

Luminescence of oxygen related defects in zirconia nanocrystals

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1 Introduction The three polymorphs of zirconia (ZrO_2) are known—monoclinic, tetragonal and cubic. Only the monoclinic phase of pure ZrO_2 crystals is stable at room temperature [1], the tetragonal and cubic phase crystals need the admixture of stabilizer. The stabilized ZrO_2 contains oxygen vacancies and the luminescence due to oxygen vacancies in stabilized tetragonal ZrO_2 was investigated [2]. However the tetragonal phase ZrO_2 nanocrystals with size below 30 nm are stable at room temperature [3] without any admixture. Therefore the study of luminescence from pure tetragonal phase ZrO_2 nanocrystals is possible. Since the tetragonal phase of ZrO_2 is controlled by oxygen vacancies [4], the oxygen related defects contribution in luminescence could be highlighted. The luminescence band peaking at 4.2–4.4 eV was observed in ZrO_2 films at 10 K [5]. This luminescence was suggested to be intrinsic from self-trapped excitons. A number of luminescence bands were observed at room temperature [6] in the yttrium stabilized cubic phase ZrO_2 . The origin of luminescence bands observed at 2.69, 2.25 and 2.07 eV was suggested to be defects - F-centre, F_A -centre and F_{AA} -centre [7]. The luminescence band at 2.58 eV was observed in undoped ZrO_2 [7], however the unexpected impurity - Ti^{4+} ion substituting for Zr^{4+} is suggested to be responsible for this luminescence. The yellow-orange luminescence was observed in yttrium stabilized tetragonal structure ZrO_2 [8], the band position of this luminescence was not mentioned. The possible role of Zr^{3+} in the luminescence was discussed in [9]. Hence, mainly the three kinds of luminescence were described: (I) intrinsic from self-trapped excitons; (II) from intrinsic defects (F-centres, Zr^{3+}) and (III) from unexpected impurity (Ti^{3+}). It could be underlined the luminescence from doped ZrO_2 was known and described also. The present study is devoted to the investigation of luminescence from undoped, oxygen deficient tetragonal phase ZrO_2 nanocrystals.

2 Experimental The ZrO_2 nanocrystals were obtained in microwave assisted hydrothermal process ascribed in [10]. Structure of nanocrystals was determined by XRD and a result shown that tetragonal phase ZrO_2 is dominant. The nanocrystals were annealed at 340 °C in oxygen–nitrogen gases mixtures, the total pressure was 1000 mbar. The oxygen partial pressure was variable from 2.1 mbar up to 23.4 mbar, the rest in all cases was nitrogen, in the text the volume % of oxygen is used also. The luminescence excitation spectra were measured using deuterium light source and two monochromators—one for excitation selection, other for luminescence spectra registration. Thus the registration of

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excitation spectrum for selected luminescence wavelength as well as registration of luminescence spectrum for selected excitation wavelength was possible. The time-resolved luminescence was measured under pulsed electron beam excitation (energy of electrons ~ 270 keV, pulse duration 10 ns) using grating monochromator (MDR 2), photomultiplier tube and digital storage oscilloscope (TEKTRONIX TDS5052), time resolution of registration ~ 12 ns. Other source for luminescence excitation was pulsed laser beam (4.66 eV, pulse duration 10 ns). The luminescence registration was conducted via monochromator using the Hamamatsu photon counting head connected to the computer controlled counter, time resolution of registration 2 ns.

3 Results and discussion The luminescence spectrum at room temperature (RT) under electron beam excitation had shown two overlapping bands – one peaking at 2.2–2.4 eV and other peaking at ~ 2.8 –2.9 eV (Fig. 1). The separation of bands was possible due to different decay time. The additional luminescence band peaking at 4.2 eV (Fig. 1) was observed at liquid nitrogen temperature (LNT).

