Hydrothermal Preparation of α-ScOOH and of γ-ScOOH

Crystal Structure of α-ScOOH

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Scandium oxide hydroxide has been prepared in two crystalline modifications, one with the boehmite structure (γ-ScOOH) and one with the diaspore structure (α-ScOOH). The diaspore structure of scandium oxide hydroxide was confirmed by X-ray analysis from powder diffractometer data. The space group is *Pbnm*, (No. 62), with $a = 4.75_5$ Å, $b = 10.30_1$ Å, and $c = 3.20_9$ Å.

The existence of a scandium oxide hydroxide isomorphous with boehmite was reported by Milligan and Weiser.[1] The investigation was based on dehydration isobars of scandium trihydroxide and on Debye-Scherrer diffraction patterns of scandium oxide hydroxide. The existence of scandium oxide hydroxide was later confirmed by Fricke and Seitz.[2]

Hydrothermal preparation of γ-ScOOH was reported by Milligan and McAtee.[3] Scandium trihydroxide was prepared by precipitating a 0.1 M solution of scandium chloride with a solution of ammonium hydroxide, and was treated with pure water in a pressure bomb at 350°C and 400 atm. for 6 days. A structure determination from the X-ray powder pattern confirmed the boehmite structure.[3]

The system Sc_2O_3-H_2O has been investigated by Shafer and Roy [4] by hydrothermal methods in the temperature range 100—600°C, and pressure range 100—850 atm. Only two stable crystalline phases were found. α-ScOOH was the stable phase at temperatures up to 395 ± 10°C, at a pressure of 680 atm., and Sc_2O_3 was the stable phase obtained above this temperature. The d-spacings of α-ScOOH obtained from an X-ray powder were reported, and a

diaspore structure was postulated. No other crystallographic data on α-ScOOH have been found in the literature.

Fricke and Seitz [5] prepared single crystals of $Sc(OH)_3$ by treating freshly precipitated scandium trihydroxide with a 12 M NaOH solution in a pressure bomb at 160°C, and later Schubert and Seitz [6] reported the structure of $Sc(OH)_3$. An unsuccessful attempt to prepare $Sc(OH)_3$ was reported by Schafer and Roy.[4]

In the present investigation γ-ScOOH and α-ScOOH have been prepared by hydrothermal methods. Preparation of $Sc(OH)_3$ using the experimental condition reported by Fricke and Seitz was unsuccessful.

EXPERIMENTAL

Chemistry. γ-ScOOH was prepared by the method reported by Milligan and McAtee,[3] and was identified by the X-ray powder pattern. The scandium chloride solution was prepared from 99.9 % Sc_2O_3 and HCl, and scandium trihydroxide was precipitated by adding a 1 M solution of ammonia. Table 1 gives the experimental conditions. α-ScOOH was obtained by treating feshly precipitated scandium trihydroxide with sodium hydroxide solutions in a 20 ml pressure bomb lined with pure silver. The balanced pressure

Table 1. Experimental conditions for hydrothermal preparations.

Expt. No.	Max.temp. °C	Pressure atm.	Time h	NaOH conc. M	Initial condition	Result
1	350	160	53	0	$Sc(OH)_3$*	γ-ScOOH
2	162	6	125	12	$Sc(OH)_3$	α-ScOOH
3	170	8	72	1	»	»
4	327	120	60	0.5	»	»
5	350	170	60	5	»	»
6	600	700	20	0.1	»	Sc_2O_3

* $Sc(OH)_3$ prepared by precipitation of Sc^{3+} with a 1 M solution of ammonia.

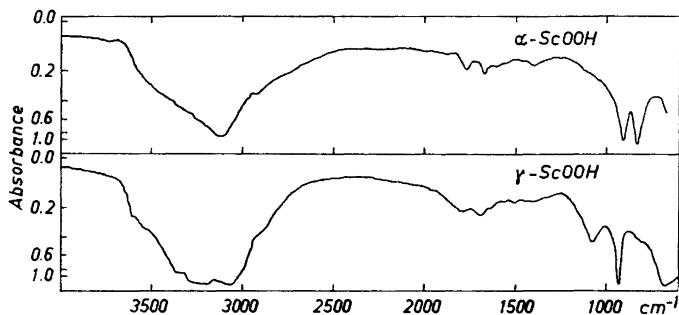*Fig. 1.* Infra-red spectra of α-ScOOH and γ-ScOOH.

technique was used. Table 1 gives the experimental conditions. The scandium trihydroxide was prepared from a scandium chloride solution by precipitation with a 0.1 M sodium hydroxide solution.

