Research Article

Upconversion Properties of Nanocrystalline ZrO$_2$:Yb$^{3+}$, Er$^{3+}$ Phosphors

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Received 30 October 2007; Accepted 26 November 2007

Recommended by Wiesław Stręk

Combustion and sol-gel methods were used to prepare the upconverting nanocrystalline ZrO$_2$:Yb$^{3+}$,Er$^{3+}$ phosphors. The crystal structure was studied by X-ray powder diffraction and the crystallite sizes were estimated with the Scherrer formula. Impurities and nanomaterials’ thermal degradation were analyzed with FT-IR spectroscopy and thermal analysis, respectively. Upconversion luminescence and luminescence decays were studied with IR-laser excitation at 977 nm. All nanomaterials possessed the cubic ZrO$_2$ fluorite-type structure except for a small monoclinic impurity obtained with the sol-gel method. The conventional NO$_3^-$ and OH$^-$ impurities were observed for the combustion synthesis products. The ZrO$_2$:Yb$_{5}$,Er$^{3+}$ nanomaterials showed red (630–710 nm) and green (510–570 nm) upconversion luminescence due to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ and ($^2H_{11/2}, ^4S_{3/2}$) $\rightarrow ^4I_{15/2}$ transitions of Er$^{3+}$, respectively. The products of the combustion synthesis exhibited the most intense luminescence intensity and showed considerable afterglow. It was concluded that excitation energy is partially trapped in the system and subsequently bleached thermally to the luminescent Er$^{3+}$ center to yield “persistent upconversion”.

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1. INTRODUCTION

One of the most sophisticated and, at the same time, the most complex applications of lanthanide luminescence is in the medical diagnostics [1]. However, there are some major problems in the use of photoluminescence based on the UV excitation in immunoassays [2]. Human blood absorbs strongly UV radiation as well as the emission of the phosphor in the visible [3]. The observation of luminescence from the lanthanide labels is thus basically disadvantageous. One of the usual ways of overcoming this problem has been the application of long-lifetime lanthanide labels (e.g., those based on terbium and europium). However, the use of these Tb$^{3+}$- or Eu$^{3+}$-based lanthanide labels in the whole-blood immunoassays is still difficult because the Tb$^{3+}$ luminescence (maximum emission at 545 nm) is in the same wavelength region as the blood absorption (<600 nm). The Eu$^{3+}$ luminescence (maximum at 615–620 nm) is also slightly overlapping with the blood absorption. Persistent luminescence is a useful method to solve the blood emission problem if the UV excitation is used [4]. Persistent luminescence can be visible for several hours after the excitation has been ceased while the luminescence lifetime of the blood is in the ns range. Although most persistent luminescence materials emit in green or blue strongly absorbed by blood, some persistent luminescence emitters in the red are known (e.g., Mn$^{2+}$) [5, 6]. However, the Mn$^{2+}$ ion needs a sensitizer (usually Eu$^{2+}$) which absorbs the exciting radiation. The upconversion luminescence where the absorption of two or more low-energy photons is followed by the emission of a photon of higher energy has witnessed numerous breakthroughs during the past decades. Upconverting phosphors have a variety of potential applications as lasers, displays, and inks for security printing (e.g., bank notes and bonds) [7–9]. In addition, another promising way to overcome the problems with the blood absorption is to use a long-wavelength excitation and benefit the upconversion luminescence [10]. There is practically no absorption by the whole-blood in the near IR region and it has no capability for upconversion in the excitation wavelength region of the conventional upconverting phosphor based on the Yb$^{3+}$ (sensitizer) and Er$^{3+}$ (activator) combination. It is also possible to find a red emitting ion (Er$^{3+}$).

For coupling to biological compounds, nanometer-sized upconverting phosphor particles are required. Moreover,
nanophosphors with high luminescent efficiency are vital in the development of novel homogeneous label technology for quantitative all-in-one whole-blood immunoassay which uses low-cost measurement devices [11].