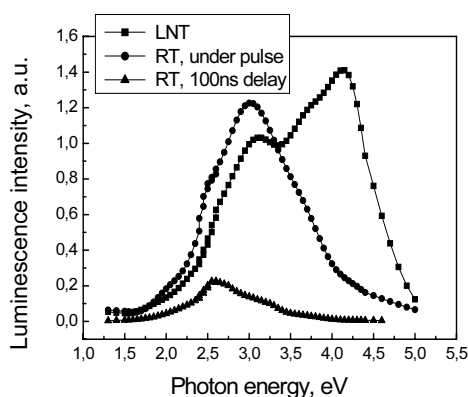


Fig. 1 Pulsed electron beam excited luminescence spectra, decay rate of overlapping bands was different.

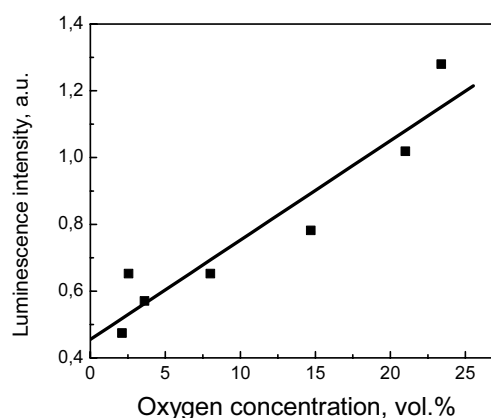


Fig. 2 Recombinative luminescence at 2.9 eV dependence on oxygen concentration.

This band was due to self-trapped excitons [5] and its appearance gives an evidence that the total amount of defects and unexpected impurities was not large. The excitation of luminescence at 2.2 eV and 2.8 eV within band gap is possible, the intensity of this luminescence was strongly suppressed in doped nanocrystals, therefore intrinsic defects were suggested to be responsible for this luminescence. The similar luminescence bands were observed by Nakajama and Mori [2] in yttrium stabilized zirconia. The luminescence spectra of nanocrystals annealed at different partial pressure of oxygen were measured at RT as well as at LNT. The shape of these spectra is similar to that shown in Fig. 1, however the relative intensities of the bands were different. The luminescence intensity dependence on oxygen partial pressure during the annealing is similar at RT and LNT. Two luminescence bands are sensitive to the oxygen content – the band peaking at 2.8 eV and the band at 4.25 eV, both bands were suppressed in oxygen deficient nanocrystals. The dependence of 2.8–2.9 eV luminescence band intensity on oxygen partial pressure during annealing is shown in Fig. 2. Note, the luminescence intensity was suppressed in nanocrystals annealed at lower partial pressures of oxygen. The intensity of this luminescence band was strongly reduced if nanocrystals were heated in vacuum. Subsequent heating of these nanocrystals in air restores the intensity of luminescence band at 2.8–2.9 eV. Therefore it was drawn out the center responsible for luminescence at 2.8–2.9 eV contains oxygen. So, the luminescence center is oxygen containing defect and it was suggested this defect is distorted (possibly strained) Zr–O bond.

The detailed study shown the luminescence excited within band-gap (photoluminescence) had a spectrum (Fig. 3) different from that obtained under electron beam excitation – a wide luminescence band

appears. Moreover – the position of photoluminescence band depends on excitation photon energy and this dependence is close to the linear (Fig. 4).

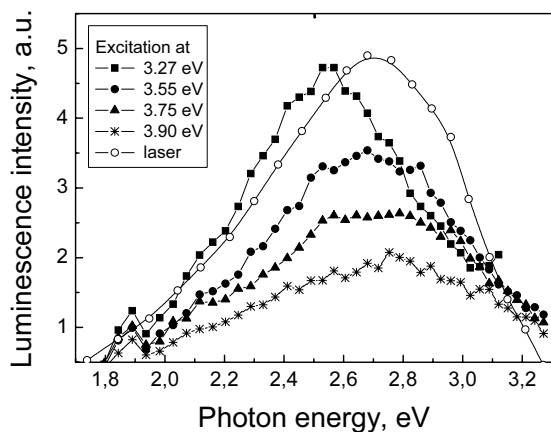


Fig. 3 Photoluminescence spectra at different excitation energy and laser (4.66 eV) excited luminescence. The excitation by laser is more intense than that by deuterium lamp, therefore the luminescence intensity is high.

