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JOURNAL OF RARE EARTHS, Vol. 34, No. 8, Aug. 2016, P. 850
JOURNAL OF RARE EARTHS
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Synthesis and characterization of monodisperse Eu^{3+} doped gadolinium oxysulfide nanocrystals

J. Cichos[1,*], M. Karbowiak[1], D. Hreniak[2], W. Stręk[2]

(1. Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie 14, Wrocław, 50-383, Poland; 2. Institute for Low Temperature and Structural Research, Polish Academy of Sciences, Wrocław, 50-383, Poland)

Received 24 February 2016; revised 12 May 2016

Abstract: $Gd_2O_2S:Eu^{3+}$ nanoparticles were synthesized using two step process consisting of sulfuration of basic carbonates obtained by homogenous precipitation. Annealing of lanthanide nitrates at total concentration of 5×10^{-3} mol/L in a water solution containing relatively high, three molar concentration of urea ensured the optimal conditions for the reproducible preparation of uniform and small spherical particles. During sulfuration step elemental sulfur was mixed with precursor which eliminated necessity of using an auxiliary furnace and provided sulfur-reach reaction atmosphere. Such optimized protocol afforded synthesis of spherical and non-agglomerated nanoparticles with diameter smaller than 100 nm. The precursors morphology was maintained, but particles size was reduced by 15%–20% during sulfuration. The results indicated that higher emission intensity was observed for $Gd_2O_2S:Eu^{3+}$(8%) oxysulfide sample synthesized using crystalline $Gd(CO_3)OH$ precursor, than for that obtained from amorphous $Gd_2(OH)_2(CO_3)_2\cdot H_2O$ precursor, although some further efforts to improve morphology of the former are still required.

Keywords: oxysulfides; nanocrystals; hydroxycarbonates; rare earths

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Lanthanide (Ln) oxysulfides emerge as promising components of thin films for use as spectral converters in solar cells[1]. However, synthesis of monodisperse Ln_2O_2S at the nanoscale still remains a challenge. The conventional methods based on the reaction of rare-earth oxide with elemental S, H_2S, CS_2 or other sulfur sources carried out at temperatures of about 500–1000 ºC in the presence of flux are not suitable since the samples are provided with good photoluminescence properties but of poor morphology. Literature survey and our own experience reveal that among different synthetic routes, hitherto reported, the most promising, in regard of both morphological and luminescent properties, is the method based on sulfuration of basic carbonate precursors[2,3]. This method, after optimization of precursor synthesis and modification of sulfuration step enabled us to obtain the $Gd_2O_2S:Eu^{3+}$ nonaglomerated nanospheres with controllable size, ranging from 60 to 500 nm. In contrast with previously reported route[4] our modified method eliminates necessity of using of an auxiliary furnace to produce sulfur vapor, which facilitates control of the process. The specific feature of the method is that particle morphology of resulting oxysulfides reproduces that of basic carbonates used as precursors. Therefore, in our work we examined amorphous and crystalline phases of basic carbonates and discussed influence of precursors morphology on morphological and photoluminescent properties of resulting oxysulfides.

1 Experimental

Europium and gadolinium nitrates were prepared by reconstitution of appropriate oxides (99.99%, Stanford Materials) in nitric acid solution (~40%) followed by evaporation of the excess of solution and drying over P_2O_5 in a vacuum desiccator for 3 d. Urea and sulfur were from Sigma-Aldrich.

Basic carbonate precursors were synthesized by homogenous precipitation method using procedure based on work by Matijevic and Hsu[5]. Three different precursors were prepared. The first precursor (precursor A) was obtained by heating water solution containing urea (3 mol/L) and lanthanide nitrates (4.6×10^{-3} mol/L $Gd(NO_3)_3\cdot6H_2O$ and 4×10^{-4} mol/L $Eu(NO_3)_3\cdot5H_2O$) in oil bath at 100 ºC under continuous stirring for 2 h. Preparation of the second one (precursor B) was conducted by heating a solution in a tightly closed Teflon bottle (100 ºC, 24 h) and the third one (precursor C) in an autoclave (120 ºC, 12 h), keeping urea and lanthanide nitrates concentrations unchanged. All samples were iso

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Foundation item: Project supported by Wroclaw Research Centre EIT+ within the project "The Application of Nanotechnology in Advanced Materials” - NanoMat (POIG.01.01.02-02-002/08) co-financed by the European Regional Development Fund (Operational Programme Innovative Economy, 1.1.2)

* **Corresponding author:** J. Cichos (**E-mail:** jakub.cichos@chem.uni.wroc.pl; **Tel.:** +48713757293)

DOI: 10.1016/S1002-0721(16)60105-9

lated by means of centrifugation and washed twice with deionized water, once with acetone and dried in vacuum. Afterwards, samples (about 100 mg) were thoroughly ground in a mortar with an excess of elemental sulfur (about 0.5–1 g) and placed in a quartz boat. The sulfuration reaction was carried out for 1 h at 950 ºC in a tubular furnace (tube diameter 25 mm, length 700 mm) (Fig. 1). Obtained oxysulfides did not require any purification steps after synthesis in this conditions.

