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journal homepage: [www.elsevier.com/locate/jlumin](http://www.elsevier.com/locate/jlumin)Intrinsic defect related luminescence in ZrO<sub>2</sub>K. Smits<sup>a,\*</sup>, L. Grigorjeva<sup>a</sup>, D. Millers<sup>a</sup>, A. Sarakovskis<sup>a</sup>, J. Grabis<sup>b</sup>, W. Lojkowski<sup>c</sup><sup>a</sup> Institute of Solid State Physics, University of Latvia, 8 Kengaraga str., Riga, Latvia<sup>b</sup> Institute of Inorganic Chemistry, Riga Technical University, 34 Miera str., Salaspils, Latvia<sup>c</sup> Institute of High Pressure Physics, Polish Academy of Science, 29/37 Sokolowska str., Warsaw, Poland

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## ABSTRACT

The studies of ZrO<sub>2</sub> and yttrium stabilized ZrO<sub>2</sub> nanocrystals luminescence as well as yttrium stabilized single crystal luminescence and induced absorption showed that the intrinsic defects are responsible for luminescence at room temperature. These defects form a quasi-continuum of states in ZrO<sub>2</sub> band gap and are the origin of the luminescence spectrum dependence on the excitation energy. Luminescence centers are oxygen vacancies related but not the vacancies themselves. At room temperature, in ZrO<sub>2</sub>, deep traps for electrons and holes exist. The oxygen vacancies are proposed to be the traps for electrons.

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## 1. Introduction

Zirconia (ZrO<sub>2</sub>) is a known material due to its widespread application—material for thermal barriers [1], solid electrolyte for fuel cells [2], material for sensors [3], for catalysts [4], for fiber optics, laser techniques, for biological labeling [5] and for jewelry. Therefore the material properties, including luminescence, were studied by a large number of researchers. However the results of the luminescence study differ.

A strong UV luminescence band peaking at 4.2 eV was observed from ZrO<sub>2</sub> tetragonal structure thin films at low temperature under excitation near the fundamental absorption edge (~5 eV) and above [6]. This luminescence was ascribed to self-trapped excitons (STE) and the material was proposed as promising for scintillators. The luminescence of STE was thermally quenched above 150 K and was not observable at room temperature (RT). The ZrO<sub>2</sub> luminescence observable at RT is from defect states. This luminescence was studied by many researchers, e.g. those of Refs. [7–13], and the number of the observed luminescence bands was within one [7] up to eight [10]. The luminescence bands observed were peaking within the spectral region from ~2 to ~3 eV. The excitation of these luminescence bands was within the band gap region (below 5 eV) and this is a strong evidence that luminescence correlate to defects. The luminescence center models proposed were different: F-centers

in different charge states, Zr<sup>3+</sup>-centers (T-centers) and various combinations of F<sub>A</sub>-centers in yttrium stabilized ZrO<sub>2</sub> (YSZ). We did not find in literature any results of luminescence dependence on oxygen content in zirconia; however oxygen vacancies are known to be responsible for the zirconia crystalline structure [14]. Thus, in current literature we did not find any clear and reasonable explanation for the ZrO<sub>2</sub> intrinsic defect related luminescence and we carried out a number of experiments for highlighting some details of this luminescence.

## 2. Experimental

## 2.1. Samples

The undoped ZrO<sub>2</sub> nanocrystals were produced by two methods: (I) plasma synthesis (PS) [15] and (II) microwave driven hydrothermal method (HT), described in detail in Ref. [16] and were used in the experiments. The commercial zirconia macroscopic powder with low Hf content (ZrO<sub>2</sub> 99.7%, Hf content less than 75 ppm, ECC No. 215-227-2) was obtained from Alfa Aesar GmbH and was used in the experiments also. The YSZ nanocrystals (Y<sub>2</sub>O<sub>3</sub> content 6 mol%) were obtained by the HT method.

As it is not possible to obtain undoped ZrO<sub>2</sub> single crystals, a ZrO<sub>2</sub>:Y (Y<sub>2</sub>O<sub>3</sub> content 9.5 mol%) single crystal plate of 10 × 10 × 1 mm size was obtained from Alfa Aesar GmbH. This single crystal was used for the luminescence and transient absorption experiments. Therefore we have the possibility to compare the luminescence from YSZ single crystal with that of

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YSZ nanocrystals as well as with undoped  $\text{ZrO}_2$  nanocrystals and check the influence of the stabilizer on the luminescence.

The nanocrystal structure was checked by XRD. The undoped  $\text{ZrO}_2$  nanocrystalline samples were mixtures of two phases—monoclinic and tetragonal. The YSZ nanocrystals have the tetragonal crystalline structure. The grain size of nanocrystals synthesized by the HT method was estimated to be  $\sim 30$  nm and for the ones synthesized by the PS method,  $\sim 110$  nm. The nanocrystals were lightly pressed into small stainless steel cells for luminescence experiments. The cells had strictly the same size for all nanocrystal samples; therefore comparison of luminescence intensity was possible.

For oxygen content influence on  $\text{ZrO}_2$  luminescence an additional set of samples was prepared. The undoped  $\text{ZrO}_2$  nanocrystals were produced by the HT method; the structure and grain size of these nanocrystals were the same as described above. The obtained crystalline powder was divided into equal parts and each part was annealed at  $340^\circ\text{C}$  in an oxygen–nitrogen gas mixture having total pressure 1000 mbar. The oxygen partial pressure was variable from 21 mbar up to 234 mbar; the rest in all cases was nitrogen; in the text the volume% of oxygen is also used. A more detailed description of the annealing procedure is in Ref. [17].

