Research Article

Synthesis and Characterization of Upconversion Fluorescent Yb^{3+} , Er^{3+} Doped CsY_2F_7 Nano- and Microcrystals

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CsY_2F_7 : 78% Y^{3+} , 20% Yb^{3+} , 2% Er^{3+} nanocrystals with a mean diameter of approximately 8 nm were synthesized at 185°C in the high boiling organic solvent *N*-(2-hydroxyethyl)-ethylenediamine (HEEDA) using ammonium fluoride, the rare earth chlorides and a solution of caesium alkoxide of *N*-(2-hydroxyethyl)-ethylenediamine in HEEDA. In parallel with this approach, a microwave assisted synthesis was carried out which forms nanocrystals of the same material, about 50 nm in size, in aqueous solution at 200°C/8 bar starting from ammonium fluoride, the rare earth chlorides, and caesium fluoride. In case of the nanocrystals, derived from the HEEDA synthesis, TEM images reveal that the particles are separated but have a broad size distribution. Also an occurred heat-treatment of these nanocrystals (600°C for 45 minutes) led to bulk material which shows highly efficient light emission upon continuous wave (CW) excitation at 978 nm. Besides the optical properties, the structure and the morphology of the three products were investigated by means of powder XRD and Rietveld method.

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1. Introduction

In recent years, a broad range of applications, ranging from display devices [1], lasers [2], and biological imaging agents [3–9], which are based on luminescent nanocrystals have been reported. Especially a subgroup of these materials which are able to convert long wavelengths radiation, for example, infrared, into shorter wavelengths by so-called photon upconversion became popular. Excitation in the NIR has some advantages, it induces only a weak autofluorescence background, avoids photodegradation in biotagging applications, and hence increases the sensitivity of the method. Very well investigated is rare earth doped sodium yttrium fluoride (NaYF_4). Many reports are focused on the synthesis and investigation of (mainly Yb, Er doped) NaYF_4 . Synthesis procedures for lanthanide doped nanocrystals of α - NaYF_4 [10–19] and β - NaYF_4 [11, 12, 18–24] have been developed. Very recently we investigated nanosized Yb^{3+} , Er^{3+} doped KYF_4 in detail. As a result of the occurred Fullprof refinement we found that KYF_4 , generated in HEEDA at 185°C, crystallizes in the cubic (alpha) NaYF_4 structure [25]. We are interested in new upconversion fluorescent materials and had decided to investigate new caesium containing compounds.

Ternary fluoride compounds of the type $\text{Cs}_x\text{Yb}_y\text{F}_z$ and $\text{Cs}_x\text{Er}_y\text{F}_z$ have been synthesized by solid state reactions or fluorination of solid compounds at high temperature and led to bulk material. For example $\text{Cs}_{3.4}\text{Yb}_{12}\text{F}_{39.4}$ and $\text{CsYb}_3\text{F}_{10}$ were synthesized and investigated by Aléonard et al. [26, 27], respectively, Marsh [28]. The structure of CsErF_4 was determined by Losch and Hebecker [29]. Other groups have investigated the nonlinear optical properties of CsY_2F_7 and CsGd_2F_7 probes doped with different rare earth ions in detail [30–33]. The samples were prepared under very drastic conditions starting from the rare earth oxides and the alkalimetal fluorides in aqueous solutions [30–34]. Schiffbauer et al. reported on the crystal structure and luminescence of Pr^{3+} doped Cs_2KYF_6 [35]. Quaternary systems like $\text{Cs}_2\text{NaLnF}_6$ were developed and investigated by Makhov et al. [36], respectively, Tanner et al. [37, 38].

Anyway, as far as we know these materials neither had been produced in the nanoscale nor the upconversion properties of Yb^{3+} , Er^{3+} codoped samples have been investigated.

