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Rare Earth Metal-Metal Halide Systems.

XVI. Scandium Sesquichloride and Sesquibromide¹

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The phase diagram for the ScBr_3 -Sc system has been investigated utilizing tantalum containers and has been found to contain only the phase Sc_2Br_3 , which melts incongruently at 880° to form metal and a solution of 23.0 mol % metal in ScBr_3 . The eutectic occurs at 817° and 19.7 mol % scandium. The ScCl_3 -Sc system was reinvestigated in order to clear up the differences between earlier reports and the present bromide findings. The crystalline sesquichloride is formed readily over a wide temperature range by a reaction of ScCl_3 vapor with a large excess of scandium metal foil. The phase melts peritectically at $877.0 \pm 0.2^\circ$. The two scandium sesquihalides are isomorphous and their crystal habits resemble that of gadolinium sesquichloride.

Introduction

Publications dealing with reduced scandium halides have been limited to two^{2,3} on the ScCl_3 -Sc system plus a brief report⁴ of the investigation of the metal-trihalide systems for chloride, bromide, and iodide, parts of which are reported in detail here. Polyachenok and Novikov² first reported a relatively large amount of reaction of the metal with liquid ScCl_3 and the formation of the solid phases ScCl_2 ,⁶⁷ and ScCl_2 . These results were disputed by Corbett and Ramsey,³ who, working in tantalum containers, found smaller solubilities of metal (~20 mol %) and no new solid phases. The apparently greater reaction in the melt reported previously was suggested to have resulted from reaction of metal with the glass container inadequately protected by a molybdenum film. However, the hindsight provided by the present investigation of the ScBr_3 - Sc_2Br_3 -Sc system also led to a reinvestigation of the chloride system and to the isolation of the analogous Sc_2Cl_3 .

Experimental Section

Materials. The metal employed had been vacuum distilled in tantalum. The metallic and hydrogen impurities were similar to those reported before,³ and oxygen and fluorine were at 90–300 and 250–360 ppm, respectively. The metal used for bromide work contained about 1800 ppm of Ta whereas this impurity constituted only about 120 ppm in that used for the chloride studies. Metal foil used in the latter was prepared by rolling a small rod at 650° while it was sealed in a stainless steel tube lined with a 2-mil thickness of tantalum. The stainless steel stripped off easily afterward and the tantalum was removed by the HF-HNO₃ solution usually employed for cleaning tantalum since the scandium remained passive. Electro-polished foil was used in several experiments in an effort to reduce the number of nucleation sites and thus obtain larger Sc_2Cl_3 crystals.

Since the trihalides and sesquihalides are very sensitive to moisture, standard vacuum-line and drybox techniques were used for all storage and handling of these materials. All samples containing reduced salt or metal were heated only in sealed tantalum containers (which in turn were contained in fused silica under inert gas or vacuum to protect them from the air).

Analyses. Several precautions were taken to avoid loss of hydrogen halide during the weighing and solution of samples prior to analysis. The preparations were first placed in small glass vials or ampoules in the drybox and these then capped and weighed in air. The samples were dissolved either in air by addition of ethanol or under vacuum by admission of distilled water into the container through a stopcock. In both cases hydrolysis products were taken up by an addition of dilute acetic acid. Scandium was titrated with

EDTA using Xylenol Orange.⁵ Chloride was determined gravimetrically after precipitation from 50% acetone; bromide was determined volumetrically using Eosin Y as the indicator.

Syntheses. ScBr_3 . The $\text{NH}_4\text{Br}-\text{Sc}_2\text{O}_3$ reaction proved not to be a very effective source of the tribromide, probably because the oxide is too stable relative to the bromide compared with lanthanide systems where the method is well known for its utility. Reaction of the metal at 1000° with an atmosphere of bromine coming from a reservoir at room temperature proved to be much more efficient. The product was sublimed several times at 700° under high vacuum onto a tantalum condenser to give a material with a Br/Sc ratio of 3.00 ± 0.02 (material balance of $100.0 \pm 0.2\%$). The ScBr_3 melted at 969° , somewhat higher than the 948° reported earlier.⁶

ScCl_3 . The initial preparation came from a scale-up of the reported⁷ synthesis of the trichloride through precipitation of the hydrated $(\text{NH}_4)_3\text{ScCl}_6$ followed by thermal decomposition and sublimation of the product trichloride. The reported method involved only 1 g of the oxide and, with a 64% yield, produced 1.3 g of the trichloride. An increase in the scale by a factor of 10 gave an inordinately slow and cumbersome process and only a 45% yield of ScCl_3 . The reaction of the metal with hydrogen chloride as before⁸ was far more expedient, producing 15 g of trichloride in nearly quantitative yield in 4–6 hr. The product sublimed in tantalum typically gave Cl/Sc ratios of 2.99 ± 0.01 with a 100.2% recovery.