## 2.2. Luminescence measurements

To get comparable results a setup with four luminescence excitation sources was used: (I) ArF laser PSX-100-2 operating at 6.42 eV; (II) diode pumped YAG Nd laser fourth harmonic at 4.66 eV; (III) nitrogen gas laser LG-21 operating at 3.67 eV and (IV) X-ray tube with W target operating at 40 kV, 10 mA. The luminescence spectra were recorded using an Andor 303i-B spectrometer equipped with a CCD camera (Andor DU-401A-BV) at its exit port.

A special luminescence excitation source, a NT342/3UV laser from Ekspla coupled with an optical parametric oscillator (OPO), was used also for luminescence excitation and emission spectra measurements. Thus the registration of the excitation spectrum for fixed luminescence wavelength as well as luminescence spectrum for fixed excitation wavelength was possible.

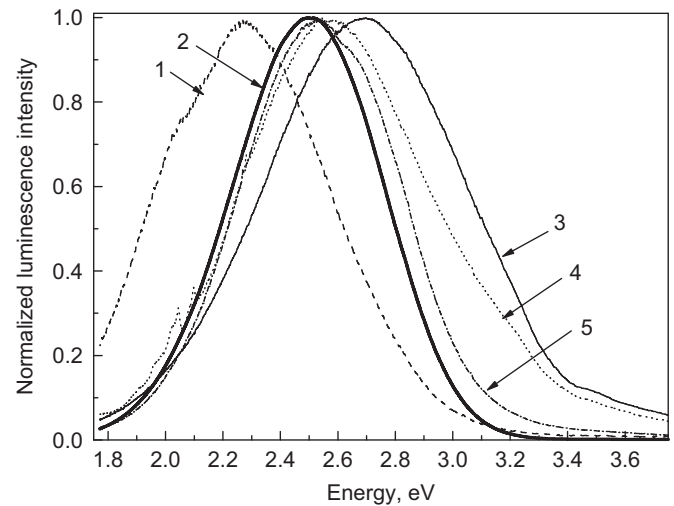
## 2.3. Transient absorption

The transient absorption was measured for YSZ single crystal only, since a transparent sample is needed for this experiment. The transient absorption was induced by a pulsed electron beam (270 kV,  $10^{12}$  el/cm<sup>2</sup> per single pulse, pulse length 10 ns). The transient absorption spectrum was measured using an MDR-2 grating monochromator for wavelength selection; the probing light was Xe flash and the signal was detected by PMT and displayed on a digital storage oscilloscope TDS5052 (TEKTRONIX). The time resolution of the equipment was limited by the PMT used and was 12 ns. The spectrum was registered point-by-point, selecting the corresponding wavelength by the monochromator. Only one pulse of electron beam hit the sample at each wavelength and induced absorption amplitude as well as kinetic were recorded at this wavelength. It was possible to use the same equipment also for luminescence registration; in this case the Xe flash was switched off.

All the luminescence and transient absorption measurements were carried out at RT.

## 3. Results and discussion

The experiments were started with luminescence spectra recording for all the samples under excitation within band gap;



**Fig. 1.** Luminescence of Y stabilized zirconia single crystal (1);  $\text{ZrO}_2$  commercial powder (2); Y stabilized nanocrystals (3); undoped nanocrystals HT (4) and undoped nanocrystals PL (5).

thus the YAG Nd laser fourth harmonic (4.66 eV) was used. The spectra obtained are shown in Fig. 1. The peak positions of luminescence bands are within 2–3.5 eV. The luminescence band for YSZ single crystal peaks in the low energy side of region whereas luminescence band for YSZ nanocrystals peaks in the high energy side. The undoped  $\text{ZrO}_2$  nanocrystal luminescence band peak positions are very close to each other.

The peak position and the band shape of the luminescence are grain size dependent—the largest size undoped nanocrystals (commercial  $\text{ZrO}_2$ ) powder showed the luminescence peaking at lower photon energies and narrower band (curve 2 in Fig. 1) than those for the smallest size nanocrystals (curve 4 in Fig. 1). Another important feature is that the YSZ nanocrystal luminescence band is noticeably shifted to the higher photon energies. This shift of the luminescence band could be due to larger concentration of oxygen vacancies incorporated in YSZ nanocrystals for yttrium charge compensation. Since the excitation of luminescence for all samples was within the band gap the luminescence is from defects and the luminescence spectra are an evidence that several kinds of defects are possible in  $\text{ZrO}_2$ . It was expected that nonselective excitation could cause luminescence of different defects; therefore the luminescence spectra were recorded under X-ray excitation for all the samples. The luminescence spectra observed for all the samples were very similar to each other (Fig. 2). A similar result was obtained under pulsed electron beam excitation [18]. Thus the observed wide luminescence band could be due to overlapping of a number of bands. A similar idea was described in Ref. [13].

Both of these excitations led to the creation of band carriers – electrons and holes – and this is similar to band-to-band excitation. The similarity of the luminescence spectra for all samples under this kind of excitation is an evidence that the radiative recombination centers in all the samples are the same. These recombination centers are  $\text{ZrO}_2$  intrinsic defects, since no difference between yttrium stabilized and pure  $\text{ZrO}_2$  samples was observed. Comparison of the radioluminescence and photoluminescence led to the hypothesis that: (I) different kinds of defects are possible in  $\text{ZrO}_2$ ; (II) defect concentration ratios for the samples produced by different methods differ and (III) direct selective excitations of these defects might be different, possibly due to different lattice surroundings.

The hypothesis was checked using three lasers with different photon energies (6.42, 4.66 and 3.67 eV) for the luminescence

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