α-ScOOH was analysed by EDTA titration.[7] (Found: Sc 55.6. Calc. for α-ScOOH: Sc 57.6). The sodium content in α-ScOOH and in γ-ScOOH was determined by flame photometry. (Found: Na 0.05 ± 0.04 in γ-ScOOH; Na 0.13 ± 0.04 in α-ScOOH). The sodium content is probably of importance for the formation of α-ScOOH. Only when sodium ions were excluded in the preparation was γ-ScOOH formed.

Physical measurements. The infra-red spectra of α-ScOOH and γ-ScOOH have been obtained over the frequency range 600 to 4000 cm^{-1} on a Perkin-Elmer Model 521

Table 2. X-Ray diffraction data for α-ScOOH. $a = 4.75_5$ Å, $b = 10.30_1$ Å, $c = 3.20_9$ Å.

| h k l	d_{obs}	d_{calc}	I_{obs}		I_{calc}
0 2 0	5.146	5.150	78		47
1 1 0	4.325	4.317	282		285
1 2 0	3.502	3.494	67		59
1 3 0	2.783	2.784	119		119
0 2 1	2.723	2.724	50		60
1 0 1	2.660	2.660	26		36
1 1 1⎫	2.575	2.576⎫	266	268⎫	304
0 4 0⎭		2.575⎭		36⎭	
1 2 1	2.362	2.363	46		56
2 1 0	2.353	2.345	13		11
1 4 0	2.264	2.264	100		95
1 3 1	2.103	2.103	5		6
0 4 1	2.007	2.008	23		25
2 3 0	1.955	1.955	7		5
1 5 0	1.890	1.890	8		3
2 1 1	1.877	1.878	49		57
1 4 1	1.850	1.850	17		16
2 2 1	1.790	1.791	110		107
2 4 0	1.748	1.747	29		27
0 6 0	1.717	1.717	15		12
2 3 1	1.670	1.669	42		52
1 5 1	1.629	1.629	85		77
0 0 2	1.604	1.604	45		50
2 5 0	1.557	1.557	31		25
2 4 1	1.534	1.534	7		6
3 2 0⎫	1.514	1.515⎫	82	28⎫	74
0 6 1⎭		1.514⎭		46⎭	
1 1 2	1.503	1.504	20		19
1 2 2	1.458	1.458	3		6
1 6 1⎫	1.439	1.442⎫	13		
3 3 0⎭		1.439⎭			
3 0 1	1.420	1.421	16		16
3 1 1⎫	1.404	1.408⎫			
1 7 0⎭		1.401⎭			
1 3 2	1.389	1.390			
3 2 1	1.370	1.370			
0 4 2	1.362	1.362			
1 4 2	1.308	1.309			
2 7 0	1.252	1.251			
1 5 2	1.227	1.223			
4 0 0	1.193	1.189			
2 4 2⎫	1.180	1.182⎫			
4 1 0⎭		1.181⎭			
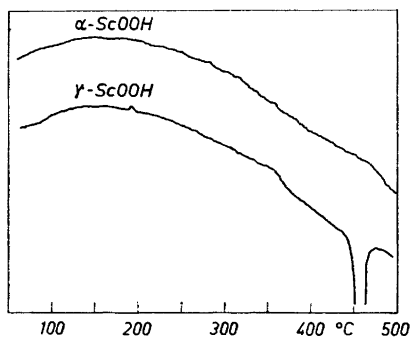
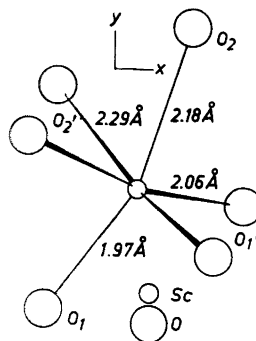Fig. 2. Differential thermal analysis diagrams of α-ScOOH and γ-ScOOH.

Fig. 3. Coordination polyhedron in α-ScOOH.

spectrophotometer. The pellet technique was used with mixtures of 4 mg of sample and 200 mg of CsI. The infra-red spectra obtained are shown in Fig. 1. α-ScOOH has an absorption band with maximum at 3100 cm^{-1} and γ-ScOOH has a broad absorption band with centre at 3200 cm^{-1}.

Differential thermal analysis were carried out with a Du Pont 900 Differential Thermal Analyzer in the temperature range 50—500°C. A heating rate of 10°C/min was used. The differential thermal analysis showed no phase transformation in α-ScOOH, but γ-ScOOH showed a phase transformation at 455°C (Fig. 2).

