Editorial

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Thin-walled Er\(^{3+}\):Y\(_2\)O\(_3\) nanotubes showing up-converted fluorescence

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Up-converted red and green fluorescence has been measured in low-crystallinity Er\(^{3+}\):Y\(_2\)O\(_3\) nanotubes upon IR excitation. A new preparation procedure for thin-walled erbium doped yttria nanotubes using alumina templates as shape defining tools and rare earth nitrates as precursors for a purely thermolytic production of erbium doped yttria was developed. The products with a diameter of approximately 40–50 nm and a wall thickness of only 6–8 nm showed up-converted fluorescence with green and red emission bands when excited at 815 nm. The fluorescence properties are compared to the ones of bulk erbium doped yttria obtained from the same precursor system.

Introduction

The capability of certain trivalent rare earth ions such as Er\(^{3+}\) to perform infrared-to-visible up-conversion is gaining increasing attention in the field of energy harvesting as this effect may help to make use of an extended spectral range of solar radiation for energy conversion.\(^1\)–\(^5\) In addition, up-conversion of IR radiation plays an important role in lasing\(^6\)\(^,\)\(^7\) and in fluorescence imaging.\(^8\)\(^,\)\(^9\) In all up-conversion materials, the efficiency crucially depends on the local environment of the emitting rare earth ion and the degree of crystallinity of the respective material.\(^10\)–\(^16\) Erbium-doped non-toxic oxides such as Er\(^{3+}\)-doped yttria show significant potential as up-conversion materials because of their strong emission bands in the green (550 nm, \(\text{S}_3/2 \rightarrow \text{I}_{15/2}\)) and the red (665 nm, \(\text{F}_9/2 \rightarrow \text{I}_{15/2}\)) region of the visible range.\(^14\) An additional enhancement of the luminescence can be achieved when the material is subjected to quantum confinement.\(^17\)

As the quality and the crystallinity of the rare earth doped host oxide have a large influence on the optical properties of the resulting materials, several approaches to nanoscale materials such as nanorods,\(^18\) nanoparticles\(^19\),\(^20\) or nanotubes\(^21\) focused on the preparation in an autoclave to obtain an optimum crystallinity of the products. For the preparation of shape-defined europium-doped yttria nanotubes porous alumina templates with a pore diameter of 70 nm in combination with a sol–gel method were used.\(^22\) In this case, as in a number of other hydrothermal or sol–gel routes, the formation of the rare earth-doped yttria is conducted under alkaline conditions.\(^11\)\(^,\)\(^18\) As porous alumina is known to be partially dissolved under basic conditions, these syntheses are not ideal for a preparation of shape defined yttria nanotubes within the template pores. The latter is inevitable for a synthetic route to very small thin-walled nanotubes, as soft templates cannot provide such delicate control over the growth of relatively small nano-objects of doped yttria. For these reasons we developed a purely thermolytic process for the formation of thin-walled erbium-doped yttria nanotubes within the pores of a porous alumina template with a nominal pore diameter of 60 nm.\(^23\)–\(^27\) Such nanotubes allow an investigation of the influence of the thin and only moderately crystalline walls on the up-conversion luminescence.

Experimental

Chemicals and materials

Y(NO\(_3\))\(_3\)-6H\(_2\)O and Er(NO\(_3\))\(_3\)-4.7H\(_2\)O were purchased from STREM and used as received. The mesoporous anodic alumina templates were produced at the Max-Planck-Institute of Microstructure Physics in Halle (Saale) via an electrochemical etching step. Details on their preparation are described elsewhere.\(^23\)–\(^27\)

Preparation of Er\(^{3+}\):Y\(_2\)O\(_3\) nanotubes and Er\(^{3+}\):Y\(_2\)O\(_3\) bulk powder

In a typical procedure 20 mg of Y(NO\(_3\))\(_3\)-6H\(_2\)O and 0.4 mg of Er(NO\(_3\))\(_3\)-4.7H\(_2\)O (depending on the desired amount of erbium) were dissolved in 2 mL of distilled water. An alumina template (pore diameter of 60 nm) was immersed into the aqueous precursor solution for two hours. Then, the template was removed from the solution and dried in air for one hour. Subsequently, the templates were calcined in air for two hours at 500 °C. After cooling to room temperature, the template was immersed into 4 M sodium hydroxide solution until the alumina layer was dissolved and a small amount of a colourless solid was released. The nanotube suspension was centrifuged and purified by removal of the supernatant, addition of distilled water and sonification. This procedure was repeated four to six times until the supernatant reacted neutral.
The released and purified nanotubes could be suspended in water or ethanol and be dropped onto any substrate.

