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Scandium fluorides

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Abstract

A new modification of scandium fluoride has been synthesised. The compound is deficient in fluorine, with the composition $ScF_{2.76}$. It belongs to the tetragonal system, lattice parameters being $a = 3.792$ and $c = 6.740$ Å and may be obtained at low temperatures by the decomposition of the precursor NH_4ScF_4. The reaction is topotactic, tetragonal parameters of the precursor are $a = 4.021$ and $c = 6.744$ Å. Structural relationships with various fluorides and ammonium aminofluorides are discussed. This synthesis route with IR-assisted decomposition should be considered as a soft-chemistry approach. © 1997 Elsevier Science S.A.

Keywords: Scandium; Fluorides; Fiber glasses

1. Introduction

The materials now known as fluoride rare-earth glasses are proving themselves the best lightguide compositions due to their stability and transparency within a wide region of infrared spectrum, where oxide-based fibers are opaque. Scandium fluoride, in particular, was recently proposed as a component of the cladding layer of the optical fiber [1]. However, a better understanding of phase relationships in binary and ternary systems as well as the possibility to make certain predictions about glass formation, require information concerning individual compounds. Evidently, it comprises explicit knowledge of various polymorphic modifications including those with structural defects. The conventional form of scandium fluoride, sometimes reported as cubic with ReO_3 structural type [2], actually belongs to the trigonal system, its angles being very close to 90° [3]. A rhombohedral modification of $ScF_{2.76}$ is characteristic for intermediate temperatures and is usually obtained by ignition [4]. Finally, a high pressure orthorhombic modification is known at 430°C after applying the pressures ≥ 100 kbar [5]. The present work reports on the synthesis and characterisation of ScF_3 low temperature form, including the study of its precursors and compounds with mixed cation.

2. Experimental details

Scandium-containing starting material was Sc_2O_3 (99.999% purity), later transformed into $Sc(OH)_3$ by dissolution in HCl and precipitation with NH_4OH. Fluorine-containing reagent was NH_4HF_2 (analytical grade purity).

In contrast to the usual method of preparation by high-temperature ignition using HF, a quite different low-temperature technique has been developed. Diluted solution of NH_4HF_2 was added to the suspension of freshly prepared scandium hydroxide. The choice of these reagents and their molar ratio (2:1) provided conditions corresponding to the crystallisation of a complex fluoride NH_4ScF_4 in the system

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NH_4F–ScF_3–H_2O [6]. With pH maintained in a very narrow range (3.4–3.5) the crystallisation is completed after 3 weeks at room temperature. Then scandium–ammonium fluoride was filtered, washed with ethanol and left for decomposing under an infrared lamp for 1 week. As a result, ammonium-free scandium fluoride was obtained. The absence of N–H bonds was checked by its IR spectrum.

After alkaline fusion and lixiviation with water, chemical analysis for scandium was performed by the ICP technique; fluorine was determined by the SPANDS method; nitrogen and hydrogen were determined by the Dynamic Flash Combustion method using elemental analyzer 1110 CHNS-O. X-ray patterns were recorded using a Siemens Kristalloflex diffractometer (Ni-filtered CuK_α radiation) provided with a graphite monochromator. Infrared spectra were run on a Nicolet Spectrophotometer FTIR IMPACT 400.

3. Results and discussion

Analysis gave the following results: (a) for scandium fluoride Sc 46.12 wt.% and F 53.7 wt.% which corresponds to a non-stoichiometric composition $ScF_{2.76}$; (b) for the precursor Sc 32.78 wt.%, F 54.20 wt.%, N 11.66 wt.% and H 2.80 wt.%, which corresponds to NH_4ScF_4 mentioned above with a slightly higher nitrogen content owing to some excessive ammonia trapped in the lattice.