Sc_2Br_3 . This phase was obtained from successive equilibrations of the tribromide-rich liquidus composition with chunks of the metal in a sealed tantalum container. These reactions were interrupted several times to break up the product in the drybox since its fibrous habit favored the retention of unreacted tribromide. The total equilibration time at 860° was of the order of 12–20 days. Typical analyses yielded Br/Sc ratios of 1.48–1.50 with recoveries of 98–99%. Most of the reduced bromide samples contained small amounts of (unweighed) tantalum from the metal used and, occasionally, traces of oxybromide from small amounts of contamination during the several handlings necessary to get a complete reduction.

The procedure for the synthesis of Sc_2Cl_3 (below) would now be the preferred one for the preparation of Sc_2Br_3 .

Sc_2Cl_3 . The material was first synthesized successfully by reaction of a metal foil about 0.5 mm thick with an approximately equal weight of trichloride in a sealed tantalum tube for 100–300 hr at 860 – 870° . A decrease in the relative weight of trichloride to 0.2–0.5 of that of the metal allowed ready quantitative synthesis of Sc_2Cl_3 in about 10 days at 650 – 750° . A typical analysis was Cl/Sc = 1.51 with a 100.4% recovery.

The tantalum tube must be sealed for these reactions; use of a sealed Vycor container with the scandium metal in an open tantalum boat resulted in substantial transport of tantalum to the glass walls.

Phase Studies. The phase diagram for the bromide system was determined by thermal analysis and equilibration techniques as already described.⁶ The tantalum containers were in all cases first cleaned by chemical means and then by induction heating and during the experiments were maintained under dynamic vacuum. The volatility of ScBr_3 at the temperatures involved required that the

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containers all be sealed. Samples of 3.5–4.5 g of ScBr_3 were used for thermal analysis studies, with subsequent composition adjustments being made by introduction of metal through an entry tube. The tube was again sealed after each addition by arc-welding under argon.

Equilibrations between the condensed phases used to establish liquidus limits in the bromide system were carried out with 1–2 g of salt and excess metal lumps sealed in 0.25-in. tantalum tubing. In order to reduce vaporization the unfilled portion of the container was crimped after a brief fusion of the contents. The samples were quenched as before⁹ after 12–35 hr.

In both systems traces of a pink transparent oxyhalide phase were occasionally encountered after equilibrations, especially after longer reactions involving a liquid salt phase when the tantalum tube was known to have leaked. In the particular case of the bromide, reaction of ScBr_3 and Sc_2O_3 in amounts appropriate to yield ScOBr at 1000° in a sealed tantalum tube gave an evidently single-phase product with a powder pattern identical with that of the pink impurity encountered in the ScBr_3 – Sc study after an errant experiment.

Powder Pattern Data. The stronger 50% of the powder diffraction patterns of the sesquihalides which occur above 1.75 Å, with relative intensities in parentheses, are as follows: Sc_2Cl_3 : 7.7 (10), 4.45 (5), 3.83 (8), 3.51 (3), 2.98 (5), 2.87 (5), 2.75 (7), 2.62 (5), 2.46 (8), 1.85 (4), 1.756 (6); Sc_2Br_3 : 8.2 (6), 4.02 (9), 3.19 (4), 3.08 (6), 3.00 (6), 2.85 (8), 2.74 (4), 2.68 (4), 2.56 (8), 2.00 (4), 1.89 (4), 1.81 (6). The powder patterns for ScCl_3 and ScBr_3 and their indexing were in excellent agreement with those reported in the literature.^{10,11}

Results and Discussion

The phase diagram adduced for the ScBr_3 – Sc system is shown in Figure 1. Faint thermal arrests to the left of the eutectic at 850° were found on reinspection of the data only after the more obvious inflection in the liquidus had been noted. However, no X-ray evidence for a new phase presumably responsible for the apparent peritectic transformation could be found, for example, in a sample containing 13.5 mol % metal quenched from the liquid state and then held overnight at 835°. The eutectic in the system occurs at 817° and 19.7 mol % metal, and the liquidus which terminates the 880° peritectic of the sesquibromide contains 23.0 mol % metal. Conversion of the liquid salt to solid sesquibromide by equilibration with excess metal is relatively difficult and requires repeated and lengthy equilibrations with fresh metal surface because of the extremely fibrous character of the product (see Experimental Section). Reaction of metal foil with gaseous trihalide as utilized for the sesquichloride synthesis (below) would doubtlessly be better.