For the preparation of the bulk powder appropriate amounts of yttrium (III) nitrate hexahydrate and erbium (III) nitrate hydrate were mixed using mortar and pestle and filled into a quartz crucible. The crucible containing the slightly pink powder was placed in an oven and calcined at 800 °C in air for up to 80 h.

Characterization methods

TG analysis was conducted with a Netzsch TG 209 cell, DSC measurements were performed in corundum crucibles with a Netzsch DSC 404 C calorimeter in nitrogen atmosphere.

X-Ray powder diffraction patterns were recorded with a STOE Stadi P transmission powder diffractometer using CuKα radiation.

Transmission electron microscopy was performed using a Jeol JEM 1010 and a Philips CM12 transmission electron microscope operated both at 100 kV (LaB6-cathode). High resolution TEM and EDX analysis was carried out with a Philips CM 20 FEG (200 kV, LaB6-cathode). For sample preparation aqueous suspensions of the nanotubes were directly dropped onto carbon coated copper grids received from Plano.

For the investigation of the up-conversion of the absorbed light in Er3+:Y2O3 we performed photoluminescence measurements (PL) with infrared excitation. The samples were deposited on a Si wafer and excited in a reflective geometry using a mode-locked titan sapphire laser with a pulse length of 2 ps. The excitation wavelength was tuned to 815 nm. The luminescence of the excited samples was detected with a 35 cm McPherson double monochromator system in subtractive mode and a peltier cooled GaAs detector.

Results and discussion

A new preparative method for the preparation of doped thin-walled yttria nanotubes was developed as the common syntheses either involve basic hydrothermal conditions, which are too aggressive for narrow porous alumina templates or the application of slurries of the yttrium and rare earth precursors where the grain size of the dispersed components may be larger than the pore diameter of 60 nm of our porous alumina templates. Therefore, a non-alkaline solution-phase approach had to be found. Before an infiltration of the pores with the precursor solution was conducted, the thermal degradation of the Y(NO3)3·6H2O precursor was investigated separately to find the optimum decomposition temperature and to assure the formation of single-phase yttria in the thermolysis. Calorimetric (DSC) measurements (Fig. 1) showed different endothermic events in the range of 25–300 °C and thermogravimetric control experiments revealed that a weight loss of 29% occurred when the precursor was heated to a temperature of 300 °C. This value is in good accord with the theoretical weight loss of 28.2% when the hexahydrate will lose its six equivalents of water. As can be seen from Fig. 1, the decomposition of the yttrium nitrate leading to the formation of yttria starts at ~335 °C and comes to completion just below 400 °C. Further annealing of the resulting yttria powder to 500 °C already gave good crystallinity and after annealing at 800 °C sharp reflections of very pure yttria were recorded (Fig. 2). All reflections were indexed for cubic Y2O3 (space group Ia3, a = 10.606(1) Å, ICSD-86813) and no reflections of any impurities were found.

Refinement of the cubic lattice parameter of the microcrystalline yttria obtained after annealing at 800 °C gave a lattice parameter of a = 10.601(2) Å, which is in excellent agreement with literature data.

Doping experiments with different amounts of Er(NO3)3·4.7H2O in the range of 1–9 at% Er3+ and subsequent co-thermolysis of the two nitrates also yielded single-phase highly crystalline materials.

For the preparation of thin-walled Er3+-doped nanotubes of yttria within the 60 nm pores of porous alumina, mixtures of yttrium nitrate and erbium nitrate with varying erbium content were prepared. The nitrates were dissolved in distilled water and the templates were infiltrated with this precursor solution by immersing them into it. The infiltrated templates were dried in air and calcined at 500 °C. Then the alumina was selectively removed by aqueous base and the nanotubes were released. The resulting tubes were investigated by transmission electron microscopy (TEM) and they showed diameters in the range of 40–50 nm (Fig. 3). Their wall thickness was determined as 6–8 nm. Electron diffraction of larger areas of

Fig. 1 DSC measurement of the thermal decomposition of Y(NO3)3·6H2O in the temperature range of 200–450 °C.

