Microwave-Assisted Synthesis, Characterization, and Thermal Decomposition of Rare-Earth Metal Disulfides *RES*₂ (*RE* = La, Pr, Nd)

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Keywords: Polychalcogenides; Rare-earth metals; Microwave-assisted synthesis; Nanostructures; Thermal decomposition

Abstract. Microwave-assisted metathesis reactions from anhydrous rare-earth metal trichlorides and alkali metal polychalcogenides in dimethylformamide in the temperature interval 160 °C $\leq T \leq 220$ °C yield sub-micron and nanometer scaled particles of the rare-earth metal disulfides *RES*₂ (*RE* = La, Pr, Nd). The samples were characterized by X-ray powder diffraction, electron microscopy, chemical analysis, and

Introduction

Polysulfides $RES_{2-\delta}$ (RE = Y, La–Nd, Sm, Gd–Lu; $0 \le \delta <$ 0.3) of trivalent rare-earth metals have been intensively studied in the last years with focus on synthesis, crystal structures, thermal properties, and thermodynamic data.^[1-7] The structures of these compounds generally consist of puckered [RES]+ double slabs and planar $[S]^{1-\delta}$ layers and can be related to the tetragonal ZrSSi type (P4/nmm, $a_0 \approx 3.8$ Å, $c_0 \approx 8$ Å^[8]). The number of chalcogen defects and their assembly determine. which kind of superstructure is realized. The planar sulfide layers in the rare-earth metal disulfides RES_2 consists of S_2^{2-1} dinuclear anions arranged in a herringbone-like pattern. Two polymorphs are known for these disulfides: The monoclinic α -RES₂ type (space group P2₁/a, lattice parameters $a \approx 8$ Å, $b \approx 4$ Å, $c \approx 8$ Å, $\beta \approx 90^{\circ})^{[3,5,7,9]}$ and the orthorhombic β -type (*Pnma*; $a \approx 8$ Å, $b \approx 16$ Å, $c \approx 3$ Å).^[3,10] The chalcogen layers of the compounds $RES_{2-\delta}$ with $\delta > 0$ exhibit defects and isolated S^{2-} anions besides dinuclear S_{2}^{2-} anions. Two commensurate superstructures of the aristotype are known for sulfur deficient rare-earth metal polysulfides $RES_{2-\delta}$: the CeS_{1.9} type, a tenfold superstructure with $\delta = 0.1$ (i.e. ten percent chalcogen defects in the planar layers)^[1,11] and the Gd₈Se₁₅ type, a 24fold superstructure ideally with $\delta = 0.125$ (12.5% chalcogen defects in the planar layers).^[6]

The ranges of existence of the binary polysulfides $RES_{2-\delta}$ depends on the sulfur vapor pressure. The phases undergo a stepwise incongruent decomposition upon heating until the sesquisulfides RE_2S_3 are finally formed as could be shown in Ref. [5], e.g.:

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 [a] Fachrichtung Chemie und Lebensmittelchemie Technische Universität Dresden Helmholtzstr. 10 01062 Dresden, Germany Raman and UV/Vis spectroscopy. The products adopt the monoclinic α -*RES*₂ type (space group *P*2₁/*a*) and form desert rose-like agglomerates. The nano-scaled samples show significantly reduced optical bandgaps compared to the bulk material. The thermal decomposition in air at 550 °C $\leq T \leq 1000$ °C yields rare-earth metal oxide sulfates *RE*₂O₂SO₄.

