JOURNAL OF SOLID STATE CHEMISTRY **13**, 368–371 (1975)

The Iodates of Scandium

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Received July 3, 1974

A dihydrate, a monohydrate, and three polymorphs of the anhydride $Sc(IO_3)_3$ have been prepared and studied. $Sc(IO_3)_3 \cdot 2H_2O$ was prepared by gel growth and by precipitation and evaporation at room temperature. The γ-anhydride can be crystallized from boiling water or nitric acid solution. The other compounds are formed on heating the dihydrate, which also dehydrates very slowly at room temperature. The α-anhydride is amorphous. The β-anhydride generates second harmonics, with about twice the efficiency of quartz. In addition differential thermal analysis (DTA), thermogravimetric analysis (TGA), infrared absorption, and powder X-ray diffraction results are presented.

A. Introduction

As part of a study of the 3*d* and 4*f* transition metal iodates (*1–6*), the iodates of scandium were prepared to continue this survey of potentially interesting nonlinear optical materials and to determine if the scandium iodates are isostructural with any of the other iodates. The only scandium iodate references appear to be the preparation of $Sc(IO_3)_3 \cdot 1\frac{1}{2}H_2O$ by Hájek and Hradilová (*7*) who gave infrared and DTA data, and the 18, 15, 13, 10 hydrates and an anhydride reported in 1908 by Crookes (*8*, *9*), characterized only by compositional analysis.

B. Experimental

The precipitation, differential thermal analysis (DTA), thermogravimetric analysis (TGA), powder X-ray diffraction, and infrared spectroscopy techniques were performed as described previously (*1*), as were the gel growth (*3*) and boiling solvent crystal growth (*10*) techniques. The Sc_2O_3 (99.99% from Research Chemicals, Div. of Nucor Corp.) was first converted to the nitrate. Transformation temperatures are estimated to be accurate to ±10°C and decomposition temperatures, which are strongly heating-rate dependent, to ±25°C.

C. Results

Room temperature precipitation of $Sc(NO_3)_3$ with HIO_3, as well as evaporation of a water solution and gel growth from acetic acid set gels (*3*) all gave the dihydrate $Sc(IO_3)_3 \cdot 2H_2O$. Analysis by DTA and TGA at 5°/min in flowing nitrogen as shown in Fig. 1 established the composition and led to the preparation of four additional compounds as summarized in Fig. 2.

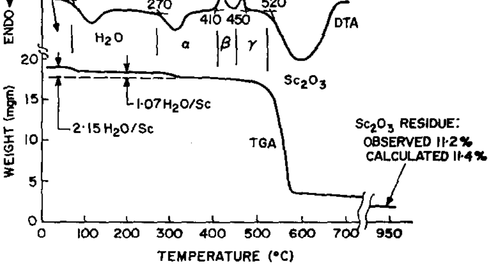

FIG. 1. Curves (DTA and TGA) of the scandium iodates at 5°/min in flowing nitrogen.

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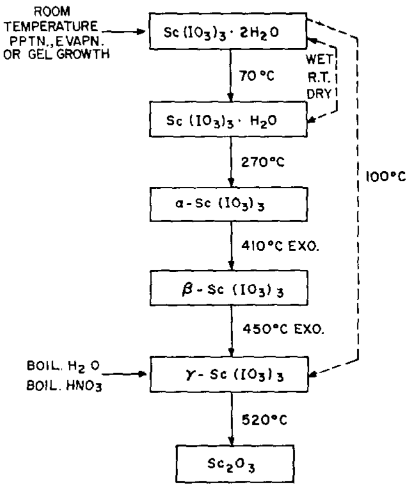

FIG. 2. Decomposition scheme of the scandium iodates (dashed lines indicate slow transformations).

The monohydrate $Sc(IO_3)_3 \cdot H_2O$ also formed slowly (several months) from the dihydrate by water loss into the ambient. This was first noted in the infrared spectrum, where the single broad 764 cm^{-1} peak of the dihydrate slowly acquired the six shoulders of the monohydrate.

Above 270°C the α-$Sc(IO_3)_3$ formed was amorphous. It is probable that it and the β-anhydride formed above 410°C are metastable since both decompose exothermally. An analogous situation occurs with the copper iodates (*3*), where in the presence of water all the other compounds transform to the $\frac{2}{3}$ hydrate. Here, however, the dihydrate appears to be the stable form.

The γ-anhydride which formed above 450°C could also be obtained by heating the dihydrate for three days at 100°C, and readily forms as small crystals from boiling water or boiling concentrated nitric acid (*10*). Above 520°C decomposition leads to Sc_2O_3, the amount remaining being very close to theoretical (Fig. 1).