Herein, two synthesis routes are presented, which are suitable in order to achieve rare earth doped crystalline material of CsY_2F_7 in a particle size ranging from less than 10 nm to more than 10 μm . The optical properties

were investigated as well as the structural properties based on powder diffractometry and Rietveld refinements. As the luminescence of the synthesized nanomaterial was very weak the heat-treated sample, consisting of micrometer-sized grains, turned to be a quite good upconversion emitter.

2. Experimental Section

2.1. Synthesis of the Yb^{3+} , Er^{3+} Doped CsY_2F_7 Particles in HEEDA. CsY_2F_7 : 20%Yb, 2%Er nanocrystals were prepared in the coordinating solvent *N*-(2-hydroxyethyl)-ethylenediamine (HEEDA) similar to the method described previously [39]. The following three solutions were used in the synthesis.

(A) *Solution of the Lanthanide Chlorides*: a clear solution of 3.55 g (11.7 mmol) of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Treibacher Industries), 1.16 g (3 mmol) of $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Treibacher Industries), and 0.115 g of (0.3 mmol) $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Treibacher Industries) in about 25 mL of methanol was combined with 25 mL of *N*-(2-hydroxyethyl)-ethylenediamine (99%, Sigma Aldrich). The methanol was removed with a rotary evaporator, and the water was distilled off in high vacuum at 75°C. The remaining slightly cloudy suspension was allowed to cool down to 60°C and kept at this temperature under dry nitrogen.

(B) *Preparation of the Caesium Alkoxide Solution*: a solution of the caesium alkoxide of *N*-(2-hydroxyethyl)-ethylenediamine (HEEDA) was prepared by dissolving 1 g (7.5 mmol) of caesium metal (Sigma Aldrich) in 10 mL of HEEDA at 20°C under dry nitrogen.

(C) *Preparation of the Fluoride Containing Solution*: 1.55 g (42 mmol) of NH_4F (98% Fluka) were dissolved in about 25 mL of methanol and combined with 25 mL of HEEDA. The methanol was removed with a rotary evaporator at 45°C and subsequently in high vacuum at 60°C. The remaining solution was kept at 45°C under dry nitrogen.

Solution A and solution B were combined and heated to 60°C. Subsequently, the fluoride-containing solution (C) which had a temperature of 45°C was added under stirring and the resulting mixture was degassed at 80°C under vacuum. The reaction mixture was heated to 185°C under dry nitrogen and kept at this temperature for 13 hours. After the transparent solution had cooled down to room temperature, the nanocrystals were precipitated by adding a mixture of 200 mL of water and 200 mL of propanol. The precipitate was separated by centrifugation and washed several times by repeatedly resuspending the solid in 2-propanol and centrifuging the suspension. Usually, the purified precipitate was directly redispersed in methanol without drying the powder (described hereafter). For XRD measurements the precipitate was dried in air (white powder, yield: 2.77 g (77%)).

2.2. Heat Treatment of the Particles. the particles were heated under air for 45 minutes at 600°C.

2.3. Microwave Assisted Synthesis. A solution containing 2.36 g (7.8 mmol) of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Treibacher Industries), 0.78 g (2 mmol) of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Treibacher Industries), 76 mg (0.2 mmol) of $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Treibacher Industries), 1.48 g (40 mmol) of NH_4F (98% Fluka) and 52 mL water was filled in the 80 mL reaction vessel of the microwave system. Subsequently, the amount of 0.89 g (5 mmol) CsF was added and the process was started. The maximum radiation power was set to 300 W, the maximum temperature was set to 200°C, and the maximum pressure was set to 13.8 bar. After radiation for 2 hours the mixture was allowed to cool down. The precipitate was separated by centrifugation and washed several times with water. For XRD measurements the precipitate was dried in air (white powder, yield: 3.45 g (71.8%)).

