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On the phase diagram of the binary system Sc_2O_3–ScF_3 in the temperature range 1400–1840 K

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Abstract

The phase diagram of the binary system Sc_2O_3–ScF_3 was investigated in the temperature range 1400–1840 K by quantitative differential thermal analysis (DTA). X-ray powder diffraction analysis revealed that at room temperature only the well-known compounds Sc_2O_3, ScOF and ScF_3 exist. At 1419 ± 3 K, the slightly non-stoichiometric compound of composition $Sc(O,F)_{1.88 \pm \delta}$ is probably formed by eutectoid reaction from Sc_2O_3 and ScOF. ScOF decomposes into $Sc(O,F)_{1.88 \pm \delta}(s)$ and $ScF_3(s)$ at 1460 ± 3 K. Eutectic melting occurs at 1627 ± 3 K for a mixture of 67 mol% ScF_3 and 33 mol% $ScO_{1.5}$. Pure ScF_3 melts at 1822 ± 3 K and does not display any solid state phase transition. The compound $Sc(O,F)_{1.88 \pm \delta}$ could not be quenched to room temperature, and therefore structural details of this presumably fluorite-related phase could not be investigated.

Keywords: Differential thermal analysis; Phase diagram; Scandium oxide fluoride; Scandium trifluoride

1. Introduction

The system Sc–O–F is characterized by the existence of three stable stoichiometric compounds at standard temperature and pressure, namely Sc_2O_3 (cubic, C-Ln_2O_3-type, space group Ia3, [1]), ScOF (monoclinic, baddeleyite-type, space group P21/c, [2]) and ScF_3 (reported to be either cubic, ReO_3-type, space group Pm3m, [3–6], or slightly rhombohedrally distorted ReO_3-type, space group R32, [7–9]). ScOF is reported to transform to the tetragonal YOF-type, space group P4/nmm, at high

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pressure [10]. At 100 kbar and 1473 K, a stoichiometric hexagonal compound of composition $Sc(O,F)_{2.66}$ and a tetragonal solid solution of composition range ScOF–$Sc(O,F)_{2.4}$ exist, which both decompose to mixtures of ScOF and ScF_3 at 773 K and normal pressure [11]. A controversy exists with respect to a possible polymorphic phase transition of ScF_3 at normal pressure. While Spedding et al. [3] did not detect such a transition, Ippolitov and Maklachkov [8], and Kommissarova and Pokrovskii [12] report transitional temperatures of 1748 ± 20 K and 1623 ± 20 K, respectively. So far a complete phase diagram of the system Sc–O–F for normal pressure conditions has not been reported. One reason for this situation may be that ScF_3 is a very high-melting but rather volatile compound, which hydrolyses easily at moderately elevated temperatures in the presence of even traces of humidity. Hence any physical investigation of ScF_3-containing samples at high temperatures has to be performed in gas-tight, high-melting and non-reactive containers.

In this paper we present the results of an investigation into the phase diagram of the binary system Sc_2O_3–ScF_3 in the temperature range 1400–1840 K by quantitative DTA and DSC.

2. Experimental

2.1. Preparation and characterization of compounds

Sc_2O_3 (stated purity 99.99%, Ventron) and ScF_3, prepared from the sesquioxide by the method described in Ref. [5] and further purified by sublimation under high-vacuum conditions inside a high-density graphite tube at 1100 K, served as starting materials. These compounds and most samples obtained after the DTA and DSC experiments were characterized by their X-ray powder patterns (Nonius Guinier-chamber, Cu $K\alpha 1$ radiation, silicon (NBS-SRM-640 A) as internal calibration standard). Sc_2O_3 and ScF_3 were both found to be cubic with $a = 984.4 \pm 0.5$ pm and 401.3 ± 0.5 pm, respectively, in very good agreement with data from the literature [1,6]. In the case of ScF_3, no reflections were observed, which would have justified the choice of a rhombohedrally distorted unit cell. ScOF was prepared by high-temperature annealing of an Sc_2O_3–ScF_3 mixture, enclosed in a gas-tight platinum capsule. The compound was found to be monoclinic with $a = 516.9 \pm 0.9$ pm, $b = 514.9 \pm 0.8$ pm, $c = 524.8 \pm 0.9$ pm and $\beta = 99°42' \pm 6'$, in very good agreement with the results of Ref. [2].

