Gmelin Handbook of Inorganic Chemistry

8th Edition

Sc, Y, La–Lu
RARE EARTH ELEMENTS

Part C 4b

Data on Individual Chlorides

System Number 39

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Data on Individual Chlorides

With 113 illustrations

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Foreword

The volumes "Rare Earth Elements" C4a and C4b deal with the rare earth chlorides and the rare earth chloride systems. Comparative and broadly valid data for these compounds and systems are presented in volume C4a, data on individual chlorides and chloride systems are given in volume C4b.

The sections on the individual chlorides in the present volume C4b are arranged according to the Periodic Table of the Elements and deal mainly with the preparation, properties, and chemical reactions of the various M-Cl compounds starting with the lowest valency states. Phase diagrams and solutions are discussed in separate sections. Generally, the subdivision and sequence of the main topics conform to those adhered to in volume C4a. References to this comparative volume, which offers additional information, are given in this volume at the head of each section on a specific rare earth element. Molecules and ions in the gas phase or as matrix-isolated species are treated only in volume C4a.

The physical properties of rare earth ions in crystal lattices as well as the chemistry of complexes are only briefly described, since these topics are reserved for later volumes of the Gmelin Handbook.

Many data in the present volume are tabulated or reproduced in figures. Values on physical properties are converted into SI units only when it seems necessary for uniformity. The most important conversion factors are compiled in a table on pp. 323/4.

Frankfurt/Main
April 1982

Hartmut Bergmann

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11.2.11 Data for Individual Chlorides

In this volume the various M-Cl systems and compounds are individually described and additional data are presented that are not considered in the comparative volume "Rare Earth Elements" C4a, 1982, Sections 11.2.1 to 11.2.10 on pp. 19/270. Molecules and ions are treated in Section 11.1 on pp. 1/19.

11.2.11.1 Scandium Chlorides

Additional data for the Sc-$ScCl_3$ system, ScCl, Sc_2Cl_3, $ScCl_2$, $ScCl_3$, $ScCl_3 \cdot n H_2O$, and $ScCl_3$ solutions are found in "Rare Earth Elements" C4a, 1982, Section 11 2.1, 11.2.2, 11.2.3, 11.2.4, 11.2.6, 11.2.7, and 11.2.8 on pp. 19, 23, 27, 29, 51, 183, and 216, respectively.

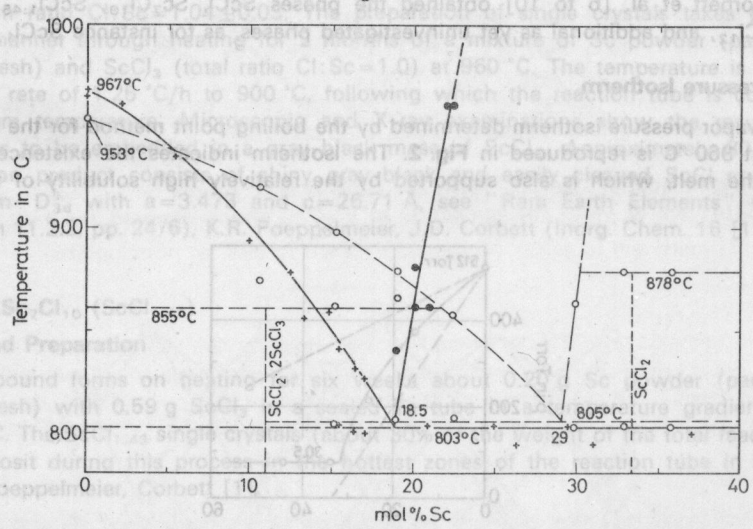
General Reference:

K.A. Gschneidner, in C.T. Horovitz, Scandium, Its Occurrence, Chemistry, Physics, Metallurgy, Biology and Technology, Academic Press, London - New York 1975, pp. 152/251, 174/81.