X-ray diffraction data were recorded at room temperature on an X'Pert Pro Diffractometer (Panalytical) with Bragg-Brentano geometry using $\text{CuK}\alpha_1$ radiation (40 kV, 40 mA) $\lambda = 1.5406 \text{ \AA}$. The average apparent crystallite size as well as the lattice parameters are evaluated by structure profile refinements of X-ray powder diffraction data collected at constant step in scattering angle 2θ using Fullprof program [40] (version February. 2007. LLB, Juan Rodríguez-Carvajal, Saclay, France). The Y_2O_3 powder standard was used to determine the instrumental resolution function of the diffractometer. Emission spectra of colloidal solutions of the nanocrystals and of the pure crystals were measured with a Fluorolog 3–22 spectrometer (Jobin Yvon) combined with a continuous wave 978 nm laser diode (LYPE 30-SG-WL978-F400). Quartz cuvettes (Hellma, QX) containing solutions of the samples or tubes with powder samples were placed inside the spectrometer and excited by the 978 nm light via an optical fiber. All spectra were corrected for the sensitivity of the monochromators and the detection system. The upconversion emission spectra of powder samples were measured with the same instrument but in front-face geometry. TEM images were taken with a 200 kV JEOL JEM-2100 microscope equipped with a charged-coupled device-(CCD-) camera (Gatan). The microwave synthesis was performed in a CEM Discover, Kamp-Lintfort, Germany.

3. Results and Discussion

Figure 1 presents the measured powder diffraction patterns together with the Rietveld refinements and diffraction lines of KEr_2F_7 (PDF 01-086-2454, ICSD 040450). Using orthorhombic KEr_2F_7 (space group Pnam, K^+ and Er^{3+} replaced by Cs^+ and Y^{3+} , resp.) as structural model for our samples leads to minimal differences between observed and calculated X-ray powder diffraction profiles. This result can be easily explained by the findings of Karbowski et al. [41], who found CsGd_2F_7 to be isostructural with KEr_2F_7 (orthorhombic, space group Pna2₁). In the case of bulk CsY_2F_7 (see Figure 1(b)), the structure was indexed with following lattice constants $a = 12.30 \text{ \AA}$, $b = 13.56 \text{ \AA}$, and $c = 7.83 \text{ \AA}$, and we deduced an estimated particle size of $>10 \mu\text{m}$. Additionally, a small trace of Y_2O_3 was observed (see the second group of Bragg lines under line 1b), revealed after the heat treatment of nanocrystalline sample (HEEDA

FIGURE 1: (a): A line pattern of orthorhombic KEr_2F_7 file number PDF 28-01-086-2454 (b): Observed X-ray powder diffraction profile of the heat treated sample of CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er (grey line), Rietveld fit (black line) and residuum, (c): observed X-ray powder diffraction profile of the microwave generated sample of CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er (grey line), Rietveld fit (black line) and residuum, (d): observed X-ray powder diffraction profile of CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er generated in HEEDA (grey line), Rietveld fit (black line) and residuum.

synthesis) under air. Powder pattern of the nanocrystalline sample gained from the microwave synthesis is presented in Figure 1(c) with Rietveld refinement yielding a value of 50 nm for the average apparent crystallite size and the lattice parameters $a = 12.11 \text{ \AA}$, $b = 13.52 \text{ \AA}$, and $c = 7.84 \text{ \AA}$. The TEM images revealed a broad size distribution from which an averaged particle size in the same range ($\sim 50 \text{ nm}$) can be extracted (Figure 2). In case of the second nanocrystalline sample (Figure 1(d)), the best agreement between observed and calculated profiles was obtained to the predefinition of elongated particles in 001 direction. Assuming elongated particles, the diffractogram is well fitted by Rietveld method yielding a value of $a = 12.37 \text{ \AA}$, $b = 13.66 \text{ \AA}$, and $c = 7.82 \text{ \AA}$ for the orthorhombic unit cell and a mean crystallite size of $10 \times 5 \text{ nm}$, a value which is in accord with the size distribution observed in TEM images of the particles (Figure 3). Obviously some particles are not single crystallites and contain more than one crystallite and hence the averaged particle size is higher than the corresponding

FIGURE 2: TEM image of CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er nanocrystals generated in the microwave synthesis apparatus.