In this work, nanocrystalline upconverting phosphors with zirconium oxide (zirconia, ZrO2) as the host lattice were prepared. The local environment, the dopant concentration, and the distribution of active ions in the host material affect the upconversion efficiency [12, 13]. Taking into account these requirements (among others), zirconia offers a very appropriate medium for the preparation of highly luminescent materials because it is chemically and photochemically stable, and has a high refractive index (2.15–2.18) and a low phonon energy. The stretching frequency of the Zr–O-bond is about 470 cm\(^{-1}\), which is much lower than for Al–O (870 cm\(^{-1}\)) or Si–O (1100 cm\(^{-1}\)) but higher than for Y–O (300–380 cm\(^{-1}\)) [12].

In the zirconia host, the lanthanide dopants possess multisite positions that improve the absorption efficiency and potentially enhance the resonant energy transfer from the sensitizer (Yb\(^{3+}\)) to the activator (Er\(^{3+}\)). The ZrO\(_2\):Yb\(^{3+}\),Er\(^{3+}\) nanophosphors were obtained with several soft chemistry methods and the possible impurities were studied mainly with FT-IR spectroscopy. Materials’ preparation and thermal degradation were studied with thermal analysis (TG, DTA). Crystal structures and phase purities were analyzed with X-ray powder diffraction (XPD). Upconversion luminescence and decays were obtained at room temperature with NIR excitation. A comparison was made between the luminescence intensities and the crystallite size, the crystal structure, as well as the impurities of the phosphors. Finally, a new phenomenon, persistent upconversion luminescence was introduced and discussed.

2. EXPERIMENTAL

The ZrO\(_2\):Yb\(^{3+}\),Er\(^{3+}\) nanomaterials were prepared with the combustion [14] and sol-gel methods [15]. The synthesis affects the type and amount of impurities as well as the crystallite size, which in turn has a profound influence on the upconversion luminescence intensity. Accordingly, the method of preparation should be chosen carefully taking into account both the crystallite size as well as the intensity and color of luminescence of the nanomaterial. This may lead to quite difficult tradeoffs.

The precursor materials of ZrO\(_2\):Yb\(^{3+}\),Er\(^{3+}\) prepared with the combustion synthesis were the aqueous solutions of zirconyl nitrate (ZrO(NO\(_3\))\(_2\)) as well as ytterbium and erbium nitrates (Yb(NO\(_3\))\(_3\) and Er(NO\(_3\))\(_3\), resp.). The nominal concentrations of Yb\(^{3+}\) (99.9%) and Er\(^{3+}\) (99.99%) were ten and four mole-%, respectively, of the Zr\(^{IV}\) amount. Glycine (NH\(_2\)CH\(_2\)COOH), semicarbazide (H\(_2\)NCONHNH\(_2\)·HCl), urea ((NH\(_2\))\(_2\)CO), citric acid (HO(COOH)(CH\(_2\)COOH)), or 2-amino-2-methyl-1,3-propanediol (AMP, (HOCH\(_2\))\(_2\)C(NH\(_2\))CH\(_3\)) served as the fuel. Additional ammonium nitrate (NH\(_4\)NO\(_3\)) was used as an oxidizer with selected fuels. The combustion reaction was carried out in a glass reactor using a weak upward air flow. Some of the products were postannealed in air at 700°C for 1 hour if the material’s crystallinity was poor.

The ZrO\(_2\):Yb\(^{3+}\),Er\(^{3+}\) nanomaterials obtained with the sol-gel method had the zirconium-n-propoxide as a precursor to which the aqueous ytterbium and erbium nitrate solutions were added. After gelation, the materials were dried and annealed for 3 or 6 hours at 400°C and for 10 or 20 hours at 1000°C in static air in a ceramic crucible with a lid.

The FT-IR spectra between 400 and 4000 cm\(^{-1}\) were measured with a Mattson Instruments GALAXY 6030 spectrometer with a 4 cm\(^{-1}\) resolution. The materials were mixed with KBr and then pressed to transparent discs.

The TG and DTA curves between 25 and 1200°C were measured in flowing air (100 cm\(^3\) min\(^{-1}\)) with a TA instruments SDT 2960 Simultaneous DTA-TGA thermoanalyzer with a heating rate of 5°C min\(^{-1}\). α-Al\(_2\)O\(_3\) was used as both the reference and crucible material.

