

Radiative Decay of Electronic Excitations in ZrO_2 Nanocrystals and Macroscopic Single Crystals

Krisjanis Smits, Larisa Grigorjeva, Donats Millers, Janusz D. Fidelus, and Witold Lojkowski

Abstract—The time-resolved luminescence was studied for $\text{ZrO}_2\text{:Y}$ single crystal and nanocrystals. The similar recombination centres were found in both—single crystal and nanocrystals. Luminescence decay is within 200 ns in nanocrystals, whereas it extends to the microseconds in single crystal. It was shown that the defects responsible for transient absorption were not involved directly in radiative recombination process.

Index Terms—Photoluminescence, scintillators, spectroscopy, ultrafast.

I. INTRODUCTION

THE zirconia (ZrO_2) is important oxide due to its widespread applications as the material for thermal coatings barriers [1], for solid electrolyte for fuel cells [2], [3], for sensors [4], for catalysts [5], as the promising material for scintillators [6]. The luminescent properties are of the high importance for the material use as a scintillator. The luminescence of zirconia was investigated by a number of researchers and today the two kinds of luminescence are established—luminescence from self-trapped excitons [6] and intrinsic defects related luminescence [7]. Luminescence of self-trapped excitons is quenched above 150 K [6] and seems not to be very attractive for scintillator since most of scintillators were used at room temperature (RT). However the zirconia defects related luminescence can be observed at RT [7], [8] and this luminescence cover spectral region 1.6–3.5 eV [9]. The complete decay of zirconia defects related luminescence is within ~ 200 ns in nanocrystals, hence this luminescence is appropriate for scintillator. The melting temperature of zirconia is high as 2700°C [10] and the phase transition (tetragonal phase to monoclinic phase) below this temperature get the growth of zirconia single crystals difficult. The zirconia tetragonal as well as cubic phase can be stabilized by additives such as Y, or Ca, or other [11]. These additives need the charge compensation and therefore the oxygen vacancies were introduced. The amount of additives is significant—up to 6% and therefore the crystallographic structure contains large amount of defects and the electronic structure changes also. However the melting temperature is high for stabilized crystals also. Therefore producing of ZrO_2 single crystals for possible applications (including scintillators) meet diffi-

culties. Other possibility is to produce the zirconia nanocrystals and try to made transparent nanostructured ceramic. The study of ZrO_2 nanocrystals luminescence is of high importance in this case and this luminescence of yttrium stabilized zirconia nanopowders and thin films were studied by several authors [12]–[15]. The observed luminescence spectrum depends on excitation wavelength [13] and the luminescence bands peaking at 2.07, 2.25, and 2.69 eV were found. More complicated photoluminescence spectrum having peaks at ~ 2.2 , 2.4, 2.8, 3.0, and 3.2 eV was described by Hachiya [14]. The time-resolved study of zirconia luminescence [16] also shown luminescence within 1.6–3.5 eV and some of possible peak positions correspond to those described in [12], [14], [15] but the spectra shapes were not the same. The oxygen vacancies were involved in the models of possible luminescence centres however the models were different. Hence, the defect related luminescence of $\text{ZrO}_2\text{:Y}$ depend on excitation wavelength and possibly on ZrO_2 powder synthesis method. The purpose of present study was to clear up are the same luminescence centres in bulk single crystal and nanocrystals. Other aim was to determine are the lattice defects involved in non-radiative recombination of charge carriers. The comparison of the time—resolved luminescence of $\text{ZrO}_2\text{:Y}$ nanocrystals with that of single crystal and transient absorption of this crystal was carried out.

II. EXPERIMENTAL

A. Samples

The $\text{ZrO}_2\text{:Y}$ (Y_2O_3 content 9.5 mol%) single crystal was obtained from Alfa Aesar GmbH. This single crystal was a $10 \times 10 \times 1$ mm plate and was used for both luminescence and transient absorption experiments. The $\text{ZrO}_2\text{:Y}$ (Y content 6 mol%) nanocrystals (nanopowder) were obtained by microwave driven hydrothermal method described in details in [17]. The nanocrystals structure was checked by XRD and the tetragonal phase was found. The grain size of nanocrystals was estimated to be ~ 30 nm. The nanocrystals were slightly pressed into a small stainless steel cell for luminescent measurements.

