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Ionic Liquid Based Approach to Luminescent $LaPO_4$:Ce,Tb Nanocrystals: Synthesis, Characterization and Application

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$LaPO_4$:Ce,Tb as a nanoscale phosphor is prepared via a microwave-accelerated synthesis in ionic liquids. The underlying approach results in non-agglomerated nanocrystals, 9–12 nm in size, and exhibiting quantum yields of 70 % (Tb-related emission) and 90 % (Ce/Tb-related emission). Based on the underlying concept of synthesis, application-oriented aspects are focused. Driven by the addition of oleylamine, first, phase transfer from the polar phase of synthesis to non-polar alkanes can be initiated. As a second aspect, dispersions of the title compound in ethanol are applied for ink-jet printing of transparent luminescent layers on polymer substrates. Finally, ethanolic dispersions of $LaPO_4$:Ce,Tb are used to realize a fully transparent dielectric barrier discharge (DBD) lamp as a prototype of a "luminescent window".

Introduction

$LaPO_4$:Ce,Tb, in general, is known as a highly relevant luminescent material, especially for application in fluorescent lamps.[1] The title compound comprises characteristic and efficient green emission of Tb^{3+}, which is most often initiated by UV excitation. On the nanoscale, $LaPO_4$:Ce,Tb is also intensely discussed aiming at novel types of application. This includes transparent fillers or markers (e.g. in/on glass, plastics, paper) as well as bio-medical purposes (e.g. bio-labeling, bio-assays, optical imaging).[1,2] Aiming at emission of green light, $LaPO_4$:Ce,Tb may also be an alternative to well-known semiconductor-type quantum dots.[3]

With concern to transparent luminescent layers and matrices, in addition to the initial particle size, stability of dispersion, degree of agglomeration and surface conditioning are also of major importance. Especially, particle agglomeration has to be excluded securely. Otherwise, even a very low number of aggregates would – in accordance with the Mie theory – cause significant scattering effects.[4] Moreover, highly crystalline, and thereby highly efficient nanophosphors are requested to ensure an intense emission of thin layers.[5] A thermal post-treatment of as-prepared nanopowders in order to remove all hydroxide contents and to boost crystallization, in general, would not be sufficient here due to extensive aggregate formation. In fact, the synthesis of $LaPO_4$:Ce,Tb applying surface-active solvents or stabilizers has been widely applied.[6] When also introducing $LaPO_4$@$LaPO_4$:Ce,Tb core-shell structures, quantum yields of 70% (Tb^{3+} emission) and 80% (Ce^{3+}/Tb^{3+} emission) have been gained.[7] However, the removal of surface-active solvents/stabilizers subsequent to synthesis as well as the application of advanced core-shell structures lead to a process that becomes more and more complicated, time-consuming, and expensive.

This investigation addresses an alternative synthetic approach to luminescent $LaPO_4$:Ce,Tb nanocrystals and has already turned out to be successful.[8] Namely, the use of ionic liquids as a solvent in liquid-phase synthesis is studied. Based on the novel strategy of synthesis as a starting point, here, the bow is bent to aspects of potential application, including ink-jet printing of transparent luminescent layers and manufacturing of a fully transparent dielectric barrier discharge (DBD) lamp.

Results and Discussion

In recent years, ionic liquids (ILs) have attracted considerable interest due to their exceptional features, including a wide liquid range, an excellent thermal stability, a wide electrochemical window, and a low vapor pressure.[9] For the preparation of high-quality $LaPO_4$:Ce,Tb nanocrystals these special features turned out to be very advantageous. First, the excellent thermal stability allows a liquid-phase synthesis at comparably high temperatures (250–350 °C). This results in highly crystalline nanoparticles with a low defect concentration, and therefore high quantum yields.[8] Driven by the polar but aprotic features of ILs, second a removal of all hydroxy contents and moisture is possible by evaporation at elevated temperatures. This effect favors

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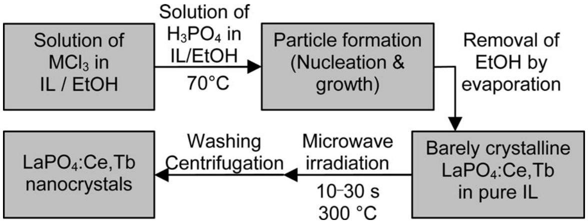
crystallization even further and eliminates OH-allocated quenching of luminescence. Due to the "non"-coordinating properties of ILs, finally, their removal after the synthesis is easy in comparison with many coordinating solvents (e.g. long-chained carbonic acids, alcohols, amines or phosphanes), which are widely applied.[6]

