

## Up-conversion luminescence dependence on structure in zirconia nanocrystals

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### ABSTRACT

The zirconia samples containing two different concentrations of Er and Yb dopants were prepared using the Sol–Gel method and up-conversion luminescence was studied using the time-resolved techniques. The up-conversion luminescence depends on the oxygen content in surrounding gasses during annealing as well as on the annealing temperature. These dependencies indicate that ZrO<sub>2</sub> intrinsic defects annealing and generation, phase transition as well as dopant redistribution take place. The possible role of these processes on up-conversion luminescence is discussed. The results of experiments confirmed that the annealing temperature has a crucial influence on up-conversion luminescence for samples containing small concentrations of Er and Yb; whereas for samples containing large concentrations of Er and Yb, the primary change of up-conversion luminescence is due to the grain size growth during annealing. The optimal annealing temperature depends upon the Er and Yb ion concentration. It is crucial to obtain up-conversion zirconia material with high quantum efficiency.

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### 1. Introduction

The up-conversion luminescence in zirconia is widely studied by a number of researchers because zirconia has many outstanding properties and it is a perspective material for applications in optics; due to its wide band-gap the material has good transparency and its refractive index and hardness of material are also high [1]. The phonon energy of the ZrO<sub>2</sub> is low (470 cm<sup>-1</sup>) and therefore the luminescence thermal quenching is less efficient than in some other optical materials [2]. On the other hand, the up-conversion processes in zirconia have a potential usage for fluorescent labeling in biology [3–5].

The up-conversion process is widely investigated in fluorides, chlorides and oxides [6–9]. In these materials the most popular dopant is Er, however, other rare earths like, Sm, Tm and Tb could be used as well [10–12]. The additional doping of up-conversion materials with Yb enhances up-conversion process efficiency due to the Yb ion large cross section for optical absorption and efficient energy transfer to Er [13].

In Er and Yb doped materials are possible three mechanisms for up-conversion luminescence. The first possibility is simple excited state absorption (ESA), where Yb<sup>3+</sup> ions do not play any role. A second possibility is energy transfer up-conversion (ETU), two excited (<sup>4</sup>I<sub>11/2</sub>) Er<sup>3+</sup> ions interact with each other and one ion is de-excited to <sup>4</sup>I<sub>15/2</sub> state whereas the other is excited to <sup>4</sup>F<sub>7/2</sub> state. A Third

mechanism for up-conversion is energy transfer from Yb<sup>3+</sup> (<sup>2</sup>F<sub>5/2</sub>) to Er<sup>3+</sup> (<sup>4</sup>I<sub>11/2</sub>) [14].

The ZrO<sub>2</sub> has three polymorphs – monoclinic, tetragonal and cubic. Only the monoclinic phase of undoped ZrO<sub>2</sub> is stable at RT; the tetragonal and cubic phases are not. However, the tetragonal and cubic phase of zirconia can be stabilized at RT by incorporation of divalent and trivalent cationic species such as Mg<sup>2+</sup>, Ca<sup>2+</sup>, Y<sup>3+</sup> [15] or other, as well as by grain size; the undoped zirconia grains smaller than 30 nm have a tetragonal structure [16]. The main agents for tetragonal and cubic phase stabilization at RT are suggested to be the oxygen vacancies [17]. Oxygen vacancy related defects are the main defects responsible for intrinsic defect luminescence [18,19], however the oxygen vacancy effect on up-conversion luminescence have not studied previously.

The up-conversion luminescence in ZrO<sub>2</sub> depends on both – rare-earth ion concentration and material structure and the intensity of up-conversion luminescence is affected by grain size and hydroxyl groups [20].

The optimal concentration of Er and Yb for green up-conversion luminescence band intensity was found to be 2 at% Yb and 0.5 at% Er [21]. One could estimate this concentration is not sufficient for stabilization of the tetragonal phase (3–6 mol%) [22].

The up-conversion process dependence on ZrO<sub>2</sub> structure is not completely understood and the processes have not been fully explained yet.

Our former studies show the intrinsic defect influence on rare earth luminescence spectral distribution in zirconia [23]. It is possible to change the intrinsic defect concentration in zirconia by

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appropriate thermal treatment [19,24,25]. We apply similar treatment to change the intrinsic defect concentration in order to determine the oxygen impact on up-conversion luminescence spectral distribution and intensity.