All five compounds are colorless. The five phases can be distinguished by the infrared spectra of Fig. 3 which are distinct from each other as well as from the many other transition

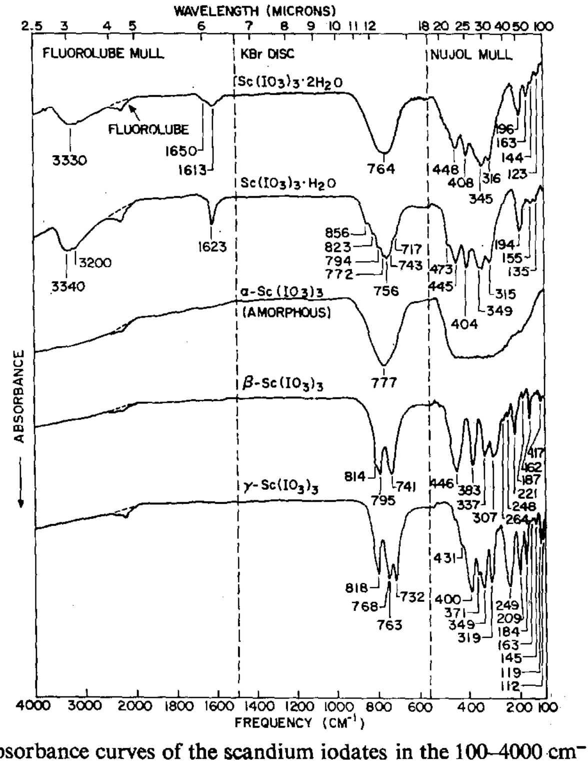

FIG. 3. Absorbance curves of the scandium iodates in the 100–4000 cm^{-1} region.

TABLE I

X-RAY POWDER DATA FOR THE SCANDIUM IODATE[a]

$Sc(IO_3)_3 \cdot 2H_2O$		$Sc(IO_3)_3 \cdot H_2O$		β-$Sc(IO_3)_3$		γ-$Sc(IO_3)_3$	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
11.44	ms	5.47	vvw	4.75	w	4.81	vw
5.79	w	5.16	vw	3.48	s	4.62	vw
4.46	vw	3.77	m	3.21	vvw	4.01	vvw
4.36	vw	3.68	m	3.12	vvw	3.35	s
3.56	m	3.21	s	2.75	m	2.89	vvw
3.47	m	3.16	m	2.66	vw	2.81	m
3.40	vw	2.94	vw	2.55	vw	2.43	vvw
3.20	s	2.88	vw	2.43	vvw	2.41	vvw
3.16	vw	2.70	w	2.39	vw	2.33	ms
2.91	w	2.61	w	2.29	vvw	2.22	vvw
2.87	vw	2.36	vvw	2.25	w	2.16	vw
2.69	w	2.07	w	2.17	m	2.10	m
2.33	w	2.04	w	2.09	vw	1.94	vvw
1.99	vw	2.00	vw	1.98	vvw	1.92	vvw
1.95	w	1.90	w	1.88	m	1.87	vw
1.79	vw	1.87	vw	1.81	vvw	1.79	m
1.74	vvw			1.78	vw	1.71	w
				1.75	vw	1.68	w
				1.70	ms	1.48	s

[a] Taken on a 114.6 mm diameter Straumanis-type Norelco camera using V filtered Cr*K*α radiation; *d* in Å; *I* is visually estimated intensity.

metal iodates examined by us (*1*, *3*, *5*, *6*). As expected, the OH features near 3300 cm^{-1} and 1600 cm^{-1} were observed only in the hydrates and the H–O–H bending mode band near 1600 cm^{-1} indicates the presence of H_2O as distinct from –OH. Hydrogen bonding is weak as in the 4*f* iodates (*5*, *6*). Quite unusual in comparison with the other iodates, even the amorphous ones in Fig. 15 of Ref. (*6*), is the absence of structure in the 777 cm^{-1} band and at lower frequencies (from vibrations involving scandium, iodine, and oxygen atoms) seen in the amorphous α-anhydride phase in Fig. 3.

The powder X-ray diffraction patterns are given in Table I; these are also distinct from each other and from those of all the other iodates studied. Examination for second harmonic generation at 1.06 μm by the powder technique showed that only the β-anhydride probably lacked a center of symmetry; it gave a signal about two times that of powdered quartz used as a reference material.

In the absence of any characterization given by him, we cannot confirm the obvious suggestion that Crookes (*8*, *9*) had excess free water in his 18, 15, 13, and 10 hydrates. Although having the same general shape, the DTA curve of Hájek and Hradilová (*7*) for their "$Sc(IO_3)_3 \cdot 1\frac{1}{2}H_2O$" is displaced about 100°C higher with respect to ours. Neither can their infrared data be made to agree with ours by postulating a mixture of mono and dihydrate due to water loss from drying at too high a temperature, although a well-decomposed mixture of dihydrate (760 cm^{-1}), β-anhydride (303, 333, 740, and 797 cm^{-1}), and γ-anhydride (210, 250, and 400 cm^{-1}) would come close. The lack of agreement here is similar to that observed by us (*5*, *6*) on the lanthanide results also presented in their paper.

Acknowledgments

We are most grateful to Miss B. E. Prescott for the infrared data and Mrs. A. S. Cooper for the powder X-ray diffraction work.

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