Crystal Structure and Thermal Behaviour of Er$_2$(SeO$_4$)$_3$·8H$_2$O

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Dedicated to Professor Kurt O. Klepp on the occasion of his 60th birthday

Single crystals of Er$_2$(SeO$_4$)$_3$·8H$_2$O were obtained by dissolving Er$_2$O$_3$ in selenic acid. The selenate crystallizes in the monoclinic space group C2/c (Z = 4, a = 1372.8(2), b = 687.5(7), c = 1860.2(3) pm, β = 101.85(2)°, R$_{all}$ = 0.0518) and contains the Er$^{3+}$ ions in eightfold coordination of oxygen atoms that belong to two crystallographically different SeO$_4^{2-}$ ions and to four H$_2$O molecules. According to DTA/TG measurements and temperature dependent powder diffraction data, Er$_2$(SeO$_4$)$_3$·8H$_2$O decomposes in several steps yielding finally Er$_2$O$_3$. Er$_2$(SeO$_4$)$_3$ and Er$_2$(SeO$_3$)$_3$ could be identified as intermediates, and for Er$_2$(SeO$_4$)$_3$ a phase transition was detected.

Key words: Erbium, Selenate, Selenite, Crystal Structure, Thermal Analysis

Introduction

Selenates of the rare earth elements have been investigated to a much lesser extent than the respective sulfates. Based on our present knowledge their structural chemistry parallels essentially the one of the respective sulfates as might be expected from the analogous structure and the comparable volume of the selenate and sulfate anion [1]. On the other hand, the thermal behaviour of sulfates and selenates is usually remarkably different. Lanthanide sulfates decompose at temperatures above 900 °C leading to oxide-sulfates and finally to oxides [2]. The decomposition of selenates starts at lower temperatures and leads in a first step to the respective rare earth selenites [3]. This is due to higher stability of Se(IV) compared to S(IV). We used this decomposition reaction to prepare single crystals of lanthanide selenites for the first time some years ago [4]. At high temperature the selenites decompose to oxides, probably with the oxide-selenites M$_2$(SeO$_3$)$_2$O as intermediates. The latter have not yet been characterized structurally, but their existence has been proved by thermochemical investigations [5]. Other intermediates might be the oxide-selenites M$_2$(SeO$_3$)$_2$O, for which the structure of the terbium compound is known [6]. Selenates of the rare earth elements are most conveniently obtained from the reaction of the respective sesquioxides with selenic acid. They crystallize as hydrates, most often with eight molecules of crystal water [1]. In this paper we describe the preparation and crystal structure of Er$_2$(SeO$_4$)$_3$8H$_2$O and its complete decomposition followed by means of DTA/TG measurements and temperature dependent powder diffraction.

Experimental Section

Pink single crystals of Er$_2$(SeO$_4$)$_3$·8H$_2$O were grown by evaporation of a solution that had been obtained by dissolving Er$_2$O$_3$ in selenic acid. The selenic acid has previously been prepared from H$_2$O$_2$ and SeO$_2$ according to the procedure given in [7]. Some of the prism-shaped crystals were mounted in glass capillaries and their quality was checked by means of orientation images on a single crystal diffractometer (STOE IPDS I). For the best specimen reflection intensity data were collected using the same diffractometer. With respect to the lattice parameters, Er$_2$(SeO$_4$)$_3$·8H$_2$O is isotopic with the respective sulfate. Assuming the space group (C2/c) and the positional parameters of the latter, a reliable structure model was refined using the program SHELXL93 [8]. The data were corrected numerically for absorption effects [9]. Details of the measurement and the crystallographic data are given in Tables 1 – 3 and are additionally available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (crysdata@FIZ-Karlsruhe.de) on quoting the deposition number given in Table 1.

DTA/TG measurements were performed with the help of a thermal analyzer (STA 409, NETZSCH). For that pur-
temperatures of the thermal effects were taken from the differentiated DTA curve following common procedures using the software delivered with the analyzer [10].