## 2. Experimental

### 2.1. Samples

The  $ZrO_2$  nanocrystals doped with Er and Yb were prepared by the Sol–Gel combustion technique [26,27], using glycine as fuel and nitric acid as oxidant. Zirconium oxychloride, erbium oxide and ytterbium oxide were dissolved in an excess of nitric acid. Chlorine was eliminated with nitric acid excess.

The molar concentration of all metal ions in the solution was adjusted to 0.2 M. The molar ratio of metal ions and glycine were 1:1.5 and molar ratio of glycine/ $NO_3^-$  was 0.7. All chemicals used were reactive grade and supplied by Aldrich. The appropriate amounts of metal solutions and glycine were mixed and the resulting mixture was then evaporated on a hot plate while stirring at 90–100 °C and concentrated until a gel consistency was reached. The gel was heated up to 300–350 °C in an open oven for 2 h to promote combustion in order to eliminate the nitric oxide; the final product was black powder. The resulting black powder annealed. Two samples with different Er Yb concentrations were prepared, Sample 1 ( $ZrO_2 \cdot 0.5 \text{ mol\%Er}_2O_3 \cdot 0.5 \text{ mol\%Yb}_2O_3$ ) and Sample 2 ( $ZrO_2 \cdot 3 \text{ mol\%Er}_2O_3 \cdot 3 \text{ mol\%Yb}_2O_3$ ). The samples were divided into equal portions and these portions were annealed at determined temperatures starting from 700 °C to 1400 °C for 2 h in order to obtain good crystalline  $ZrO_2$ :Er:Yb particles. After annealing the powder was white.

Phase composition of the prepared sample was determined using the X-ray diffraction analysis (XRD) D8 Advance, (Bruker AXS) with Cu anode ( $Cu K\alpha_1 = 1.54060 \text{ \AA}$ ). The crystallite size was calculated from broadening of diffraction maxima using Topas 3 (Bruker AXS) software.

### 2.2. Optical measurements

The samples for luminescent measurements were lightly pressed into small stainless steel cells of the same size and thus the comparison of luminescence intensities from the samples was possible. The measurements of luminescence were prepared using two different excitation sources: X-ray tube, W anode (operated @ 30 kV, 10 mA) and 975 nm laser diode L975P1WJ (Thorlabs). The luminescence spectra were recorded using the Andor Shamrock B – 303i spectrograph equipped with a CCD camera (Andor DU-401A-BV) at exit port.

For the luminescence kinetic measurements, the samples were excited by a wavelength-tuneable pulsed PG401/SH (Ekspla) solid state laser. The laser pulse exponential decay was  $\tau = 8.7 \text{ ps}$  and pulse duration was 30 ps. The luminescence spectra in time were recorded using a 250is/sm (Bruker Optics) spectrograph and detected on a streak C4334-01 (Hamamatsu) Camera. The measurements of luminescence were carried out at room temperature.

As described in our former studies [19,24,25], it is possible to vary the oxygen concentration in zirconia, by annealing the nanocrystals in gases with different oxygen concentrations. The Sample 1 annealed at 900 °C was additionally annealed in synthetic air ( $N_2 + O_2$ ) or in reducing atmosphere ( $N_2 + H_2$ ) for one hour. Sample 1 was alternately annealed in air and in reducing atmosphere and these cycles were repeated several times. The up-conversion luminescence measurements were conducted after each annealing. The luminescence of Sample 1 after annealing in air differs from its luminescence after annealing in reducing atmosphere; however,

repeated annealing in the air (or in reducing atmosphere) ever result in the same luminescence. This is evidence that the luminescence as well as the sample changes caused by annealing in air or in reducing atmosphere are reversible. A similar effect was observed for sample luminescence in vacuum and ambient atmosphere at RT.

## 3. Results and discussion

The XRD data (Fig. 1) shows that the Sample 1 ( $ZrO_2 \cdot 0.5 \text{ mol\%Er}_2O_3 \cdot 0.5 \text{ mol\%Yb}_2O_3$ ) structure depends on annealing temperature; whereas Sample 2 annealed even at 1400 °C remain in tetragonal phase. Sample 1 had dominant tetragonal structure when annealed at temperatures up to 900 °C; the sample when annealed at 1000 °C consisted of a tetragonal and monoclinic phase mixture and the sample which annealed at 1400 °C had a monoclinic structure.

