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STUDIES ON LANTHANOID SULFITES. PART VI*. THERMOGRAVIMETRIC STUDY OF SCANDIUM SULFITE PENTAHYDRATE

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SUMMARY

Scandium sulfite was found to crystallize as a pentahydrate both at 25 and 90 °C when precipitated by the action of sulfur dioxide on aqueous suspensions of $Sc(OH)_3$. Thermogravimetric analysis showed that the anhydrous sulfite is formed by 200 °C but it starts to decompose immediately after its formation. The decomposition leads to an intermediate phase which is stable up to 700 °C in inert (nitrogen) and air atmospheres but decomposes earlier in reductive (hydrogen) environment. The weight remaining, which corresponds to the intermediate level, varies between 58 and 43 % depending on experimental conditions and thus cannot be assigned to a single compound such as $Sc_2O_2SO_4$ or $Sc_2O_2SO_3$. The intermediate phase is amorphous to X-rays but IR spectra indicate the presence of both sulfite and sulfate ions pointing to a mixture. In all atmospheres studied the final decomposition step is the formation of scandium sesquioxide.

INTRODUCTION

The preparation and properties of lanthanoid sulfites, including those formed by scandium and yttrium, have been recently reviewed (refs. 1,2). There are only a very few reports on scandium sulfites which give partially contradictory data as regards the water content (refs. 3,4). Preparative conditions, however, may greatly affect the stoichiometries of the precipitated phases. For instance, Kuntsevich et al. (ref. 5) report that only basic sulfites $ScOHSO_3$ and $Sc_3OH(SO_3)_4$ are formed when scandium thiosulfate solutions are hydrolyzed by boiling at pH 4 and 2, respectively.

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[*] For Part V, see ref. 6.

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As part of our systematic investigation into the preparation and properties of rare earth sulfites (ref. 6), we are now reporting the results of a thermogravimetric study of $Sc_2(SO_3)_3 \cdot 5H_2O$.

EXPERIMENTAL

Scandium sulfite pentahydrate was prepared *via* $Sc(OH)_3$ which was obtained by dissolving Sc_2O_3 in nitric acid and precipitating with aqueous ammonia. The gel-like hydroxide was filtered, washed and dried *in vacuo*. An aqueous suspension of the hydroxide (1 g/100 ml H_2O) was treated with SO_2 by slowly passing the gas through the suspension. Scandium hydroxide does not dissolve completely, contrary to other rare earth oxides and hydroxides, but after passing SO_2 a few hours the light hydroxide powder is slowly converted to a heavier precipitate. This precipitate was filtered, washed with ethanol and dried in air. According to chemical analyses the stoichiometry of the precipitate was very close to $Sc_2(SO_3)_3 \cdot 5H_2O$ in analogy with the corresponding sulfate (ref. 7). The X-ray diffraction measurements showed that the products prepared both at room temperature and at 90 °C were identical (Fig. 1) which is also contrary to the behaviour of other rare earth sulfite hydrates where the water content depends greatly on the crystallization temperature (refs. 6,8).

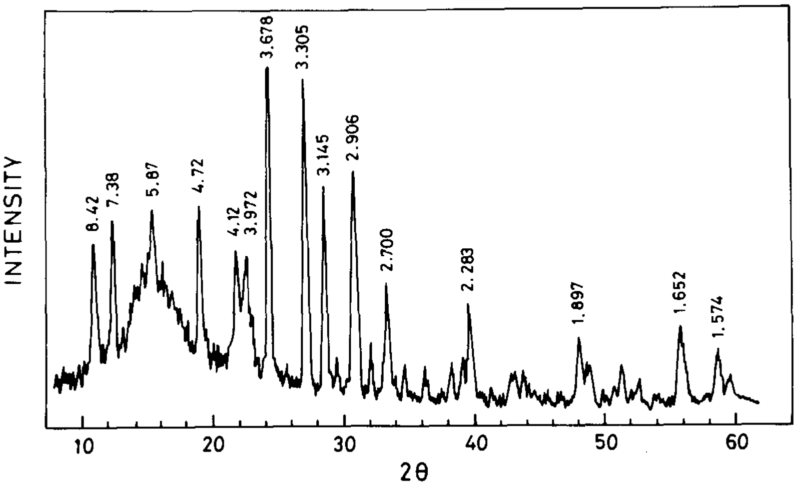

Fig. 1 The X-ray diffraction pattern of $Sc_2(SO_3)_3 \cdot 5H_2O$. Radiation used CuKα, internal standard Si. *d*-values given for the most intense reflections are in Å.