Temperature dependent powder diffraction data were collected using a powder diffractometer (Stadi P, STOE&CIE) equipped with a position sensitive detector and a graphite furnace providing a temperature accuracy of ±0.3 °C. The finely powdered sample was filled in a silica capillary (⌀ 0.3 mm) and sealed with grease. Data were collected in Debye-Scherrer geometry in the range of 2θ = 7° – 60°. The temperature range was 50 to 900 °C with intervals of 25 °C between 50 and 200 °C, and 50 °C between 200 and 900 °C. After each heating period the system was allowed to equilibrate for 30 min. The data were processed applying smoothing and background corrections using the program package VISUAL XPOW (STOE&CIE) [11]. The same program also allowed for lattice parameter refinements based on least square procedures.

Results and Discussion

Crystal structure

Er$_2$(SeO$_4$)$_3$ · 8H$_2$O (monoclinic, C$_2$ / c, Z = 4, a = 1372.8(2), b = 687.5(1), c = 1860.2(3) pm, β = 101.85(2)°) is isotypic with the respective erbium sulfate hydrate [12]. In accordance with the smaller volume of SO$_4^{2-}$ compared to SeO$_4^{2-}$ the lattice parameters of Er$_2$(SO$_4$)$_3$ · 8H$_2$O (a = 1346.4(3), b = 667.2(1), c = 1816.1(6) pm, β = 101.90(3)°) are remarkably smaller. In the crystal structure of Er$_2$(SeO$_4$)$_3$ · 8H$_2$O the Er$^{3+}$ ions are in eightfold coordination of oxygen atoms that belong to four water molecules and four monodentate selenate groups. The distances Er-O range from 226.5(7) up to 247.5(7) pm (Table 3) and compare well with the data for the respective sulfate. One of the two crystallographically different se-
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**Fig. 1.** Crystal structure of Er$_2$(SeO$_4$)$_3$·8H$_2$O viewed along [100] (on top). The Er$^{3+}$ ions are connected to layers by tridentate (light grey tetrahedra) and bidentate (dark grey tetrahedra) selenate ions. The layers Er$_2$(SeO$_4$)$_3$·8H$_2$O are stacked in the [20 1] direction and linked only via hydrogen bonds (at bottom).

Selenate ions, Se(2)O$_4^{2-}$, is located on a special position (4e) of the space group C2/c, the second one, Se(1)O$_4^{2-}$, resides on a general site (8f) (Table 2). The Se(1)O$_4^{2-}$ anion connects three Er$^{3+}$ ions with each other, Se(2)O$_4^{2-}$ only two, leading to layers according to $\frac{2}{3}$[Er(H$_2$O)$_{1/1}$]Se(1)O$_4^{3/3}$(Se(2)O$_4^{1/2}$) (Fig. 1). Within the selenate ions typical distances Se-O between 161.9(7) and 166.6(7) pm are observed (Table 3). The angles O-Se-O show also the expected values (106.5(4)$^\circ$ to 113.1(6)$^\circ$) and prove that the tetrahedra are only slightly distorted. The layers are connected via hydrogen bonds, and even if the hydrogen atoms of the H$_2$O molecules could not be located, it can be assumed that the non-coordinating oxygen atoms of the selenate ions act as acceptors and the water molecules as donors, in accordance with the findings for Er$_2$(SO$_4$)$_3$·8H$_2$O [12].

**Thermal behaviour**

According to the DTA/TG measurement the thermal decomposition of Er$_2$(SeO$_4$)$_3$·8H$_2$O starts at 122 $^\circ$C with the loss of the crystal water (Fig. 2, Table 4). The dehydration is a two–step process, although a little shoulder is discernible in the DTA curve for the first step. With respect to the mass loss the intermediate is the trihydrate, Er$_2$(SeO$_4$)$_3$·3H$_2$O. At two–step dehydration has been observed also for Er$_2$(SO$_4$)$_3$·8H$_2$O, but in contrast to the latter the onset temperature for the dehydration is about 20 $^\circ$C higher in the present case and the resolution of the two steps in both DTA and TG curve is not clearly observable. This is also reflected by the temperature dependent X-ray powder diffraction experiment which does not allow the detection of the diffractogram of Er$_2$(SeO$_4$)$_3$·3H$_2$O, although this was possible for the sulfate trihydrate.