Pyrohydrolysis of ScF_3 at 1300 K in air yielded an Sc content of 44.10% by weight, in good agreement with the expected content, 44.17%.

2.2. DTA and DSC measurements, apparatus and procedures

The DTA measurements were performed in a Netzsch STA 429 apparatus for simultaneous DTA and TGA. Carefully homogenized Sc_2O_3–ScF_3 mixtures, weighing approximately 100 mg, were enclosed in sealed, gas-tight platinum capsules (length, approx. 10 mm; outer diameter, 5 mm). An identically enclosed corundum powder sample served as the inert reference material. The temperature difference was measured with Pt/Pt + Rh thermocouples, kept in direct contact with the platinum capsules. This sample-holding arrangement resulted in optimal sensitivity and very good reproducibility and resolution of the DTA signals. For equilibration purposes, each enclosed Sc_2O_3–ScF_3 mixture was first annealed at 1800 K for 3 h and then run through four heating–cooling cycles between the minimum and maximum temperatures of the experiment with a rate of 5 K min^{-1} in dry, standing air. In most cases, equilibrium had already been attained after the first cycle, and the average signal temperatures and peak areas of cycles 2–4 could then be considered as the final results. Undercooling effects were generally observed. Therefore only the signals obtained on heating were used for the data evaluation. The signal temperatures were derived from the extrapolated peak onsets in the usual fashion. A temperature calibration of the instrument was carried out by measuring the melting points of NaCl and CaF_2 (reagent grade and suprapur, respectively, Merck AG) and a solid state phase transition of $SrCO_3$ (ICTA standard GM 760). The observed melting and transition temperatures, 1071 ± 3 K, 1690 ± 3 K and 1201 ± 3 K, respectively, were found to be in very good agreement with literature data, 1074 K [13], 1691 K [13] and the certified ICTA value, 1201 K. Hence an accuracy of the temperature measurements of ± 3 K was assumed for the whole temperature range. TGA was performed simultaneously in order to be certain that the composition of the samples had not changed during the runs, either by loss of gaseous ScF_3 or due to hydrolytic attack by traces of humidity. The observed mass losses were always $< \pm 0.3$ mg and, hence, could be neglected.

DSC measurements were performed in a Netzsch DSC 404 apparatus in order to gain better information on the relative enthalpy changes accompanying the various thermal effects. The samples were contained in covered platinum crucibles and had been equilibrated in sealed platinum capsules at 1530 K for 48 h prior to use.

The normalized signal intensities, as derived from the DSC and DTA peak areas, were used to determine the composition ranges relating to the thermal transformations.

3. Results and discussion

Four DTA signals, designated $T_1 - T_4$, are the characteristic thermoanalytical features of the system Sc_2O_3–ScF_3 in the temperature range 1400–1840 K. The results of this study are summarized in Table 1, which in column 1 contains the compositional index x related to the general analytical formula $Sc(O,F)_x$ ($1.5 \leq x \leq 3.0$) of the samples, and in columns 2–5 gives the equilibrium signal temperatures. A tentative phase diagram based on these results is presented in Fig. 1.

The signal T_1 occurs at 1419 ± 3 K within the composition range $1.5 \leq x < 2.5$. Its intensity increases from zero at $x = 1.5$ to a maximum at $x = 1.88$, and then drops to almost zero at $x = 2.0$. For the composition range $2.0 \leq x \leq 2.5$, the behaviour of this signal proved to be different depending on whether the samples were cycled in the temperature range 1300–1700 K or in the range 1300–1500 K: In the former case, the signal was generally observed, although with unusually scattered intensities, until close to $x \approx 2.5$ when it could no longer be detected reliably. In the latter case, however, the signal was definitely absent for $x > 2.0$. For $1.5 \leq x \leq 2.0$, signal T_1 is attributed to the