 $\begin{array}{l} 20RES_{2.00}(s) \rightarrow 20RES_{1.90}(s) + S_2(g), \\ 40RES_{1.90}(s) \rightarrow 40RES_{1.85}(s) + S_2(g), \\ 25RES_{1.85}(s) \rightarrow 25RES_{1.77}(s) + S_2(g), \\ 7.41RES_{1.77}(s) \rightarrow 7.41RES_{1.50}(s) + S_2(g). \end{array}$

The stability of a given rare-earth metal polysulfide structure type is structurally correlated to the size of the rare-earth metal cations RE^{3+} . With decreasing atom size antibonding interactions between the S_2^{2-} and S^{2-} anions in the planar sulfide layers increase, leading to a destabilization of the crystal structure.^[6] As a result, only disulfides of the larger trivalent rare-earth metals La, Ce, Pr, and Nd are accessible by conventional syntheses under ambient pressure conditions.

To prepare stoichiometric disulfides of the lighter rare-earth metals and to overcome the increasing decomposition pressure, two general approaches seem possible: the application of highpressure synthesis conditions or a considerable reduction of the reaction temperature. The first possibility has recently proven its capability again.^[5,7] The general obstacle for the low-temperature routes is the allocation of a sufficient amount of activation energy. It has, however, been demonstrated already in the 1970ies, that metathesis is a possible reaction route to synthesize transition metal sulfides in aprotic solvents at moderate temperatures, cf. Ref. [12], e.g., and microwaveassisted syntheses have been successfully applied for the preparation of sulfides of other trivalent metals like Bi2S3 and Sb₂S₃.^[13] The synthesis of nano-scaled rare-earth metal sulfides and oxide-sulfides is described in the literature.^[14] However, literature featuring nano-scaled polychalcogenides of trivalent rare-earth metals is scarce.[15]

We performed a series of microwave-assisted metathesis reactions in organic solvents in order to explore, if rare-earth metal disulfides might also be accessible under these specific low-temperature conditions. Phase pure crystalline samples of the disulfides of La, Pr, and Nd could be prepared and the results are presented.

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Results and Discussion

General Results

The microwave assisted syntheses starting from anhydrous rare-earth metal trichlorides and sodium polysulfides yields ocher-orange colored powder samples. After leaching out the sodium chloride with an ethanol/water mixture, the powder X-ray diffraction patterns for RE = La, Pr, and Nd reveal reflections of the monoclinic α -RES₂ type samples, cf. Figure 1. The crystal structure of α -NdS₂^[3] is shown in Figure 2 as an example. Sulfur, generated as by-product during the synthesis, deposits most probably amorphously and is usually rinsed completely during the washing process if Na₂S₂ was chosen as sulfide source. This observation has also been made for conventional metathesis reactions.^[16] For reactions starting with Na₂S₄ sulfur is sometimes found as by-product in the powder X-ray patterns of the respective samples (cf. also Figure 11 and Figure 13). Like the bulk material, the sub-micron and nanostructured α -RES₂ samples are not sensitive to atmospheric conditions. The broad reflections in the X-ray pattern can be taken as a first evidence for the formation of small particles. Moreover, the peak broadening observed in the power diagrams is clearly *hkl*-dependent: reflections with l = 0 show a significantly lower full width at half maximum (FWHM) (cf. Figure 1, e.g.) indicating, that the samples should consist of anisotropic particles with their smallest dimension along [001].



Figure 1. Diffraction pattern of a NdS_2 sample; top: measured pattern of the nano-structured sample; bottom: pattern calculated for α - NdS_2 .^[3]

In accordance with the lanthanide contraction, the diffraction angles increase from α -LaS₂ to α -NdS₂, as shown in Figure 3.



Figure 2. Crystal structure of α -NdS₂, projection of the unit cell (right), planar layer with dinuclear S₂²⁻ anions (left).^[3]



Figure 3. Diffraction patterns of nano-structured samples of α -LaS₂, α -PrS₂, and α -NdS₂.

