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Intrinsic defect related luminescence in ZrO₂

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A R T I C L E I N F O

A B S T R A C T

The studies of ZrO₂ and yttrium stabilized ZrO₂ 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 ZrO₂ 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 ZrO₂, deep traps for electrons and holes exist. The oxygen vacancies are proposed to be the traps for electrons.

1. Introduction

Zirconia (ZrO₂) 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 ZrO₂ 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 ZrO₂ 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, Zr³⁺-centers (T-centers) and various combinations of F_A-centers in yttrium stabilized ZrO₂ (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 ZrO₂ 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 ZrO₂ 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 (ZrO₂ 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 (Y₂O₃ content 6 mol%) were obtained by the HT method.

As it is not possible to obtain undoped ZrO₂ single crystals, a ZrO₂:Y (Y₂O₃ 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 ZrO_2 nanocrystals and check the influence of the stabilizer on the luminescence.

The nanocrystal structure was checked by XRD. The undoped 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 ∼30 nm and for the ones synthesized by the PS method, ∼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 ZrO_2 luminescence an additional set of samples was prepared. The undoped 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 °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^2 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 of.

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

3. Results and discussion

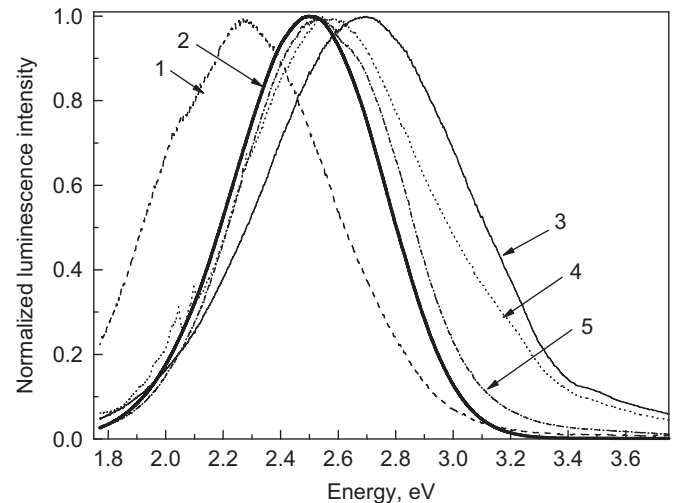The experiments were started with luminescence spectra recording for all the samples under excitation within band gap;