Magnetic susceptibility measurements (Faraday method) on the sesquibromide showed it to be very slightly paramagnetic (Table I). The material has almost a zero gross susceptibility at room temperature, and the diamagnetic correction remains larger than the observed value down to near 77°K.

After completion of the above phase study it was noted that the liquidus between the trihalide and the eutectic for the bromide system was extremely similar to that reported earlier³ for the chloride system. The melting points of the trihalides differ by only 2°, and, as shown in Figure 2, the liquidus curves indeed must be displaced in order to be distinguished down to 15 mol %. At this point the 850° transition in the bromide system decreases the rate of freezing point depression and makes the eutectic 14° higher than with the chloride. As with evidently all of the rare earth metal-metal halide systems^{8,12} the dilute solutions of scan-

Table I. Magnetic Susceptibility Data for Sc_2Br_3

Temp, °K	$10^6 \chi_M$, emu mol ⁻¹		Temp, °K	$10^6 \chi_M$, emu mol ⁻¹	
	Obsd	Cor ^a		Obsd	Cor ^a
77	126.4	250	189	62.6	187
113	93.8	218	242	45.0	169
142	74.4	198	299	37.4	161

^a After diamagnetic correction, $\chi_D = -124 \times 10^{-6}$ emu mol⁻¹.

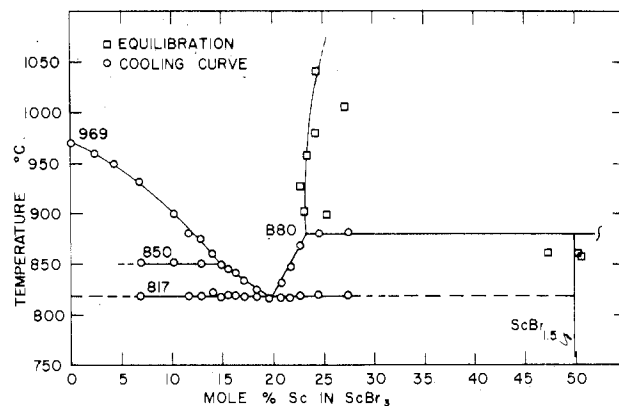


Figure 1. The phase diagram of the system ScBr_3 – Sc : ○, thermal analysis—cooling; □, equilibration followed by quenching and analysis.

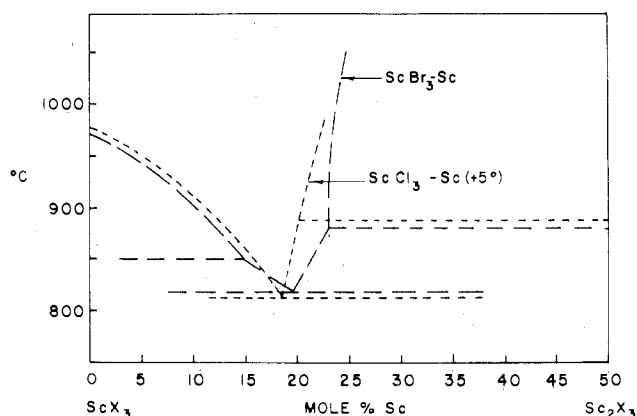


Figure 2. Comparison of the phase diagrams of ScCl_3 – Sc_2Cl_3 ³ (with peritectic transition added) and ScBr_3 – Sc_2Br_3 . The chloride diagram has been raised 5°.

dium metal in these two trihalides also appear to contain the simple Sc^{2+} ion, giving cryoscopic numbers of 2.5 ± 0.2 (vs. 3.0 theoretically) out to about 10 mol % metal according to a recent ΔH_f for ScCl_3 .¹³ There is some suggestion of solid solution behavior on the trihalide side of the eutectics so that these numbers could be low.

