

Flame Synthesis of Complex Fluoride-Based Nanoparticles as Upconversion Phosphors[†]

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Abstract

Recent improvements in precursor chemistry, reactor geometry and run conditions extend the manufacturing capability of traditional flame aerosol synthesis of oxide nanoparticles to metals, alloys and inorganic complex salts. As an example of a demanding composition, we demonstrate here the one-step flame synthesis of nanoparticles of a 4-element non-oxide phosphor for upconversion applications. The phosphors are characterized in terms of emission capability, phase purity and thermal phase evolution. The preparation of flame-made β -NaYF₄ with dopants of Yb, Tm or Er furthermore illustrates the now available nanoparticle synthesis tool boxes based on modified flame-spray synthesis from our laboratories at ETH Zurich. Since scaling concepts for flame synthesis, including large-scale filtration and powder handling, have become available commercially, the development of industrial applications of complex nanoparticles of metals, alloys or most other thermally stable, inorganic compounds can now be considered a feasible alternative to traditional top-down manufacturing or liquid-intensive wet chemistry.

Keywords: flame pyrolysis, upconversion, sodium yttrium fluoride, rare earth, luminescence, nanoparticles

1. Introduction

Nanoparticle powder technology is a widely applied industrial process for the preparation of advanced functional materials (Hosokawa, 2008). Pre-designed and engineered nanostructures attract the interest of research and industry communities. Various methods of synthesis and control of these objects are constantly being developed and appear in high-impact journals, symposia and discussions. Despite a dramatic gap between academic methods for laboratory synthesis and the technological implementation on an industrial scale, various materials based on nanotechnologies are already available from large-scale production. Among the most promising methods are: CVD process for carbon nanotubes (Cassell et al., 1999); emulsion methods for polymer-

ic nanoparticles (Muller et al., 2006) in drug delivery applications (PLGA, (Musyanovych et al., 2008)); sol-gel, e.g. LiFePO₄ (Lee et al., 2010); precipitation, e.g. BaSO₄, (Adityawarman et al., 2005); and hydrothermal methods (Chen et al., 2009) for various nanoparticles. However, the aforementioned methods are often inapplicable for metastable phases which often possess high functional characteristics.

Gas-phase synthesis stands aside as an independent process to fabricate nanopowders, particularly with aerosol methods. This technique allows a multi-scale and cheap production of nanoparticles. It is a relatively flexible technology by which also metastable phases can be obtained. Flame pyrolysis is currently applied in the large-scale production of SiO₂ and TiO₂ nanoparticles. The method is also promising for the production of nanostructured carbonates, e.g. CaCO₃ (Huber et al., 2005) and SrCO₃ (Strobel et al., 2006), sulfides, e.g. PbS and ZnS (Athanasios et al., 2010), highly reactive metals, e.g. Co (Grass and Stark, 2006) and Ni (Jung et al., 2005), alloys, e.g. Cu-Ni (Jung et al., 2003), glasses, e.g. SiO₂-CaO-P₂O₅-Na₂O (Brunner et al., 2006), and halides, e.g. NaCl,

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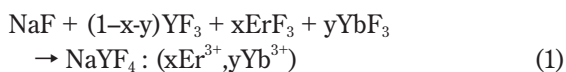
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BaF₂, and CaF₂, (Grass and Stark, 2005). An overview of nanoparticles prepared by flame-spray pyrolysis is shown in **Fig. 1**. The established materials, namely spherical oxide nanoparticles, a straightforward product of gas-phase synthesis, stand at the origin of the graph. This group typically includes titanium, silicon, and aluminum oxides. There has been evidence for more complex materials prepared by flame pyrolysis, e.g. Sr₅(PO₄)₃Cl:Eu²⁺ (Kang et al., 2003). A reducing atmosphere helps to step away from oxidic nanoparticles towards metallic compounds. Acetylene-fed flames form carbon shells on the surface of metallic nanoparticles (Grass et al., 2007). Such carbon coatings allow chemical functionalization strategies of the nanoparticle surface to use them in filtration and purification (Rossier et al., 2011), magnetic chemical reagents (Wittmann et al., 2010) and catalysts (Zeltner et al., 2011). Sulfides derived from flame pyrolysis belong to another group of widely applied chalcogenide salts. Recently, Athanassiou et al. successfully prepared doped ZnS:Mn²⁺ nanoparticles (Athanassiou et al., 2010).