The "non"-coordinating properties of ILs, however, can also be regarded as a drawback since the colloidal stabilization of nanoparticles at the elevated temperature of synthesis is limited. To avoid extensive aggregate formation, fast and short-timed heating is prerequisite. To this concern, microwave-accelerated heating is performed at 300 °C; this temperature is reached within 10 s. In summary, microwave-accelerated synthesis of $LaPO_4$:Ce,Tb in ILs is carried out according to Scheme 1. Particle formation for optimal conditions of nucleation and growth is performed at 70 °C in a mixture of $N(CH_3)(n\text{-}C_4H_9)_3][N(SO_2CF_3)_2])$ as the IL and ethanol as a cosolvent. The role of the cosolvent, on the one hand is to reduce the viscosity of the IL for practical handling, and on the other hand is to increase the solubility of the starting materials, such as MCl_3 (M = La, Ce, Tb). Subsequent to particle formation and evaporation of the cosolvent, barely crystalline $LaPO_4$:Ce,Tb is obtained. To boost crystallization, microwave-accelerated heating in the pure ionic liquid is performed next.



Scheme 1. Course of reaction with concern to the microwave-accelerated synthesis of nanocrystalline $LaPO_4$:Ce,Tb in ionic liquids (M: La, Ce, Tb; IL: $[N(t\mathrm{Bu})_3(\mathrm{Me})][N(SO_2CF_3)_2]$).

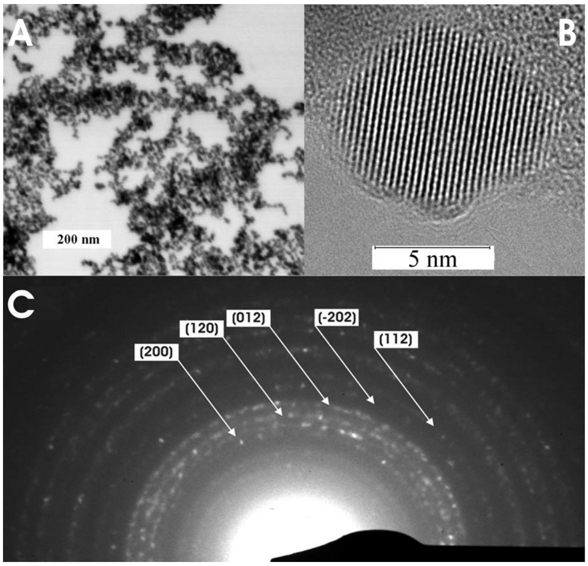


Figure 1. TEM/SEM images of as-prepared $LaPO_4$:Ce,Tb: A) STEM micrograph indicating the uniformity of particles; B) HRTEM micrograph showing lattice fringes; C) Electron diffraction pattern of a bundle of particles including Miller indices.

Electron microscopy evidences the presence of very uniform and non-agglomerated particles with spherical to slightly ellipsoidal shape (Figure 1). Statistical evaluation of about 100 particles results in an average diameter of 11 nm. According to HRTEM micrographs, $LaPO_4$:Ce,Tb nanoparticles turn out to be single-crystalline and exhibit well-ordered lattice fringes, even at the surface of the particles. The observed lattice spacing confirms the monoclinic monazite type of structure.[10]

As-prepared nanocrystalline $LaPO_4$:Ce,Tb (45 mol-%, 15 mol-%) can easily be redispersed in alcohols such as methanol, ethanol or diethylene glycol. The resulting suspensions turned out to be colloidally stable within weeks. Such a dispersion in ethanol is shown in part A of Figure 2. Intense green emission is observed when exciting with UV light (254 nm). This holds even for dispersions in protic solvents, which normally quench luminescence to some extent.[11] Luminescence is quantified by recording excitation and emission spectra (Figure 2, B). Herein, intense and broad $4f^05d^1 \rightarrow 4f^1$ absorption (240–320 nm) and the pertinent emission (320–380 nm) of Ce^{3+} are visible. Followed by efficient energy transfer from Ce^{3+} to Tb^{3+}, $^5D_4 \rightarrow {}^7F_J$ relaxation accompanied by intense and characteristic emission of green light occurs.[12] Previous investigations show the quantum yield of $LaPO_4$:Ce,Tb to be 70% considering Tb^{3+}-related green emission, and 90% when considering a certain Ce^{3+}-related UV emission, too.[8] These values are even more surprising since neither strongly coordinating solvents or stabilizers nor advanced core-shell structures are applied to protect the surfaces of the nanoparticles.[7]

