COMPARISION OF ZrO$_2$:Y NANOCRYSTALS AND MACROSCOPIC SINGLE CRYSTAL LUMINESCENCE

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Abstract. The luminescence spectra of a tetragonally structured ZrO$_2$:Y single crystal and nanocrystals were compared. It was found that the number of luminescence centers contributed to the spectra. The excitation of luminescence within the band gap region led to different luminescence spectra for the single crystal and nanocrystal samples, whereas recombinative luminescence spectra were the same for both samples. The origin of this difference is that in the nanocrystals, even under excitation within the band gap, charge carriers were created. Zirconium- oxygen complexes distorted by intrinsic defects were proposed to be the luminescence centres responsible for the wide luminescence band observed.

1. Introduction

Zirconia (ZrO$_2$) is a material known to have very wide range of applications, such as in catalysts, high temperature and corrosion resistant coatings, and sensors. Therefore, the material properties, including optical properties, are of high interest. ZrO$_2$ luminescence is known to have been studied for single crystals, ceramics, and micro- and nano- sized crystals. However, the luminescence spectra obtained by different researchers were rather different. The luminescence band within 4.2-4.4 eV was observed at 10K in ZrO$_2$ films [1], and self-trapped excitons were suggested to be responsible for this luminescence. The wide luminescence band peaking at 2.58 eV in undoped ZrO$_2$ was described in [2]. The luminescence centre was assumed to be a Ti^{4+} ion in the Zr^{4+} site with a distorted oxygen surrounding. Three luminescence bands peaking at 2.69, 2.25, and 2.07 eV were detected in yttrium-stabilized cubic structure ZrO$_2$ [3] under laser beam excitation of different wavelengths. The F-centre, F$_A$-centre, and F$_{AA}$-centre were suggested to be responsible for the luminescence bands at 2.69, 2.25, and 2.07 eV, respectively. The decay of yellow-orange luminescence (without more definite band position) in yttrium-stabilized tetragonal and cubic structure polycrystalline ZrO$_2$ was discussed in [4], and it was suggested that some structure disorder could be responsible for the complicated decay kinetics of luminescence. The detailed luminescence centre model was not described; however, it was assumed that some point defects were involved. The Zr^{3+} state was supposed to be involved in the luminescence centre [5]. It will be pointed out that the Zr^{3+} in ZrO$_2$ was detected by ESR [6]. However, it was noted that Zr^{3+} could be found mainly on the crystal surface. One can conclude from the aforementioned that the luminescence described in [1] could be intrinsic, from relaxed excitons, whereas intrinsic defects as well as unexpected impurities would be responsible for the luminescence described in the majority of papers. Details of the ZrO$_2$:Y luminescence were described poorly. Moreover, to our knowledge, the luminescence of a macroscopic single crystal had never been

compared in the literature with that of nanocrystals. The purpose of the present paper is to make such a comparison.

2. Experimental

2.1. Samples

The tetragonal structure ZrO_2:Y sample was a plate 10x10x1 mm obtained from Alfa Aesar. The ZrO_2:Y nanocrystals (nanopowders) were prepared by microwave driven hydrothermal synthesis described elsewhere [7]. The concentration of Y was 6 mol%, and XRD data shows that the nanocrystals had a tetragonal structure. The sizes of the nanocrystal grains were between 13 nm and 24 nm. The ZrO_2:Y nanopowder was slightly pressed into a small stainless – steel cell to perform the luminescence measurements.