Fig. 1. Luminescence of Y stabilized zirconia single crystal (1); 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 singe crystal peaks in the low energy side of region whereas luminescence band for YSZ nanocrystals peaks in the high energy side. The undoped 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 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 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 ZrO_2 intrinsic defects, since no difference between yttrium stabilized and pure ZrO_2 samples was observed. Comparison of the radioluminescence and photoluminescence led to the hypothesis that: (I) different kinds of defects are possible in 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
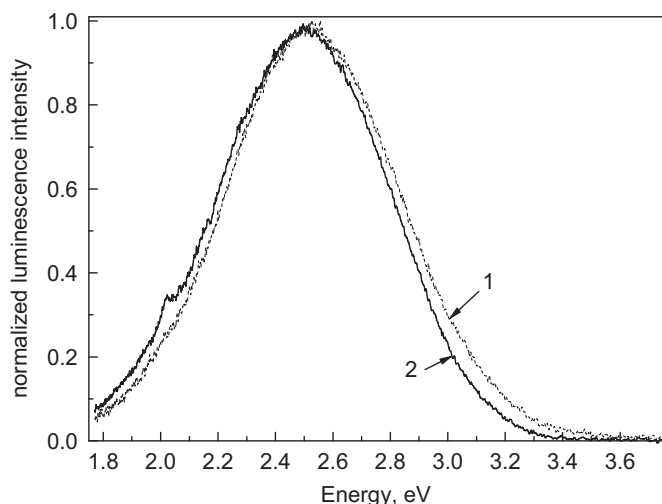
Fig. 2. Luminescence spectra for pure ZrO_2 nanocrystals (1) and Y stabilized single crystal (2) under X-ray excitation (the X-ray excited luminescence was similar for all the samples).
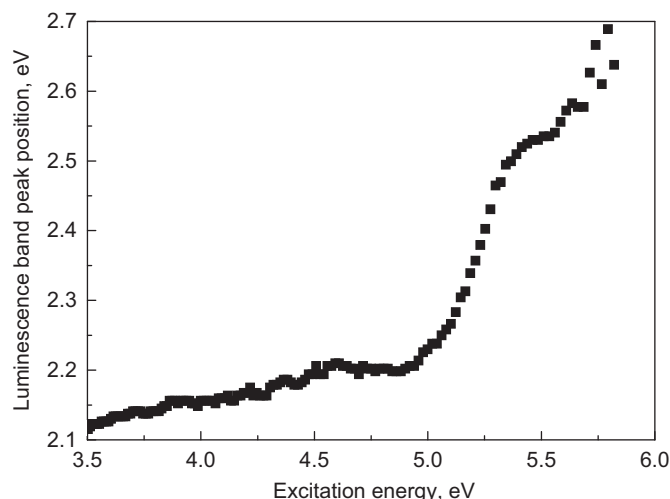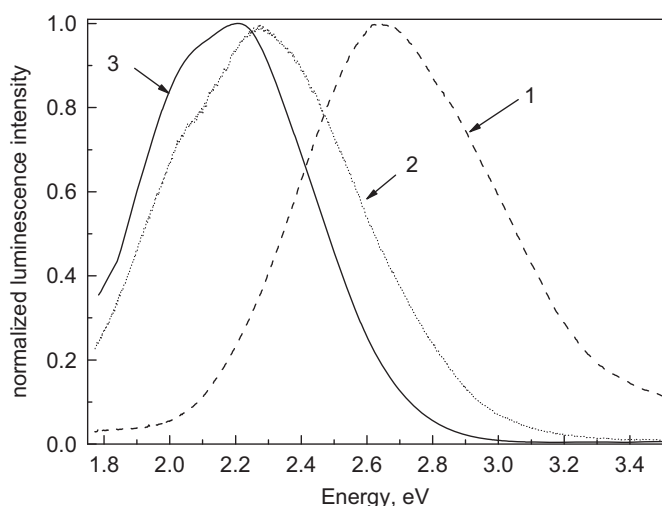

Fig. 3. Luminescence spectra of Y stabilized ZrO_2 single crystal under 6.42 eV excitation (1), 4.66 eV excitation (2) and 3.67 eV (3) excitation.

excitation. The result for YSZ single crystal is shown in Fig. 3. The three well resolved luminescence bands were observed and the luminescence band peak position energy sequence in the spectrum follows that of excitation photons: the lower the excitation photon energy, the lower the energy of the luminescence band peak position.

Therefore even in YSZ single crystal there are several kinds of different defects (at least four), which are responsible for the observed luminescence. A similar effect of the luminescence band position dependence on the excitation photon energy was also observed for nanocrystals [18], although the luminescence band positions and band separation differ for nanocrystals and YSZ single crystal. These results suggested that possibly a set of slightly different defects would be responsible for ZrO_2 luminescence. An experiment was carried out to check this proposition. The laser supplied with OPO was used as the excitation source. The excitation photon energy was from 5.82 eV (213 nm) to 3.5 eV (354 nm) with the step of 1 nm and the luminescence spectrum was recorded at each excitation step. Thus a family of luminescence spectra was obtained and the maximum position for each spectrum was determined. This data was used for

Fig. 4. Luminescence band positions dependence on the excitation energy.

building up the luminescence band position dependence on the excitation photon energy. The result for YSZ single crystal is shown in Fig. 4. This dependence shows two regions: one below 5 eV, other above 5 eV.