Another group of industrially valuable non-oxidic salts are halides. Chlorides and fluorides of alkaline and alkaline-earth metals have been successfully obtained by gas-phase synthesis yielding nanoparticles of various morphologies and structures. Fluorides have unique optical and electronic properties which are widely used in biomaterials and electronic applications, though the need of more complex phosphors requires the preparation of glasses and mixed fluorides.

Recently, upconversion (UC) phosphors based on the rare earth and alkaline-earth materials have been investigated. In a UC process several low energy photons are absorbed, their energy is converted and finally a photon of higher energy is emitted. UC is also known as anti-Stokes emission (Auzel, 2004). It is known for f-elements such as the lanthanide ions Er³⁺ and Tm³⁺, as well as U³⁺, and several d-element ions embedded into specific matrices (Auzel, 2004).

Upconversion phosphors such as β-NaYF₄: Yb, Tm or Yb, Er are regularly synthesized as bulk microcrystalline materials by high-temperature solid-state synthesis:



Targeting molecules in biological applications and thin coatings for solar cells imply size limits of the embedded upconversion particles from tens to hundreds of nanometers. For the same purposes, it is

preferable to produce upconversion nanoparticles with high luminescence intensity. Few approaches in the production of nanocrystalline UC phosphor materials are known: decomposition of multiprecursors (Yi et al., 2004), co-precipitation (Martin et al., 1999), hydrothermal and solvothermal methods (Zeng et al., 2005). Nonetheless, those methods are limited to predictable crystallite morphology, low production rates and complicated synthesis schemes. Hexagonal sodium yttrium fluoride is one of the most efficient host matrices for NIR-to-visible upconversion phosphors (Sommerdijk, 1973). The upconversion efficiency of sodium yttrium fluoride host matrices is 20 times higher compared to La₂O₃ and 6 times - to La₂(MoO₄)₃ crystal matrices (Blasse and Grabmaier, 1994). NaYF₄: Yb,Er or Yb,Tm upconversion phos-

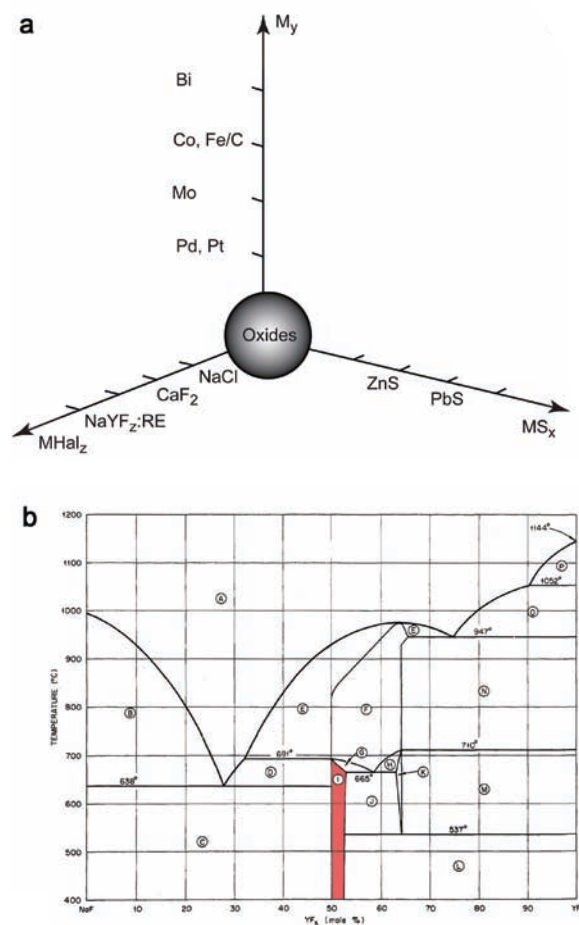


Fig. 1 (a) Schematic representation of various nanostructures currently available by the flame-pyrolysis technique and (b) phase diagram of the NaF-YF₃ system (Thoma et al., 1963). The shaded area marks the hexagonal NaYF₄ stability region. Adapted with permission from Thoma et al., 1963. Copyright 1963 American Chemical Society.

