Single-crystalline hexagonal Sr-Er- and Sr-Dy-sialon microtubes

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Regularly shaped single-crystalline, hexagonal, and hollow Sr-Er- and Sr-Dy-sialon microtubes were yielded by high-temperature reaction using a radio-frequency furnace at 1600 °C and 1670 °C, respectively. Starting materials were silicon diimide (Si(NH)$_2$), AlN, Sr and Er or Dy, respectively. The carbonates Er$_2$(CO$_3$)$_3$ and SrCO$_3$, respectively, have been used as oxygen providing reactants. The sialon microtubes had an average diameter between 3 and 25 μm and an average length between 30 and 150 μm. © *2000 Kluwer Academic Publishers*

1. Introduction

Ceramic materials are very useful for a wide range of applications [1]. Especially whiskers, filaments, and fibers have attracted significant attention in the context of tailor-made ceramics and they are considered to play an important role for the progress of emerging technologies over the next few decades. Among the non-oxidic materials predominantly the nitridic ceramics acquired much attention due to their outstanding properties.

Oxonitridoalumosilicates (sialons) are a special class of ceramic materials. Their systematic investigation has started in the 70s [2–5]. The first sialons were synthesized by the reaction of Si$_3$N$_4$ and Al$_2$O$_3$ and these compounds were called α- or β-sialons because of their structural similarity to α- or β-Si$_3$N$_4$, respectively. In the meantime several other sialons were obtained, and most of them exhibit structural relationships to well-known oxides or nitrides [6].

Sialons are remarkable materials in spite of their physical properties. Their exceptional hardness and their enormous thermal and chemical stability must be emphasized [7–9]. Several sialons have been synthesized in the past but only a very few of them have been fully characterized using single-crystal X-ray methods [10] or reliable structural investigations using powder X-ray, synchrotron [11], or neutron diffraction data [12].

Recently we extended our synthetic attempts from the nitridosilicate class of compounds to products in the system Si-Al-O-N. As starting materials we used rare earth metals, strontium, different carbonates, silicon diimide Si(NH)$_2$, and aluminum nitride. Similar to the nitridosilicates we have synthesized several sialons as coarsely crystalline products by high-temperature reactions. The new compounds have been fully characterized by single-crystal X-ray investigations in combination with lattice energetic calculations [13–16].

Additionally, we have performed combined differential thermal analysis and thermal gravimetry which revealed no weight loss or melting up to 1800 °C for the sialons. Very recently mechanical investigations using the vickers method have revealed a hardness of nearly 22 GPa for Sr and Pr containing sialon single crystals [17].

Besides the structural investigations of single-crystalline products also the synthesis of microstructured species like fibers and whiskers are important goals with respect to an application of these materials. Especially hollow ceramic micro- and nanotubes are considered to exhibit outstanding materials properties. Rodriguez *et al.* have reported about partially filled β-sialon fibers with an average diameter between 7 and 30 μm [18].

In this paper we are now reporting about the first hollow sialon microtubes which were yielded by high-temperature reaction using a radio-frequency furnace.

2. Experimental procedure

The synthetic procedure using a radio-frequency furnace for high-temperature syntheses primarily in our laboratory was developed for the preparation of nitridosilicates [19, 20]. We now have adopted this method for the synthesis of several new sialons [13–16]. Details of the experimental setup are given in [14]. As starting materials for the preparation of the sialon microtubes we used silicon diimide (Si(NH)$_2$), aluminum nitride (AlN), strontium carbonate, erbium carbonate, and the powdered metals Sr, Dy, and Er, respectively.