In thermoanalytical investigations a set of Perkin-Elmer TG-DSC series 7 instruments was employed. The sample size was usually 20 mg and the heating rate varied between 1 and 10 °C/min. The heating was performed using standard crucubles in air and nitrogen atmospheres or in hydrogen which contained argon (5:95, v:v).

The infrared spectra were recorded with a Bruker IFS 313V FTIR apparatus using the ATR technique, the sample was spread on a Ge or ZnSe crystal. The X-ray diffraction measurements were carried out with a Philips powder diffractometer.

RESULTS AND DISCUSSION

Upon heating $Sc_2(SO_3)_3 \cdot 5H_2O$ starts to loose water immediately. The three-step dehydration corresponds to the release of one, three and one water molecules. The steps are not very distinct, however. The dehydration process is slow up to 100 °C, fast between 100 and 140 °C, and slow again above 140 °C. A weight plateau corresponding to $Sc_2(SO_3)_3$ is reached at 200 °C (Fig. 2). The dehydration process is similar in all atmospheres studied; the heating rate has expected effect on the temperatures only.

The anhydrous phase is not stable but decomposes slowly. Above 250 °C the decomposition rate increases and around 350 °C in air an intermediate plateau occurs at 53-54 wt-% when heating rate is 1 °C/min but at 57-58 wt-% when a heating rate of 10 °C/min is employed. The intermediate phase is stable up to

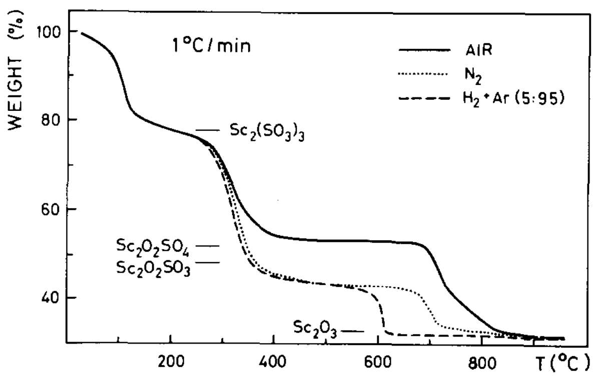

Fig. 2. TG curves of $Sc_2(SO_3)_3 \cdot 5H_2O$ heated with a rate of 1 °C/min in different atmospheres. Calculated weight losses are indicated by lines with corresponding chemical formulas.

700-780 °C after which it decomposes in a two-stage process to oxide (Figs. 2,3). Pure oxide is obtained above 850-930 °C, depending on the heating rate. In air the two last reaction steps occur so successively that no distinct intermediate plateau can be observed.

The anhydrous phase is no more stable in an inert or reductive atmosphere than in air. On the contrary, in nitrogen or hydrogen/argon mixture more weight is lost than in air. The intermediate plateau is found at 44 wt-% in the both atmospheres when a slow heating rate is employed; with a faster rate it occurs at 48 wt-% in nitrogen and at 45 wt-% in the hydrogen/argon mixture. Judging from decomposition temperatures, the stability order of the intermediate phase thus follows the order: air > N_2 > H_2/Ar (Figs. 2,3). The final product in both inert and reductive atmospheres is the sesquioxide. This is surprising because usually when the rare earth sulfites are fired in reductive atmospheres the oxysulfide phase is formed (refs. 9,10).

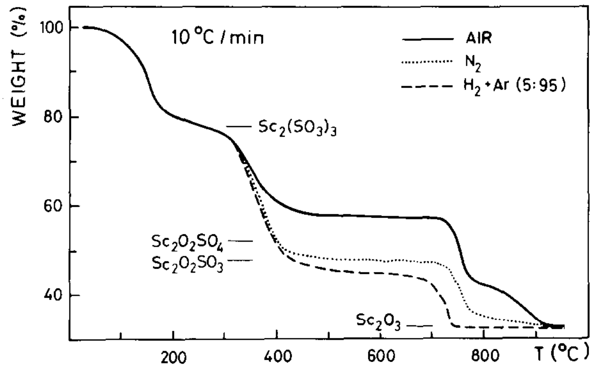

Fig. 3. TG curves for $Sc_2(SO_3)_3 \cdot 5H_2O$ heated at 10 °C/min in different atmospheres.