The annealing results in grain size growth. The estimated mean grain sizes were 18 nm for the sample 1 annealed at 700 °C and 50 nm for that annealed at 1400 °C.

The grain size for Sample 1 annealed at 1000 °C was  $\sim 40 \text{ nm}$  and this is more than the known upper limit (30 nm) for tetragonal phase stabilization in pure zirconia due to excess surface energy [16]. The grain size combined with the Er and Yb concentration determines the phase in zirconia nanocrystals.

Doping concentration of 3–6 mol% is suggested to stabilize the tetragonal phase [22]. Therefore, Sample 2 which has a 3 mol% $Er_2O_3$  3 mol% $Yb_2O_3$  rare earth concentration was prepared to avoid the phase transformation from tetragonal to monoclinic.

The up-conversion luminescence spectra for Sample 1 reveals well known Er emission lines (Fig. 2). Sample 1 annealed at different temperatures was used to clarify the structure impact on up-conversion luminescence. The up-conversion luminescence intensity was strongly suppressed in Sample 1 annealed at temperatures over 900 °C.

The luminescence intensity dependence on Sample 1 annealing temperature was monitored in the more intense line peaking at 549 nm (Fig. 3).

As expected, the annealing increased the luminescence intensity due to grain size growth and due to the decrease of the hydroxyl content at higher temperatures, which helps to reduce the non-radiative relaxation process (Fig. 3 line 1). However, in samples annealed at temperatures above 900 °C up-conversion luminescence intensity decreases (Fig. 3b line 2). A similar effect was described by [1,28]. The annealing time prolongation at high

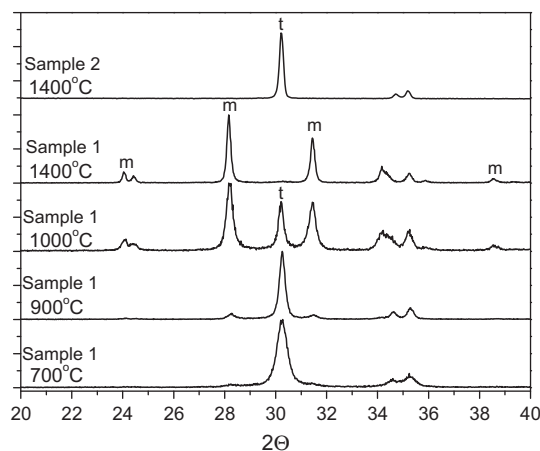
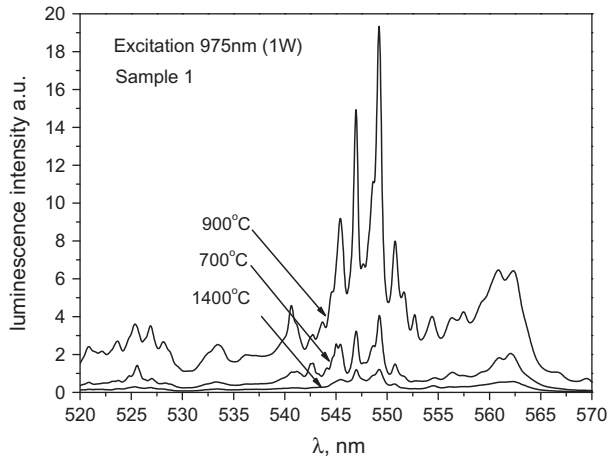
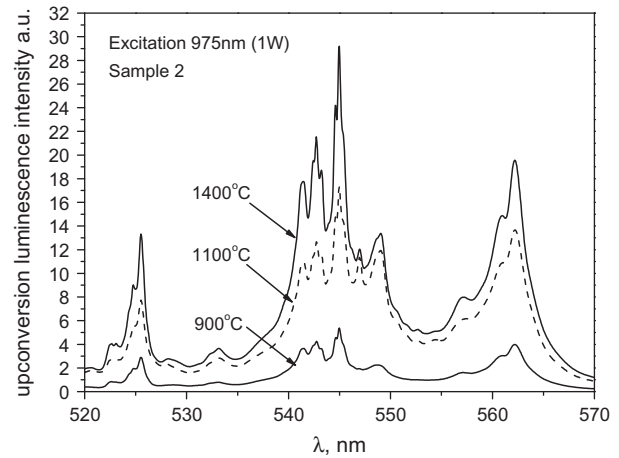