B. Luminescence Measurements

The excitation of luminescence was completed either by a pulsed laser beam at 4.66 eV (within band gap region) 8 ns pulses or by a pulsed electron beam: 270 KeV, 10 ns, flux 10^{12} el/cm². The irradiation with electron beam produces the electrons and holes, not the new defects in crystalline lattice, since electron energy above 300 KeV is needed for oxygen shift from its lattice site due to direct collision in a number of oxides. In the case of luminescence excited by laser beam the registration was by photon counting in 2 ns time bins

Manuscript received June 18, 2007; revised April 11, 2008. This work was supported in part by the Latvian National Program and European social foundations.

K. Smits, L. Grigorjeva, and D. Millers are with the Institute of Solid State Physics, Riga LV-1063, Latvia (e-mail: smits@cfi.lu.lv).

J. D. Fidelus and W. Lojkowski are with Institute of High Pressure Physics, Warszawa 01-142, Poland.

Digital Object Identifier 10.1109/TNS.2008.924077

(Hamamatsu photon counting head H8259 and Fast Com Tec multiscaler P7888-1(E)). The decay kinetics of luminescence were measured for the wavelengths over all spectrum, thereby the family of kinetics was obtained and the spectra can be drawn out for different delay relative to the excitation pulse as well as the spectrum integrated within definite time interval. If the integration time interval is wide enough then spectrum is the same as recorded by conventional method without time resolution. The registration of luminescence excited by the electron beam was by photomultiplier tube (PMT) and digital storage oscilloscope (Tektronix TDS 5052). The time resolution was 12 ns and it was limited by PMT output signal. This registration was used for transient absorption measurements also. The grating monochromator MDR-2 was used for the luminescence as well as transient absorption spectra measurements.

C. Transient Absorption Measurements

The transient absorption measurements were possible only under pulsed electron beam irradiation. The electron beam parameters were the same as for luminescence measurements. The equipment used for luminescence measurements was modified by adding the probe light source—Xenon flash lamp. The probe light pulse have flat top within 15 μ s and limited the transient absorption measurement time interval. The probe light was collimated and directed on the one side of sample so that light reaches the irradiated surface of the sample, undergoes the total reflection from this surface and comes out from sample via opposite side. The probe light after passing the sample was collected at the entrance slit of monochromator. This geometry was necessary since the penetration depth of electrons in $\text{ZrO}_2\text{:Y}$ was estimated to be ~ 0.2 mm. Therefore the optical path in normal direction to the irradiated surface was short. Using the described geometry the light beam passes sample practically along the irradiated surface and the optical path through the irradiated layer is ~ 35 times longer. The longer optical path allows detecting the smaller changes of induced optical density.

III. RESULTS AND DISCUSSION

The luminescence spectra for ZrO_2 single crystal and nanocrystals under laser beam excitation are shown at Fig. 1. The both spectra contain a wide band which origins from overlapping of several bands. However, the peak positions of these wide luminescence bands were within 2.0–2.25 eV for single crystal and at ~ 2.8 eV for nanocrystals. The band gap of $\text{ZrO}_2\text{:Y}$ is above 5 eV [18] and the excitation with laser beam at 4.66 eV was within band gap. Therefore the luminescence was defect related and different spectra are a witness that in single crystal and nanocrystals luminescence the contribution from various defects is different. The 2.8 eV band was observed in single crystals [15] under 240 nm (5.17 eV) excitation. The excitation by laser beam in our experiments was at 266 nm (4.66 eV) and it could be the reason why this band was not observed in the crystal. Since the excitation by laser beam within band gap was selective only a fraction of all defects could be responsible for luminescence observed. Thus the experiment using electron beam excitation was carried out. This kind of excitation creates the band carriers and during recombination the excited states of defects could be created. This kind of

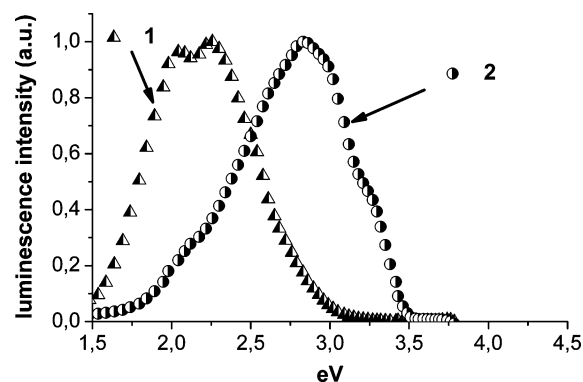


Fig. 1. Luminescence spectra under laser beam excitation. 1—single crystal; 2—nanocrystals.