Previous studies have already shown the IL constituents to be adhered on the surface of the nanocrystals via charge interaction. Due to the "non"-coordinating properties of the IL, its constituents can be removed completely just by washing with ethanol that is saturated with NaCl.[8] Considering this finding, other types of specific surface modification should also be possible. To this concern, phase transfer of elemental metals driven by amines such as oleylamine or 4-(dimethylamino)pyridine (DMAP) is well known.[13] It turned out that such a phase transfer works also very well in case of as-prepared $LaPO_4$:Ce,Tb. After addition of oleylamine, by stirring the nanocrystals can be transferred from a polar, hydrophilic phase (e.g. methanol, ethanol, diethylene glycol) to a non-polar, hydrophobic dispersant (e.g. hexane, toluene) (Figure 3). Such a phase transfer for application-oriented issues is important in order to embed or to attach luminescent nanocrystals in or on non-polar substrates (e.g. plastics).

Nanoscale luminescent materials are in great demand as embeddings in transparent matrices (e.g. glass, plastics) or as transparent luminescent layers (e.g. on glass, plastics, metal, paper) for labeling, signaling and design purposes.[14] In this context, ink-jet printing of dispersions containing as-prepared $LaPO_4$:Ce,Tb on standard overhead trans-

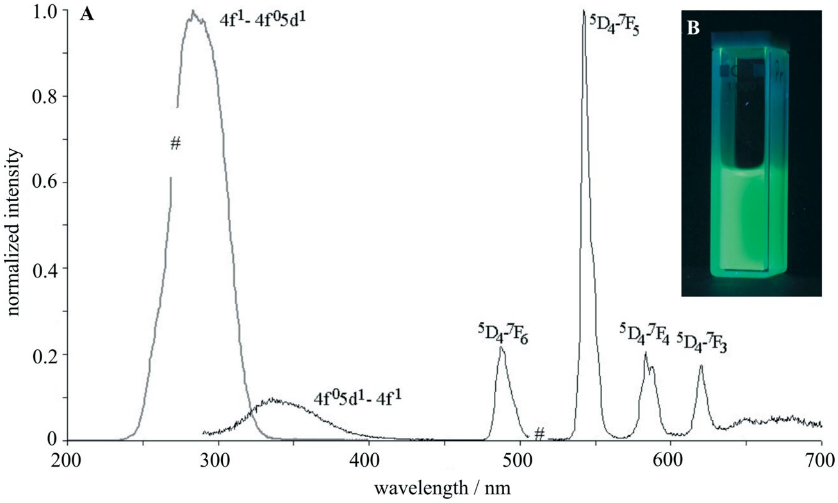


Figure 2. Emission ($\lambda_{emission}$ = 543 nm) and excitation ($\lambda_{excitation}$ = 254 nm) spectra of $LaPO_4$:Ce,Tb (A) as well as transparent dispersion thereof in ethanol under UV excitation (B).

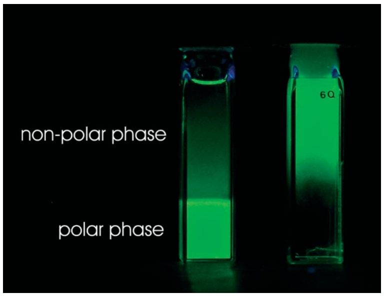


Figure 3. Oleylamine-driven phase transfer of nanocrystalline $LaPO_4$:Ce,Tb from the polar phase (A, e.g. methanol, ethanol, diethylene glycol) to a nonpolar dispersant (B, e.g. hexane, toluene).