phors convert, e.g. continuous-wave 980-nm laser excitation into NIR, visible and UV emissions. Cost-effective diode lasers can be used to obtain UC emissions from transparent nanoparticle solutions (Heer et al., 2004). The prospective applications of such phosphors include bio labels (Wang et al., 2009), solar cells (Richard and Shalav, 2005) and solid-state lasers (Sandrock et al., 1997).

Lim et al. (Lim et al., 2009) successfully produced sub-10-nm polydisperse UC nanophosphors by flame-spray pyrolysis in a one-step continuous synthesis. The host matrix used for their study was cubic Y_2O_3 which is less efficient than hexagonal $NaYF_4$ (Auzel, 2004). Grass et al. (Grass and Stark, 2005) proposed a fluoride doping with rare earth elements by flame synthesis. As a result, it appeared feasible to synthesize upconverting sodium yttrium fluoride nanoparticles doped with Yb-Tm or Yb-Er, although the cubic phase might be obtained instead of the hexagonal phase which shows better UC properties. Due to the limited thermodynamic stability of the hexagonal low-temperature phase, see the phase diagram in **Fig. 1b**, the cubic high-temperature phase of $NaYF_4$ might be obtained from the synthesis as metastable kinetic product.

In the present work, flame pyrolysis is used to prepare nanoparticles of non-oxidic, doped rare earth fluorides. The upconversion emission during excitation with NIR laser and the thermal behavior of the derived phosphors are analyzed. The cubic-to-hexagonal phase transition of $NaYF_4$ will be examined for various syntheses and thermal treatment conditions.

2. Experimental

Preparation of $NaYF_4$: Yb (Tm, Er) nanoparticles

Powders of nano-sized upconversion particles (UCNP, $NaYF_4$: Yb,Tm) were fabricated by flame-spray pyrolysis. Precursors of yttrium, ytterbium, erbium, and thulium were prepared from rare earth acetates $Tm(CH_3CO_2)_3 \cdot xH_2O$, $Y(CH_3CO_2)_3 \cdot xH_2O$ (Fluka, 99.90% metal trace), and $Yb(CH_3CO_2)_3 \cdot xH_2O$ (Acros Organics, 99.90% metal trace) by refluxing them with 2-ethylhexanoic acid (Fluka, puriss.) (Stark et

al., 2003, 2004, 2005) and removal of acetic acid, for experimental conditions see **Table 1**. In the case of erbium-doped phosphors, $Er(CH_3CO_2)_3 \cdot xH_2O$ (Fluka, 99.90% metal trace) was dissolved in 2-ethylhexanoic acid and the solution was directly combusted in the flame. $NaHCO_3$ (Ph Eur, Applichem Co.) was mixed with 2-ethylhexanoic acid to obtain the sodium precursor. Each precursor solution was diluted with xylene (technical grade) to adjust the metal content to 1M and was filtered before combustion.

The prepared stoichiometric mixtures of rare earth ethylhexanoates, sodium 2-ethylhexanoate, and fluorobenzene (ABCR-Chemicals, 99%) were combusted to produce $NaYF_4$ nanoparticles, doped with 25 mol.% Yb and 0.3 mol.% Tm, i.e. $NaY_{0.747}Yb_{0.25}Tm_{0.003}F_4$, and 20 mol.% Yb and 2 mol.% Er, i.e. $NaY_{0.78}Yb_{0.2}Er_{0.02}F_4$. The solution was pumped through a 0.4-mm-diameter capillary at rates of 3, 5, 7, and 9 l min^{-1} into fuel flames. Alternatively, the liquid solution was dispersed into an aerosol and burnt in oxygen (99.8%, Pan Gas) at rates of 7, 5, and 3 l min^{-1} with a pressure drop at the capillary tip of 1.5 bar. A steady combustion was achieved by an oxygen (99.8%, Pan Gas) sheath gas flow of 230 l h^{-1} through a concentric sinter metal ring. A Teflon filter was used to collect the prepared particles of UCNP. The particles remained stable at ambient conditions. In the case of the reducing flame pyrolysis, the precursors were burned in a nitrogen-rich atmosphere using a nitrogen (5N, PanGas) glove-box with gas flow (Grass et al., 2007). This flow was circulated by a vacuum pump (Busch, Seco SV1040CV). The oxygen concentration was fixed below 100 ppm (volumetric) for the reducing flame pyrolysis.