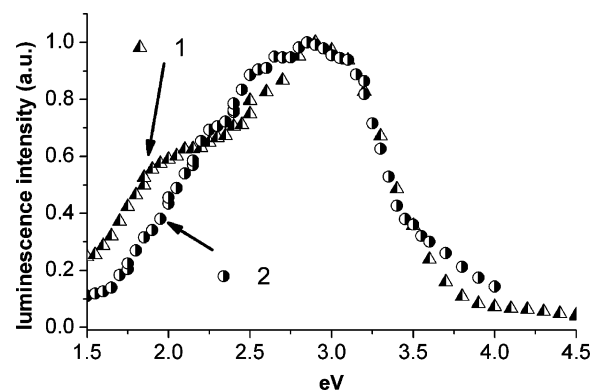


Fig. 2. Luminescence under electron beam excitation. 1—single crystal; 2—nanocrystals.

excitation was not selective and it was expected more types of defects could be involved. The single crystal and nanocrystal luminescence spectra at the end of electron beam pulse were shown at Fig. 2.

The comparison of spectra at Fig. 1 and Fig. 2 led to the following. The single crystal spectra under laser beam and electron beam excitation were different. The spectrum under electron beam excitation is wider and peak position is shifted to the ~ 2.9 eV. The luminescence bands peaking at ~ 2.0 and 2.25 eV under laser beam excitation (Fig. 1) forms a shoulder in the same spectral region (Fig. 2) under electron beam excitation. Hence, the single crystal luminescence spectrum is a superposition of a number of overlapping bands and during the recombination process more kinds of luminescence centres were excited than under laser beam irradiation. Under electron beam excitation the single crystal luminescence spectrum was similar to that of nanocrystals (Fig. 2). Therefore the defects involved in electron—hole recombination were the same in both samples. The luminescence decay kinetics for single crystal and nanocrystals differ (Fig. 3 and Fig. 4).

More over—luminescence decay in the single crystal is different for laser beam and electron beam excitation. The well resolved two components were in in luminescence kinetics under laser beam excitation—initial fast decay was followed by slow one, extended in the microsecond range. In the case of electron beam excitation the contribution from initial fast decay was large, up to $\sim 90\%$ from total intensity during first 100 ns,

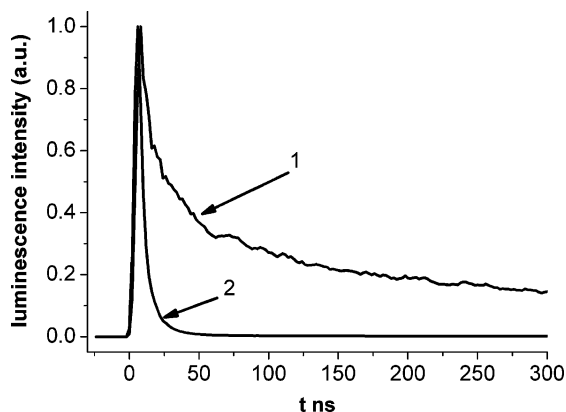


Fig. 3. Laser beam excited luminescence decay kinetics at 2.6 eV. 1—single crystal; 2—nanocrystals.