11.2.11.1.1 The Sc-$ScCl_3$ System

Phase Diagram

Fig. 1



Phase diagram of the Sc-$ScCl_3$ system according to Corbett, Ramsey [1] (heavy lines) and Polyachenok, Novikov [2] (thin lines). The crosses and empty circles denote thermal analyses, the full circles equilibration experiments.

The salt-rich region between 780 and 980 °C is presented in **Fig. 1**, p. 1, based on thermal analyses (cooling curves) as well as on investigations of samples in equilibrium with excess metal. The metal shows a very noticeable solubility in the melt: 18.5 mol % ($\triangleq ScCl_{2.45}$) at 803 °C (eutectic) and 22.2 mol % at 960 °C. An intermediate phase was not found, Corbett, Ramsey [1].

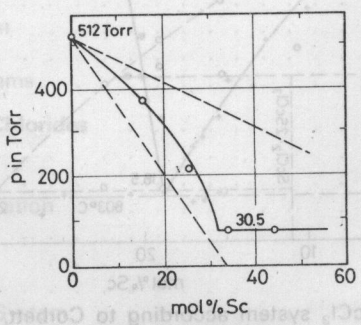
Polyachenok, Novikov [2, 3] determined a substantially higher solubility for Sc in the melt by thermographic investigations and vapor pressure measurements; their results are entered in Fig. 1 for comparison. In the paper [4] these Russian authors report the solubility of Sc in $ScCl_3$ at 960 °C as 31 mol%. In contrast to the results of [1], the phases $ScCl_2$ and $ScCl_2 \cdot 2ScCl_3$ ($\triangleq ScCl_{2.67}$) are found by [2, 3]. The latter melts incongruently at 855 °C [2]. The dichloride $ScCl_2$ is said in [3] to melt with decomposition at 806 °C. An incongruent melting point of 878 °C for $ScCl_2$ is attributed by [1] to [2]; however, according to [2], the very small thermal effect at 878 °C is due to a monotectic (?) transformation, while the incongruent melting point of $ScCl_2$ practically coincides with the eutectic temperature. The discrepancy between the two diagrams is attributed by [1] primarily to the reaction of $ScCl_3$ melt and vapor with the containers used by [2, 3], fused silica ampules protected only imperfectly by an Mo coating; they themselves used Ta vessels.

However, since the phase diagram of [1] is very similar to that for the Sc-$ScBr_3$ system from McCollum et al. [5], see "Seltenerdelemente" C6, 1978, p. 48, these authors [5] have conjectured that an intermediate chloride phase was overlooked by [1] due to the inadequacies of the experimental technique. By a partial reinvestigation of the hypereutectic liquidus line on annealed samples, they in fact succeeded in proving this, and then further in preparing a phase of the composition $ScCl_{1.5}$ ($\triangleq Sc_2Cl_3$, cf. p. 6) which melts peritectically at 877.0 ± 0.2 °C, i.e., approximately at the 878 °C transition temperature given by [2]. By reduction of $ScCl_{1.5}$ or $ScCl_3$ with excess Sc above the melting point of $ScCl_{1.5}$, or through the action of gaseous $ScCl_3$ on the metal, Poeppelmeier, Corbett et al. [6 to 10] obtained the phases ScCl, Sc_7Cl_{10}, $ScCl_{1.45}$, Sc_5Cl_8, and Sc_7Cl_{12}, and additional as yet uninvestigated phases, as for instance $ScCl_{1.40}$..

Vapor Pressure Isotherm

The vapor pressure isotherm determined by the boiling point method for the Sc-$ScCl_3$ system at 960 °C is reproduced in **Fig. 2**. The isotherm indicates the existence of Sc^{2+} ions in the melt, which is also supported by the relatively high solubility of the metal

Fig. 2



Vapor pressure isotherm of the Sc-$ScCl_3$ system at 960 °C. The dashed lines are theoretical curves assuming the existence of Sc^{2+} and Sc^0, respectively, in the melt.

in melts of the trichloride, Polyachenok, Novikov [2], see also [3]. Also, the cryoscopic evaluation of the liquidus curve (cryoscopic number $n=2.5\pm0.2$ vs. the theoretical value 3.0) speaks for the occurrence of monomeric Sc^{2+} ions in melts with $\leqq$10 mol% Sc, McCollum et al. [5].