Characterization of UC phosphors

The specific surface area was calculated by measuring the nitrogen adsorption at 77 K on a Tristar (Micromeritics Instruments) following the Brunauer–Emmett–Teller (BET) method. Prior to the surface area determination, samples were preheated in vacuum at 150°C with $p < 0.1$ mbar during 1 hour.

The prepared $NaYF_4$ nanoparticles with Yb-Tm and Yb-Er rare earth dopants were sintered at various temperatures (500 – 800°C) in air or nitrogen flow during 2 or 3 hours at heating rates of 10°C min^{-1} . A “fast” heating of the $NaYF_4$:Yb, Er upconversion phosphors was achieved by placing the powders directly in an 800°C preheated furnace.

The relative upconversion luminescence was measured according to the following procedure: Powders of the UC phosphors were filled in glass tubes of 1

Table 1 Precursor synthesis conditions

Salt ion	Temperature, °C	Distillation time, hours	Concentration, wt. %
Y^{3+}	130	6	6.3
Yb^{3+}	110	12	8.32
Tm^{3+}	120	2	0.7

mm inner and 1.5 mm outer diameter and then fixed in a sample holder. The powder densities were the same for all samples, as the powders were pressed into the glass tubes with glass tips. The samples were excited by a 980-nm IR laser diode coupled to a 1-mm-diameter fiber. The non-focused laser beam illuminated the sample in a spot of about 1 mm² at a distance of 2-3 mm from the surface. The UC emission was collected by a Y-fiber, i.e. parallel to the excitation light, and measured by an Ocean Optics SD1000 spectrometer. The reflected IR laser light was blocked by a filter in front of the spectrometer. The laser power was measured by a power meter. The luminescence spectra were corrected for the spectral response of the detection system. The integrated emission peaks yielded the relative UC efficiencies of the powder samples with a reproducibility of 5%.

The size and shape of the as-prepared upconversion nanoparticles were characterized by transmission electron microscopy (TEM) with a Philips CM30 ST (LaB₆ cathode, operated at 300 kV, point resolution 4 Å). Morphologies were also analyzed by scanning electron microscopy (SEM) with a Zeiss LEO 1530 Gemini. The phase composition was characterized by X-ray diffraction (XRD) patterns recorded with a PANalytical XPert PRO-MPD (CuK α radiation, X'Celerator linear detector system, step size of 0.033°, ambient conditions). The mean crystallite size was estimated from X-ray diffraction patterns by the Scherrer equation.

3. Results and Discussion

Flame-spray powder morphologies and phase analysis

NaYF₄:Yb,Tm powders were prepared by flame-spray synthesis. The obtained nanoparticles had diameters of 20-40 nm. The fuel/oxygen flow rates of 3/7, 7/3, and 7/9 L/min resulted in the formation of cubic α -NaYF₄ particles, see **Fig. 2a**. Equation (2) shows the reaction scheme,



where liquid corresponds to the melt in the flame before cooling down at the Teflon filter.

The medium 5/5 l min⁻¹ feeding rate led to a mixed product with hexagonal(β) and cubic(α) phases of sodium yttrium fluoride, see **Fig. 2a**.

The TEM analysis of this powder revealed the presence of hexagonal particles. The particles have sizes of about 10 nm with agglomerates up to 50 nm, see **Fig. 2b**.