2.1. Silicon diimide

Using Si(NH)$_2$ instead of the relatively unreactive Si$_3$N$_4$ as starting material proved to be advantageous

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for the synthesis of the nitridosilicates [19, 20] and this also holds for the sialons. Si(NH)$_2$ was obtained by ammonolysis of SiCl$_4$ in CHCl$_2$ followed by a thermal treatment at 600 °C under an atmosphere of pure NH$_3$ according to reaction (1.)

$$SiCl_4 + 6NH_3 \xrightarrow[\text{2. 600° C}]{\text{1. CH}_2\text{Cl}_2} Si(NH)_2 + 4NH_4Cl \qquad (1)$$
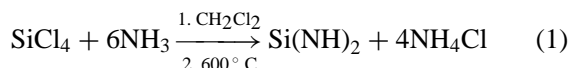
A detailed description for the synthesis of Si(NH)$_2$ is given in [21]. Si(NH)$_2$ is an X-ray amorphous and relatively undefined but reactive product which converts to amorphous Si$_3$N$_4$ at temperatures above 900 °C. It is an important precursor for the technical production of Si$_3$N$_4$ ceramics.

2.2. Aluminum nitride

Single-phase and crystalline aluminum nitride was obtained by reaction of Al (purity > 99%, Fluka) in a continuous stream of nitrogen (purity 5.0, Linde). Five reaction cycles of 2 h each at 900 °C (heating rate 1 °C/min, cooling rate 20 °C/min) with subsequent grinding of the sintered product were performed. IR-spectroscopic investigations excluded the presence of N-H groups in the product. Furthermore the purity was checked by X-ray powder diffraction.

2.3. High temperature synthesis of Sr-Er- and Sr-Dy-sialon microtubes

For the synthesis of the Sr-Er-sialon microtubes 0.47 mmol (80.0 mg) erbium powder (ABCR), 1.16 mmol (101.7 mg) metallic strontium (ABCR), 1.58 mmol (80.5 mg) Si(NH)$_2$, 0.19 mmol (100.2 mg) Er$_2$(CO$_3$)$_3$ (ABCR), and 1.23 mmol (50.4 mg) AlN were thoroughly mixed under pure argon atmosphere in a glove box and than transferred into a tungsten crucible, which was positioned in the center of a water
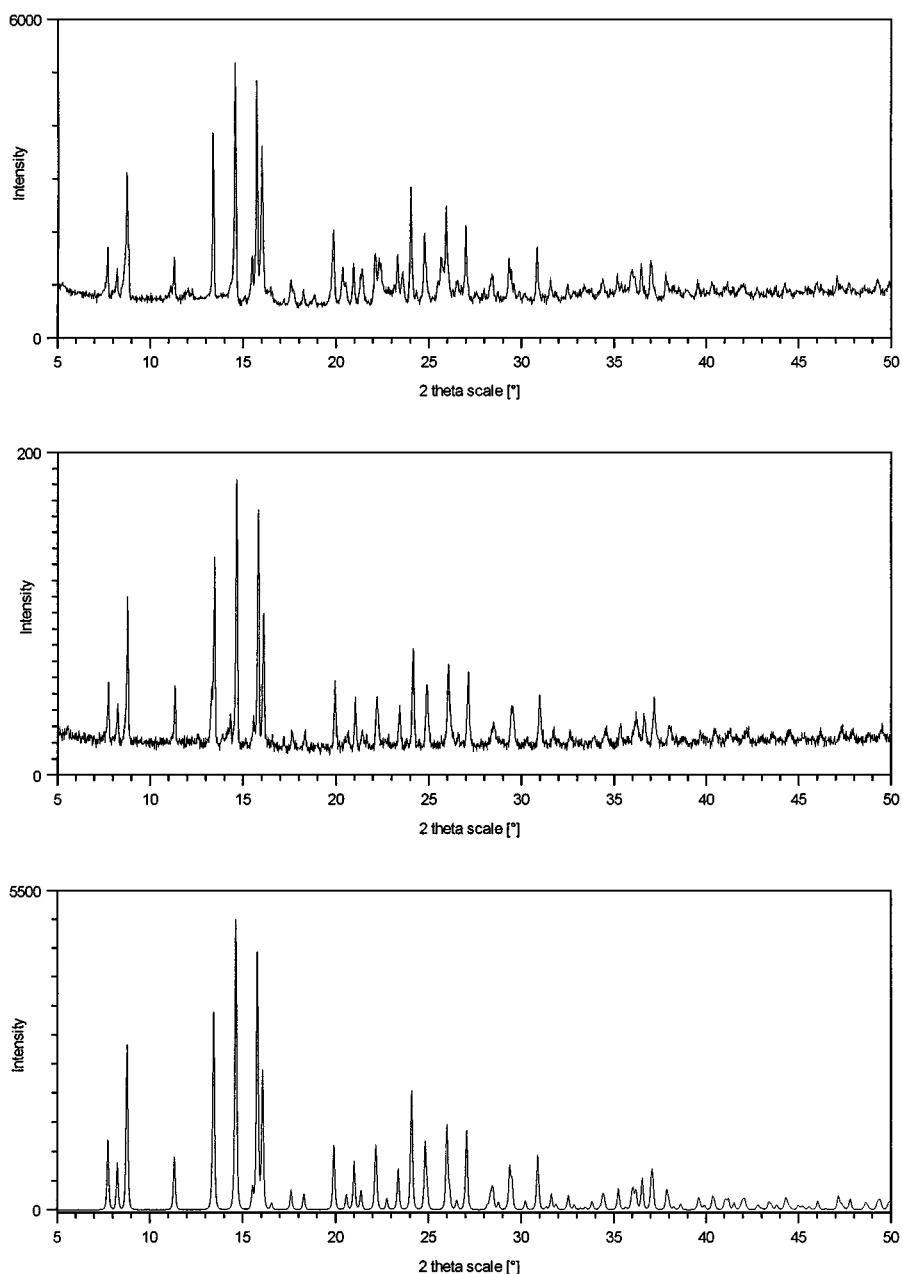

