH)_6$ was investigated using three dimensional Patterson and Fourier functions and was refined to a conventional R-value of 5.4 %. The structure is very similar to that of indium trihydroxide. The space group is $Pn3$ with $a = 7.85$ Å.

I. HYDROTHERMAL INVESTIGATION

The preparation of some hydroxy stannates has been reported and some of the compounds have been characterized by their X-ray powder patterns.[1-3]

Hydrothermal recrystallisation yielded the crystalline hydroxy stannates $CaSn(OH)_6$, $MnSn(OH)_6$, $FeSn(OH)_6$, $CoSn(OH)_6$, and $ZnSn(OH)_6$. A compound containing calcium and tin, presumably a calcium stannate, was also obtained in the hydrothermal experiments.

Experimental

Chemistry. In a typical hydrothermal experiment 5 ml of a 0.1 M solution of sodium stannate and 5 ml of a 0.1 M solution of the metal chloride or of the metal nitrate were mixed in a thick-walled pyrex ampoule. The sealed ampoule was heated for 24 h in a thermostated oven kept at $180° \pm 1.5$°C. The crystalline reaction product was thoroughly washed with water and dried at 25°C. All manipulations with compounds and solutions containing Mn^{2+} or Fe^{2+} were performed in an oxygen free glove box.

In the hydrothermal preparation of $CaSn(OH)_6$ and of the calcium stannate the freshly precipitated calcium hydroxy stannate was treated with water or solutions of sodium hydroxide in a 20 ml pressure bomb lined with pure silver. Table 1 gives the experimental conditions. The tin content of $CaSn(OH)_6$ and of the calcium stannate was determined by neutron activation analysis. (Found: Sn 44.0. Calc. for $CaSn(OH)_6$: Sn 45.6. Found: Sn 63.0. Calc. for $CaSnO_3$: Sn 57.5). Differential thermal analyses of $CaSn(OH)_6$ and of the calcium stannate were obtained with a heating rate of 10°C/min in the temperature range from 50°C to 500°C. For $CaSn(OH)_6$ a transformation was observed at 355°C, corresponding to a loss of water.

Table 1. Experimental conditions.

Temp. °C	Pressure atm.	Time h	Conc. of NaOH M	Product
150	7	24	0	$CaSn(OH)_6$
222	24	24	0	do.
298	82	24	0	do.
350	162	24	0	Calcium stannate
350	180	25	0.1	do.
395	500	48	0	do.

X-Ray technique. The powder patterns of the hydroxy stannates and of the calcium stannate were obtained with a Guinier-de Wolff camera using Cu$K\alpha$ radiation, $\lambda = 1.5418$ Å. Germanium was used as internal standard, $a_{Ge} = 5.6576$ Å. From the powder patterns of the hydroxy stannates the unit cell parameters were calculated using a least squares program.[4] The results are given in Table 2. For comparison some previously reported values are given also.

Table 2. Unit cell parameter of hydroxy stannates. (Å).

	This work	Ref. 1	Ref. 2	Ref. 3
$CaSn(OH)_6$	8.150(2)	8.135	8.128(2)	8.15(1)
$MnSn(OH)_6$	7.885(2)	7.88	7.892(2)	
$FeSn(OH)_6$	7.630(6)	7.79	7.757(2)	
$CoSn(OH)_6$	7.757(1)	7.78	7.749(2)	
$ZnSn(OH)_6$	7.772(2)		7.765(2)	7.80(1)

Discussion

The hydrothermal investigation shows that the hydroxy stannates can be recrystallised, and that powders giving sharp X-ray powder patterns can be obtained. Calcium hydroxy stannate can be recrystallised at temperatures up to 298°C. Hydrothermal treatment of $CaSn(OH)_6$ at temperatures over 350°C yields a product that presumably is a calcium stannate. The neutron activation analysis does not agree well with the formula $CaSnO_3$, but it must be emphasised that it is usually difficult to obtain reproducible tin analyses by neutron activation analysis. However, this method was chosen, as the hydrothermally prepared calcium stannate was difficult to dissolve quantitatively.

The hydroxy stannates investigated are all cubic with space group *Pn*3.[3] The unit cell parameters obtained in this investigation are slightly different from previously reported values (see Table 2). The new parameters are considered to be of greater precision than others previously reported, since a Guinier camera of 114.6 mm diameter was used in the investigation and since an internal standard has been used in the data processing of the patterns.

II. STRUCTURE OF $MnSn(OH)_6$

An investigation on the crystallisation of cassiterite (SnO_2) from freshly precipitated SnO_2,xH_2O by treatment with sodium hydroxide solutions using hydrothermal techniques yielded, in one experiment, a dark powder containing a few colourless cubic crystals. The product proved to have a high content of iron and manganese presumably from corrosion of the pressure bomb. A three-dimensional single-crystal X-ray analysis was carried out to determine the structure and chemical composition of the cubic crystals. The investigation proved that the crystals had the formula $MnSn(OH)_6$.