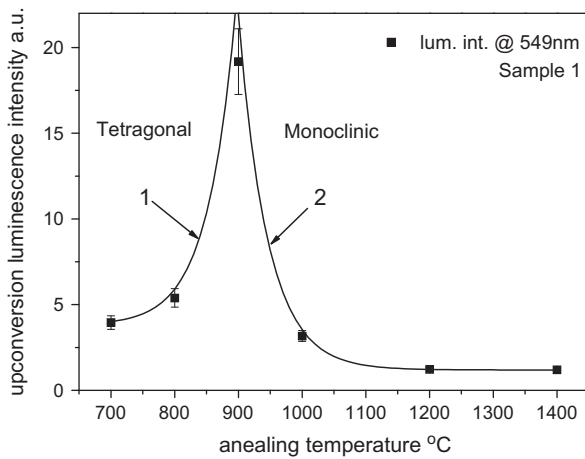
Fig. 1. XRD patterns for Sample 1 and Sample 2 annealed at different temperatures (m corresponds to zirconia monoclinic and t to tetragonal phase).



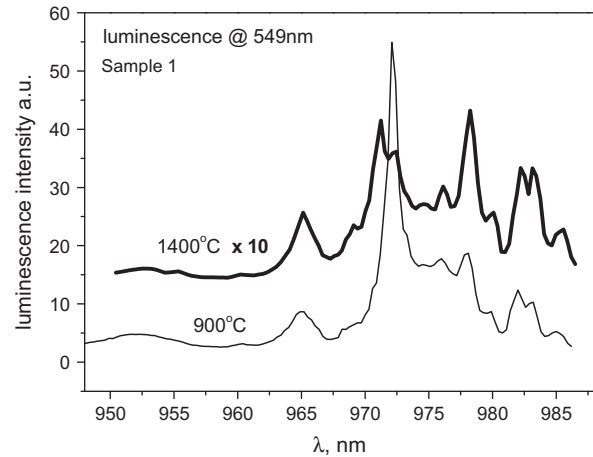
**Fig. 2.** Up-conversion luminescence spectra dependence for Sample 1 ( $\text{ZrO}_2 \cdot 0.5 \text{ mol}\% \text{Er}_2\text{O}_3 \cdot 0.5 \text{ mol}\% \text{Yb}_2\text{O}_3$ ) annealed at different temperatures.



**Fig. 4.** Luminescence spectra for Sample 2 ( $\text{ZrO}_2 \cdot 3 \text{ mol}\% \text{Er}_2\text{O}_3 \cdot 3 \text{ mol}\% \text{Yb}_2\text{O}_3$ ) and annealed at different temperatures.



**Fig. 3.** Up-conversion luminescence intensity dependence on annealing temperature for Sample 1.



**Fig. 5.** Excitation spectra for Sample 1 annealed at 900 °C and 1400 °C (the excitation spectra for sample annealed at 1400 °C is multiplied by factor of 10).

temperatures led to the similar change of luminescence [29]. XRD data indicated (Fig. 1) that within 900–1200 °C the phase transitions from tetragonal to monoclinic take place.

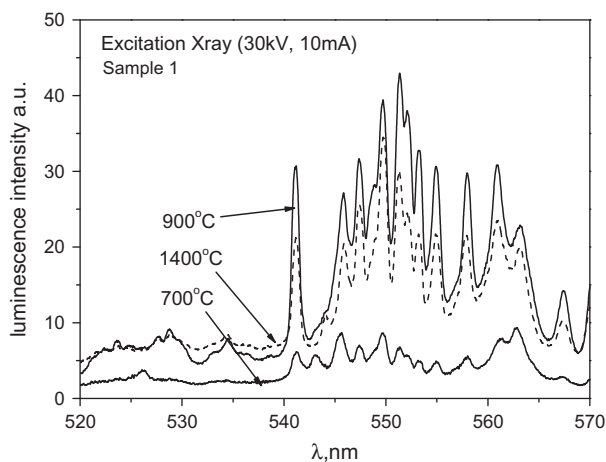
However, for Sample 2 where the tetragonal phase is stabilized by sufficient Er and Yb concentration, the up-conversion luminescence also increases for temperatures over 900 °C (Fig. 4). The luminescence intensity is higher for larger size grains due to relatively less contribution in non-radiative transitions from surface states.