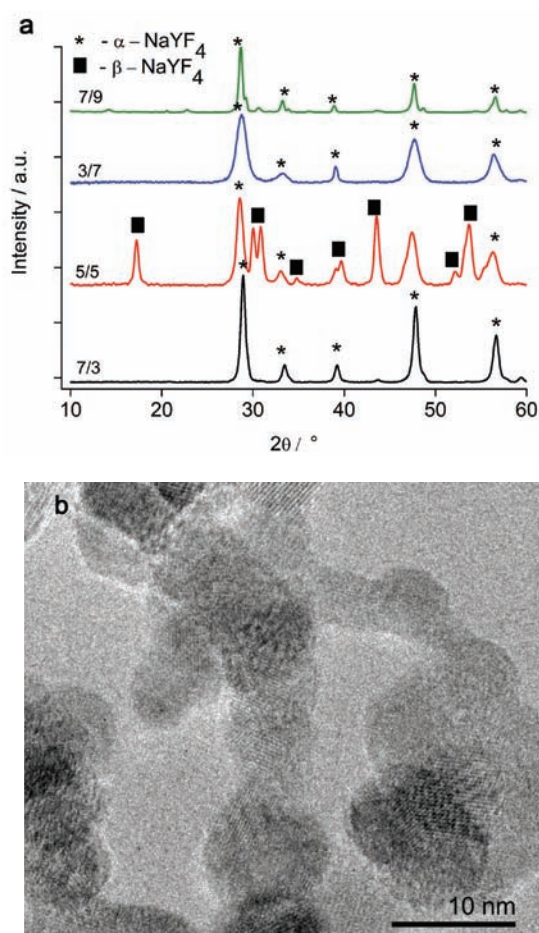


Fig. 2 (a) X-ray diffraction patterns of NaYF₄:Yb,Tm nanoparticles from different fuel/oxygen flow rates and (b) Transmission electron microscopy image of hexagonal NaYF₄:Yb,Tm nanoparticles obtained from fuel/oxygen flow rates of 5/5 L/min.

By the BET method, specific particle surface areas from 29.5 to 31 m² g⁻¹ were determined for nanoparticles prepared in oxidic or reduced atmospheres.

The calculated particle diameters according to equation (3) were 47 and 45 nm, respectively,

$$d_{BET} = \frac{6}{\rho \cdot SSA} \quad (3)$$

where $\rho = 4.3 \text{ g cm}^{-3}$ is the density of β -NaYF₄ (Sobolev, 2000) and SSA is the specific surface area (Sobolev et al., 1963).

The SEM micrographs of flame-sprayed NaYF₄:Yb,Tm also demonstrated the homogeneous distribution of nanoparticles without any visible micron-sized agglomerates, see **Fig. 3a**. These particles are stable at room temperature under atmospheric conditions. Images of the as-prepared NaYF₄:Yb,Er nanoparticles show agglomerated clusters in the 100-nm range with

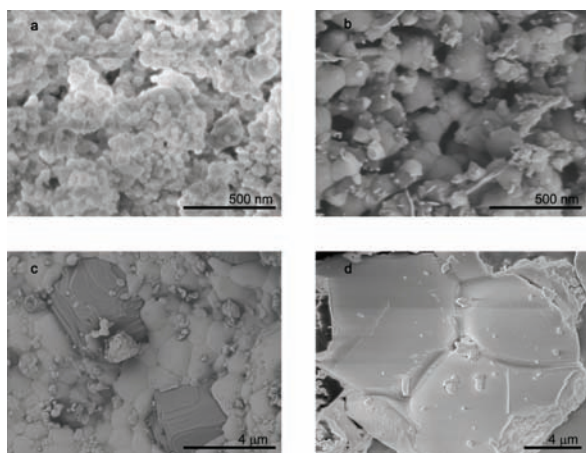


Fig. 3 SEM micrographs of sodium yttrium fluorides prepared by the flame-spray method. (a) and (b) show highly anisotropic hexagonal nanoparticles of NaYF₄:Yb, Tm and NaYF₄:Yb, Er, respectively. (c) and (d) show images of micron-sized crystallites of NaYF₄ and cubic Y₂O₃, respectively, after sintering at 700°C in ambient atmosphere.

hexagonal crystallites of less than 50 nm in size, see **Fig. 3b**. It correlates to previously measured BET and TEM particle size estimations. During sintering, the grains grow and micron-sized cubic crystals of Y₂O₃ form, see **Fig. 3c**. The image of a fragment in **Fig. 3d** shows narrow grain boundaries of β-NaYF₄ crystals after 3 hours sintering at 700°C under constant nitrogen flow.