The crystal structure and phase purity of the ZrO\(_2\):Yb\(^{3+}\),Er\(^{3+}\) nanomaterials were analyzed with the X-ray powder diffraction (XPD) measurements. The patterns were collected with a Huber 670 image plate (2θ range: 4–100°) Guinier-camera (CuK\(_{\alpha1}\) radiation: 1.5406 Å).

The crystallite size of each ZrO\(_2\):Yb\(^{3+}\),Er\(^{3+}\) nanomaterial was estimated from the diffraction data by using the Scherrer formula [16]

\[
d = \frac{0.9 \times \lambda}{\beta \times \cos \theta}
\]

where, in this formula, \(d\) (m) is the mean crystallite size, \(\lambda\) (m) the X-ray wavelength, \(\beta\) (rad) the full width at half maximum (FWHM) of the [111] reflection (2\(\theta\) = 30.2°), and \(\theta\) (°) half of the Bragg’s angle (2\(\theta\)).

The reflection broadening due to the diffractometer setup was eliminated from the \(\beta\) value by using a microcrystalline ZrO\(_2\) reference (\(\beta_{zr}\)):

\[
\beta^2 = \beta_r^2 - \beta_s^2.
\]

The upconversion luminescence spectra of the nanomaterials were measured at room temperature with an Ocean Optics PC2000-CCD spectrometer. The excitation (\(\lambda_{exc}\) = 977 nm) source was an HTOE FLMM-0980-711-1300m IR laser diode. The decay curves were measured with the same excitation source at 650 nm. The width of the excitation pulse was 1 millisecond. After each pulse there was a 9-millisecond delay before the next pulse. One measurement consisted of 1000 pulse-delay cycles.

3. RESULTS AND DISCUSSION

3.1. Material impurities

The FT-IR spectra of the ZrO\(_2\):Yb\(^{3+}\),Er\(^{3+}\) nanomaterials revealed the presence of the conventional impurities (NO\(_3\), OH\(^-\)) in the materials prepared by the combustion synthesis (see Figure 1). The amount of these impurities depended on the fuel used; the highest amount of impurities was observed when urea was used as a fuel. The organic compounds (fuels) were mainly decomposed to CO\(_2\), H\(_2\)O, and NO\(_3\), but it is possible that the nanomaterials contain also some carbon residue since the ZrO\(_2\) nanomaterials prepared with the
The TG curve of the ZrO₂:Yb³⁺,Er³⁺ nanomaterial, prepared with the combustion synthesis, showed a practically constant weight. No signals were observed below 200°C. With glycine used as the fuel, a further mass change was observed between 500 and 650°C. This change is due to the decomposition of zirconium oxycarbonates/oxynitrates which are surprisingly stable to high temperatures as are the corresponding rare earth oxycarbonates/oxynitrates [17, 18]. The exothermic signal in the DTA curve around 700°C can be related to the appearance of a crystalline phase of ZrO₂:Yb³⁺,Er³⁺ as indicated by the XPD patterns. The gradual weight loss at higher temperatures can be taken as an indication of evaporation of tightly bound species, for example, OH⁻ groups (as water). The presence of these impurities may have a nefarious effect on the luminescence performance of these nanomaterials.

The TG curve of the material prepared with the sol-gel method showed a practically constant weight. No signals were observed in the DTA curve either.

### 3.3. Crystal structure and crystallite sizes

The XPD measurements revealed that the structure of the ZrO₂:Yb³⁺,Er³⁺ nanomaterials was that of the typical cubic yttria stabilized zirconia (the cubic YSZ phase: space group Fm 3 m, no. 225, Z = 4) [19]. The nanomaterials, prepared with the combustion synthesis (see Figure 3), were essentially pure, whereas small amounts of the monoclinic zirconia phase (P2₁/a, no. 14, Z = 4) [19] as an impurity was found in the materials prepared with the sol-gel method (see Figure 4). The presence of the monoclinic phase is probably due to the partial segregation of ZrO₂:Yb³⁺,Er³⁺ to the individual ZrO₂ and (Yb,Er)₂O₃ phases since very weak reflections belonging to R₂O₃ were noticed in the XPD patterns. The crystallite sizes estimated with the Scherrer equation [16] were 5–30 and ca. 50 nm for materials prepared with the combustion synthesis and the sol-gel method, respectively.