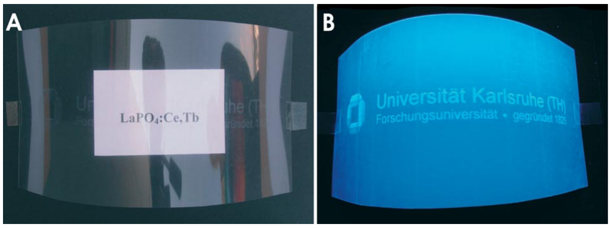


Figure 4. Picture with ink-jet printed $LaPO_4$:Ce,Tb on overhead transparency: in daylight (A) and under UV excitation (B, $\lambda_{excitation}$ = 254 nm).

parencies was studied (Figure 4). Due to the ink-jet equipment applied, dispersions in ethanol were limited to solid contents of 2 wt.-% in order to avoid nozzle clogging. Printing was repeated for several times until sufficient layer thickness (about 30 nm) was achieved. Black letters on paper, which are positioned behind the overhead transparency, qualitatively confirm its transmittance to be almost unaffected after printing. The printed structure is only barely visible in daylight (Figure 4, A), but can clearly be recognized with UV light excitation (Figure 4, B). Due to optical bleachers in commercial overhead transparencies, blue emission is observed in addition. Additive color mixing altogether results in a greenish white appearance of the printed structure. Aspects such as viscosity, solids content and composition of the ink, adhesion, haze and definition of the layer as well as the printing equipment itself have not been optimized so far. Consequently, a substantial increase in layer quality can be expected by application of optimized professional printing procedures.

As a second example of potential technical application, a fully transparent dielectric barrier discharge (DBD) lamp is aimed. DBD lamps, in general, are relevant for general lighting as an alternative to standard fluorescent lamps (FL). This is especially for environmental issues, namely to substitute the mercury discharge used in FL lamps by a xenon discharge.[15] Driven by a pulsed voltage, the latter is applied in DBD lamps and leads to an Xe-excimer emission, exhibiting its highest intensity at 173 nm. This vacuum ultraviolet (VUV) emission is converted into visible light by a phosphor layer, which is located on the inside of the glass bulb. Figure 4 (A) schematically shows the construction of

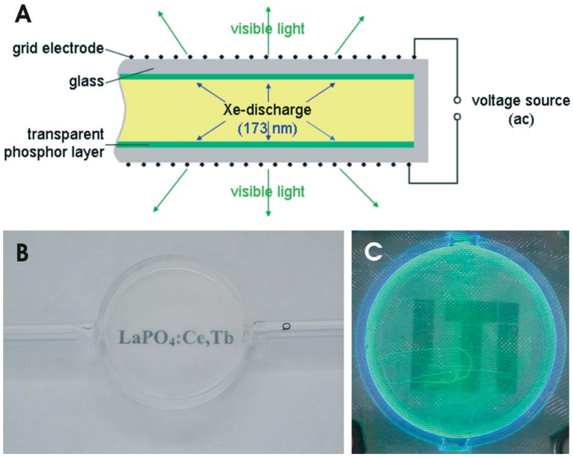


Figure 5. Scheme (A) and photos of dielectric barrier discharge (DBD) lamp subsequent to $LaPO_4$:Ce,Tb layer deposition (B) and under conditions of Xe discharge (C).

such a DBD lamp. As a state-of-the-art, the phosphor layer consists of micron-sized phosphor particles (5 to 8 µm in diameter). Due to the scattering of this layer the lamp for physical reasons cannot be transparent. While introducing nanoscale $LaPO_4$:Ce,Tb as a phosphor layer, however, all scattering in the visible can be excluded (Figure 5, B). Subsequent to evacuation, careful removal of all moisture, filling with xenon and connecting to two grid electrodes, the Xe discharge can be turned on. Indeed, green emission of $LaPO_4$:Ce,Tb is observed (Figure 5, C). With this prototype a first fully transparent DBD lamp containing nanoscale luminescent materials is shown.[16] In principle, such a device can be interesting as a kind of a "luminescent window", which has to be transparent throughout the day, but which can be illuminated during the night by means of labelling, signalling or advertising. Subsequent to optimizing, for instance, the thickness of the phosphor layer and after exchanging the metal grid by ITO (indium tin oxide) electrodes, also extended transparent flat light sources might be within reach.