Thermal treatment of UC phosphors

The thermal behavior of the synthesized powders was studied by differential thermal analysis (DTA), see **Fig. 4a**. At low temperatures, the adsorbed water was released from the sample according to a weight loss of 0.3 wt%. In addition, the DTA signal indicates a minor exothermic peak at 380°C. It may correspond to the formation of traces of cubic yttrium oxide. At 400-500°C, the TG curve shows a step correlated to an endothermic peak on the DTA curve.

Analysis of the phase composition of upconversion phosphors sintered at 500°C showed decreasing half-widths of the Bragg peaks which correspond to an increased size of the crystallites. The NaYF₄:Yb, Tm powders were sintered at temperatures from 500°C to 800°C. The XRD curves up to 700°C give no hint for a phase transition, see **Fig. 4b**. The sintering at 800°C shows a partial transition of sodium yttrium fluoride from its cubic to the hexagonal phase. According to the NaF-YF₃ (Thoma et al., 1966) phase diagram, see **Fig. 1b**, the hexagonal β-NaYF₄ phase is stable at room temperature whereas the high-temperature

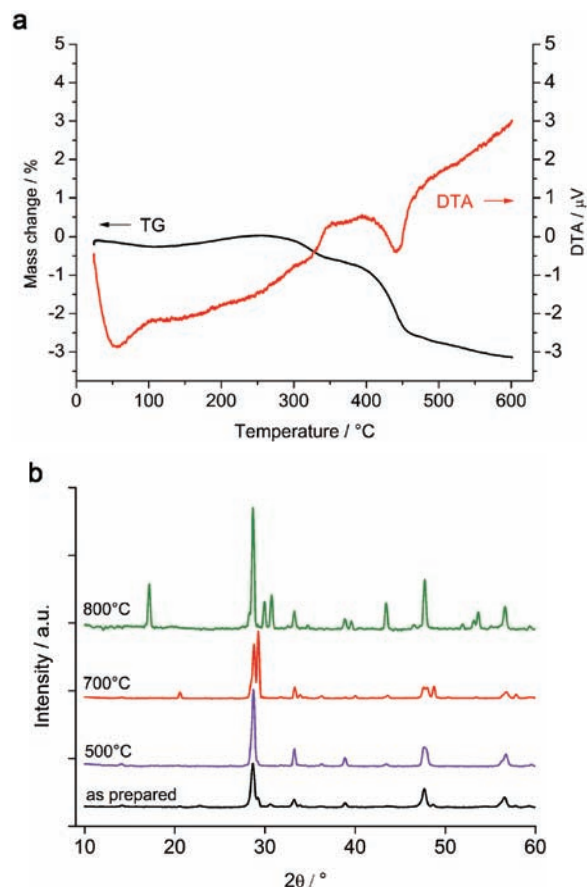


Fig. 4 (a) Differential thermal analysis (DTA) and thermal gravimetric (TG) signals of NaYF₄:Yb, Tm nanoparticles and (b) XRD diffraction patterns for different sintering temperatures of NaYF₄:Yb, Er. 500°C and 700°C sintering was applied at a 10°C min⁻¹ heating rate. For 800°C, a “fast” heating is achieved by placing the powder directly into the preheated furnace.

cubic α-phase is stable above 691°C. Thus cubic NaYF₄ is obtained in the synthesis as a metastable, kinetically stabilized phase. Only at high enough temperatures, close to the α-β phase transition, can the α-phase overcome the activation energy barrier and transform into the β-phase. The ‘800°C’ curve in **Fig. 4b** shows a partial α-β phase transition. The sample temperature had obviously not been 800°C in this experiment, because then no β-phase would be obtained at all, but it had been high enough to partially activate the transition.

