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Luminescence properties of zirconia nanocrystals prepared by solar physical vapor deposition

Krisjanis Smits [a,*], Larisa Grigorjeva [a], Donats Millers [a], Karlis Kundzins [a], Reinis Ignatans [a], Janis Grabis [b], Claude Monty [c]

[a] Institute of Solid State Physics, University of Latvia, Riga, Latvia
[b] Institute of Inorganic Chemistry, Riga Technical University, Latvia
[c] Procédés, Matériaux et Energie Solaire CNRS, France

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ABSTRACT

Zirconia nanocrystals have attracted considerable interest as biolabels, which can be used as probes for medical imaging and biosensor applications. However, zirconia particle agglomeration forms a major limitation to its use for biolabeling. In this backdrop, for the first time, well-separated zirconia nanocrystals were obtained in a Heliotron reactor (PROMES CNRS, France) via the solar physical vapor deposition (SPVD) method. As the raw material target for solar evaporation, zirconia nanopowders obtained via the sol–gel process were used. The luminescence and upconversion luminescence properties of the Sol Gel nanopowders were compared with those of the SPVD nanocrystals. Erbium was chosen as the luminescence center with ytterbium as the sensitizer, and along with these two dopants, niobium was also used. Niobium acts as a charge compensator to compensate for depletion in the charge due to the introduction of trivalent erbium and ytterbium at tetravalent zirconium sites. Consequently, the oxygen-vacancy concentration is reduced, and this results in a significant increase in the upconversion luminescence.

The SPVD-prepared samples showed less agglomeration and a fine crystal structure as well as high luminescence, and thus, such samples can be of great interest for biolabeling applications.

1. Introduction

Zirconia (ZrO_2) is considered an excellent material for use in optics due to its wide bandgap, good transparency, and high refractive index and material hardness [1]. On the other hand, the phonon energy of ZrO_2 is low, and therefore, its luminescence thermal quenching is less efficient than in certain other optical materials.

The intrinsic luminescence of zirconia is relatively weak, and therefore, for practical luminescence applications, zirconia is doped with rare earth (RE) ions. The RE-ion luminescence characteristics in zirconia are concentration-dependent, and concentration quenching of RE ions in zirconia nanocrystals can be observed at relatively high concentrations, which indicates that the RE distribution in nanocrystals is homogeneous [2]. The RE-ion luminescence in ZrO_2 depends on its nanocrystal grain size [3]. On the one hand, increase in the grain size reduces the surface defect concentration, thereby reducing the possibility of excitations recombining in a nonradiative manner. On the other hand, an increase in the grain size for doping concentrations less than 3 mol% could lead to the compound's phase transition from tetragonal to monoclinic.

We have recently demonstrated the possibility of using zirconia-nanocrystal upconversion luminescence in biolabeling [4]. Such applications have also been reported by other researchers [5]. Zirconia nanocrystals can be prepared by different chemical methods; however, in most cases, the final products mostly agglomerate even upon using surfactants. However, for biolabeling applications, separated (not agglomerated) nanocrystals are necessary. Our previous study on zirconia powder prepared in plasma [6] resulted in significantly reduced agglomeration. It is expected that similar or better results can be obtained using the SPVD method. Further, the morphology of SVPD-prepared oxide nanocrystals strongly differs from those of samples obtained via the Sol Gel method [7]. In addition, the SPVD sample quantities are smaller in comparison with those obtained via the plasma method. This provides an easy approach to test the differences in composition between the two methods.

* Corresponding author. Tel.: +371 26538386.
E-mail address: smits@cfi.lu.lv (K. Smits).

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Zirconia nanocrystals are non-toxic (zirconia are often used in biological implants), and therefore, the possible application of zirconia for biolabeling has attracted strong interest. However, the downside of using zirconia in biolabeling is its relatively weak luminescence compared with certain fluorides. Nevertheless, we have recently shown the reason for the decrease in the upconversion luminescence intensity [8] and how this reduction can be avoided by adding Nb dopant [9].

For the upconversion luminescence center, we chose Er ions as the dopants; additional doping with Yb enhances the upconversion process efficiency (due to the large absorption cross-section of the Yb ions) for optical absorption and effective energy transfer to Er ions. Both Er and Yb are incorporated in Zr^{4+} sites as RE^{3+}; therefore, for charge compensation, oxygen vacancies can also be incorporated in zirconia. As assumed by Fabris et al. [10], oxygen vacancies stabilize tetragonal or even cubic zirconia phases; however, oxygen vacancies could affect the energy transfer from one RE ion to another.