Conclusions

$LaPO_4$:Ce,Tb is successfully realized via microwave-accelerated synthesis in ionic liquids as a novel experimental approach. The particles turned out to be non-agglomerated and very uniform in size and shape. Due to the excellent crystallinity of the particles, very high quantum yields are achieved. The quality of $LaPO_4$:Ce,Tb altogether confirms a substantial advantage of ILs concerning to chemical synthesis and materials science. To this end, the high boiling point and the polar, but aprotic properties can be denoted to be advantageous features of the IL. According to its "non"-coordinating properties, furthermore, phase transfer of $LaPO_4$:Ce,Tb from polar to non-polar dispersants is easy to perform. Due to microwave irradiation, heating is extremely fast (10–30 s at 300 °C), resulting in an almost instantaneous crystallization of particles. As a proof of concept, application of $LaPO_4$:Ce,Tb as a transparent luminescent layer on plastics as well as a fully transparent DBD lamp is evaluated.

Experimental Section

General: Scanning electron microscopy (SEM) was carried out with a Zeiss Supra® 40VP: The nanocrystals were deposited on silicon wafers and sputtered with platinum. Characterization was carried out at room temperature at an acceleration voltage of 10 kV and a working distance of 3 mm. Transmission Electron Microscopy (TEM) and electron diffraction were performed on a Philips CM200 FEG/ST operating at 200 kV. Samples were prepared by ultrasonic nebulization of ethanolic dispersions on a Lacey film copper grid. Photo luminescence (PL) was recorded with a Jobin Yvon Spex Fluorlog 3 equipped with a 450 nm Xe-lamp and double grating excitation and emission monochromator. $LaPO_4$:Ce,Tb dispersions in ethanol were measured in standard quartz cuvettes at ambient temperature. The synthesis of $LaPO_4$:Ce,Tb (45 mol-%, 15 mol-%) nanocrystals via a microwave-accelerated approach in ionic liquids has been described in detail elsewhere.[8] Subsequent to synthesis, dispersions of $LaPO_4$:Ce,Tb in $[MeBu_3N][(SO_2CF_3)_2N]$ as the ionic liquid were diluted with ethanol and placed in an ultrasound bath. The nanocrystals were collected by centrifugation. Thereafter, the nanocrystals were washed thrice by redispersion in ethanol and repeated centrifugation. Finally, the resulting colorless powder could be redispersed in methanol, ethanol, diethylene glycol or mixtures thereof.

Phase Transfer: For phase transfer $LaPO_4$:Ce,Tb dispersed in ethanol (10 mL, 2 wt.-%) was mixed with 0.5 mL of oleylamine and covered with 10 mL of hexane. After 30 min of stirring, $LaPO_4$:Ce,Tb was extracted from the hydrophilic to the hydrophobic phase. The process was followed qualitatively by $LaPO_4$:Ce,Tb-related light emission.

Inkjet Printing: For printing, as-prepared $LaPO_4$:Ce,Tb nanocrystals were redispersed in ethanol/methanol mixtures (50:50) with a solid content of 2.0 wt.-%. Layer formation was performed with a standard ink-jet printer (Lexmark® Z735, HP Deskjet® 540). In order to gain a sufficient layer thickness, printing was repeated 10 times as a layer-by-layer process. The layer thickness was estimated to 30 nm based on tilted samples in the electron microscope. Since the printing equipment is made for liquids, not dispersions, the quality of layers is limited due to nozzle clogging. Moreover, solids content, viscosity and evaporation of the dispersion have not been optimized sufficiently yet.

Dielectric Barrier Discharge (DBD) Lamp Preparation: A homemade quartz bulb (40 mm in diameter, 5 nm in thickness) was used to establish a prototype DBD lamp. via two glass tubes positioned on opposite sides of the bulb, first, layer formation of $LaPO_4$:Ce,Tb was performed via repeated solvent evaporation of dispersions in ethanol. Subsequent to drying (80 °C, 5 h), evacuation, removal of traces of moisture by driving a plasma and flushing the glass bulb with pure xenon (200 mbar), the lamp was closed by two valves. After being positioned between two metal grid electrodes, an Xe excimer discharge was established, which was driven by an unipolar pulsed voltage (3 kV peak, 40 kHz).

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