The thermal treatment at 700°C in an air flow during two hours led to the formation of Y₂O₃. This hydrolysis results in HF gas evolution and leaves Y₂O₃ and NaF behind, cf. equation (4).



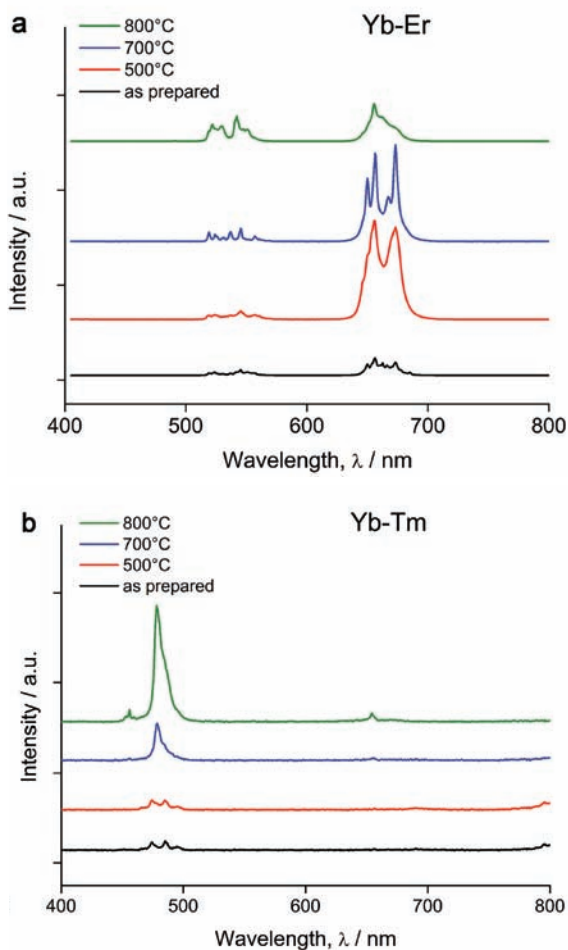


Fig. 5 Upconversion luminescence emission of NaYF₄ with Yb-Er (a) and Yb-Tm (b) rare earth dopant couples. The relative peak intensities increase after sintering from 500°C to 800°C.

In order to transform the cubic phase towards the more favorable hexagonal phase, the powders were sintered in vacuum. The X-ray diffraction patterns of samples treated at 500°C demonstrate the growth of crystals, see **Fig. 4b**, but no formation of hexagonal NaYF₄. Crystallite sizes derived from the Scherrer Equation show a growth from 40 nm to 80 nm. Sobolev et al. (Sobolev et al., 1963) earlier demonstrated that the NaYF₄ hexagonal phase undergoes a phase transition into NaYF₄ with cubic symmetry at 600°C.

Further examinations of the flame-spray synthesis conditions and thermal treatment modes such as cooling rate are required. Flame pyrolysis allows the synthesis of nanocrystalline upconversion phosphors with a high surface area which show luminescence (**Fig. 5b, 6a and b**).

Thermal behavior and luminescence of NaYF₄:Yb, Er

NaYF₄:Yb, Er samples were prepared using a 7/9 (L/min) feeding rate. The particles revealed green and red luminescence on excitation with a 980-nm IR laser. After sintering at 500°C and 700°C, the luminescence intensity increased because the crystallites grew in size. Fast heating, i.e. placing powders into a preheated furnace at 800°C, resulted in rapid formation of hexagonal sodium yttrium fluoride, see **Fig. 4b**. As a result, the green emission intensity increased, see **Fig. 5a**. Phosphors sintered under an inert atmosphere formed oxide phases, which in turn intensified the red emission in the UC luminescence spectrum, see **Fig. 5a**. Yttrium oxide formation in the inert atmosphere is based on phase kinetics and prior built-in oxygen. This embedding happens during flame pyrolysis in an oxygen-containing environment. The formation of micron-size crystallites is observed on the SEM micrographs, see **Fig. 3c**. A slow heating rate of 10°C min⁻¹ yielded a mixture of yttrium oxide and cubic NaYF₄; the fast heating leads to hexagonal NaYF₄ formation.