The close similarity of the two systems suggested that a reduced chloride phase might have been missed in the earlier study. Some new liquid salt–solid metal equilibrations gave encouraging results, and so the system was partially reinvestigated. In the time elapsed since the first study, considerable success had been achieved in difficult systems with the synthesis of the lowest halide in high yield and purity, ZrCl and HfI_3 for example,¹⁴ by reaction of gaseous higher halide with metal in the form of a foil with a large surface area. For ScCl_3 – Sc , reaction of such foil with trihalide *via* the gas phase for a few days readily gave complete conversion to

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sesquichloride over a range of temperature from 650 to 860°. The tantalum container when opened was found to be apparently completely filled with long fibers of Sc_2Cl_3 which were only a few microns in diameter and resembled polyglass string. The principal amount of product occurs inside this cocoon-like shell on the metal as a hard crust with a dark brown to golden appearance. This is actually a very dense "forest" of thin fibers which grow normal to the metal surface, the individual "trunks" ($\sim 100\text{-}\mu$ diameter, 1–4 mm long) actually being composed of bundles which fray into smaller fibers ($\sim 3\text{--}10\ \mu$) when cut or rubbed. (The assembly also resembles the fibers in a cigarette filter.) The product is single phase to the microscope and to X-rays and is clearly isostructural with the sesquibromide, with lattice spacings about 6% smaller (see Experimental Section). The Sc_2Cl_3 melts peritectically at $877.0 \pm 0.2^\circ$, about 3° lower than the sesquibromide. The recombination reaction between ScCl_3 and the finely powdered metal produced on melting is evidently quite rapid as judged from the fact that the eutectic is not observed on cooling a decomposed 0.5-g sample from 877° to the expected 803° at $0.7^\circ \text{ min}^{-1}$. The transition is of course found on faster cooling.

The technique of premelting metal into 0.25-in. tantalum tubes prior to equilibration with liquid ScCl_3 was used in the previous chloride study³ in order to avoid problems of metal suspension which otherwise produced high and erratic solubilities, particularly above 900° . However this same technique also obscured the formation of Sc_2Cl_3 below 877° since the hard, thin layer of product formed on the limited surface readily blocked further reaction. The compositions determined³ below 880° were actually those of the Sc_2Cl_3 -saturated melt; the diffraction pattern of the sesquichloride is not evident in the powder pattern of such quenched samples. Nonetheless, the cooling curves were inadequately interpreted since some clearly showed the peritectic transition supercooled about 20° .

The only other element which forms a high-melting sesquihalide as the lowest phase is gadolinium,⁹ and, interestingly, the crystal habit of the two scandium sesquihalides greatly resembles that already known for Gd_2Cl_3 , where a remark-

able metal chain structure has been determined.¹⁵ The scandium phases would appear thermodynamically to be considerably more stable than Gd_2Cl_3 , however, melting almost 250° higher and notably less incongruently. The slight paramagnetism found for Sc_2Br_3 is not in conflict since such a small effect would be undetected in the large susceptibility background of the $4f^7$ metal cores observed for Gd_2Cl_3 .¹⁶ It is interesting to note that both elements form evidently metallic iodides, namely, ScI_2 ,¹⁵ and GdI_2 ,⁹ another constitution which doubtlessly also requires substantial orbital extension for the differentiating electrons. No further evidence is available at present concerning the possible structural similarities of the scandium and gadolinium compounds. Predictions^{17,18} of dihalide stability notwithstanding, scandium remains the only 3d element lacking a simple dihalide in the solid state. Of course the metal-reduced melt does contain substantial amounts of Sc^{2+} according to cryoscopic evidence, up to about 69 mol % ScX_2 in ScX_3 if this is the sole product, and so the solid dihalides may not be very far from stability. The alternate solid phases actually found for scandium do appear a good deal more interesting, however.

Registry No. Sc_2Cl_3 , 12-432-552; ScBr_3 , 13465-59-3; $(\text{NH}_4)_3\text{ScCl}_6$, 38136-16-2; ScCl_3 , 10361-84-9; Sc_2Br_3 , 12-431-582; NH_4Br , 12124-97-9; Sc_2O_3 , 12060-08-1.

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Ionic Radii for Spherical Potential Ions. I

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Experimental ionic radii (r_c) are available for several cations from X-ray density maps. Ionic radii for other cations with a rare gas configuration are derived from an empirical relation between r_c and the intermetallic distance of the corresponding metal. These are termed radii for spherical potential ions (SPI) and receive theoretical justification from the calculations of Paschalis and Weiss showing contraction of anions and expansion of cations in spherical potential wells of opposite sign. Expansion of cations in crystals is small and definite values of cation radii can be established. However, variable radii are proposed for anions to take into account the relatively large contraction of anions in the field of cations.

Introduction

The use of ionic radii and covalent radii¹ (which are ex-

remely crude representations) along with sophisticated quantum mechanical calculations using accurate wave functions for electrons is one of the anachronisms of present day chemistry and physics.

Fajans² has long emphasized the deviations from additivity of internuclear distances in crystals and has shown, *e.g.*, that

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