Usually the rare earth sulfites decompose in air and nitrogen atmospheres *via* an oxysulfate phase, $Ln_2O_2SO_4$ (refs. 1,2). This corresponds to a weight remaining of 51.9 % starting from $Sc_2(SO_3)_3 \cdot 5H_2O$. Our TG results indicate that the intermediate plateaus observed in air are located above the theoretical weight level corresponding to the formation of oxysulfate while the plateaus observed in inert or reductive atmospheres are below this value. Moskalenko *et al.* (ref. 4) have reported the formation of an oxysulfate phase without any deviations from ideal stoichiometry. Kuntsevich et al. (ref. 5), on the other hand, have obtained $Sc_2O_2SO_3$. The oxysulfite phase corresponds to 48.0 wt-% measured from scandium sulfite pentahydrate. It is interesting to note that the values observed in nitrogen and hydrogen are very close to 48 % but in air the $Sc_2O_2SO_3$ level is far from that observed.

The identification of the intermediate products obtained is difficult because they are amorphous. Despite of isothermal heatings lasting several hours, crystalline material could not be obtained. However, the isothermal firings in thermobalance showed the great stability of the intermediate phases. IR spectroscopy remained one of the very few practical ways to investigate the intermediate phases. Unfortunately, the infrared spectrum of $Sc_2(SO_3)_3 \cdot 5H_2O$ showed only two strong peaks (889 and 924 cm^{-1}) in the S-O stretching region 1300 - 800 cm^{-1} (Fig. 4). The spectrum is similar to that observed by Moskalenko et al. for $Sc_2(SO_3)_3 \cdot 3H_2O$ (ref. 4) who noted that the distortion of

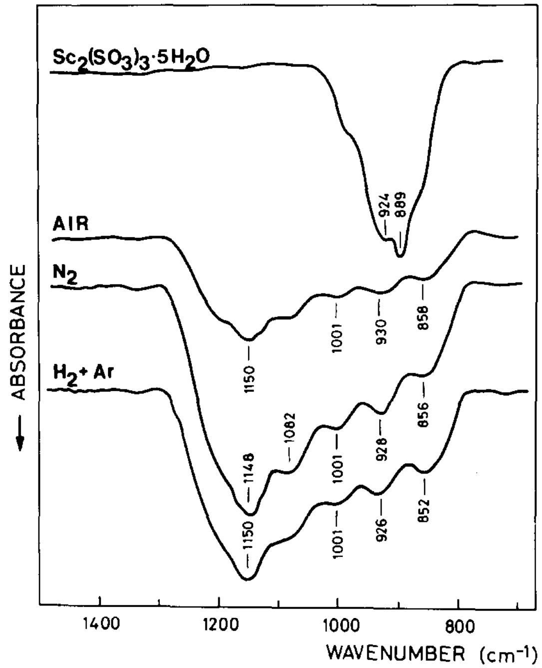

Fig. 4. IR spectra in the region 1400 - 700 cm^{-1} for scandium sulfite and samples prepared thereof by firing in air, nitrogen and hydrogen atmospheres for 4 hrs.

the $\underline{C}_{3v}$ symmetry in SO_3^{3-} groups is minimal. Based on this observation they suggested the presence of an outer-sphere sulfito complex but concluded that this would be improbable because there are only three water molecules in the compound. Even with a higher water content, as in the present compound, this coordination seems unlikely (ref. 1).

The IR spectra of the isothermally fired samples differ from that of the unfired sample (Fig. 4). Samples fired in static atmosphere appear to contain both sulfate and sulfite (ref. 11). The number of peaks has increased and the absorption peaks above 1000 cm^{-1} are typical for rare earth sulfates (ref. 12). It is interesting to note that the spectra are identical and independent of the firing atmosphere. Thus it seems that the intermediate product always contains both sulfite and sulfate ions and no pure stoichiometric compounds can be obtained.

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