X-Ray technique. The X-ray powder pattern of α-ScOOH was obtained by using a Guinier de Wolff camera. $CuK\alpha$ radiation was used. Purified sodium chloride was chosen as standard. The powder pattern had sharp lines, and was similar to the powder pattern previously reported for α-ScOOH;[4] it could be indexed on an orthorhombic cell with $a = 4.75_5$ Å, $b = 10.30_1$ Å and $c = 3.20_9$ Å. The indexing of the powder pattern is given in Table 2. Optical densities of the lines in the Guinier powder pattern were measured using a recording Joyce-Loeble double beam micro-densitometer. In order to confirm that α-ScOOH had a diaspore structure intensities of 29 lines in the powder pattern were collected with an automatic powder diffractometer, using $CuK\alpha$ radiation. From the single peaks in the pattern 26 independent structure factors were calculated. The overlapping reflections (111) (040), (320) (061) and (161) (330) were excluded. The intensities of the reflections (021), (140), (221), (002) and (112) from the Guinier film and from the diffractometer measurement were significantly different; this was probably due to preferred orientation. The intensities of these reflections used in the structure factor calculation are average values from the two measurements. No absorption correction has been applied in the structure factor calculation.

CRYSTAL DATA

The investigation showed α-ScOOH to be isostructural with α-AlOOH.[8] The space group of the diaspore structure is *Pbnm* (No. 62) and all the atoms are situated on mirror planes with $z = \pm \frac{1}{4}$. In α-AlOOH the coordinates for Al^{3+}, O^{2-}, and the oxygen atom in the OH^- ion are (0.0451, —0.1446, 0.25), (0.7120, 0.1989, 0.25) and (0.1970, 0.0532, 0.25), respectively. These coordinates were used for Sc and O atoms in the structure factor calculation; the coordinates and temperature factors were then refined by the method of Bhuiya and Stanley.[9] The structure factors were calculated using the atomic scattering factors from Vol. III of *International Tables of X-ray Crystallography* and the

Table 3. Fractional atomic-coordinates, and temperature factors with their standard deviations.

Atom	x	σx	y	σy	z	B (Å²)	σB (Å²)
Sc	0.065	0.003	−0.148	0.001	0.25	0.2	0.3
O	0.689	0.009	0.201	0.003	0.25	0.2	1.1
O	0.211	0.009	0.053	0.004	0.25	0.3	1.0

interpolation formula of Bassi.[10] The refinement gave a conventional R-value of 8.5 %.

Table 3 gives atomic coordinates and temperature factors with their standard deviations. From this set of coordinates a set of calculated intensities $(I = jF^2 (1 + \cos^2 2\theta)/(\sin^2\theta\cos\theta)$ was obtained. (Table 2). Table 4 gives some bond angles and interatomic distances. Fig. 3 shows the distorted octahedron.

Table 4. Bond angles and interatomic distances with standard deviations.

Angles about Sc (degrees)	v	σv
$O_1 - Sc - O_1'$	97.9	1.3
$O_1' - Sc - O_1'$	102.2	1.4
$O_1 - Sc - O_2'$	89.2	1.4
$O_1' - Sc - O_2$	94.0	1.3
$O_1' - Sc - O_2'$	83.9	1.1
$O_2 - Sc - O_2'$	77.3	1.3
$O_2' - Sc - O_2'$	88.9	1.1

Distances within coordination polyhedra (Å)

	l	σl
$Sc - O_1$	1.97	0.04
$Sc - O_1'$	2.06	0.03
$Sc - O_2$	2.18	0.04
$Sc - O_2'$	2.29	0.03

Distances along the hydrogen bond (Å)

$O^{2-} - OH^-$	2.73	0.06

DISCUSSION

In general the boehmite structure is the metastable structure and the diaspore structure is the stable structure of an oxide hydroxide. The present investigation shows that both α-ScOOH and γ-ScOOH can be prepared by hydrothermal methods. It is assumed that it is essential to avoid sodium ions in the preparation if the boehmite structure is to be obtained.

The atomic coordinates and interatomic distances in α-ScOOH have not been determined with a high precision because of the limited amount of data. However, two sets of Sc$-$O distances have been obtained, one set with an average Sc$-$O distance of 2.02 $\pm$ 0.04 Å and one set with an average Sc$-$O distance of 2.24 $\pm$ 0.04 Å. The two sets are significantly different and correspond to Sc^{3+}$-$O^{2-} distances and Sc^{3+}$-$OH$^-$ distances, respectively. The Sc$-$O distance of 2.02 Å is comparable with the corresponding distances of 2.06 and 2.08 Å found in γ-ScOOH,[3] and the distances of 2.10 Å found in Sc$_2$O$_3$.[11] The Sc$-$O distance of 2.24 Å is comparable with the corresponding distance of 2.17 Å found in γ-ScOOH.[3] A Sc$-$O distance of 2.08 $\pm$ 0.05 Å was found in Sc(OH)$_3$.[6] The hydrogen bond of 2.73 Å is comparable with the hydrogen bond of 2.70 Å found in γ-ScOOH.[3]

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