FIGURE 3: TEM image of CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er nanocrystals prepared in HEEDA.

size of the crystallites. It should be remembered at this point that there is a limit to the amount of information that can be retrieved from a powder diffraction pattern and, therefore, we cannot completely assume at this time that the structure of our CsY_2F_7 samples is totally identical to orthorhombic KEr_2F_7 .

The samples were doped with the sensitizer/activator ion couple $\text{Yb}^{3+}/\text{Er}^{3+}$ and the emission behaviour upon excitation in the NIR was investigated. Figure 4 shows the light emission of a 1 wt.-% colloidal solution of microwave generated CsY_2F_7 : Yb, Er particles in methanol upon excitation in the NIR. The laser power was about 30 W mm^{-2} , the overall laser power was 4.5 W. The emitted light appears pale green to the eye. The corresponding emission spectrum can be taken from Figure 5. The spectrum is similar to those of Yb,Er doped NaYF_4 but there are differences concerning to the splittings of the emission lines which are not yet understood. Generally, rare earth fluorides doped with the Yb^{3+} and Er^{3+} ion couple show light-emission mainly in the

FIGURE 4: Image of the upconversion luminescence in 1 wt.-% colloidal solutions of CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er nanocrystals in methanol. Excitation at 978 nm with a power density of about 30 W mm^{-2} . Overall laser power: 4.5 W. The laser is positioned on the right side.

FIGURE 5: Emission spectrum of a 1 wt.-% colloidal solution of CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er nanocrystals in methanol.

green ($\text{Er}^{3+} \ ^2\text{H}_{11/2}, \ ^4\text{S}_{3/2} \rightarrow \ ^4\text{I}_{15/2}$) and red ($\text{Er}^{3+} \ ^4\text{F}_{9/2} \rightarrow \ ^4\text{I}_{15/2}$) spectral region after excitation in the NIR. The green to red ratio (GRR), defined as the intensity ratio between the emission bands centered at about 550 nm and 670 nm, depends on the particle size, the crystallographic phase as well as on the doping concentration. A GRR value of about 0.3 can be extracted from the spectrum measured in solution. Mai et al. obtained a very high GRR value of 30 for hexagonal phase NaYF_4 : Yb, Er nanocrystals, the highest GRR value reported to our knowledge [42]. For cubic NaYF_4 and cubic KYF_4 we determined values of about 0.2 [39], respectively 0.26 [25]. Very recently we found a value of 0.6 in case of hexagonal NaYF_4 [24].

Unfortunately the luminescence efficiency of the nanoparticles received from the HEEDA synthesis was extremely

FIGURE 6: Emission spectra of the pure crystals of (a): CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er nanocrystals generated in HEEDA, (b): CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er nanocrystals generated in the microwave synthesis apparatus. (c): CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er nanocrystals generated in HEEDA and heat treated for 45 minutes at 600°C , (d): Hexagonal bulk NaYF_4 : 18% Yb^{3+} , 2.0% Er^{3+} .

low. Even at high laser power ($>6 \text{ W}$) it was not possible to detect visible light emission in transparent solutions of the nanocrystals ($\sim 1 \text{ wt. \%}$) in methanol under excitation in the NIR. The dried powder sample however showed visible light emission upon excitation in the NIR at a laser power of about 3 W.

In order to evaluate the upconversion quality of the particles, the samples were compared with other well known upconversion phosphors. We used hexagonal bulk NaYF_4 : 18% Yb^{3+} , 2% Er^{3+} synthesized by Krämer (University of Bern) as reference substance. Figure 6 presents the emission spectra of the two nanocrystalline samples (a, b) together with the heat treated sample (c) and the reference substance (d) obtained after excitation at 978 nm with a laser power of about 3.5 W. The green to red ratios differ distinctly. The corresponding GRR values are 0.2 (nanocrystals from HEEDA synthesis), 0.24 (nanocrystals from the microwave assisted synthesis), respectively, 0.05 in case of the heat treated nanocrystals. Figure 7, displaying double logarithmic plots of the emitted light intensity versus the power density of the exciting light, shows the upconversion efficiency of the synthesized probes in detail.