2.2. Luminescence measurements

Four different excitation sources were used: (I) a diode pumped YAG laser fourth harmonic (4.66 eV, pulse length 8 ns); (II) a nitrogen laser (3.67 eV, pulse length 8 ns); (III) a deuterium lamp (DDS-400, 400W); (IV) a pulsed electron accelerator (270 keV, 10^{12}el/cm^2, pulse length 10 ns). When the deuterium lamp was used, the excitation light was selected by a SPM-1 monochromator with fused quartz optics. Two kinds of luminescence registration were possible. Registration of luminescence under photon excitation was prepared by a photon counting system (Hamamatsu H8259 and H8259-02 photon counting heads and PC compatible FAST ComTec P7888-1E multiscaler). The time resolution of the luminescence registration channel was 2 ns. The luminescence under pulsed electron beam irradiation was detected by a PMT and the signal was displayed on a digital storage oscilloscope TDS 5052 (TEKTRONIX). In this case the time resolution was limited by the PMT and was 12 ns. The monochromator MDR-2 was used to record the luminescence spectra. During the luminescence measurements the sample was kept under vacuum on the cold finger of a cryostat. The cryostat had a heater; the temperature was controlled by a thermocouple. Luminescence measurements at temperature between 85 K and 350 K were possible. The accuracy of the temperature measurements was approximately $\pm$ 1 K.

Results and discussion

The luminescence spectra of tetragonal structure the ZrO_2:Y single crystal and the nanocrystals are shown in Fig.1. The luminescence was excited by a 4,66 eV laser beam at room temperature (RT).
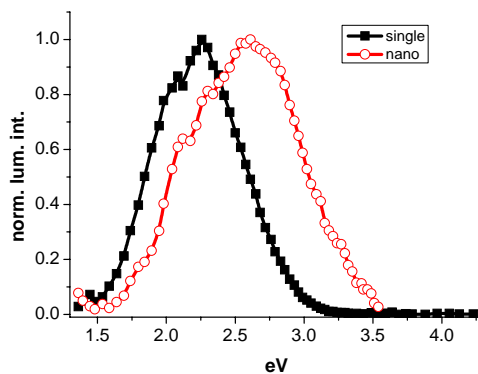

Figure 1. Normalized luminescence spectra of ZrO_2:Y single crystal (filled symbols) and nanocrystals (open symbols). Single crystal luminescence shows bands at 2.1 eV and 2.25 eV. These bands can be resolved in the nanocrystal spectrum also.

Since the band gap of tetragonal ZrO_2 is expected to be above 5 eV [8, 9 and references therein] the luminescence observed was from defects. A number of undoped ZrO_2:Y nanocrystalline samples were studied and all of them reveal the same luminescence. Thus, it is supposed that the luminescence is

related to intrinsic defects in ZrO_2:Y. One can see that there are two shoulders at 2.10 and 2.25 eV at low energy side of nanocrystals luminescence spectrum. The position of first shoulder matches well with the position of corresponding shoulder in the spectrum of single crystal; the position of second shoulder corresponds to the peak position of the luminescence band of the single crystal. Hence, the same luminescence centres were responsible for the luminescence of the single crystal and the nanocrystals between ~1.5 eV and 2.5 eV. However, the main peak position of nanocrystal luminescence is shifted to the high energy side of the spectrum (~ 2.7 eV). This shift indicates that more of luminescence centres were involved in the nanocrystals than in the single crystal. The peak positions of the nanocrystal luminescence spectrum coincide with those observed and described in [4, 10]. The luminescence of nanocrystals between 2.5 and 3.5 eV is also defect related. There could be similar luminescence centres possible in single crystals is discussed bellow, together with results obtained under electron beam excitation. The shapes of the luminescence spectra (bandwidth, shoulders) suggested that a number of bands overlap. Thus, excitation with photons of different energy could change the luminescence spectrum. We used 4.66 eV and 3.67 eV photons for luminescence excitation. The single crystal luminescence (Fig. 2) shows that the relative intensities of overlapping bands changes, and for excitation with lower energy photons, the lower energy luminescence band became dominant. Possibly, only two luminescence bands overlap. The change in the nanocrystal luminescence spectrum was somewhat similar (Fig. 3) – the luminescence peaks at lower energy if excited by a lower energy photon. However, the spectral region covered is
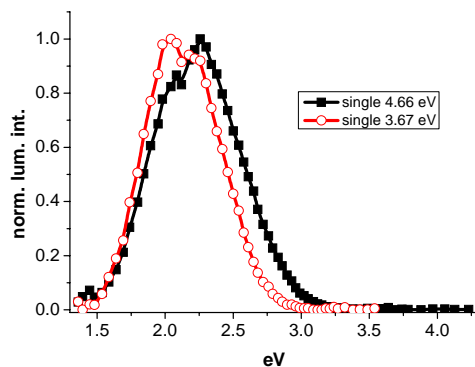