Sample 1 annealed at both 1200 °C and 1400 °C have monoclinic phase; however, the up-conversion intensity of 1400 °C is slightly lower (Fig. 2). The grain size in case of 1400 °C is bigger, so it is expected that the up-conversion luminescence will be higher. We postulate that at high temperatures the Er and Yb ion diffusion and formation of agglomerates or relocation closer to grain surfaces occurs.

The change in zirconia structure could cause the rare earth luminescence spectral distribution changes. Therefore, to ensure clarity and avoid the possibility that under 975 nm excitation only a fraction of ions in specific surrounding/phase is excited, we measured the up-conversion luminescence excitation spectra. The excitation spectra for Sample 1 annealed at 900 °C (tetragonal) and 1400 °C (monoclinic) differs (Fig. 5). However, the excitation

spectra shape around the 975 nm is very similar and the efficiency of excitation for the sample annealed at 1400 °C is weaker than that for sample annealed at 900 °C. The overall excitation efficiency also is weaker for the sample annealed at 1400 °C.

The X-ray excited luminescence also corresponds to the emission from Er (Fig. 6); nevertheless, the relative intensity of luminescence lines differ from those excited in the up-conversion process. This luminescence intensity shows an increase for Sample 1 annealed in temperatures up to 900 °C and a decrease of luminescence intensity for samples annealed above 900 °C. However, the luminescence decrease was minor (compared with up-conversion luminescence decrease) for Sample 1 annealed at higher temperatures (Fig. 6). In case of up-conversion luminescence, the energy transfer from one RE ion to another RE ion occurs, but in the case of X-ray excitation, electron hole pairs are created and they can be trapped directly by RE ions built in different sites – regular site, defect associated site, etc. as described in [23]. The X-ray excited luminescence intensity increase for samples annealed from 700 °C to 900 °C could be due to grain size growth. The slight reduction in luminescence intensity for samples annealed at temperatures above 900 °C could be caused by Er or Yb ion agglomeration or relocation closer to grain surfaces. The luminescence decrease is smaller due that not all Er ions are involved in X-ray excited luminescence.



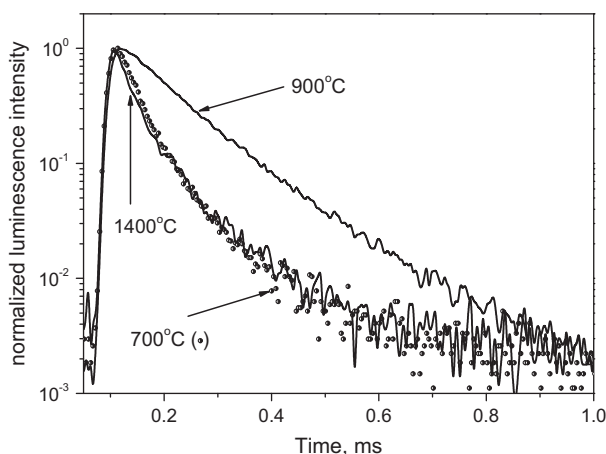
**Fig. 6.** X-ray excited luminescence spectra for Sample 1 annealed at different temperatures.

The tetragonal structure has higher symmetry than monoclinic; therefore the luminescence decay should be slower. Indeed when the annealing temperature is increased, the luminescence intensity increases and also luminescence decay time increases. It could be relevant that after synthesis the oxygen vacancies or other intrinsic defects are located closer to Er. When annealing starts the oxygen vacancies distribute evenly in crystals and grain size also grows, thus the surrounding Er and Yb is in higher symmetry.