Figure 1 XRD patterns (MoK$_\alpha$ radiation) of Sr-Dy- (above) and Sr-Er-sialon microtubes (middle) in comparison with a simulated diagram for SrErSiAl$_3$O$_3$N$_4$ [14] on the basis of the single crystal data (below).

cooled quartz reactor of the radio-frequency furnace. The crucible was heated under pure nitrogen atmosphere by inductive coupling through a water-cooled induction coil, which was connected to the radio-frequency generator (Hüttinger, Freiburg, Germany, Type IG 10/600, frequency 600 kHz, electrical output 0–12 kW). The reaction mixture was first heated to 1200 °C within 60 min, then to 1600 °C within 60 min. The temperature was held at 1600 °C for 30 min. Afterwards the mixture was cooled down to 900 °C within 44 h. Room temperature was reached in additional 5 min.

For the synthesis of the Sr-Dy-sialon microtubes 0.68 mmol (110.0 mg) Dy (ABCR), 0.54 mmol (80.0 mg) $SrCO_3$ (Fluka), 1.04 mmol (60.3 mg) $Si(NH)_2$, and 0.98 mmol (40.2 mg) AlN were thoroughly mixed under pure argon atmosphere in a glove box and filled into a tungsten crucible. The crucible was treated as described before. The mixture was heated up to 1200 °C within 60 min and then to 1670 °C within 60 min. The temperature was now held for 30 min and than cooled down to 900 °C over a period of 65 h. Room temperature was reached within additional 5 min.

2.4. Chemical analyses

A scanning electron microscope (Jeol JSM 6400, Institute for Materials Research, University of Bayreuth, Germany) was used for the investigation of the morphologies and the growth features of the sialon microtubes. For the analyses of the element contents we applied the technique of quantitative electron dispersive X-ray micro-analysis (EDX). X-ray diffraction patterns showed a high rate of crystalline perfection for both species of the sialon microtubes.