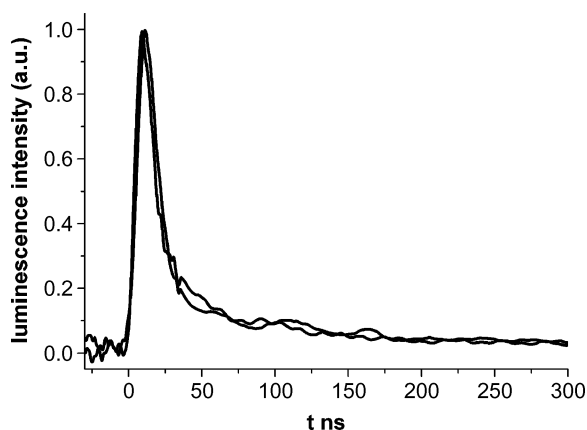


Fig. 4. electron beam excited luminescence decay kinetics at 2.6 eV. 1—single crystal; 2—nanocrystals.

whereas laser beam excited luminescence decay was $\sim 65\%$ at the same time. The slow decaying component became negligible after $\sim 2 \mu\text{s}$. The luminescence decay in nanocrystals was close under both kinds of excitation and was faster—the luminescence intensity diminished to undetectable level 200 ns after excitation pulse. This difference in laser beam excited luminescence decay was due to the different surrounding of luminescence centres. The relative long radiation life-time (above $10 \mu\text{s}$) indicates that the semi-forbidden transitions were responsible for luminescence. It is known that for lower symmetry semi-forbidden transition probability increases and the decay of luminescence in this case is faster. It was suggested in the single crystal the fraction of luminescence centers has more regular surrounding than in nanocrystals and it is the reason for different decay time of luminescence. The luminescence decay under electron beam excitation was the same for single crystal and nanocrystals (Fig. 4). The coincidence of luminescence decay need further, more detailed study.

The luminescence main band peak position in the nanocrystals is the same under laser beam excitation (Fig. 1) and electron beam excitation (Fig. 2), whereas for the single crystal not. Similar feature was observed by Petric *et al.* [12] for ZrO₂:Y cubic phase single crystal—luminescence bands 2.07 eV and 2.25 eV were observed under excitation within band gap region and band peaking at 2.69 eV under band-to band excitation. The following

interpretation of luminescence centres was [12]: for the bands peaking at 2.07 eV, 2.25 eV and 2.69 eV responsible were F_{AA}^+ , F_A^+ and F^+ -centres correspondingly. We assume that the luminescence centres could be similar in cubic and tetragonal phase ZrO₂:Y. On the other hand it was shown that in ZrO₂ nanocrystals the oxygen deficient defects were responsible for the luminescence band at 2.9 eV [9], [15], [17]. Hence, the luminescence band peaking at 2.9 eV could be from F^+ -centres or from Zr-O bond perturbed by oxygen deficient defect [9]. If the F^+ -centres were involved the obtained results then can be explained by a hypothesis as follows. The fraction of oxygen vacancies in the single crystal was associated with one or two yttrium ions, these vacancies has trapped one electron (F_A^+ , F_{AA}^+ -centres). The other fraction of oxygen vacancies was in the regular ZrO₂ environment and has trapped two electrons (F-centre). The excitation with 4.66 eV photons creates F_A^+ and F_{AA}^+ -centres excited states and luminescence bands peaking 2.0–2.25 eV were observed. The F-centres either were not excited by these photons or the excitation did not result in luminescence observable in our experiments. If the band carriers were created then the sequent trapping of hole and electron can create F^+ -centre excited state and luminescence band peaking at 2.9 eV was observed in the single crystal. In the nanocrystals dominant fraction of oxygen vacancies was not associated with yttrium ions, therefore the large number of F^+ -centres was. The 4.66 eV photons excite F^+ -centres and in nanocrystals luminescence at 2.9 eV appear. One could see at the Fig. 1 and Fig. 2 that the nanocrystals luminescence spectrum was wider under electron beam excitation than that under laser beam excitation and spectrum cover the region down to 1.5 eV, thus it is not excluded that a small number of F_A^+ and F_{AA}^+ -centers in nanocrystals were.

It could be noted the luminescence spectra under electron beam excitation were extended to larger photon energy side also, therefore besides F^+ type centers some unidentified centers contributed in luminescence.