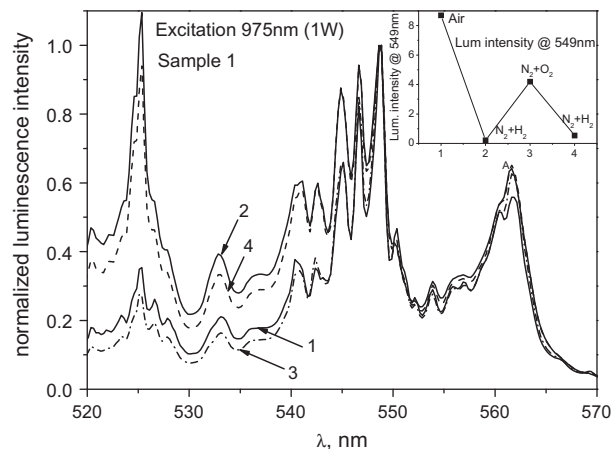
When the phase transformation to monoclinic occurs, then vacancies or even dopant ions relocate. Symmetry for monoclinic phase is also lower, which leads to a decrease in luminescence decay time (Fig. 7).

In our opinion, only the phase transition itself could not be the reason for up-conversion luminescence suppression. The oxygen vacancies could affect the up-conversion luminescence intensity. To increase the oxygen vacancy concentration the sample was annealed at reducing atmosphere. With the increase of vacancy concentration in zirconia the luminescence spectral distribution changes (Fig. 8, main graph). This change could be related to the local surrounding change by oxygen vacancy. The additional oxygen vacancies quench the up-conversion luminescence intensity (Fig. 8, insert graph). Therefore oxygen vacancies are considered a drawback for optimal up-conversion process.

In the case of the tetragonal phase, we assume that the rare earth ions incorporate in the regular  $Zr^{4+}$  sites in the zirconium



**Fig. 7.** Decay kinetics of the up-conversion luminescence at 545 nm for the Sample 1 annealed at different temperatures.



**Fig. 8.** Up-conversion luminescence spectra for Sample 1 subsequently annealed at 900 °C in  $N_2H_2$  (reducing atmosphere) and at 900 °C in  $N_2 + O_2$  (synthetic air) for two cycles.

sublattice. The deficiency of positive charge is compensated by oxygen vacancies in the oxygen sublattice. These oxygen vacancies are the main agents for tetragonal (or cubic) phase stabilisation [17].

It is expected that in tetragonal phase, the oxygen vacancies are more or less evenly distributed in the volume of the nanocrystal; however, the distribution of Er or Yb is not clear. Two RE ions for charge compensation need one oxygen vacancy. The support for the above assumptions is that the EXAFS spectra analysis showed that in tetragonal and cubic phases, mostly the oxygen vacancies are associated with the Zr rather than dopants [30,31] also dielectric measurements indicated similar result [32].

The cation diffusion in tetragonal Ce and Yb doped zirconia was noticed at 1200 °C; however, the anion diffusion is six orders of magnitude faster [33].

When phase transition to monoclinic occurs, there is no need for even distribution of oxygen vacancies and the temperature is high enough for vacancy relocation closer to Er and Yb, which thus strongly reduces the up-conversion intensity. In case of phase transition at temperatures above 900 °C, the temperature is high enough to produce a new equilibrium of point defects (including impurities) in the crystal and the relaxation of stresses by means of the oxygen vacancy migration.

#### 4. Conclusions

It was shown that the presence of oxygen vacancies in zirconia has an important impact on up-conversion luminescence.

The up-conversion luminescence intensity was monotonically growing with annealing (annealing) temperature in zirconia containing an appropriate amount of rare earth dopants for tetragonal phase stabilization.

When the rare earth ion concentration is small, the increase of annealing temperature can lead to the phase transformation from tetragonal to monoclinic, and luminescence intensity is quenched. The up-conversion luminescence quenching could be related to oxygen vacancy migration closer to Er and Yb. Also dopant relocation on the grain surface and agglomerate formation could additionally reduce the up-conversion intensity.

The present research shows that if the rare earth concentration in zirconia was below that necessary for tetragonal phase stabilization, the material annealing temperature is crucial for obtaining intense up-conversion luminescence.

In our opinion the optional Er and Yb ion concentration should be reviewed to take into account the optimal annealing temperature for each Er and Yb concentration.

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