References:

[1] J.D. Corbett, B.N. Ramsey (Inorg. Chem. **4** [1965] 260/2). – [2] O.G. Polyachenok, G.I. Novikov (Zh. Neorgan. Khim. **8** [1963] 2819/21; Russ. J. Inorg. Chem. **8** [1963] 1479/80). – [3] O.G. Polyachenok, G.I. Novikov (Zh. Obshch. Khim. **33** [1963] 2797; J. Gen. Chem. [USSR] **33** [1963] 2725). – [4] O.G. Polyachenok, G.I. Novikov (Vestn. Leningr. Univ. Fiz. Khim. **1963** No. 3, pp. 133/4; C.A. **60** [1964] 4875). – [5] B.C. McCollum, M.J. Camp, J.D. Corbett (Inorg. Chem. **12** [1973] 778/80), B.C. McCollum, J.D. Corbett (Chem. Commun. **24** [1968] 1666).

[6] K.R. Poeppelmeier, J.D. Corbett (Inorg. Chem. **16** [1977] 294/7). – [7] K.R. Poeppelmeier, J.D. Corbett (Inorg. Chem. **16** [1977] 1107/11). – [8] K.R. Poeppelmeier (Diss. Iowa State Univ. 1978, pp. 1/196; Diss. Abstr. Intern. B **39** [1979] 3323). – [9] J.D. Corbett, R.L. Daake, K.R. Poeppelmeier, D.H. Guthrie (J. Am. Chem. Soc. **100** [1978] 652/4). – [10] K.R. Poeppelmeier, J.D. Corbett (J. Am. Chem. Soc. **100** [1978] 5039/44).

11.2.11.1.2 ScCl

The ScCl phase was first obtained in an extremely small yield by reduction of $ScCl_{1.5}$ with Sc metal foil in sealed tantalum tubes above 877 °C (incongruent melting point of $ScCl_{1.5}$). For improvement of the yield Sc metal powder (particle size <100 mesh; ca. 0.25 g) was welded in a small Ta tube with $ScCl_3$ (0.4 g); the tube was then surrounded by a quartz glass jacket and heated for several weeks at 800 °C. In this manner the reaction components were completely consumed and a black crystalline mass was formed with the atom ratio $Cl:Sc=1.04\pm0.03$. The preparation of single crystals takes place in a similar manner through heating for 2 months of a mixture of Sc powder (particle size <100 mesh) and $ScCl_3$ (total ratio $Cl:Sc=1.0$) at 960 °C. The temperature is then lowered at a rate of 1.25 °C/h to 900 °C, following which the reaction tube is cooled in air to room temperature. Microscopic and X-ray examinations show the resulting single crystals to be embedded in a gray-black mass of $ScCl_3$. Approximately 80 wt% of the reaction product consists of shiny gray-black and easily cleaved ScCl crystals (trigonal $R\bar{3}m-D^5_{3d}$ with $a=3.473$ and $c=26.71$ Å, see "Rare Earth Elements" C4a, 1982, Section 11.2.2, pp. 24/6), K.R. Poeppelmeier, J.D. Corbett (Inorg. Chem. 16 [1977] 294/7).

11.2.11.1.3 Sc_7Cl_{10} ($ScCl_{1.43}$)

Formation and Preparation

The compound forms on heating for six weeks about 0.20 g Sc powder (particle size <100 mesh) with 0.59 g $ScCl_3$ in a sealed Ta tube in a temperature gradient of 880 to 900 °C. The $ScCl_{1.43}$ single crystals (about 30% of the weight of the total reaction product) deposit during this process in the hottest zones of the reaction tube in form of needles, Poeppelmeier, Corbett [1].

Crystallographic Properties

The crystals are monoclinic, more needle-shaped than fibrous, but easily broken up into fibers. The space group is $C2/m-C^3_{2h}$ (No. 12). The lattice constants are $a=18.620$,