Transient absorption was measured only for single crystal under electron beam excitation. The origin of transient absorption is recharging of some defects under electron beam irradiation. Since the absorption decay takes place at RT the recharged defect levels were not deep traps. The transient absorption spectrum is a wide band (Fig. 5) and the induced absorption decay within band was different—low energy side of spectrum decays faster. Hereby absorption spectrum is a result of several bands overlapping. The induced absorption decay is slow (Fig. 6) and at 2.5 eV within $10 \mu\text{s}$ the 30% of initial optical density decays; at 1.3 eV two decay components were and during $10 \mu\text{s}$ the $\sim 80\%$ of initial optical density decays, however after initial $3 \mu\text{s}$ optical density change was very small. The absorption decay is much longer than luminescence decay and the charges released from the slow decaying defects responsible for transient absorption undergoes nonradiative recombination. Hence, this process reduces the number of charges which create the excited states of luminescence centers and luminescence efficiency was reduced also.

IV. CONCLUSION

The luminescence spectrum of ZrO₂:Y was a result of several overlapping bands. The luminescence bands at 2.0 and

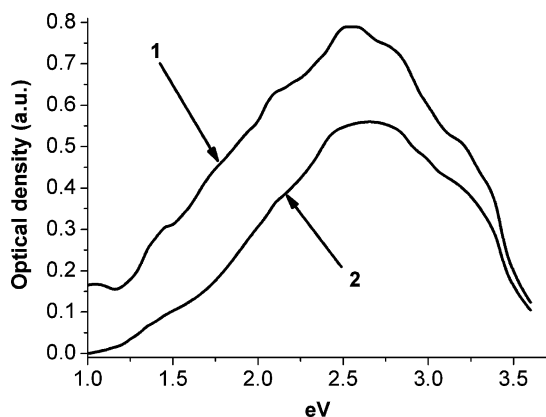


Fig. 5. Transient absorption spectra: 1—under excitation pulse; 2—delay for $10 \mu\text{s}$ relative to excitation pulse end.

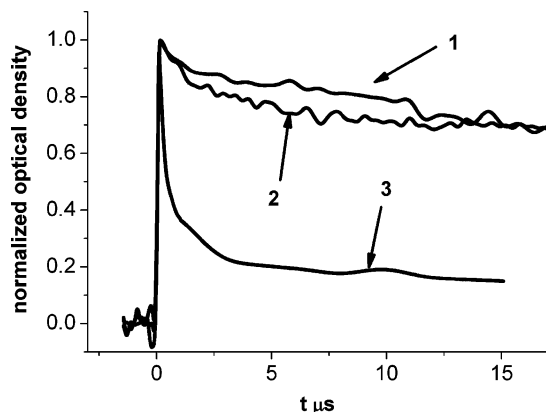


Fig. 6. Transient absorption decay kinetics for: 1— 3.2 eV ; 2— 2.5 eV ; 3— 1.3 eV .

$\sim 2.2 \text{ eV}$ well resolved in the bulk single crystal under 4.67 eV excitation were due to F_{AA}^+ and F_A^+ centers. The luminescence bands peaking at $\sim 2.9 \text{ eV}$ in nanocrystals and bulk single crystal was due to F^+ centers. The centers responsible for main fraction of recombinative luminescence were the same in nanocrystals and bulk single crystal, however the surrounding of these luminescence centers are different in bulk single crystal and nanocrystals. Besides F_{AA}^+ , F_A^+ centers another unidentified luminescence centers contributed in recombinative luminescence.

The number of electrons and holes fills traps responsible for transient absorption. These electrons and holes undergoes non-

radiative recombination and therefore reduce the luminescence yield.