### 3.4. Upconversion luminescence

The excitation process for the upconversion emission of Er³⁺ ions (see Figure 5) under infrared excitation (λ_exc = 977 nm)
has been well established in the literature, for example, [20–22]. Though this mechanism is well known, in view of the phenomenon described later on, it is presented here as well. The first photon of near-infrared (NIR) radiation excites the Yb\(^{3+}\) ion to the sole excited \(^{2}F_{9/2}\) level from which the excitation may relax radiatively back to the ground \(^{2}F_{7/2}\) level. Taken into account the long radiative life time of the excited \(^{2}F_{9/2}\) level (typically 1 millisecond), the Yb\(^{3+}\) ion may transfer the excitation energy to an Er\(^{3+}\) ion with higher probability than decaying radiatively. The Er\(^{3+}\) ion is first promoted to the \(^{4}I_{11/2}\) level, and further to \(^{4}F_{7/2}\) due to absorption and energy transfer of another NIR photon. Then Er\(^{3+}\) decays rapidly and nonradiatively to the \(^{2}H_{11/2}\), \(^{4}S_{3/2}\) or \(^{4}F_{5/2}\) (or lower) levels. The upconversion emission is customarily assigned to the following transitions: green emission in the 510–570 nm region to the \(^{2}H_{11/2} \rightarrow ^{4}I_{15/2}\) transitions; and red emission in the 630–710 nm region to the \(^{4}F_{9/2} \rightarrow ^{4}I_{15/2}\) transitions of the Er\(^{3+}\) ion. It should be noted that other pathways (including the initial ground-state absorption (GSA) and further excited-state absorption (ESA)) may be possible involving the Er\(^{3+}\) ions only, though their probabilities are low, partly due to the low Er\(^{3+}\) concentration.

In the ZrO\(_2\) matrix, the luminescence transitions are rather broad and without evident crystal field fine structure. This observation is in agreement with the multisite positions occupied by the trivalent Yb\(^{3+}\) and Er\(^{3+}\) ions. This is due to the lack of any trivalent ion site in the ZrO\(_2\) structure and the creation of oxide vacancies (Kröger-Vink notation: \(V_{O}^{\prime}\)) results from the Yb\(^{3+}\) and Er\(^{3+}\) ions occupying the tetravalent Zr\(^{IV}\) site (Yb\(_{Zr}\) or Er\(_{Zr}\)) in the cubic fluorite type structure. At least three different sites with different point symmetries due to the different position of the oxide vacancies around the R\(^{3+}\) ion have been found for the ZrO\(_2\):Yb\(^{3+}\), Eu\(^{3+}\) system with the use of optical site selective excitation techniques [23] and EXAFS measurements [24]. Moreover, the inhomogeneous broadening of the Eu\(^{3+}\) emission lines was taken as an indication of a relaxation of the oxide sublattice towards the oxide vacancies creating a number of sites with rather similar point symmetries. There is no doubt that similar charge compensation schemes are present in the ZrO\(_2\):Yb\(^{3+}\), Er\(^{3+}\) nanomaterials because of the similar size of the Yb\(^{3+}\) and Y\(^{3+}\) dopants when compared to Zr\(^{IV}\).

The highest luminescence intensity was obtained from the ZrO\(_2\):Yb\(^{3+}\), Er\(^{3+}\) nanomaterials obtained with the combustion synthesis with semicarbazide used as the fuel (see Figure 6). This is due to the structurally pure (cubic) material, whereas the material prepared with the sol-gel method was a mixture of both the cubic and monoclinic forms. The difference between the luminescence intensities might also be due to the different surrounding microdomains of the Yb\(^{3+}\) and Er\(^{3+}\) ions, and due to other impurities.

The heating of the nanomaterial prepared with the combustion synthesis at 1100°C for 2 hours did not increase
were also quite equal.

of the equal crystallite sizes, the luminescence intensities of
the crystallite size. This might be due to a too low
heating temperature and/or too short heating time. Because
of the equal crystallite sizes, the luminescence intensities
of the both materials prepared with the combustion synthesis
were also quite equal.