To determine the phase of the samples X-ray powder diffraction (XRD) experiments were carried out on a Bruker D8 Advance diffractometer equipped with Cu X-ray lamp and Vantec detector. The particle size and morphology of the samples were examined by a scanning electron microscope (SEM) using Hitachi S-3400N with Thermo Scientific Ultra Dry EDS detector.

The emission and excitation spectra were recorded using an Edinburgh Instruments FLSP 920 spectrofluorimeter with resolution of 0.5 nm. Emission decay time was evaluated using FAST software and uncertainties of determined values did not exceed 5%.

2 Results and discussion

2.1 Optimization of synthesis

2.1.1 Synthesis of hydroxycarbonate precursor

Synthetic procedure of $Gd_2O_2S:Eu^{3+}$ nanoparticles (NPs) adapted in the present paper is carried out in two steps. The first step includes the preparation of basic carbonate precursors, which in a second step are converted to oxysulfides in the sulfuration process. The first step is crucial, because conversion of precursor to oxysulfides occurs without change in morphology. This allows the control of size and uniformity of oxysulfides by controlling the morphology of the precursors.

It has been reported[6] that monodisperse lanthanide basic carbonate colloid spheres could be produced via an urea-based homogeneous precipitation method. The synthetic procedure is based on work by Matijevic and Hsu[5]. Their method enables producing of well-defined, uniform and monodisperse spherical particles of submicron size by aging solutions of rare-earth salts at elevated temperatures in the presence of urea. This procedure is adapted here as a starting point for synthesis of precursor A. The morphology of particles obtained according to this procedure depends strongly on a number of parameters, among which the most important are the concentrations of lanthanide ions and of urea, starting pH, temperature, aging time and the kind of anions. Therefore, our initial efforts were aimed at optimization of these synthetic parameters.

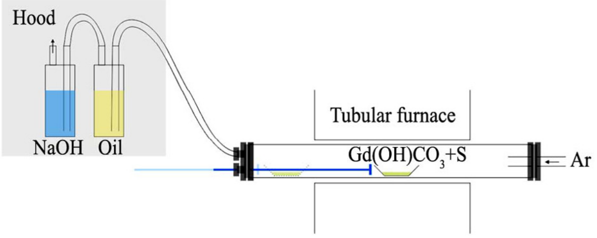

Fig. 1 Scheme of experimental setup used for sulfuration

The presented results confirm observation[5] that in the precipitation of basic gadolinium carbonates, decomposition of urea in solution containing nitrate ions appears to yield a larger number of nuclei and smaller particles than in the same process in the presence of chloride ions. This corroborates with other reported results, where it has been observed that precipitation from lanthanide chloride solutions yield NPs usually larger than 200 nm[3], whereas from nitrates the size is in the 100–200 nm range[1,4,6,7]. A similar effect of stabilizing small particles by nitrate ions has been noticed during study of rare-earth oxide precursors[8].

Matijevic and Hsu[5] have determined optimum concentrations of lanthanide nitrates and urea as 5.6×10^{-3} mol/L and 0.5 mol/L, respectively. The same concentrations were subsequently employed in Ref. [6] for preparation of gadolinium-europium hydroxycarbonate particles with the average diameter from 164+/–22 nm to 240+/–19 nm, and in Ref. [1] for synthesis of the $Gd(OH)CO_3:Eu^{3+}$ particles with an average diameter of 149+/–11 nm. For the same reactants concentrations, particles with a mean diameter of 107+/–9 nm have been obtained if an aqueous solvent containing 20 vol.% EtOH was used instead of pure water[4]. Luo et al.[7] modified the procedure[5] by adding oleic acid to 1 mol/L urea solution. Although hydroxycarbonate precursors with a mean diameter of about 50 to 60 nm were obtained, they were not stable and underwent a change when exposed to the electron beam during TEM measurements, which is a typical behavior for small OA-capped nanocrystals. Much more stable particles were obtained when their size was above 150 nm.

In the course of our studies we have noticed that the best conditions for the reproducible preparation of uniform and small spherical particles is concentration of 5×10^{-3} mol/L for lanthanide nitrates, only slightly smaller than optimal 5.6×10^{-3} mol/L determined in original paper by Matijevic and Hsu[5], however concentration of urea should be significantly increased up to 3 mol/L. If lower concentrations of urea were used, maintaining all other reaction parameters unchanged, bigger particles were produced. For example, if 3 mol/L solution of urea was used the obtained particles were in 60–80 nm range, whereas for 2 mol/L urea their diameter increased to 110–140 nm (Fig. 2). Moreover, we found that for better morphology it is beneficial to increase the decomposition temperature from 85 ºC proposed by Matijevic and Hsu[5] to 90–95 ºC. It seems that both higher temperature and higher urea concentration lead to faster nucleation, thus larger number of nuclei is produced and smaller particles are obtained. To obtain the smallest particles the reaction