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Studies on Lanthanoid Sulfites. Part VII.* Preparative and Thermal Study on Rare Earth Sulfite Sulfate Hydrates**

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The existence of metal sulfite sulfate hydrates in the solid state has been detected recently. Peterson *et al.* have studied the rare earth (La, Ce, Pr) sulfite sulfate hydrates [1, 2], while Cohen and Zangen have focused their research on the corresponding calcium complexes [3–5]. The interest in the rare earth sulfite sulfates stems from the reaction of these materials with iodine which yields the sulfate in the solid phase and HI in the gas phase. A water splitting thermochemical cycle is formed with HI is catalytically decomposed to hydrogen and the solid phase is fired and recycled [6, 7].

Insoluble rare earth disulfite sulfate hydrates, $Ln_2(SO_3)_2SO_4 \cdot nH_2O$ (Ln = lanthanoids), can be prepared by the reaction of the corresponding oxosulfate, $Ln_2O_2SO_4$, with sulfur dioxide in aqueous media at 25–90 °C. The reaction product is non-stoichiometric, which in the case of lanthanum means that the sulfite coefficient ranges from 0.2 to 1.8 and that of sulfate from 0.8 to 1.0, depending on the experimental conditions. The water content (n) varies from 2.8 to 6.8 [8] and part of the oxosulfate starting material may also remain in the product. Besides crystallizing from solution, both types of cerium sulfite sulfate compounds ($Ce_2(SO_3)_2SO_4$ and $Ce_2SO_3(SO_4)_2$) have been obtained as intermediates in the thermal decomposition of cerium sulfite hydrate [9]. The other rare earth sulfite which shows a similar oxidation behavior under heating in air is europium sulfite [10].

On the other hand, calcium sulfite sulfate hydrate can be crystallized by adding Ca^{2+} ions into a solution of sodium sulfite and sulfate [3–5]. The $SO_3{}^{2-}$/$SO_4{}^{2-}$ ratio in the solid phase is always close to 2. The sulfite sulfate solution is surprisingly stable in air. It may be assumed therefore that when calcium solutions are utilized in the removal of sulfur from utility stack gases, the calcium sulfur waste formed is not pure gypsum but at least partly calcium sulfite sulfate hydrate.

In view of the interesting chemical properties and potential applications, the present study was initiated. Its aim was to systematically investigate the preparation of stoichiometric rare earth sulfite sulfate hydrates by the solution process and to characterize the solid compounds by X-ray diffraction and thermoanalytical methods.

Experimental

A series of rare earth sulfite sulfate hydrate complexes was prepared by dissolving Ln_2O_3 at room temperature in a sulfuric acid solution saturated with SO_2 and precipitating at 90 °C. The volume of the sulfuric acid was typically 60 cm^3 (0.05 mol/dm^3 = 0.003 mol $SO_4{}^{2-}$) and the amount of oxide was about 1 g (= 0.006 mol Ln^{3+}; Ln^{3+}: $SO_4{}^{2-}$ ratio 2:1). The oxides dissolve immediately but the precipitation takes place slowly at 90 °C in an SO_2 atmosphere. Changing the SO_2 atmosphere gradually to nitrogen improves the yield. The precipitate was filtered, washed and dried in vacuum. $Ce_2(SO_3)_2SO_4 \cdot 4H_2O$ was also prepared by mixing aqueous solutions of $Ce_2(SO_3)_3$ and $Ce_2(SO_4)_3$ in the molar ratio 2:1 and warming at 90 °C in an SO_2/N_2 atmosphere.

The products were characterized by X-ray powder diffraction and thermal analysis, and the rare earth content was checked by firing the rare earth compound to oxysulfate or oxide. In the thermoanalytical measurements a set of Perkin-Elmer instruments (TGS-2 and TADS) was employed. The sample sizes varied between 10 and 20 mg and two heating rates, 1 and 10 °C/min, were used. The heatings were performed both in air and nitrogen atmospheres.

Results and Discussion

The lanthanoids from lanthanum to neodymium form, under the experimental conditions used in this study, disulfite sulfate tetrahydrates, $Ln_2(SO_3)_2SO_4 \cdot 4H_2O$. Haas *et al.* [8] obtained non-stoichiometric $La_2(SO_3)_{2.32}(SO_4)_{0.68} \cdot 4.9H_2O$ by nearly the same method as we have used. They showed, however, that even small changes in the experimental conditions affect the composition. In our studies the number of water molecules was three only for samarium, while for the lanthanoids from europium to ytterbium, including yttrium, n was 2.2–2.5. The sulfite/sulfate ratio was always stoichiometric, *viz.* 2.

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X-ray Diffraction

The disulfite sulfate hydrates obtained were reasonably crystalline powders according to the XRD patterns. Structurally at least two groups were observed: (i) the tetrahydrates (Ce–Nd) are isomorphous, and (ii) the rest of the lanthanoids (Sm–Yb, incl. Y) form another isomorphous series despite the small differences found in their water content. Lanthanum alone possibly forms a structure type of its own. The results of the first group are in good agreement with those reported by Haas *et al.* for the cerium complex [8]. The XRD pattern of $La_2(SO_3)_2SO_4 \cdot 4H_2O$ clearly differs from that of the Ce and Nd complexes when the strongest reflections are compared (for La, $d = 6.46_{100}$, 3.32_{100}, 2.964_{70}, 2.718_{60}, 4.90_{50} Å; and for Nd, $d = 6.24_{100}$, 3.44_{90}, 4.62_{50}, 2.686_{50}, 3.26_{50} Å). On the other hand, when compared to the d-values of $La_2(SO_3)_{2.32}(SO_4)_{0.68} \cdot 4.9H_2O$ [8] ($d = 6.78$, 3.30, 2.98, 2.71, 4.70 Å) our first and fifth reflections differ also.