Our previous researches show the possibility of varying the oxygen vacancy concentration in zirconia [6,8] thereby allowing for the examination of the influence of oxygen vacancies on the luminescence properties. Another possible method to vary the vacancy concentration in zirconia doped with trivalent dopants is to add Nb^{5+} [11–13], which also leads to increase of dopant luminescence [9].

In this article, we describe our investigation of the luminescence properties of Er-, Yb- and Nb-doped zirconia nanocrystal samples prepared via SPVD and our comparison of these properties with those of nanocrystals prepared via the classical Sol Gel method.

2. Experimental

2.1. Sample preparation

Erbium-, ytterbium-, and niobium-doped zirconia samples were prepared by the Sol Gel and SVPD methods. Further, samples with only Er and Yb (without Nb) were also prepared for purposes of comparison in the backdrop of our previous research that describes the role of Nb in luminescence increase [9]. This study focuses mainly on Nb-doped samples. We primarily compare SPVD 12-8 samples with sample Sol Gel 13-8a samples. The sample names and descriptions are listed in Table 1.

Er and Yb concentrations for the Sol Gel method were chosen such that the resulting concentrations for the both the SPVD and Sol Gel samples were identical. The Sol Gel sample synthesis method has been described previously [8,14,15].

The SPVD samples were prepared in a Heliotron reactor (PROMES CNRS) in a manner similar to that described by Kouam et al. [16]. The target pellets for SVPD experiments were synthesized by the Sol Gel method with 1 and 2 mol% of Er and Yb, respectively, and 3 mol% Nb. However, subsequent to SPVD, the Er and Yb amounts in the resulting nanocrystal powder were significantly lower. The Er and Yb quantities were reduced by factors of five and two, respectively, while the final Nb concentration was larger. These differences can be attributed to the different melting temperatures and different phase diagrams corresponding to these materials.

2.2. SPVD method

Zirconia is a high-temperature material, and therefore, the evaporation temperature for zirconia in the Heliotron reactor is estimated to be about 3000 °C. Such temperatures are achieved with heat transfer via concentration of solar radiation focused to small spot sizes. The estimated maximal power density can reach up to 5 kW/cm^2. The schematic of the SPVD method is shown in Fig. 1 along with the evaporation process in Fig. 2.

The mobile plane mirrors follow the movement of the sun and reflect solar radiation onto the parabolic mirror, whose emission is concentrated on the sample with spot sizes below 1 cm^2. For power control, the flaps between the mobile plane mirrors and the parabolic mirror are used. The target material is placed at the focus of the parabolic mirror in a water-cooled target holder, which is placed at the center of the glass balloon of the reactor. This setup facilitates variation of the ambient gas and gas pressure while also allowing gas flow for controlled material transport. The evaporated particles are transported by gas flow along the cooling part (the cold finger) to nanoporous ceramic filters. Such particle transport reduces the particle condensation on the walls and allows controlled particle collection at the filters. The power density, gas type, pressure, and flow rate in the reactor also affect the properties of the prepared samples.

2.3. Morphology and structure measurements

Energy dispersive X-ray (EDX) analysis of the samples (using the Eagle III XPL) was carried out for controlling the dopant content and detecting unexpected impurities. The crystalline structure of the samples was examined via X-ray diffraction (XRD) using an X-ray diffractometer (X'Pert Pro MPD) with Cu Kα radiation (λ = 0.154 nm). The crystalline size verification and morphology studies were performed using a transmission electron microscope (TEM, Tecnai G20, FEI) operated at 200 kV. An ultrasonic bath was used for powder treatment. Sol Gel samples when mixed in ethanol undergo partial precipitation, thereby indicating the presence of large agglomerations of the particles, whereas the SPVD samples remain milky; in this manner, the difference in terms of agglomeration between samples obtained by the two methods can be compared. The samples for TEM studies were placed on a carbon-coated grid. For verification of the dopant incorporation in nanocrystals, we performed STEM observations with an EDX detector.

2.4. Optical measurements

The luminescence measurements were carried out at room temperature. The luminescence measurements were carried out using three different excitation sources: (I) YAG laser FQSS266 (CryLas

Table 1
Sample names used in text with corresponding structure, grain sizes, doping content, and annealing temperatures.

Sample name	Structure	Grain sizes (nm)		Dopands (mol%)			Annealing T (°C)
		M	T	Er	Yb	Nb	
Sol Gel 12-8	T	–	–	1	2	3	1000
Sol Gel 12-10	T	–	–	1	2	0	1000
SPVD 12-8	T	–	21–22	0.2	1.12	4.4	None
SPVD 12-10	T	–	15–17	0.22	1.18	0	None
Sol Gel 13-8a	T65% + M35%	35–40	20	0.2	1.12	4.4	800
Sol Gel 13-8b	M68% + T32%	40–45	35	0.2	1.12	4.4	1000