Experimental

Chemistry. A sample of 10 g freshly precipitated SnO_2,xH_2O was treated with 45 ml of a 1 M sodium hydroxide solution in a 99 ml pressure bomb for 90 h. The temperature was 500°C, and the pressure was measured as 660 atm. The sample was kept in an ampoule of pure silver, and the balanced pressure technique was used. The pressure bomb was constructed from a Cr—Ni—Mo-steel. (Fe: 65.00. C: 0.07. Si: 0.34. Mn: 1.55. Ta and Nb: 0.80. N_2: 0.10. Cr: 16.57. Mo: 1.47. Ni: 13.25. V: 0.85). The experiment resulted in heavy corrosion of the pressure bomb. A black layer was found at the outside of the silver ampoule, and the sample in the ampoule was a dark powder containing a few colourless cubic crystals. A qualitative test on the sample for iron and manganese was positive.

X-Ray technique. With a Guinier-de Wolff camera powder patterns were taken of the black deposit from the outside of the ampule and of the dark product. Cu$K\alpha$ radiation was used (1.5418 Å). The black deposit was magnetite, Fe_3O_4, and the dark product had lines corresponding to the powder pattern of $MnFe_2O_4$, (ASTM 10-319). The dark product was not further characterized.

A single crystal of the cubic phase with the dimensions 0.05 mm × 0.05 mm × 0.05 mm was investigated by Weissenberg and precession methods. Integrated Weissenberg photographs were taken with Zr-filtered Mo$K\alpha$ radiation of ($0kl$), ($1kl$), ($2kl$), ($3kl$), and ($4kl$), using the multiple film technique. No absorption correction was applied.

Structure determination

The symmetry of the Weissenberg and precession photographs corresponded to the space group *Pn3m* (No. 224). However, it was later found that the space group is *Pn*3 (No. 201), and that the crystal was extensively twinned, which resulted in the apparent mirror plane.

A three-dimensional Patterson function gave positions of heavy atoms at (0,0,0) and at (0.5, 0.5, 0.5). Tin atoms were inserted at these coordinates. A three-dimensional Fourier function gave the possible position of a light atom at approximately (±0.05, ±0.05, 0.25). During the refinement the temperature factor of the tin atom at (0,0,0) increased, and the temperature factor of the tin atom at (0.5, 0.5, 0.5) decreased, and became negative and the later refinements were carried out both with iron and with manganese at (0,0,0). If an oxygen atom is inserted at (0.05, 0.05, 0.25) or at (—0.05, —0.05, 0.25) short oxygen-oxygen distances of 2.1 Å to 2.2 Å will occur, and consequently the oxygen atom position (—0.05, 0.05, 0.25) in space group *Pn*3 was chosen. The reflections hkl and khl do not have to be equal and the refinement was carried out with the not averaged data-set. An oxygen atom inserted at (0.05,

—0.05, 0.25) gives approximately the same overall agreement. The strong reflections ($h+k=2n$, $h+l=2n$) to which Sn and Mn (or Fe) contribute hardly showed any difference. Four pairs of weak reflections to which only the oxygen atoms contribute showed, however, that the crystal must be twinned. Averaged structure factors were then used and were compared with the root mean square values of the calculates structure factors. After this the agreement was considered good also for the weak reflections.

The refinement proceeded to an R-value of 5.4 % with the formula $MnSn(OH)_6$ and to an R-value of 5.7 % if an iron atom was inserted instead of the manganese atom. This difference is of low significance but together with the fact that the parameter of the unit cell was $a=7.85(1)$ Å it indicated, that the composition probably is $MnSn(OH)_6$; see Table 2.

The structure is very similar to that of indium trihydroxide [5] and it is likely to be hydrogen bonded in the same way. Hydrogen atoms were therefore inserted at positions corresponding to those found in $In(OH)_3$ but no improvement was observed.

Coordinates and isotropic temperature factors were refined by the method of Bhuiya and Stanley [6] using a program written by Danielsen.[7] The atomic scattering factors used were those reported by Forsyth and Wells.[8]

Crystal data

The compound $MnSn(OH)_6$ is cubic, $a=7.85(1)$ Å, space group: $Pn3$ (No. 201). Density calculated for four formula units in the unit cell, 3.79 g/cm^3. Absorption coefficient $\mu=82$ cm^{-1} for Mo$K\alpha$ radiation ($\lambda=0.7107$ Å).

Table 3 gives atomic coordinates and temperature factors with their standard deviations. Table 4 gives interatomic distances. Table 5 is a list of observed and calculated structure factors. Fig. 1 shows coordination polyhedra in the structure.

Table 3. Atomic coordinates and temperature factors.

Atom	x	σx	y	σy	z	σz	B (Å^2)	σB (Å^2)
Sn	0.5		0.5		0.5		0.49	0.03
Mn	0.0		0.0		0.0		0.85	0.07
O	0.081	0.003	0.930	0.003	0.255	0.004	1.59	0.28

Table 4. Interatomic distances in Å.