3. Results and discussion

Under the applied reaction conditions the regularly shaped hexagonal Sr-Er- and Sr-Dy-sialon microtubes were obtained as the only crystalline products. They were yielded in an amount of nearly 40% in both cases. The nearly perfect hexagonal symmetry of the sialon-microtubes indicates that the species are built up of six single-crystalline domains. Further

by-products were X-ray amorphous Sr-Er- or Sr-Dy-sialons which were identified by EDX analyses. The length, wall thickness, and the diameter of the sialon microtubes varied in a relatively wide range (Sr-Er-sialon microtubes: length: 30–100 μm, wall thickness: 2–5 μm, diameter: 5–20 μm, Sr-Dy-sialon microtubes: length: 50–150 μm, wall thickness: 2–5 μm, diameter: 3–25 μm). Often the tubes grow radially arranged from a common center, in other cases they grow isolated. In contrast to this Rodriguez et al. reported about partially filled β-sialon fibers which grow closely together [18].

The two types of microtubes (Sr-Er- and Sr-Dy-sialon) are quite different concerning their macroscopic habit. The Sr-Er-microtubes grow regularly shaped with a hexagonal morphology and a smooth surface similar to the Si_3N_4 microtubes which recently have been described [22]. In contrast to this the Sr-Dy-microtubes are not always regularly formed and they exhibit a severe scale-like surface. Under an optical microscope it is visible, that the Sr-Er-microtubes are transparent with a rose color. The Sr-Dy-microtubes are transparent and colorless.

Fig. 1 shows the observed X-ray powder diffraction pattern of the Sr-Er- and the Sr-Dy-sialon microtubes in comparison with the XRD pattern of $SrErSiAl_3O_3N_4$ [14]. The refined unit cell dimensions for both species after hexagonal indexing (Sr-Er-sialon microtubes: $a = 607,0(1)$, $c = 986.6(3)$ pm; Sr-Dy-sialon microtubes: $a = 607.8(2)$, $c = 988.1(4)$ pm) are very close to the refined lattice parameters of $SrErSiAl_3O_3N_4$ [14] ($a = 606.53(3)$, $c = 985.90(8)$ pm, space group P6$_3$mc). Both XRD patterns exhibit a good agreement concerning their reflection profiles and intensities. Apparently there is a tight structural relationship between $SrErSiAl_3O_3N_4$ and the Sr-Er-sialon microtubes. Quantitative EDX measurement indicated for the Sr-Er-species a higher content of Si and N in comparison with the values obtained for $SrErSiAl_3O_3N_4$. This corresponds to a formula $SrErSi_{4-x}Al_xO_xN_{7-x}$ with $x \approx 1.7$ for the Sr-Er-sialon microtubes (Fig. 2).

Up to now no direct experimental evidence for the explanation of the growth mechanism of these Sr-Er- and Sr-Dy-sialon microtubes is available. Therefore, only presumptions are possible. The composition the starting materials used for the preparation of both species
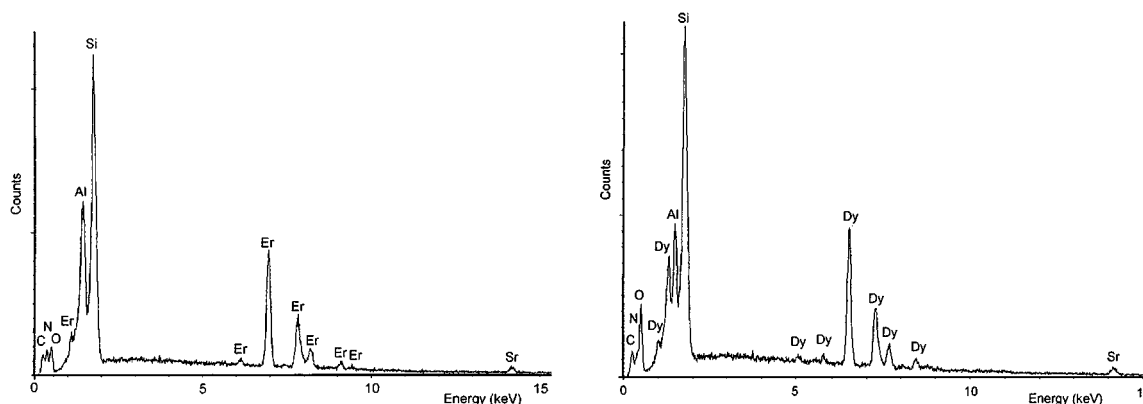