SEM and TEM images confirm the plate-like shape of the RES₂ particles (Figure 4, Figure 5 and Figure 6). The sizes of the particles depend on the individual reaction conditions. Short reaction times ($t \approx 20$ min) and lower reaction temperatures $(T \approx 160 \text{ °C})$ generally favor the formation of smaller particles of lateral dimensions about 25-100 nm and heights of about 5-10 nm. Reaction times of about 90 min and temperatures in the range $180 \le T \le 200$ °C yielded plates of approximate dimensions of $(200 \times 200 \times 10)$ nm³. Moreover, the particle anisotropy deduced from the X-ray powder patterns is clearly confirmed in the micrographs. The α -RES₂ particles were generally found agglomerated, in most cases desert rose-like structures are formed (cf. Figure 4 and Figure 6). Due to the agglomeration the determination of a particle size distribution by dynamic light scattering (DLS) did not yield reliable results. The application of the Scherrer formula^[17] to extract particle sizes is also of limited scientific value. As stated above, the α -RES₂ compounds crystallize in the monoclinic space group $P2_1/a$ with nearly tetragonal unit cell dimensions of $a \approx 8$ Å, $b \approx 4$ Å, $c \approx 8$ Å, and $\beta \approx 90^{\circ}$ and hence largely overlapping reflections are recorded. A mathematical peak deconvolution is thus difficult, especially taking the considerably broad reflections and the hkl-dependent line broadening into account. The reported particle sizes in this contribution thus

stem from SEM and TEM micrographs. N. B.: As the dedicated formation of monodisperse RES_2 nanoparticles was not the aim of this work, improvements of nucleation and growth processes as well as optimization procedures to determine the particle size distribution were not undertaken.



Figure 4. SEM images of nano-structured α -NdS₂ (left) and α -LaS₂ (right) samples.





0 nm

Figure 5. TEM image of agglomerated particles of α-NdS₂.



Figure 6. SEM-images of microcrystalline α -LaS₂ (left) and nanostructured α -PrS₂ with similar intergrowth of the particles.

Raman spectra of the α -*RES*₂ samples show the typical signal for the S–S stretching mode at about 400 to 420 cm⁻¹ (Figure 7) consistent with literature data for LaS₂, e.g.^[18]. Probably due to scattering effects in the small particles the Raman signals appear somewhat broadened as compared to the bulk samples.

Figure 7. Relevant section of the Raman spectra showing the stretching mode of the disulfide anions S_2^{2-} for α -LaS₂ and α -NdS₂ samples obtained under different reaction conditions.

The size of the particles also influences the electronic properties of the α -*RES*₂ compounds. Rare-earth metal disulfides are semiconductors and macroscopic crystals are of deep red color (cf.^[3] e.g.). In accordance with the quantum size effect the optical absorption edge shows a blue shift from roughly 450 nm for samples consisting of micrometer-sized particles obtained from conventional solid state reaction to about 350 nm for the nano-sized samples. This corresponds to an increase of the bandgap from approximately 2.5 to 3.5 eV, respectively, as shown for α -NdS₂ in Figure 8.



Figure 8. UV/Vis-spectra of different α -NdS₂ samples illustrating the shift of the optical absorption edge.

EDX analyses as well as ICP-OES data confirm the metal/ sulfur ratio within experimental errors. Both methods indicate, however, a considerable amount of carbon (up to 20 atom-%) and oxygen (up to 50 atom-%) in the α -RES₂ samples. As no evidence for rare-earth oxides (RE₂O₃), oxide–sulfides (RE₂O₂S or RE₁₀OS₁₄) or carbon containing phases are found by X-ray powder diffraction and in the spectroscopic investi-

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gations, we assume contamination of the sample surfaces due to the reaction conditions and the rinsing process.

Reaction Temperature

The overall crystallinity – as judged by absolute peak intensities and reflection/background ratios – of the synthesized samples can be influenced by the reaction temperature (cf. Figure 9). The variation of the reaction temperature between 160 °C and 220 °C was tested for the Discover microwave system keeping the other reaction parameters constant [reaction time t = 2 h, V(DMF) = 15 mL, reactant amounts: 1 mmol]. An optimized reaction temperature of T = 180 °C was made out. Samples prepared at lower temperatures were found with lower overall crystallinity while samples prepared at $T \ge 220$ °C generally show good crystallinity but are in some cases accompanied by side-products like rare-earth metal oxides and sulfur. The particle size and shape is not much affected if the synthesis is conducted within the temperature interval $180 \le T \le 200$ °C, as can be seen from Figure 10.