The ZrO2:Yb3+,Er3+ nanomaterials exhibit a very high
Ired/Igreen ratio (note the logarithmic y-scale in Figure 7)
compared to other host materials (e.g., NaYF4) [25]. This
is due to the very low intensity of the green luminescence.
In the ZrO2 host, there are three main reasons for the weak
green luminescence: the multiphonon relaxation, the cross-
relaxation, and trapping of excitation energy by lattice de-
fecrs. The prerequisites for efficient multiphonon relaxation
are an energy level close below the luminescent level and/or
high-energy phonon(s). The energy difference between the
4S3/2 (2H11/2) levels yielding the green luminescence and the
next lower level (4F9/2) is ca. 3000 cm⁻¹ (ca. 3700). The Zr–O
phonon energy is 470 cm⁻¹ [12] and the Er–O energy is
approximately the same. In pure materials, the multiphonon
relaxation process is not probable because too many (six or
seven) lattice phonons are needed to quench the green luminescence. However, when the crystallite size is smaller, there
exist impurities (e.g., NO3, OH⁻) on the large surface area
to facilitate the quenching. The surface itself may act as a
quenching center too. The probability of the multiphonon
relaxation is increased because the impurities have higher
phonon energies (up to 1500 and 3500 cm⁻¹ for NO3 and
OH⁻) and thus less phonons (one or two) are needed for
quenching. Finally, the multiphonon relaxation of the green
luminescence enhances the intensity of the red luminescence
by populating the 4F9/2 level.

The energy difference between the 4F9/2 level yielding
the red luminescent and the next lower 4I9/2 level is also ca.
3000 cm⁻¹. The probability for the multiphonon relaxation of
the red luminescence should be comparable to that of the
green one. However, the red emission is much stronger and
thus the multiphonon relaxation seems to be inefficient in
this case. Finally, it should be noted that both the green and
red luminescence of the ZrO2:Yb3+,Er3+ nanomaterials are
rather weak when compared to other host lattices studied
(e.g., NaYF4 and Y2O2S) [25]. The multiphonon relaxation
processes can thus explain the weakness of the total but not
the individual green luminescence alone.

The second process that may affect the luminescence
intensities is cross-relaxation. There may be three possible
cross-relaxation processes resulting in the quenching of the
green luminescence. First of all, the quenching of the green
emission from 4S3/2 proceeds via the thermally activated
3H11/2 level. The first process involves the 3H11/2→4I15/2
relaxation and the 4I9/2→4I15/2 excitation; the energy be-
coming ca. 12500 cm⁻¹. In the second possible cross-relaxation
process, there are coupled the 2H11/2→4I9/2 relaxation and the
4I13/2→4I15/2 excitation [13]. The energy difference
related to these processes is ca. 6700 cm⁻¹. It has been claimed
that the two cross-relaxation mechanisms are experimentally
indistinguishable [26]. The two cross-relaxation processes
are competing with the green luminescence, with the mul-
tiphonon relaxation, with each other, and also with the trap-
ing of energy. There are no known cross-relaxation pro-
cesses for the red luminescence of Er3+ because of the lack
of appropriate energy levels.

The third cross-relaxation process involves the higher ex-
cited 4F9/2 level of Er3+ which relaxes to the red emitting
4F9/2 level bypassing the green emitting levels [27]. The energy
balance (ca. 5000 cm⁻¹) is conserved by the excitation of Er3+ to
the 4F9/2 level from the 4I11/2 level which is populated due to
the NIR laser pumping. Indeed, this process would favor the
red emission.

The cross-relaxation processes of Er3+ is naturally fa-
vored by the rather high erbium concentration in the
ZrO2:Yb3+,Er3+ nanomaterials (nominal four mole-%) be-
cause then the erbium ions can locate near each other.
As a special feature in the zirconia host, the Er3+ ions can
form pairs with the aid of the oxide vacancy, that is,
Er3+−V0••−Er3+ (cf. above). In addition to the intratia cross-
relaxation processes, the interior ions can thus occur more
easily between the Er3+ ions and decrease the intensity of the
green luminescence.