Table 1
DTA and DSC signal temperatures for samples of analytical composition $Sc(O, F)_x$, with $1.5 \leq x \leq 3.0$, for the binary system $ScO_{1.5}$–ScF_3

x	T_1/K [a]	T_2/K [a]	T_3/K [a]	T_4/K [a]
1.655	1419	–	–	–
1.750	1421	–	–	–
1.841	1421	–	–	–
1.850	1419 [b]	–	–	–
1.876	1421	–	–	–
1.895	1418 [b]	–	–	–
1.897	1415	1445	–	–
1.900	1421	–	–	–
1.903	1419	1460	–	–
1.915	1419 [b]	1467	–	–
1.950	1419 [b]	1465	–	–
1.972	1416	1463	1626	–
1.990	1418 [b]	1466	–	–
2.000	1420 [b]	1467	–	–
2.001	1419	1462	1628	–
2.024	–	1459	1626	–
2.050	–	1459	1626	–
2.073	–	1462	1630	–
2.100	–	1461	–	–
2.125	–	1461	1628	–
2.149	–	1458	1618	–
2.200	–	1457	1619	–
2.445	–	1454	1617	1745
2.465	–	1453	1620	1733
2.490	–	1457	1625	–
2.499	–	1461	1629	–
2.525	–	1458	1628	–
2.549	–	1463	1628	–
2.650	–	1456	1625	1683
2.750	–	1456	1629	1723
2.840	–	1456	1619	1748
2.940	–	1458	1627	1798
3.000	–	–	–	1822

[a] Accuracy ± 3 K.
[b] DSC data.

eutectoid formation of a phase of composition $Sc(O,F)_{1.88}$ according to

$$0.24ScO_{1.5}(s) + 0.76ScOF(s) \longrightarrow Sc(O,F)_{1.88}(s) \tag{1}$$

The inconsistent behaviour of signal T_1 for $x > 2.0$ in the case of samples which had been cycled through the temperature range 1300–1700 K, can be interpreted as being caused by incomplete equilibration. This temperature range also includes the transformations relating to signals T_2–T_4 (see below), and the otherwise optimal cooling rate

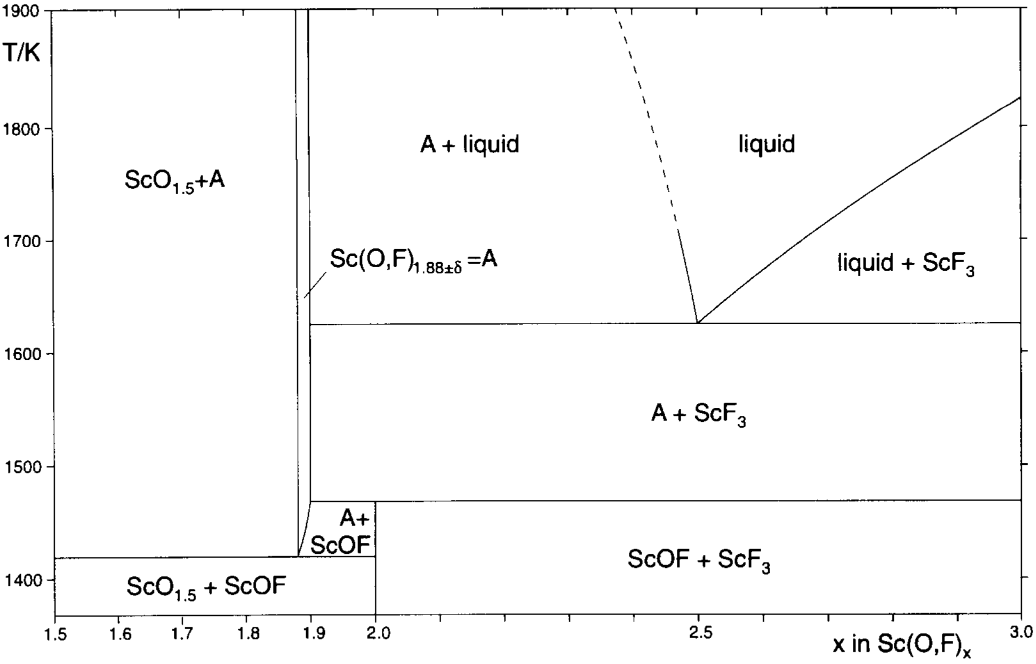

Fig. 1. Tentative phase diagram of the binary system Sc_2O_3–ScF_3 in the temperature region 1400–1822 K.