The dehydration is complete at 213 $^\circ$C and leads to the anhydrous selenate Er$_2$(SeO$_4$)$_3$. In the powder diffraction investigation the pattern of Er$_2$(SeO$_4$)$_3$ can be detected at 175 $^\circ$C and the diffractogram can be indexed unambiguously assuming the trigonal-rhombohedral structure of Sc$_2$(SO$_4$)$_3$ [13]. The latter...
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<table>
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<th>Reaction</th>
<th>T_{onset} [°C]</th>
<th>T_{end} [°C]</th>
<th>T_{max} [°C]</th>
<th>Mass loss/% obsd. calcd.</th>
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<td>122</td>
<td>172</td>
<td>157</td>
<td>10.0 9.9</td>
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<td>Er2(SeO4)3 · 3H2O → Er2(SeO4)3</td>
<td>157</td>
<td>213</td>
<td>192</td>
<td>15.6 15.9</td>
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<td>681</td>
<td>686</td>
<td>23.8 21.2</td>
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<tr>
<td>Er2(SeO3)3 → Er2(SeO3)O2</td>
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<td>737</td>
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<td>959</td>
<td>947</td>
<td>56.6 57.8</td>
</tr>
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</table>

Table 4. DTA/TG results of the thermal decomposition of Er2(SeO4)3 · 8H2O.

that the dehydration leads to Er2(SO4)3 in the trigonal-rhombohedral form (I) proving the dimorphism of the sulfate. The same dimorphism occurs for Er2(SeO4)3 as may be seen from the diffractogram at 250 °C (Fig. 3). This pattern shows clearly the orthorhombic modification of Er2(SeO4)3 (II). The structures of the two modifications of Er2(SeO4)3 are very similar as it has been described in more detail for the pair Sc2(SO4)3/Y2(SO4)3 [13]. The coordination is octahedral in both cases and the kind of linkage of [ErO6] octahedra and [SeO4] tetrahedra remains the same. That might be the reason why the phase transition cannot be observed in the DTA curve. A further noteworthy detail of the temperature dependent X-ray diffraction can be seen from the refined lattice parameters: The values for Er2(SeO4)3-I decrease when going from 175 to 200 °C, indicating negative thermal expansion. The same effect has been observed for Er2(SO4)3-I [12] and in more detail for Sc2(SO4)3 [14]. On the other hand, Er2(SeO4)3-II exhibits a volume expansion with increasing temperature that interestingly is due to the lengthening of only the a-axis while the other two axes remain the same within the standard deviations.

The orthorhombic form of Er2(SeO4)3 exists up to 658 °C when the decomposition to Er2(SeO3)3 is observed in the DTA/TG measurements (Table 4). However, the respective effect is severely obscured by that of a second step that indicates the formation of the oxide–selenite Er2(SeO3)O2 between 682 and 777 °C (Fig. 2). Nevertheless, the powder diffractograms at 700 °C and even at 750 °C can be unambiguously assigned to Er2(SeO3)3 whose crystal structure has recently been reported [4]. The difference in the results of the DTA and powder diffraction measurements may be attributed to the different conditions of the two methods. The diffractogram at 800 °C shows a new phase, which probably is Er2(SeO3)O2 as suggested by the DTA data. Above 900 °C, Er2O3 is found as the final product of the thermal decomposition.
Our current investigations aim at the preparation of Er$_2$(SeO$_4$)$_3$ and Er$_2$(SeO$_3$)$_2$O in single crystalline form in order to allow a complete characterization of the observed intermediates.

Acknowledgments

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