Fig. 2 X-Ray powder diffractogram of microcrystalline yttria obtained after annealing at 800 °C and indexed for cubic Y2O3 (Ia3).
nanotubes showed the expected reflections of cubic yttria and the reflections were indexed accordingly (Fig. 3). Bundles of erbium doped yttria tubes were investigated by EDX analysis and the EDX spectra revealed the presence of yttrium and erbium in the product (Fig. 4). The amount of erbium found in such nanotubes was in good accordance with the erbium contents of the initial precursor solution that was infiltrated into the template pores.

In addition to the analysis and characterization of larger fields and bundles of nanotubes we also investigated the products on a single tube basis. One important aspect for the optical quality of the nanotubes is a homogeneous distribution of the erbium dopant in the yttria host lattice. Thus we performed line scan analysis of single nanotubes to look for potential formation of erbium-rich regions and phase segregated areas within the tube walls. No such phenomena were observed and all line-scans showed the typical concentration profile of a tubular morphology (Fig. 5). The yttrium profile and the erbium profile are correlated and determined by the shape of the nano-objects. No other type of erbium ion distribution was detected in the tubes.

The second major parameter that governs the line width and the efficiency of erbium luminescence in Er\(^{3+}\)-doped yttria is the crystallinity of the products and the degree of order around the emitting rare earth ions. This is one of the most challenging aspects of nanotube synthesis in general. Often, thin-walled nanotubes are of poor crystallinity and annealing at higher temperatures will destroy their tubular structure. A closer TEM investigation of the walls of the yttria nanotubes produced in this thermolytic approach revealed polycrystalline walls showing mostly (222) lattice planes in HRTEM images (Fig. 6), but also some small amorphous regions in between. An average size of the individual nano grains of 3–4 nm was determined by HRTEM analysis. This grain size was found for all tubes that were investigated and no larger distribution of grains sizes was observed. Several attempts to improve the crystallinity of the tube walls by higher annealing temperatures or steeper heating ramps during thermolysis of the precursors within the pores did not succeed. The presence of the amorphous pore wall of the alumina template seems to decrease the tendency of the initially formed primary grains to form larger crystalline areas. In addition, the wall thickness of only 6–8 nm is also disadvantageous for an ordering of more extended areas of the tubes. The rather low tendency to develop long range order found in these tubes cannot be attributed to the presence of Er\(^{3+}\), as pure yttria tubes made from the yttrium nitrate precursor in the same way showed the same degree of crystallinity.

Despite the moderate crystallinity of the thermolytically produced thin-walled nanotubes, they were investigated...
regarding potential up-converted fluorescence. Nanorods of Er\textsuperscript{3+} doped yttria showed up-conversion to the visible range when excited in the infrared range at 810 nm.\textsuperscript{18} The dominant emission bands of the trivalent erbium ion are well known to be the \( ^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2} \) transition (centered at 550 nm for bulk material) and the \( ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2} \) transition (centered at 565 nm for bulk material) in the bright green region of the visible range and the \( ^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2} \) transition (centered at 665 nm for bulk material) leading to a red luminescence.\textsuperscript{6,14,17,28}