Figure 2 Electron probe microanalysis (EPMA) spectra of Sr-Er-sialon microtubes (left), and Sr-Dy-sialon microtubes (right), adjusted for both cases on a tube edge.

differs only by the choice of the metals. In the case of the Sr-Er-microtubes the content of the metals was higher. All other reaction conditions (e.g. heating and cooling rates, maximum reaction temperature) are similar. The maximum reaction temperatures are in both cases significantly above the melting points of the metals. Therefore, Sr, Er, and Dy are melting while in the same temperature range the carbonates $SrCO_3$, $Er_2(CO_3)_3$, and $Si(NH)_2$ already are dissociating. Solely AlN and the metal oxides remain as solids under these conditions and probably these solids act as reactive substrates on which the metallic melting drops are absorbed. Consequently volatile N- and Si-species from the vapor phase diffuse into the metallic melting drops finally yielding a supersaturation. This initiates the nucleation and crystal growth of the microtubes (Fig. 3) proceeding until the melting drops are completely consumed [23]. Therefore the characteristic drops which usually are observed at the end of whiskers or microtubes formed by the VLS mechanism (VLS = vapor liquid solid) are not observed in case of the sialon microtubes investigated here. Accordingly a VLS mechanism might be responsible for the formation of these microtubes. Crystal growth caused by the VLS mechanism leads to regularly formed crystals with a smooth surface and not to a scale-like microstructure as it has been observed for the Sr-Dy-sialon microtubes (Figs 4–6). Nevertheless,
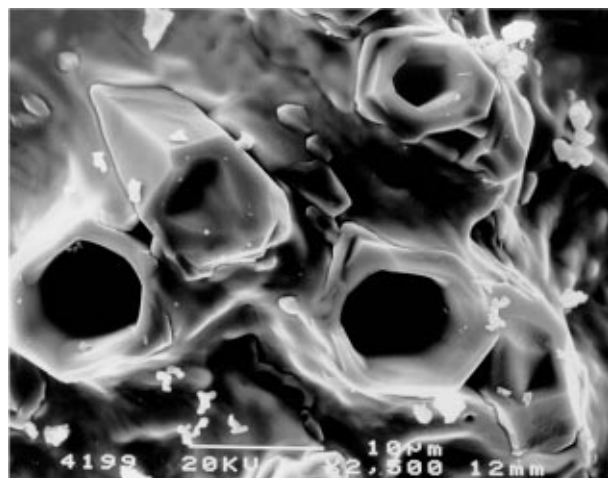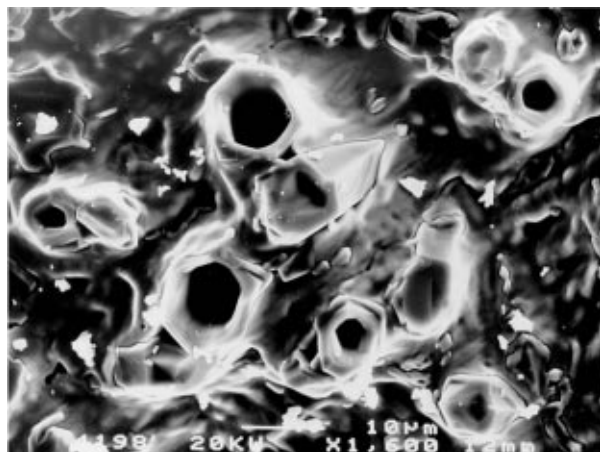

Figure 4 SEM micrograph; fully developed Sr-Er-sialon microtube with sharply formed edges.