The very weak green luminescence can thus be explained
with both the multiphonon and the cross-relaxation pro-
cesses but the strong red luminescence only with one of the
cross-relaxation processes. However, in order to judge the
relative probabilities of these processes, much more detailed
spectroscopic work is needed. At the moment, this is out of
the scope of the present work.

The energy trapping caused by the oxygen vacancies (cf.
the discussion about the color centers above and Section 3.5)
is also a competing process with the multiphonon and cross-
relaxation processes. The total luminescence intensity can be
quenched due to the absorption of the excitation energy but
it may also affect the relative intensities of the green and red
luminescence.

3.5. Upconversion luminescence decay

The study of the dynamics of the Er3+ red upconversion
luminescence from the ZrO2:Yb3+,Er3+ nanomaterials was

Figure 7: Upconversion luminescence intensities of selected
ZrO2:Yb3+,Er3+ nanomaterials.
processes involved in the upconversion (absorption by Yb$^{3+}$ and energy transfer to Er$^{3+}$) were examined in detail. It is evident with the one-millisecond excitation pulse. The Yb$^{3+}$-to-Er$^{3+}$ energy transfer is not exceedingly efficient since the other processes involved in the upconversion (absorption by Yb$^{3+}$ (and Er$^{3+}$) and relaxation from the higher Er$^{3+}$ levels to the emitting 4$^2$F$_{9/2}$ level) should take only a fraction of time when compared to the customary one-millisecond decay time of Yb$^{3+}$. The probability of the Yb$^{3+}$-Er$^{3+}$ energy transfer can be deduced to be of the same order of magnitude as the emission from Yb$^{3+}$. This is supported by the luminescence feeding curve which barely achieves the saturation point during the one-millisecond excitation pulse. The Yb$^{3+}$-to-Er$^{3+}$ energy transfer seems to be the rate determining step in the excitation process and thus the time to reach the saturation can give some information about the probability of the energy transfer process.

The second part of the decay kinetics proved to be as complex as the first part. However, due to a more expanded time scale, some quantitative measurements and calculations could be accomplished. The fitting of the red upconversion luminescence decay curves, clearly multieponential or even more complicated, could be carried out to individual exponential components in the linear part of the curves immediately after the influence of the feeding processes had ceased. The results of these calculations showed that there are at least two different luminescence lifetimes in a range from ca. 100 to ca. 300 microseconds. These values are quite typical for the regular red Er$^{3+}$ luminescence [27] and the number of different decay times is consistent with the multisite positions occupied by the Er$^{3+}$ ion. The decay curves show also that there is no significant difference between the different preparation methods when the shorter lifetimes are considered. Nevertheless, there is a significant difference in the long lifetimes of the nanomaterials prepared with different methods. For the ZrO$_2$:Yb$^{3+}$,Er$^{3+}$ nanomaterials prepared with the combustion synthesis (and subsequently heated at 1100°C for 2 hours), there was observed severe afterglow. The total length of this afterglow could not be measured because of the experimental setup but it will definitely extend to several tens of milliseconds. This afterglow was hardly observed by the naked eye adapted to darkness and thus does not fulfill the requirements of the term “persistent luminescence” in the strictest meaning of the definition (light observed at the illumination level of 0.32 mcd m$^{-2}$). However, it should be noted that the ZrO$_2$:Yb$^{3+}$,Er$^{3+}$ nanomaterials for which this afterglow was observed were not optimized for this effects, for example, by adding agents to create lattice defects. The intense and long upconversion luminescence indicates that there occurs trapping of the excitation energy in the system followed by thermal bleaching of this energy and feeding to a luminescence center. In that sense, this emission can be called “persistent upconversion luminescence”.