Figure 9. Diffraction patterns of α -LaS₂ samples synthesized at 220 °C (grey) and 180 °C (black).



Figure 10. SEM images of α -LaS₂ samples synthesized at 220 °C (left) and 180 °C (right).

Reaction Time

The reaction time for the synthesis was varied systematically for the Discover microwave system between t = 20 min. and t = 3 h keeping the remaining reaction parameters constant [T = 180 °C, V(DMF) = 10 mL, reactant amounts: 1 mmol]. A formation of the target product can be affirmed yet after 20 min of reaction although the X-ray pattern exhibits only broad reflections and a poor signal/background ratio. However, side products were not detected. The optimized reaction time was found to be 90 min. Shorter as well as longer reaction times give lower levels of crystallinity. Figure 11 shows the powder X-ray patterns of four α -NdS₂ samples prepared at different reaction times. It is not yet clear why a prolongation of the reaction time decreases the crystallinity of the sample. This observation is, however, also supported by SEM images, in which the faceting of the particles is found less pronounced in the respective samples.



Figure 11. Diffraction patterns of α -NdS₂ samples synthesized with different reaction times. Reflections of sulfur as by-product in the 3-h-sample are indicated by arrows.

Solvent Volume and Reactant Concentration

As can be expected, the solvent volume and the effective reactant concentration also influence the crystallinity of the products. As shown for α -NdS₂ in Figure 12, the crystallinity decreases rapidly with increasing solvent volume (decreased reactant concentration). For absolute solvent volumes less or equal to 5 mL in a 35 mL vessel (Discover SP system) the



Figure 12. Diffraction pattern of α -NdS₂ samples synthesized with different solvent volumes.

desired products could not be obtained because of complete evaporation of the solvent and a lack of reaction media.

Figure 13 shows the powder X-ray patterns of two lanthanum samples, synthesized from initial concentrations of 1 mmol and 2 mmol of LaCl₃ and Na₂S₂, respectively, [Discover SP system, T = 180 °C, V(DMF) = 10 mL, t = 1.5 h]. Significant differences can't be made out although the sample obtained from the higher concentrated starting mixture exhibits slightly broader reflections and traces of sulfur.



Figure 13. Diffraction patterns of a-LaS₂ samples synthesized with different initial reactant concentrations, the sample obtained from the higher concentration shows some additional peaks of sulfur as marked by arrows.

Thermal Decomposition

Thermal treatments of the submicron- and nano-scaled α -RES₂ samples in air were performed to check, if rare-earth metal oxides RE_2O_3 can be obtained under retention of the plate-like appearance of the disulfide particles. Interestingly, the oxides could not be obtained by heat treatment up to 1000 °C. Instead rare-earth metal oxide sulfates $RE_2O_2SO_4^{[19]}$ resulted in the oxidation at temperatures $T \ge 550$ °C as can be seen in the X-ray powder pattern in Figure 14. The reaction proceeds via the oxide sulfide $RE_2O_2S^{[20]}$ in the intermediate temperature range 350 °C $\leq T \leq$ 550 °C as Bragg reflections of these phases can be detected in the X-ray powder patterns of the respective samples. Due to the high surface area of the nano-structured α -RES₂ particles and possibly due to the oxidic surface contamination the oxidation is quick. The ochercolored samples of α -LaS₂ turn white almost immediately when placed in a pre-heated furnace even at moderate temperatures of T = 350 °C. The particle morphology of the oxidized products is retained in the first place. After prolonged thermal treatment at $T \ge 850$ °C the faceting of the particles is, however, less pronounced and further agglomeration towards compact samples can be observed (Figure 15).