REFERENCES

- [1] H. Zhou, F. Li, B. He, J. Wang, and B. de Sun, "Air plasma sprayed thermal barrier coatings on titanium alloy substrates," *Surface Coatings Technol.*, vol. 201, no. 16–17, pp. 7360–7367, 2007.
- [2] N. Nguyen, "Ceramic fuel cells," *J. Amer. Ceramic Soc.*, vol. 76, no. 3, pp. 563–588, 1993.
- [3] B. C. H. Steele, "Material science and engineering: The enabling technology for the commercialisation of fuel cell systems," *J. Mater. Sci.*, vol. 36, no. 5, pp. 1053–1068, 2001.
- [4] O. L. Figueroa, C. Lee, S. A. Akbar, N. F. Szabo, J. A. Trimboli, P. K. Dutta, N. Savaki, A. A. Soliman, and H. Verweij, "Temperature controlled CO, CO₂, NO_x sensing in diesel engine exhaust stream," *Sensors Actuators B: Chem.*, vol. 117, no. 2, pp. 839–848, 2005.
- [5] A. V. Emeline, G. N. Kuzmin, L. L. Basov, and N. Serpone, "Photoactivity and photoselectivity of a dielectric metal-oxide photocatalyst (ZrO₂) probed by the photoinduced reduction of oxygen and oxidation of hydrogen," *J. Photochem. Photobiol. A: Chem.*, vol. 174, pp. 214–221, 2005.
- [6] M. Kirm, J. Aarik, M. Jurgens, and I. Sildos, "Thin films of HfO₂ and ZrO₂ as potential scintillators," *Nucl. Instrum. Meth. Phys. Res. Sect. A*, vol. 537, no. 1–2, pp. 251–255, 2005.
- [7] Z. Wang, B. Yang, Z. Fu, W. Dong, Y. Yang, and W. Liu, "UV-blue photoluminescence from ZrO₂ nanopowders prepared via glycine nitrate process," *Appl. Phys. A*, vol. 81, pp. 691–694, 2005.
- [8] E. de la Rosa-Cruz, L. A. Diaz-Torres, P. Salas, D. Mendoza, J. M. Hernandez, and V. M. Castano, "Luminescence and thermoluminescence induced by Gamma and UV-irradiation in pure and rare earth doped zirconium oxide," *Opt. Mater.*, vol. 19, pp. 195–199, 2002.
- [9] K. Smits, L. Grigorjeva, W. Lojkowski, and J. D. Fidelus, "Luminescence of oxygen related defects in zirconia nanocrystals," *Physica Status Solidi C*, vol. 4, no. 3, pp. 770–773, 2007.
- [10] P. Li and I. W. Chen, "X-ray absorption studies of zirconia polymorphs. I. Characteristic local structures," *Phys. Rev. B*, vol. 48, no. 14, pp. 10063–10073, 1993.
- [11] V. Ramaswamy, M. Bhagwat, D. Srinivas, and A. V. Ramaswamy, "Structural and spectral features of nano-crystalline copper-stabilized zirconia," *Catalysis Today*, vol. 97, pp. 63–70, 2004.
- [12] N. G. Petrik, D. P. Taylor, and T. M. Orlando, "Laser-stimulated luminescence of yttria-stabilized cubic zirconia crystals," *J. Appl. Phys.*, vol. 85, no. 9, pp. 6770–6776, 1999.
- [13] S. E. Paje and J. Llopis, "Disorder effects on the luminescence decay in yttria-stabilized zirconia polycrystals," *J. Phys. D: Appl. Phys.*, vol. 29, pp. 442–445, 1996.
- [14] K. Hachiya, H. Oku, and J. Kondoh, "Photoluminescence in yttria-stabilized zirconia of aging effects," *Phys. Rev. B*, vol. 71, pp. 064111-1–064111-7, 2005.
- [15] H. Nakajima and T. Mori, "Photoluminescence excitation bands corresponding to defect states due to oxygen vacancies in yttria-stabilized zirconia," *J. Alloys Compounds*, vol. 408–412, pp. 728–731, 2006.
- [16] S. E. Paje and J. Llopis, "Luminescence of polycrystalline cubic and tetragonal yttria-stabilized zirconia," *J. Phys. Chem. Solids*, vol. 55, no. 8, pp. 671–676, 1994.
- [17] J. D. Fidelus, W. Lojkowski, D. Millers, L. Grigorjeva, K. Smits, and R. R. Piticescu, "Zirconia based nanomaterials for oxygen sensors—Generation, characterisation and optical properties," *Solid State Phenomena*, vol. 128, pp. 141–150, 2007.
- [18] N. Nicoloso, A. Lobert, and B. Leibold, "Optical absorption studies of tetragonal and cubic thin film yttria stabilized zirconia," *Sensors Actuators B: Chem.*, vol. 8, no. 3, pp. 253–256, 1992.