The upconversion efficiency of pure crystals of bulk hexagonal NaYF_4 : Yb, Er is, depending on the laser power, 1-2 orders of magnitudes higher than for the heat treated sample. For example at 4 W laser power the emission intensity of the reference phosphor is about 12 times as high as that of the particles from the HEEDA synthesis treated at 600°C for 45 minutes. The efficiency ratio between the reference material and the microwave sample is at 4 W laser-power 345. As mentioned before the nanomaterial generated in the HEEDA synthesis is a very weak upconversion emitter. The upconversion efficiency of the bulk reference material is approximately 1.5×10^5 times higher than for the nanomaterial generated in HEEDA. The result of this comparison was a little bit disappointing but nevertheless it

FIGURE 7: Double logarithmic plots of the emitted light intensity versus the power density of the exciting light for pure crystals of (a): CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er generated in HEEDA, (b): CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er generated in the microwave synthesis apparatus. (c) : CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er generated in HEEDA and heat treated for 45 minutes at 600°C , (d): Hexagonal bulk NaYF_4 : 18% Yb^{3+} , 2% Er^{3+} .

FIGURE 8: Infrared spectrum of (a): CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er generated in the microwave synthesis apparatus, (b): CsY_2F_7 : 78% Y, 20% Yb, 2.0% Er generated in HEEDA, (c): the solvent *N*-(2-hydroxyethyl)-ethylenediamine (HEEDA).

is noteworthy to keep in mind that the microwave generated material is about 430 times more efficient than the material generated in the organic solvent HEEDA. To sum up we can say that the upconversion efficiency of the synthesized probes increases with increasing particle size. This finding is not surprising and can be easily explained by the increment of the surface to volume ration with decreasing particle size. It is well known that the quantum yield of luminescent nanoparticles is strongly affected by surface properties of the particles. In the case of lanthanide doped materials the quantum yield and, hence, also the upconversion efficiency can be strongly reduced if OH, NH_2 , or other groups with vibrational modes of high energy are located in close

proximity to the lanthanide ions. Therefore, the surface ligands and the solvent strongly affect the optical properties of these nanomaterials. In case of high surface to volume ratio (small particles) this lowering effect is of course quite strong, vice versa. The used solvent HEEDA contains a lot of these hampering molecule fragments and hence the probe generate in this solvent shows the lowest UC efficiency. The presence of NH_2 and OH groups of HEEDA molecules had been proven by FTIR. Figure 8 shows the results of the FTIR measurements. The curve (c) belongs to the solvent HEEDA, the curve (b) belongs to the particles gained from the HEEDA synthesis and the curve (a) belongs to the sample from the microwave assisted synthesis. HEEDA molecules on the surface in combination with a very high surface to volume ratio explain the very low upconversion efficiency of the particles gained from the HEEDA synthesis.

4. Conclusion

We demonstrated simple routes for the synthesis of nano- and microcrystalline Yb^{3+} , Er^{3+} doped CsY_2F_7 . Depending on the starting material and the reaction conditions the particle sizes vary. Whereas the reaction carried out in water starting from CsF lead to bigger particles, the reaction carried out in HEEDA starting from the corresponding Cs HEEDA alkoxide lead to real nanosized material. So the nature of the caesium source seems to influence the particle growth which we do not understand up to now. Fullprof refinements of the powder diffraction data of the probes led to the conclusion that CsY_2F_7 , generated in a way presented in this article, crystallizes in an orthorhombic structure known from KEr_2F_7 . The average particle sizes, which were also extracted from these Rietveld refinements, are in accordance with the corresponding values derived from the TEM images. The samples showed visible upconversion emission upon excitation in the NIR. Nevertheless, in comparison with the most efficient upconversion phosphor known today, hexagonal bulk NaYF_4 : 18% Yb^{3+} , 2% Er^{3+} , the upconversion efficiency especially of the sample generated in HEEDA, was very low.

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