Figure 2. Normalized luminescence spectra under different energy (4.66eV and 3.67eV) excitation for ZrO_2:Y single crystal
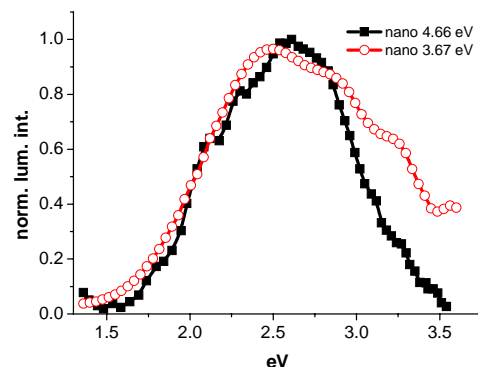
Figure 3. Normalized luminescence spectra for nanocrystals. The position of main peak in the spectrum depends on excitation photon energy.

wider, and the relative contribution of luminescence between 3.0 eV and 3.5 eV is larger for the case of 3.67 eV excitation than for excitation at 4.66 eV. One can conclude that the spectrum of nanocrystal luminescence observed under excitation within the band gap region results from the overlapping of a larger number of bands than in the case of single crystal. The luminescence of undoped nanocrystals was studied for excitation at different photon energies with a deuterium lamp as a UV source and a monochromator to select the exciting wavelength. The other monochromator was used to measure the luminescence spectra. The luminescence spectra obtained covered a wide region that ranged from 1.7 eV to 3.3 eV. Possibly, this band has some poorly resolved structure; however each spectrum has a main peak, which corresponds to the position of maximum –luminescence (Fig.4). The dependence of the position of the luminescence peak on the exciting photon energy was linear (Fig.5). It follows from this dependence that the Stokes shift change follows a similar linear dependence for luminescence centres excited in the region from 3.0 eV to 4.0 eV. The shift of the main luminescence peak is continuous and did not show well resolved discrete bands. However, the structure of the spectrum in Fig.1 showed that there were discrete bands. The luminescence spectrum of nanocrystals seems to be the superposition of a wide unstructured or very weakly structured band and some

narrower discrete bands. The origin of this wide luminescence band could be a large number of slightly different centres. It is doubtful that the electronic transitions in discrete
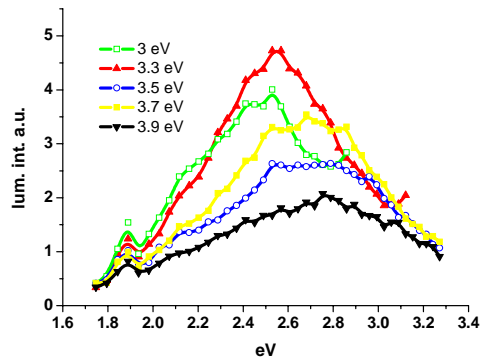

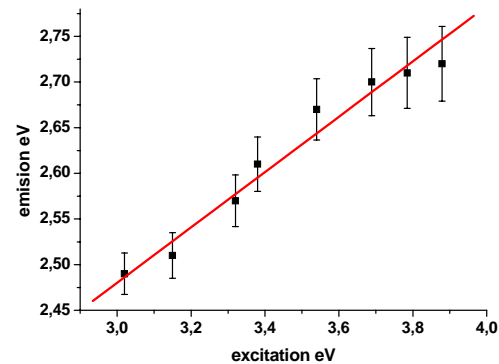**Figure 4.** The luminescence spectra of nanocrystals under excitation by photons of different energy

Figure 5. The dependence of the peak position on the excitation photon energy.