The second structural series of $Ln_2(SO_3)_2SO_4 \cdot 2\text{–}3H_2O$ (Ln = Sm–Yb, Y) appears to be a new phase as no literature data have been found. The d-values of the ten strongest reflections for the holmium complex are: 6.11_{60}, 5.62_{100}, 4.70_{40}, 3.35_{60}, 3.28_{60}, 2.894_{100}, 2.858_{100}, 2.823_{60}, 2.607_{50}, 2.166_{40} Å. All disulfite sulfate hydrates appear to have low crystal symmetry and consequently unit cell calculations [11] from the powder XRD data failed.

Thermal Analysis

The dehydration between 150 and 350 °C is a single-step reaction under the conditions studied (Figs. 1–4). Only for the Nd complex is the last water molecule released in a separate step. The anhydrous phase is somewhat more stable in air than in nitrogen. The stability range in nitrogen decreases with the increasing atomic number, but in air this trend is reversed. Thus, for example, $Nd_2(SO_3)_2SO_4$ is stable in air up to 600 °C and in nitrogen up to 570 °C (Fig. 1), while $Er_2(SO_3)_2SO_4$ is stable in air up to 700 °C (Fig. 4) but in nitrogen only up to 490 °C (Fig. 3).

The decomposition of the disulfite sulfate phase takes place in air in a single step to the oxosulfate, $Ln_2O_2SO_4$, which was the final product in the temperature range studied. In nitrogen, the TG curve shows at least two steps. In some cases a distinct level can be observed corresponding to an intermediate stage where the sulfite has decomposed to oxosulfate, *i.e.*, 2/3 $Ln_2O_2SO_4$ + 1/3 $Ln_2(SO_4)_3$, (Fig. 1) but intermediate levels of variable composition also exist (Figs. 2 and 3). The final product in nitrogen is also the oxosulfate.

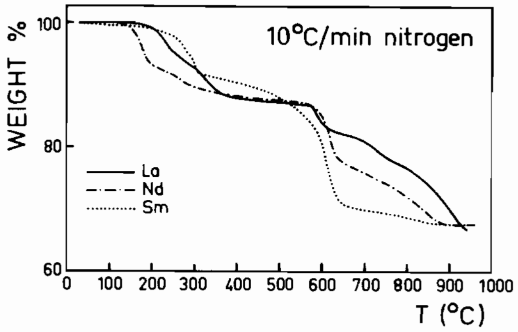

Fig. 1. The TG curves for $Ln_2(SO_3)_2SO_4 \cdot nH_2O$ (Ln = La, Nd, $n = 4$; Ln = Sm, $n = 3$) heated in nitrogen (heating rate 10 °C/min, sample size 12–16 mg).

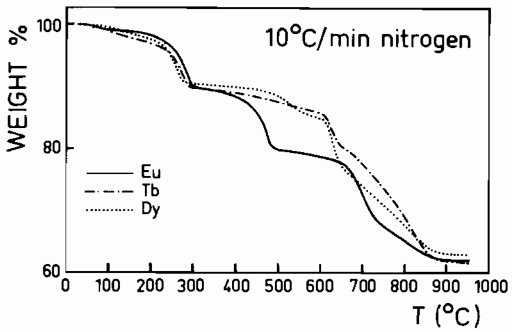

Fig. 2. The TG curves for $Ln_2(SO_3)_2SO_4 \cdot 2\text{–}3H_2O$ (Ln = Eu, Tb, Dy) heated in nitrogen (heating rate 10 °C/min, sample size 12–18 mg).

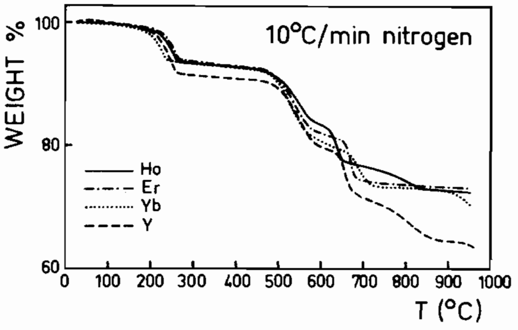

Fig. 3. The TG curves for $Ln_2(SO_3)_2SO_4 \cdot 2\text{–}3H_2O$ (Ln = Ho, Er, Yb, Y) heated in nitrogen (heating rate 10 °C/min, sample size 6–9 mg).

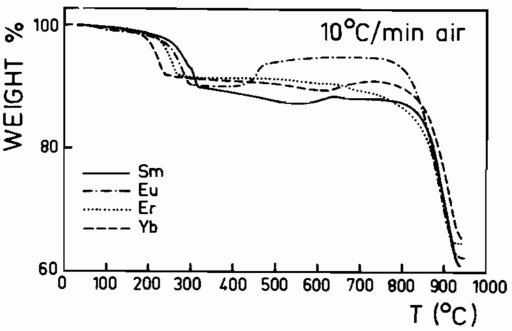

Fig. 4. The TG curves for $Ln_2(SO_3)_2SO_4 \cdot 2\text{–}3H_2O$ (Ln = Sm, Eu, Er, Yb) heated in air (heating rate 10 °C/min, sample size 9–14 mg).

The anhydrous disulfite sulfate phases of Sm, Eu and Yb behave differently in air: the weight increases above 450 ℃ (Fig. 4). The increase is strongest for the Eu complex and the level reached corresponds to the formation of the sulfite disulfate phase, $Eu_2SO_3(SO_4)_2$. The oxidation behavior may be connected with the oxidation reduction potential of these cations. Above 850 ℃ a single-step decomposition yields the oxosulfate as final product.

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