The luminescence band position depends slightly on the excitation energy within 3.5 and 5 eV, whereas the dependence above 5 eV is more explicit. We surmise the first region is due to direct excitation of defects (luminescence centers); the second one seems to be due to defect interaction with excitons and a transfer process might be involved. However clearing up the mechanism of the second region needs further study. This dependence of the luminescence band position on excitation photon energy strongly shows that there is a set of defects responsible for the luminescence and the energy levels of these defects form a quasi-continuum in ZrO_2 band gap. Similar quasi-continuum of defects energy states was found in ZrO_2 nanocrystals [18]; however in this case we did not have the possibility to cover the excitation range above 3.9 eV. The quasi-continuum of defect energy states seems to be the reason why different positions and numbers of luminescence bands can be found in literature. These defects could be lattice cells distorted by oxygen vacancy, because there is a quasi-continuum of defect energy states due to the different distances to oxygen vacancy. The luminescence of the undoped nanocrystalline ZrO_2 samples annealed at different oxygen partial pressures was studied for clearing up the oxygen vacancy role. It was found that the luminescence intensity under excitation within the band gap increases for ZrO_2 nanocrystals annealed at low oxygen partial pressure (oxygen deficient samples) whereas under band-to-band excitation, luminescence intensity of the same samples decreases. The effect depends on the partial pressure of oxygen during annealing of ZrO_2 nanocrystals—the lesser the partial pressure, the higher the luminescence intensity under excitation within the band gap (Fig. 5).

This is a strong evidence that the intrinsic defects responsible for the luminescence are oxygen vacancy related; however most of these defects were not oxygen vacancies themselves, since oxygen deficient samples showed reduced luminescence intensity under band-to-band excitation. On the other hand the F^+- as well as F-centers cannot have quasi-continuum of energy levels. The reason for the luminescence intensity reduction in oxygen deficient samples under band-to-band excitation is an additional channel for recombination—the band carriers trapping at deep traps followed by non-radiative recombination. Theoretical estimations show that oxygen vacancy is a deep trap for electrons
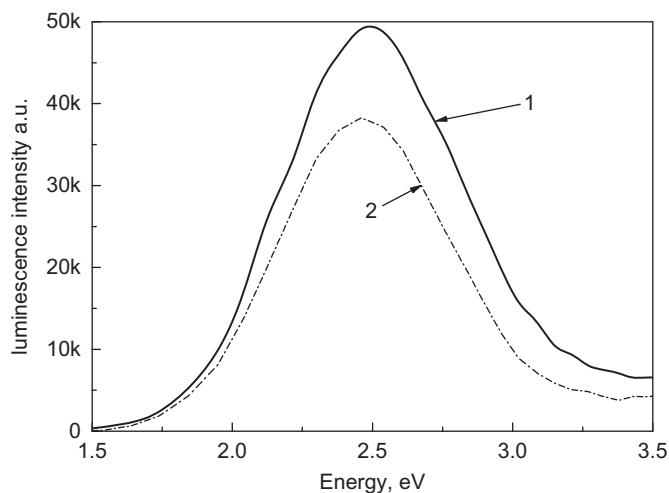
Fig. 5. Photoluminescence dependence on oxygen treatment: (1) 2% O_2 content in gas mixture and (2) 21% O_2 content in gas mixture.

Fig. 7. Luminescence decay and induced absorption relaxation kinetics.

luminescence centers. Since the decay of the transient absorption is not followed by luminescence it is suggested that this absorption is a competitive channel for the luminescence. The relatively slow decay of the transient absorption at RT indicates that the charge was trapped in the deep trap. The simplest origin of the transient absorption decay is thermostimulated release of the charge from the trap followed by its migration and recombination with opposite sign trapped charge. In this case both – the electrons and holes – must be localized in deep traps. These deep traps for the electrons can be oxygen vacancies; this proposition is supported by the fact that luminescence intensity under band-to-band excitation was suppressed in oxygen deficient ZrO_2 nanocrystals containing larger concentration of oxygen vacancies, which serve as electron traps.

The trap for the holes is not clear; however the valence band top is formed from the oxygen 2p states [23] and theoretical calculation and some experiments showed the holes localized on oxygen [19,24,25]. Since the STE was observed [6] the self-trapped hole could also exist and a configuration similar to the self-trapped hole localized at some defect could be a hole center participating in non-radiative recombination. The details of this relatively slow (in the microseconds range) non-radiative recombination as well as the nature of the hole centers require further studies.
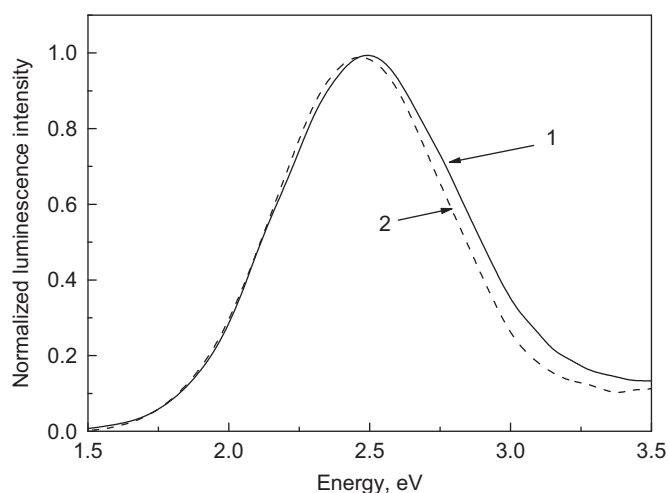