point defects, e.g. Zr^{3+} and/or defects containing vacancies, could produce such a continuous shift of the luminescence peak position as a function of excitation photon energy. The extrapolation of the straight line in Fig. 5 to an emission of 4.2 eV yields an excitation energy of 5.8 eV, which is close to the excitation energy of excitons [1]. The centres responsible for this wide luminescence band are suggested to be distorted zirconium-oxygen (Zr –O) complexes. The distortion of these complexes can vary slightly with position and with distance relative to the intrinsic defect (e.g., oxygen vacancy). This variation in distortion causes the surrounding of centres to relax differently, and, as a result, a continuous spectrum shift as well as a change of Stokes shift was observed. We emphasize that the Zr-O complex can be a luminescence centre, since self – trapped exciton luminescence was observed [1], and a self – trapped exciton is an electronic excitation trapped in the regular lattice.

   The excitation of luminescence by photons within the band gap is selective: only a fraction of all possible kinds of luminescence centres was excited. Band–to–band excitation led to recombination and more, possibly all, kinds of luminescence centres could be involved. We used electron beam irradiation for band-to-band excitation. In a number of oxides it is possible to create new lattice defects by means of direct collisions. In oxides this defect creation is common if the electron energy exceeds 300 kV. Thus it was expected the the 270 kV electrons do not have sufficient energy to create defects in ZrO_2:Y and that the irradiation would result in the creation of band carriers. The ZrO_2:Y luminescence spectra (Fig.6) under electron beam irradiation were very similar for the single crystal and for the nanocrystals. Thus, the radiative recombination (luminescence) centres were the same in both kinds of samples - single crystal and nanocrystals. Therefore, the luminescence from distorted Zr-O complexes is possible in the single crystals also. Luminescence decay kinetics over the spectrum were slightly different (Fig.7), which confirms that, in the case of recombinative luminescence, luminescence bands also overlap. The luminescence decay kinetics did not obey a simple exponential law, and they were different for the single crystal and for the nanocrystals. Another important feature is that the luminescence spectrum is wider under band-to-band excitation than under excitation by photons with energies within the band gap region (Fig.1 and Fig.6). The reason for this difference is that, under selective excitation with photons from the band gap region, only a fraction of all kinds of luminescence centres was excited. We point out that the well resolved luminescence bands (2.10 and 2.25 eV, Fig.1 and Fig. 2) observed in the single crystal under laser beam excitation can be related to discrete defects: either to electron transitions in defects or to transitions in the Zr-O complex which contains the defect.

The luminescence spectra of nanocrystals under excitation by 4.66 eV photons and band-to-band excitation were very similar (compare spectrum depicted in Fig.1. with that in Fig.6.), whereas for the single crystal there were significant differences. The similarity of the nanocrystal luminescence spectra under both kinds of excitation suggested that in nanocrystals band carriers were created under both kinds of excitation. The creation of band carriers is possible if, when nanocrystals are irradiated with photons from the band gap region, at least two processes take place:
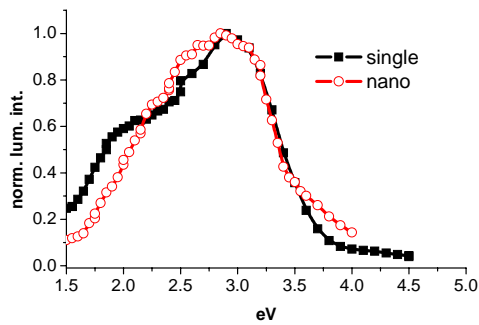

Figure 6. Normalized luminescence spectra of ZrO_2:Y under electron beam irradiation. The spectrum of the single crystal is similar to that of nanocrystals.
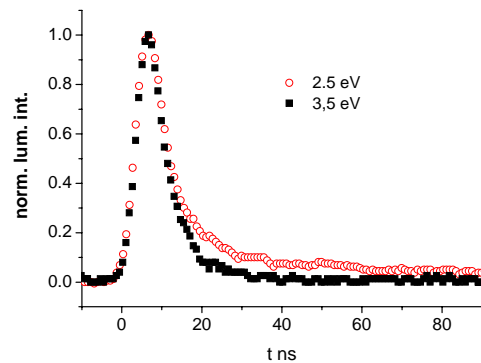

Figure 7. The decay kinetics of the single crystal at different spectral positions.