Figure 5 SEM micrograph; Sr-Er-sialon microtubes completely grown.

it is not completely excluded that there is a combination of the VLS and the VS (vapor solid) mechanism, because the reaction temperature in both cases was 1600 °C in minimum. Therefore a significant ratio of the reactants might be transferred into the vapor phase, except AlN and the metal oxides. After the beginning of the crystal growth from the melt the additional

Figure 3 SEM micrographs showing the beginning of growth of the hexagonal Sr-Er-sialon microtubes. The lower picture is an enlarged section of the upper one.
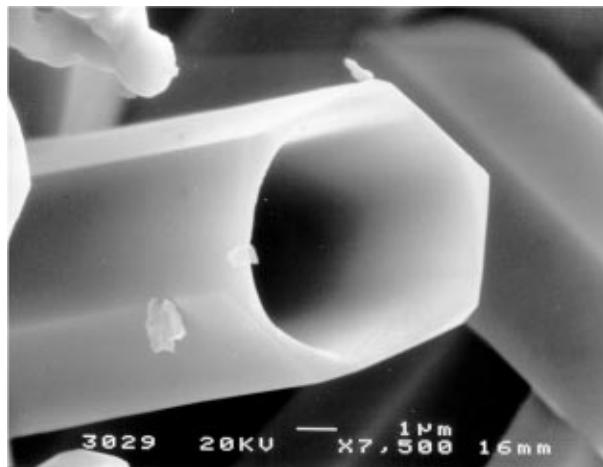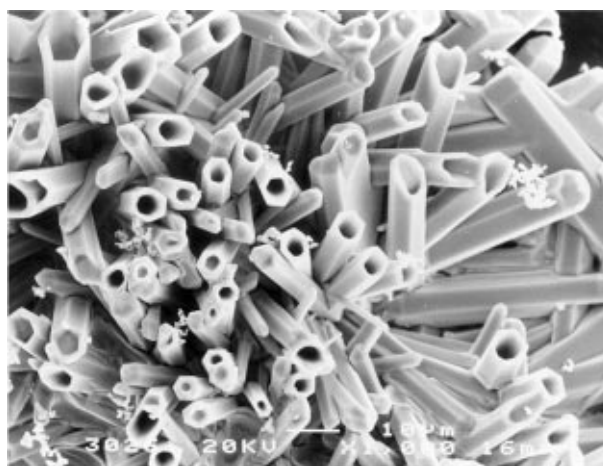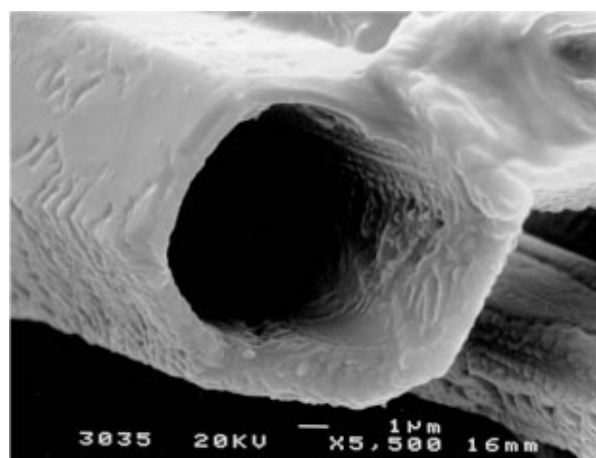

Figure 6 SEM micrograph of Sr-Dy-sialon microtubes with typical scale-like microstructure.

separation of reactants might follow through the vapor phase. This might have caused the scale-like and irregular microstructure of the Sr-Dy-sialon microtubes (Fig. 6) which is more typical for a crystal growth following the VS mechanism. In this case the diffusion of the reactants in the melt is kinetically hindered and it is superseded by the direct absorption of further reactants from the vapor phase.

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