Fig. 6. Normalized photoluminescence dependence on oxygen treatment: (1) 2% O_2 in gas mixture and (2) 21% O_2 in gas mixture.

[19–21]; therefore the luminescence intensity reduction can be due to the electron trapping at oxygen vacancies. The luminescence spectrum of oxygen deficient ZrO_2 samples slightly differs from this for the sample annealed in oxygen–nitrogen mixture containing 21 vol% oxygen (artificial air). The luminescence spectrum of oxygen deficient sample is wider and slightly shifted to higher energy (Fig. 6); this indicates that in these samples more defects are responsible for the luminescence at higher photon energies. Hence the annealing of the sample in oxygen–nitrogen mixtures changes defect concentrations and this concentration change was not evenly shared over all kinds of defects.

The induced absorption in YSZ single crystal under pulsed electron beam irradiation showed a strong and wide transient absorption band peaking at ~2.6 eV [22]. In the present study under pulsed electron beam the transient absorption spectrum and luminescence decay kinetics were studied for YSZ single crystal. Since the energy of electrons was below the threshold for new defect creation only recharging of the existing defects must be responsible for the appearance of transient absorption. The transient absorption decay is relative slow—no more than 20% from initial optical density decays within 2 μs, whereas most of the luminescence decays (> 97%) during the first 100 ns (Fig. 7).

This difference in the decay times is a strong evidence that the centers responsible for the transient absorption are not
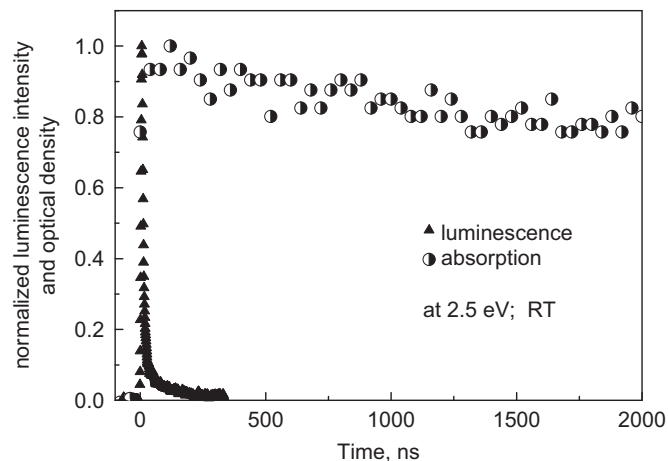
4. Conclusions

The centers responsible for YSZ as well as undoped ZrO_2 luminescence at RT are intrinsic defects, possibly the oxygen vacancy distorted ZrO_2 lattice cells.

Since the distortion of lattice by oxygen vacancy is distance dependent the distorted lattice cells could be responsible for quasi-continuum of states in ZrO_2 band gap. The distorted lattice cells can be represented as the ZrO_2 intrinsic defects and these defects were similar in undoped ZrO_2 nanocrystals, YSZ nano-crystals and YSZ single crystals; however the relative contribution of different defects differs.

Only a fraction of electrons and holes created by band-to-band excitation undergoes radiative recombination at distorted lattice sites; the other fraction was trapped and gave rise to transient absorption. The slow decay of transient absorption at RT was due to the trapping of both – electrons and holes – at relatively deep traps. The oxygen vacancies in ZrO_2 are deep traps for electrons; the nature of traps for holes is not clear. The centers responsible for the luminescence and transient absorption were not the same.

The luminescence spectrum as well as band position strongly depends on the excitation wavelength due to the quasi-continuum of states.

Acknowledgements

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