As for the mechanism(s) of this persistent upconversion, there are two main possibilities: the trapping of the excitation energy can take place either after the absorption by Yb$^{3+}$ (the sensitizer) or after the final excitation processes by Er$^{3+}$ (the activator). The slightly more probable choice is the energy storage in the vicinity of Yb$^{3+}$ since the decay time of Yb$^{3+}$ is 3 to 10 times that of Er$^{3+}$. As a further proof to the existence of persistent luminescence for either Yb$^{3+}$- or Er$^{3+}$-doped materials, one can find experimental data for (strong) afterglow from Yb$^{3+}$-doped garnets [28, 29], Er$^{3+}$-doped silicons, and oxysulfides [28, 30, 31]. It can be thus as-sumed, though not yet proved, that the persistent upon-version in the ZrO$_2$:Yb$^{3+}$,Er$^{3+}$ nanomaterials is possible. The resolution of the exact mechanism(s) requires further work, however.

Even without further studies, it is clear that there are vacancies (together with other impurities, e.g., OH$^-$ groups) present in the ZrO$_2$:Yb$^{3+}$,Er$^{3+}$ nanomaterials both due to the size and charge mismatch between the trivalent Yb$^{3+}$ (and Er$^{3+}$) and the tetravalent Zr$^{4+}$ ions as well as to the soft chemistry preparation methods used. Similar defects are known to store energy in the persistent luminescence materials (such as Eu$^{2+}$-doped alkaline earth aluminates and silicates) [32] as well as in the photostimulated materials (such as Eu$^{2+}$-doped BaF(Cl,Br)) [33]. In the case of the ZrO$_2$:Yb$^{3+}$,Er$^{3+}$ nanomaterials, the depths of these traps are compatible with the thermal energy (kT) at room temperature and thus the feeding from the traps can occur.

The probability of trapping the excitation energy can be assumed to be a few orders of magnitude lower than the energy transfer to Er$^{3+}$ or the emission of the Yb$^{3+}$ ion. This can, however, be improved by careful engineering of these materials, as has been done with the alkaline earth aluminates and silicates. It can be assumed that the major advantages of combining the persistent luminescence and IR up-conversion are that it can lead to efficient immunoassay materials.
4. CONCLUSIONS

The combustion method was found to be an efficient way to prepare the nanocrystalline upconverting ZrO$_2$:Yb$^{3+}$,Er$^{3+}$ luminescence materials with the cubic ZrO$_2$ structure. The sol-gel method yielded a mixed product with slightly larger crystallite sizes, however. All materials showed very efficient red upconversion luminescence with broad features due to multiple Er$^{3+}$ sites originating from different charge compensation schemes because of aliovalent substitution of Zr$^{4+}$ with R$^{3+}$. As a result of the structural purity, the combustion route yielded products with the highest luminescence intensity. The red/green intensity ratio was found to increase with the decreasing crystallite size due to the weakening of the green luminescence. This may be due to a very complex relaxation process involving the multiphonon, cross-relaxation, as well as energy trapping caused by lattice defects. Only one of several cross-relaxation processes can explain at the same time the weak green and strong red luminescence, however. This process must thus be considered as the dominating relaxation process of the green luminescence.

The luminescence decay characteristics with at least two different lifetimes in the range typical of red Er$^{3+}$ luminescence agreed with the multisite nature of the ZrO$_2$ lattice. The materials obtained with different methods showed considerable differences in the longer lifetimes. Moreover, severe afterglow, that is, persistent upconversion luminescence, was observed for the products of the combustion route indicating the inherent energy storage capability of the ZrO$_2$:Yb$^{3+}$,Er$^{3+}$ materials.

For efficient use in bioassays, more work is needed to yield nanomaterials with smaller and more uniform crystallite sizes. Surface modifications need to be studied to allow for the dispersion in aqueous solutions. On the other hand, further work must be carried out to optimize the persistent luminescence of the ZrO$_2$:Yb$^{3+}$,Er$^{3+}$ nanomaterials to allow for their use as efficient immunoassay nanomaterials combining the advantages of both upconversion and persistent luminescence.

ACKNOWLEDGMENTS

Financial supports from the Finnish Funding Agency for Technology and Innovation (Tekes) and the Graduate School of Materials Research (Turku, Finland) for L. Pihlgren and from the Graduate School of Chemical Sensors and Microanalytical Systems (Espoo, Finland) for I. Hyppänen are gratefully acknowledged.

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