(I) the direct excitation of luminescence centres and (II) the ionization of some defects. The ionization of defects by UV light in the previously irradiated single crystal was observed by C.B. Azoni and A. Paleari [11], and it was concluded that holes and electrons were created. The ionization of defects in nanocrystals led to the appearance of recombination luminescence in our experiments. A corresponding ionization of defects in the single crystal did not take place, obviously because of the absence of the same charged defects that were responsible for ionization process in the nanocrystals.
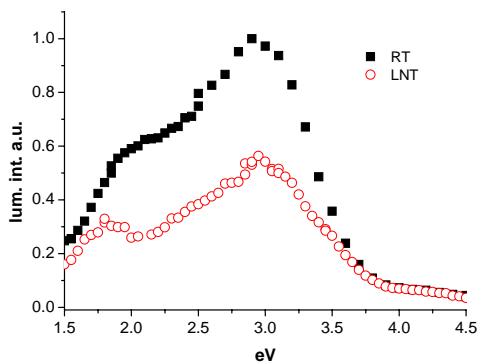

Figure 8. Luminescence spectra of ZrO_2:Y single crystal at RT and 85K under e-beam irradiation; at low temperature the recombinative luminescence intensity was suppressed.
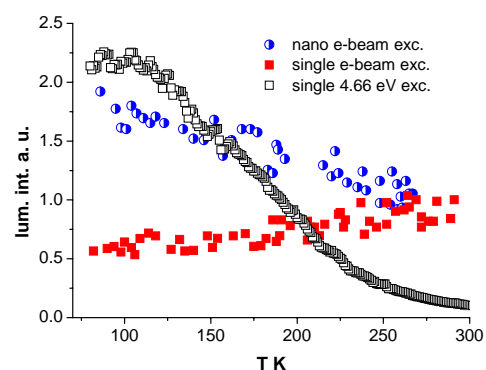

Figure 9. Luminescence intensity dependence on temperature: filled squares and half-filled circles - single crystal and nanocrystals, respectively under electron beam irradiation; open squares - single crystal under 4.66 eV laser beam excitation.

This is the reason why the luminescence spectra of the single crystal and of the nanocrystals under laser beam excitation (Fig.1) were different. Additional evidence that some defects in the single crystal and in the nanocrystal differed was obtained from the dependence of the luminescence intensity on temperature. The recombinative luminescence intensity for the single crystal at 85 K was a factor of two less than at room temperature (RT) over the entire spectrum (Fig. 8), whereas for nanocrystals the lowering of temperature causes a slight increase of the luminescence intensity. In Fig. 9 the dependence of luminescence intensity on temperature is depicted for two kinds of excitation. The decrease of the recombinative luminescence intensity and the increase of photoluminescence intensity in the single crystal when temperature decreases is strong evidence that some defects act as shallow traps in the single crystal. These defects did not act as luminescence centres, since the spectra at RT and 85 K in the case of the single crystal were similar. The dependence of the luminescence intensity of the nanocrystals on temperature showed that there were no defects acting as shallow traps, since the intensity of luminescence was not reduced at 85 K (Fig. 9).

3. Conclusions

The luminescence spectrum of ZrO_2:Y contains a wide band from 1.5 eV to 3.5 eV, and some narrower bands that can be observed on the background of this wide band. The wide luminescence band is caused distorted Zr-O complexes; the variety of these complexes is due to their different positions relative to intrinsic defects. The narrow luminescence bands at 2.10 and 2.25 eV are due to electron transitions in intrinsic defects or Zr-O complexes that contain an intrinsic defect. The centers of recombinative luminescence are the same in the single ZrO_2:Y crystal and in the nanocrystals. The ZrO_2:Y single crystals contain defects which act as shallow traps for charge carriers.

4. References

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