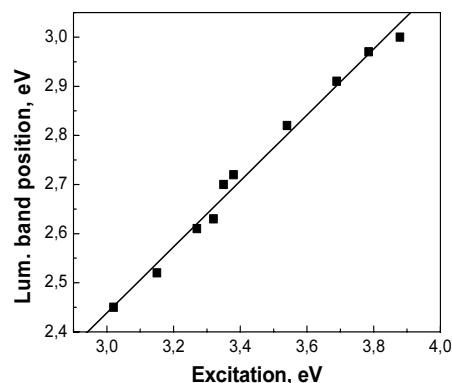


Fig. 4 Photoluminescence band position dependence on excitation.

This result clearly indicates the numbers of slightly different defects contribute in photoluminescence and the band observed is superposition from a number of overlapping bands. The low intensity band peaking at ~ 1.85 eV appears in all photoluminescence spectra and this band seems to be due to trace of Hf, which was observed in the raw material also. The luminescence spectrum excited by laser beam pulse (4.66 eV) contain well resolved band peaking at ~ 2.8 eV. This luminescence band is narrower, than those in Fig. 1, excited by pulsed electron beam, possibly due to that narrow excitation line from laser excited only some kinds of defects, whereas the pulsed electron beam creates band carriers that can be trapped at all kinds of defects and therefore the luminescence spectrum is wider. The intensity of this luminescence band depends on oxygen partial pressure during annealing also but this dependence was opposite to that observed under electron beam excitation. The intensity of this photoluminescence was higher for nanocrystals annealed at lower partial pressure of oxygen (Fig. 5).

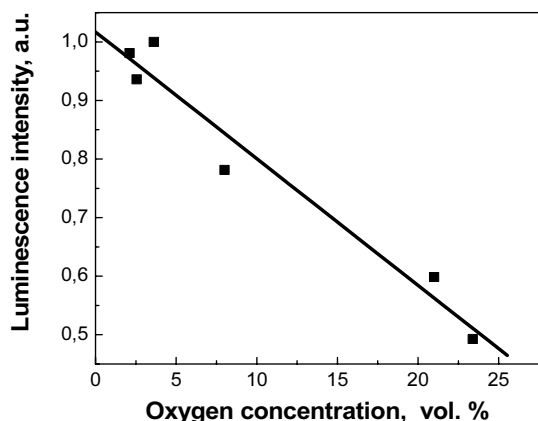


Fig. 5 Photoluminescence intensity dependence on oxygen concentration.

The difference between electron beam excited luminescence and photoluminescence dependence on oxygen partial pressure during nanocrystals annealing arises from different excitation processes.

The electron beam creates band carriers—electrons and holes. These carriers undergo the mutual recombination at recombination center. The recombination center as it is shown above is somewhat distorted oxygen bond. During the nanocrystal annealing in oxygen deficient gases mixture these distorted oxygen bonds were broken and oxygen was released from nanocrystal, thus the number of recombination centers was reduced and intensity of corresponding luminescence was suppressed. The release of oxygen from nanocrystal led to the increase of oxygen deficiency defects (e.g. oxygen vacancies) content in nanocrystal. Since the photo-luminescence excitation within band-gap occurs, the direct excitation of oxygen deficient defect takes place, not the creation of free electrons and holes. Therefore the nanocrystals containing larger concentration of oxygen deficient defects showed more intense luminescence.

4 Conclusions The intrinsic defects were responsible for undoped ZrO_2 nanocrystal luminescence within 2.0–3.2 eV range. The distorted ZrO_2 bond was the main recombination center for band carriers. A number of slightly different defects were involved in photo-luminescence. The 4.66 eV photons excited some oxygen deficient defect and corresponding luminescence band peaks at ~3.0 eV.

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