of 5 K min^{-1} was apparently still too high to attain equilibrium and hence to assure the complete disappearance of $Sc(O,F)_{1.88}$ at temperatures below 1419 K.

The shapes of signal T_1 for compositions in the neighbourhood of $x = 1.9$ imply the possibility that the compound $Sc(O,F)_{1.88}$ is slightly non-stoichiometric, and $Sc(O,F)_{1.88\pm\delta}$ would therefore be a more appropriate formula. We were, however, unable to derive an exact value for the width of a potential homogeneity region.

The signal T_2 occurs at 1460 ± 3 K within the composition range $1.9 \leq x \leq 3.0$ with an intensity maximum at $x = 2.0$. It is attributed to the peritectoid decomposition of ScOF according to reaction (2)

$$ScOF(s) \longrightarrow 0.892Sc(O,F)_{1.88}(s) + 0.108ScF_3(s) \quad (2)$$

This interpretation is corroborated by our finding that pressures of $ScF_3(g)$ in equilibrium with ScOF(s), as measured by the Knudsen effusion method at $T > 1460$ K, practically equal the vapour pressures of pure $ScF_3(s)$ in the same temperature range [5, 14].

The signal T_3 occurs at 1627 ± 3 K within the composition range $1.9 < x \leq 3.0$ and displays an intensity maximum at $x = 2.5$. This signal can be attributed to eutectic melting of a mixture of 67 mol% ScF_3 and 33 mol% $ScO_{1.5}$. The liquidus line could be accurately determined for $2.5 \leq x \leq 3.0$, but it could not be reliably detected for $1.9 \leq x \leq 2.5$. Following the reasonable assumption that $Sc(O,F)_{1.88\pm\delta}$ is a very high-melting compound one has to conclude that the liquidus line is extremely steep for $x<2.5$. Since the maximum temperature obtainable with our DTA equipment was approx. 1850 K, it is immediately evident that in this region the liquidus signals are only reliably observable very close to the eutectic composition.

The signal T_4 at 1822 ± 3 K for $x=3.0$ represents the melting point of ScF_3, in very good agreement with the results of Ippolitov and Maklachkov [8], 1823 ± 20 K, and of Spedding et al. [3], 1825 K, but deviating from the value given in Ref. [12], 1803 ± 20 K. In the range $2.5<x<3.0$, the temperatures T_4 do in fact increase and the signals display typical liquidus shapes. The authors of Refs. [8] and [12] claim to have observed a polymorphous transition of ScF_3 at 1748 ± 20 K and 1623 ± 20 K, respectively. Since neither Spedding et al. [3] nor ourselves were able to detect this transition when studying practically oxide-free ScF_3, we are inclined to conclude that the effect reported in Refs. [8] and [12] was actually the eutectic signal at 1627 ± 3 K, which is easily observable even if the oxide-fluoride content of the trifluoride sample is very small.

Since the phase $Sc(O,F)_{1.88\pm\delta}$ could not be quenched to ambient temperature, no hint can be given as to the crystal chemical nature of this compound. Bevan [15] has found that baddeleyite-type YbOF decomposes at about 1275 K by a eutectoid reaction into YbF_3 and a non-stoichiometric, monoclinic, fluorite-related phase of approximate composition $Yb(O,F)_{1.9}$. One may hence tentatively assume that the crystal chemical features of $Sc(O,F)_{1.88\pm\delta}$ are similar to those of the compositionally comparable phase in the Yb–O–F-system.

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