Figure 14. Diffraction pattern of an oxidized sample (La₂O₂SO₄ from α -LaS₂ after heat treatment at T = 850 °C for 24 h, calculated pattern according to reference^[19]).



Figure 15. SEM image of an oxidized sample $(La_2O_2SO_4 \text{ from } \alpha\text{-}LaS_2 \text{ after heat treatment at } T = 850 \text{ °C for } 24 \text{ h}; \text{ same material as used for Figure 14}.$

Conclusions

Phase pure samples of the monoclinic α modifications of LaS₂, PrS₂, and NdS₂ (space group $P2_1/a$) were prepared by microwave assisted metathesis reactions starting from anhydrous rare-earth trichlorides and sodium polysulfides in dimethylformamide. According to SEM micrographs the products consist of plate-like particles. The sizes of the primary particles vary approximately between $(25 \times 25 \times 5)$ nm³ and $(200 \times 200 \times 10)$ nm³. The α -RES₂ plates tend to form larger, sand-rose like agglomerates which hinders the determination of a meaningful size distribution. The optimized reaction parameters to get phase pure material of adequate crystallinity were determined to: T = 180 °C, t = 1.5 h, V(DMF) = 10 mL, $n(RECl_3) = n(Na_2S_x) = 1 \text{ mmol}; 35 \text{ mL}$ silica vessel in a Discover SP microwave system. With these parameters, particles of about 200 nm lateral dimensions and thicknesses of about 10 nm were found by SEM. Raman spectra confirm the presence of S_2^{2-} dinuclear anions by their characteristic stretching S-S mode and a blue shift of the optical absorption edge for

	MARS 5	Discover SP	
Vessel type	PTFE and silica with PTFE cap	Silica with PTFE cap	
Vessel volume	120 / 80 mL	35 mL	
Temperature range	160–220 °C		
Pressure range	0–3 bar excess pressure		
Solvent volume	30–50 mL	5–20 mL	
Product amount	1–2 mol	0.5–2 mol	
Reaction time	1–24 h	0.33–8 h	

Table 1. Reaction variables and system parameters of the used microwave systems.

the nano-sized samples was observed in UV/Vis spectra. The synthesis of α -*RES*₂ samples by microwave assisted synthesis for Ce, Sm, and Gd was not successful yet. Heat treatments of the α -*RES*₂ samples in air in the interval 550 °C $\leq T \leq$ 1000 °C gave the rare-earth metal oxide sulfates *RE*₂O₂SO₄ as oxidation products.

Experimental Section

Synthesis: All manipulations with the starting reagents were carried out in purified argon (99.999%, Air Liquide) in a glove box (Unilab, MBraun). Nano-scaled *RES*₂ are obtained by metathesis reactions of adequate amounts of anhydrous rare-earth metal trichloride (LaCl₃, PrCl₃, NdCl₃, all: >99.9%, ABCR) and sodium polysulfides (Na₂S₂ or Na₂S₄) in dried dimethylformamide (DMF) by microwave-assisted metatheses reactions according to the scheme:

 $2RECl_3 + 3Na_2S_2 \rightarrow 2RES_2 + 6NaCl + 2S$

Anhydrous DMF (< 0.005% water, stored over molecular sieve, Sigma Aldrich) was degassed by a continuous argon flow for at least 30 min prior to use. Na₂S₂ and Na₂S₄ were obtained by reaction of the elements (Na: ingot, 99.99%, Chempur, S: 99.95%, Alfa Aesar, re-crystallized from CS₂ and twice sublimed prior to use) in dried and oxygen-free ethanol or tetrahydrofuran.