Several nanotube samples with different concentrations of trivalent erbium in the yttria matrix (1–9 at\%) were prepared and microcrystalline yttria with the same concentrations of Er\textsuperscript{3+} was synthesized in parallel. Whereas the microcrystalline samples also showed bright up-converted emission in the green and the red region at concentrations between 5\% and 9\% erbium, the nanotubes only gave satisfying up-converted fluorescence at very low erbium contents such as 1.3 at\% Er\textsuperscript{3+}. The lack of detectable visible emission for higher concentrations can likely be attributed to concentration quenching\textsuperscript{29} in the thin-walled tubes. The up-converted fluorescence of the nanotubes with low erbium content was compared to the emission bands of microcrystalline erbium doped yttria powder (Fig. 7). Both samples exhibit the three most intense emissions of trivalent erbium ions due to the transitions from the \( ^2\text{H}_{11/2} \) state, the \( ^4\text{S}_{3/2} \) state and the \( ^4\text{F}_{9/2} \) level to the \( ^4\text{I}_{15/2} \) ground state. When compared to the microcrystalline powder, the emission bands of the rare earth doped nanotubes are significantly broadened and slightly shifted in their positions. The \( ^4\text{S}_{3/2} \) emission and both branches of the red \( ^4\text{F}_{9/2} \) emission band are red shifted by 8–11 nm. In the case of the \( ^4\text{S}_{3/2} \) band this leads to an emission maximum at 568 nm for the nanotubes instead of 560 nm in the bulk erbium doped yttria. The two branches of the red \( ^4\text{F}_{9/2} \) emission are red-shifted from 659/681 nm for the microcrystalline material to 668/689 nm for the nanotubes. In contrast to these two emissions, a small but detectable blue-shift was found for the \( ^2\text{H}_{11/2} \) band. The center of this green fluorescence shifts from 550 nm for the microcrystalline powder to 545 nm for the Er\textsuperscript{3+}-doped yttria tubes.

The dominant phenomena of peak broadening and red-shifts of the emission bands were also found by Qi et al.\textsuperscript{16} in nanocrystalline Eu\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} with a particle size of only 9 nm. As the grains in the thin walls of the Er\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} investigated here are even smaller, such broadening effects that are attributed to non-homogeneous coordination spheres around the trivalent rare earth\textsuperscript{15,16} are even more likely to be found. In the case of Eu\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} it was shown, that the coordination number of six that all trivalent ions in the bixbyite structure type adapt is expanded to an average coordination number of 6.8 for yttrium ions and even of 7.9 for europium ions.\textsuperscript{16} Such a pronounced distortion of the parent structure type leads to a larger distribution of rare earth–oxygen distances and also allows the emitting rare earth ions to couple to a broader range of vibrational states in the crystal structure. As each of these effects is expected to contribute to an overall broadening of the rare earth emission

![Fig. 6](image_url) TEM image of a single Er\textsuperscript{3+}-doped yttria nanotube (a) with two HRTEM areas (b and c) showing (222) lattice planes of individual grains in the polycrystalline pore walls.

![Fig. 7](image_url) Up-converted room temperature luminescence spectra of thin-walled Er\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} nanotubes ((a), 1.3 at\% Er\textsuperscript{3+}), and microcrystalline Er\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} (b), both prepared thermolytically from mixtures of erbium nitrate and yttrium nitrate.
states, the changes in the structure of the fluorescence spectrum of the Er$^{3+}$:Y$_2$O$_3$ nanotubes can be rationalized. The photoluminescence behaviour of rare earth metal ions in inorganic–organic hybrid materials has been investigated by Karmaoui et al.$^{30,31}$ The structures consisted of very thin alternating layers of various rare earth metal oxides ($\sim 0.6$ nm) and benzoate molecules ($\sim 1.2$ nm) and mainly showed rather broad reflections in their X-ray diffraction patterns. Nevertheless, rather sharp emission bands in the visible could be detected in e.g. gadolinium/terbium and gadolinium/ europium based materials. $^{31}$ This indicates that peak broadening can be suppressed when a high degree of short range order is achieved, even in materials consisting of very small crystalline domains. In contrast, if there are relevant distortions in the first coordination sphere of the emitting ion due to weak crystallinity a broadening of the emission bands is observed.

Conclusions

A new thermolytic synthesis of thin-walled erbium-doped yttria nanotubes with a diameter around 50 nm was found and used to produce nanotubes that exhibit up-conversion from the infrared to the visible range. With a doping level of 1.3\% Er$^{3+}$, a slight shift of the green and the red emission bands was observed, most likely due to the moderate degree of crystallinity in the tube walls and a resulting distribution of local coordination environments of the emitting Er$^{3+}$ ions. Here, the strategy of a very low doping level to avoid rare earth ion clustering in the relatively small volume of the thin walls was successful and both prominent emissions were detected. These results demonstrate that even in thin-walled nanotubes lacking high crystallinity up-converted fluorescence in the visible range can be obtained by Er$^{3+}$ doping.

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