The luminescence spectra of upconversion phosphors doped with Yb³⁺ and Tm³⁺ show two characteristic visible emissions upon 980-nm excitation, see **Fig. 5b**. The red emission originates from the ¹G₄ → ³F₄ transition. The blue emission consists of the two neighboring transitions of ¹G₄ → ³H₆ and ¹D₂ → ³F₄. Upconversion luminescence spectra also show emissions in the ultraviolet range (¹D₂ → ³H₆ and ¹I₆ → ³F₄). Higher sintering temperatures increase the luminescence intensity because larger crystallites have a smaller surface-to-volume ratio and therefore less defects (Suyver et al., 2006). The Yb³⁺, Er³⁺-doped α-NaYF₄ shows a significantly higher red (⁴F_{9/2} → ⁴I_{15/2}) than green (⁴S_{3/2} → ⁴I_{15/2}) emission, see **Fig. 5a**. However, for the “fast heating” at 800°C sample, the green-to-red emission ratio becomes higher because hexagonal β-NaYF₄ formed which has a significantly stronger green emission. Photographs of the UC emission of the respective samples are shown in **Fig. 6**.

4. Conclusions

Pre-designed complex nanostructures with characteristic properties are built up by assembling their functional units step by step. In this regard, gas-phase methods have a great potential for industrially realizing some of the promises of nanotechnology. Their scaling potential and access to various types of precursors covers a plethora of nanostructures such as metals, oxides, salts, and complex compounds.

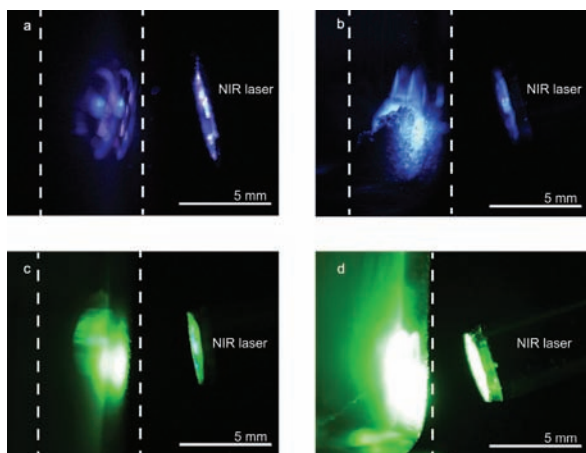


Fig. 6 Photographs of the UC luminescence of Yb^{3+} , Tm^{3+} (a, b) and Yb^{3+} , Er^{3+} (c, d)-doped nanophosphors. The thermal treatment of powders at 800°C significantly increased the intensity of the visible emissions for the Yb^{3+} , Tm^{3+} (b) and the Yb^{3+} , Er^{3+} (d) phosphors.

In the present work, a successful bottom-up access through a refined flame-spray technique provides access to complex non-oxide particles such as rare-earth-doped sodium yttrium fluorides. The co-doping with Yb-Tm and Yb-Er ion couples leads to blue and green upconversion luminescence, respectively. Particles of less than 50 nm in size were obtained under reducing conditions as cubic NaYF_4 . It was possible to tune a cubic to hexagonal phase transition by thermal treatment of the nanomaterial. A strongly enhanced UC luminescence intensity was observed for the β - NaYF_4 . Upconversion luminescence spectra showed a correlation between crystallite size (i.e. low surface area) and luminescence intensity. Oxide impurities reduced the green and increased the red UC emissions in Yb^{3+} , Er^{3+} -doped phosphors.

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Wendelin J. Stark received his master's degree in chemistry in 2000, followed by a PhD in mechanical engineering in 2002, both from ETH Zurich. In 2004, he founded the Functional Materials Laboratory within the Departments of Chemistry and Applied Bioscience at the ETH Zurich. His research group pursues application-oriented research at the interface of chemistry with materials science and medicine.