$ScF_{2.76}$ is a colourless powder. Its X-ray pattern was indexed in tetragonal system with parameters $a = 3.970$ and $c = 6.740$ Å. It is isostructural with the γ-form of indium fluoride [7], certainly due to the proximity of Sc and In ionic radii. The compound we obtained is a new, non-stoichiometric form of scandium fluoride. The deviations of the cationic/anionic ratio from the stoichiometric values are well known for the elements of lanthanide series although their syntheses were performed by solid-state reactions at high temperatures. These phases with a deficit in fluorine are considered as limiting compositions having a tysonite structural type before its sharp transition into the structural type of fluorite [8]. The contraction along the c-axis with a slight distortion of angles may lead to the trigonal lattice with the parameter $a = 4.021$ Å. Finally, under certain experimental conditions (temperature, pressure) and lesser fluorine contents we might expect additional polymorphic modifications of scandium fluoride. In this case scandium is much closer to Al, Ga and In fluorides with the difference that the stable tetragonal phases formed by these elements are always stoichiometric [7].

The ammonium complex NH_4ScF_4 belongs to a family of non-stoichiometric fluorides $(NH_4)_n(NH_3)_mMe(III)F_{n+3}$ [9,10] which tend to absorb and storage NH_3 and hydrazine. So, when discussing the mechanism of $ScF_{2.76}$ formation, it is logical to suggest that the elimination of ammonia trapped in NH_4ScF_4, in addition to the elimination of NH_4F, may be responsible for the formation of non-stoichiometric fluoride. Fluorine removal may be due to the formation of intermediate dimerized ammonia and its fluorides N_2H_5F and/or $N_2H_4F_2$. Schemes for ammonia dimerization are not so exotic as once they were [11].

Fittingly, the IR spectrum of ammonium aminofluoride shows that apart from the frequencies characteristic of N–H bonds (1433, 2323, 2891 and 3223 cm^{-1}), there are weak bands corresponding to the vibrations of groups amino (1260 and 1626 cm^{-1}), cations NH_3^+ (1124 and 2690 cm^{-1}) and bridges N–N (955 and 985 cm^{-1}). These data are in accordance with the results of previous spectroscopic studies carried out for structurally related indium and gallium aminofluorides [7,9] and hydrazine scandium fluorides [12]. As to the Sc–F vibration (ν_3), in the spectre of NH_4ScF_4 it is split into two components, 490 cm^{-1} (s) and 553 cm^{-1} (sh), these distortions being usually explained as being due to the rotation of $Me(III)F_6^{3-}$ octahedra.

Under IR radiation the reaction of NH_4ScF_4 decomposition is slow but occurs with noticeable rate because kinetics factors are significant and NH_4F acts as mechanical agitator. No major changes in the X-ray patterns are observed during the heating. Actually, we could confirm that NH_4ScF_4 is isostructural with the above non-stoichiometric fluoride, its parameters being $a = 4.021$ and $c = 6.744$ Å. The a parameter of NH_4ScF_4 is larger than that of scandium fluoride due to the presence of NH_4^+ ions in the network, but there is no corresponding increase in the c-parameter. So gradual loss of ammonia and its volatile fluoride seems to be a topotactic process, as was proposed elsewhere [10].

Rapid heating does not allow the preservation of the initial tetragonal network, the structure collapses and the common rhombohedral form of scandium fluoride is obtained at 270°C. No reflections of ScN [13] have been observed on X-ray patterns. In contrast to InN [9], this compound is not formed in the process of scandium–ammonium fluoride decomposition.

For synthesising materials including two different cations, it is preferable to introduce them both bound in the common crystalline lattice. In view of possible applications we reproduced the same synthesis using the mixture (1:1) of two hydroxides, $Sc(OH)_3$ and $In(OH)_3$, as starting reagents. In contrast to the pair Lu–Sc with comparable ionic radii [2], isomorphic relationships between γ-phases of In and Sc fluorides permitted the crystallisation of a fluoride with mixed cation which maintains the structure of γ-InF_3 and may be used as a starting material for fiber glasses. As to the absorption in the near IR region, their properties are the less troublesome in fluoride glass preparation. The investigation of other fluorides with mixed cations is now in progress.

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