Sn—O	2.10 (3)
Mn—O	2.17 (3)
O—O	2.83 (3)
O—O	2.65 (3)

Table 5. Observed and calculated structure factors ($\times 10$) for $MnSn(OH)_6$. Film data. $R = 5.4$ %.

h	k	l	Fobs	Fcal
16	0	0	469	469
16	2	0	371	444
16	4	0	395	413
14	0	0	618	598
14	2	0	499	535
14	4	0	572	556
14	6	0	455	470
14	8	0	474	453
12	0	0	878	869
12	2	0	741	739
12	4	0	674	694
12	6	0	478	532
12	8	0	483	526
12	10	0	377	449
12	12	0	491	424
10	0	0	877	895
10	2	0	866	899
10	4	0	876	898
10	6	0	837	823
10	8	0	662	699
10	10	0	521	557
8	0	0	1139	1163
8	2	0	1257	1299
8	4	0	1036	1021
8	6	0	973	1008
8	8	0	765	760
6	0	0	1093	994
6	2	0	1411	1470
6	4	0	1303	1306
6	6	0	1377	1461
4	0	0	1888	2145
4	2	0	2025	2114
4	4	0	1617	1510
2	2	0	1842	2000
3	1	0	695	631
5	3	0	471	387
3	3	0	342	320
1	1	1	930	931
1	3	1	746	734
1	5	1	715	648
1	7	1	532	502
1	9	1	490	492
3	3	1	690	672
3	5	1	637	604
3	7	1	544	527
3	9	1	432	463
5	5	1	509	509
5	7	1	473	490
7	7	1	482	476
3	2	1	435	359
14	2	2	522	515
14	4	2	487	549
14	6	2	406	500
12	2	2	717	684
12	4	2	698	691
12	6	2	578	598
12	8	2	577	552
10	2	2	935	888
10	4	2	858	865
10	6	2	752	787
10	8	2	622	678
10	10	2	499	553
8	2	2	1352	1292
8	4	2	1029	986
8	6	2	884	877
8	8	2	725	717
6	2	2	1557	1578
6	4	2	1266	1221
6	6	2	1278	1150
4	2	2	1982	1988
4	4	2	1575	1469
2	2	2	1781	1790
5	3	2	306	214
3	3	2	261	239
1	1	2	196	144
3	3	3	782	624
5	3	3	531	564
12	4	4	626	617
12	6	4	614	566
12	8	4	540	491
10	4	4	851	794
10	6	4	710	698
10	8	4	644	607
10	10	4	498	519
8	4	4	1148	1039
8	6	4	944	923
8	8	4	814	798
6	4	4	1342	1254
6	6	4	1177	1068
4	4	4	1567	1440

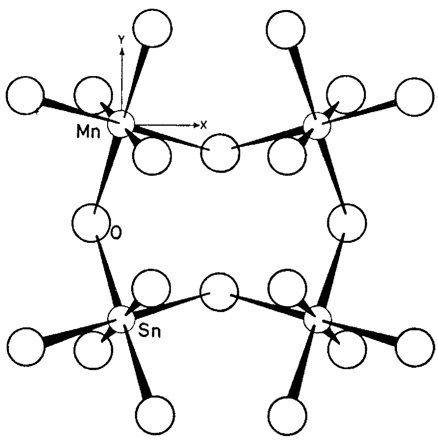

Fig. 1. Projection in the [001] direction of four of the eight octahedra in the unit cell of $MnSn(OH)_6$.

Discussion

In hydrothermal syntheses corrosion of the pressure bomb can be a serious problem. Corrosion products can contaminate the crystals that are to be prepared. As found in the present investigation this resulted in the formation of compounds, which were not expected to be formed in the preparation of cassiterite crystals. The use of a silver ampoule has in the present case not been a sufficient protection of the cassiterite against contamination.

The hydrothermal experiment yielded the compounds Fe_3O_4, $MnFe_2O_4$, and $MnSn(OH)_6$. From a chemical point of view the composition of the cubic phase, $MnSn(OH)_6$, is acceptable as compounds containing the Mn^{2+} ion should be formed in favour of a compound containing the Fe^{2+} ion, *e.g.*

$FeSn(OH)_6$, in a hydrothermal synthesis at the experimental conditions used. A structure determination of $FeSn(OH)_6$ based on an X-ray diffraction powder pattern was reported by Strunz and Contag,[1] and a structure determination of $CaSn(OH)_6$ and $ZnSn(OH)_6$ also based on X-ray diffraction powder patterns was reported by Cohen-Addad.[3] The present investigation is in agreement with the structure reported in Ref. 3.

In the structure of $MnSn(OH)_6$ the metal atoms are octahedrally coordinated with oxygen atoms and the structure is very similar to that of $In(OH)_3$.[5] The Mn—O distances of 2.17 Å with a standard deviation of 0.03 Å are comparable with the Mn—O distances of 2.207 Å, standard deviation 0.006 Å, found in $Mn(OH)_2$,[9] and the Sn—O distance of 2.10 Å with a standard deviation of 0.03 Å is comparable with the Sn—O distances of 2.040, standard deviation 0.007 Å, found in $Na_8Sn_4Ge_{10}O_{30}(OH)_4$.[10] The structure is hydrogen bonded, presumably in the same way as the structure of indium trihydroxide.[5]

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