The reactants were put into polytetrafluoroethylene (PTFE) or silica microwave vessels in an argon atmosphere and the vessels were closed with a PTFE cap. The reaction mixtures were heated with a microwave system MARS 5 or Discover SP (both: CEM GmbH). Both systems and their characteristics are listed in Table 1. A heating ramp of 5 min to reach the reaction temperature T (160 $\leq T \leq 220$ °C) was used. The reaction mixtures were held at this temperature between 30 min and 24 h, while stirring. Afterwards, the vessels were cooled down to room temperature by switching off the microwave energy. The resulting ocher-orange colored powders were washed with a 1:1 ethanol/water-mixture and dried under dynamic vacuum supported by an ultrasonic treatment.

Attempts to prepare samples of RES_2 for RE = Ce, Sm, and Gd under the experimental conditions stated above were not successful. After rinsing, the X-ray powder pattern indicated the presence of RE_2O_3 or *REOCl* and elemental sulfur in the respective samples.

X-ray Powder Diffraction: X-ray powder diffraction patterns were recorded with a PANalytical X'Pert diffractometer with $Cu-K_{\alpha 1}$ -radiation and Bragg-Brentano setup. The instrument settings were kept identical and the same type of sample holders (to ensure approximate

equal sample amounts) was used for a better comparability of the sample characteristics. Only the measured angular range was changed in some cases to allow for different overall scanning times. Theoretical patterns were calculated with the WinXPow software package.^[21]

Electron Microscopy and Energy Dispersive X-ray Spectroscopy: Scanning electron micrographs of the samples were recorded with a DSM 982 Gemini or with an UltraPlus SEM (both Carl Zeiss NTS). Energy dispersive X-ray spectroscopy (EDX) was performed with a Si(Li) detector (Voyager, Noran) attached to the Zeiss 982. Transition electron microscopy (TEM) studies were conducted with a Philips EM-208 (Philips) with an acceleration voltage of 100 kV.

Chemical Analyses: Besides EDX determinations, the compositions of selected samples were also determined by atomic emission spectroscopy (ICP-OES). For that, samples were sealed into capillaries, which were cracked in an autoclave with PTFE inlay and digested using a 4 M HNO₃/HCl solution. The standard solutions as reference for the rare-earth metals and sulfur were taken from Johnson Matthey.

Optical Spectroscopy: Raman spectra were recorded with a Renishaw RM 2000 Raman microscope equipped with a 633 nm He/Ne laser in the range from 100 nm to 500 nm.

UV/Vis spectra using $BaSO_4$ (Merck, white standard DIN 5033) as standard were measured with a Varian Cary 4000. Measurements were performed in the range from 350 nm to 900 nm with a Varian Praying Mantis device for diffuse reflectometry. The size of the bandgap was estimated from the onset-wavelength at the absorption edge.

Dynamic Light Scattering (DLS): Apart from particle size estimations based on SEM images, dynamic light scattering (DLS) was performed to confirm these results with a Malvern Zetasizer ZS at a wavelength of $\lambda = 688$ nm. The samples were suspended in ethanol. However, the DLS results are heavily biased by particle agglomeration and were deemed unrepresentative. The data are thus not given here.

Thermal Treatment: Thermal decompositions of the nano-structured α -*RES*₂ were performed in air at temperatures 350 °C $\leq T \leq 1000$ °C. The samples were filled in alumina boats, which were placed in a furnace for reaction times between 1 min and 24 h. After cooling, the samples were checked by powder X-ray diffraction and SEM imaging.

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG, Bonn, Germany). We thank *Ellen Kern, Susanne Goldberg* (Department of Chemistry and Food Chemistry, TU Dresden), and *Regine Boldt* (Leibnitz Institut für Polymerforschung, Dresden) for REM imaging and EDX analyses, *Gudrun Auffermann* (Max Planck Institute for Chemical Physics of Solids, Dresden) for

Zeitschrift für anorganische und allgemeine Chemie

chemical analyses and *Christoph Ziegler* (Department of Chemistry and Food Chemistry, TU Dresden) for Raman measurements and TEM imaging.

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Received: May 29, 2012 Published Online: October 19, 2012