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LUMINESCENCE OF ZIRCONIA NANOCRYSTALS

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Luminescence of Zirconia Nanocrystals

(Abstract)

Zirconia (ZrO_2) has a number of unique properties; therefore, it is widely used in industry. Information about luminescence and the explanations of its origin as described in scientific papers are unclear and even contradictory.

A study of time-resolved luminescence of zirconia was carried out. It was found that excitation of the intrinsic defect luminescence band is possible within band gap and also in band - to - band region. The continuous shift of luminescence band position on excitation photon energy was observed. This effect was thought to be due to the quasi-continuous energy spectrum in band gap. Transient absorption measurements for ZrO_2:Y_2O_3 single crystals were carried out for first time.

The Eu^{3+} luminescence spectral dependence on activators concentration in ZrO_2 nanocrystlas was shown. It was found that with an increase of Eu concentration the phase transition occurs and tetragonal and even cubic phase is stabilized.

These new findings about zirconia nanocrystal luminescence properties provide additional information about physical processes in zirconia. This knowledge should be used in further studies for material applications in oxygen sensors.

Table of Contents

1. Introduction

ZrO_2 (Zirconia) is a wide band gap crystal (~5eV) with many practical applications in: jewelry, fuel cells, oxygen sensors, semiconductors, optics, metallurgy, ceramics and catalysts. The defect luminescence of ZrO_2 has been studied by a number of researchers; however, the research has been done along narrow, specific lines without an overview about the related physical processes.

ZrO_2 has been widely studied, but the research mostly covers a relatively limited sphere not considering the interaction of the physical processes. For example, many research papers have been published on the optical properties of ZrO_2, but the data and the explanations of the physical processes vary, sometimes being even contradictory. These uncertainties in the sources of scientific literature show that there are multiple unsolved questions; this provides strong motivation for doing corresponding scientific research to find an explanation for the physical processes that occur in the material.

The previously mentioned wide usage of ZrO_2 is possible because of the unique properties of the material – good ionic conductivity, low thermal conductivity, high melting temperature, chemically inert and consistent against ionizing radiation, very hard and bears a large index of refraction. Both the wide range of application possibilities and the optical properties of the material have made ZrO_2 an interesting material for wider research.

The most appropriate materials for the application of their luminescent properties are transparent materials – big single crystals, glasses and, in some cases, ceramics. During the last century, wide attention was turned to obtaining different kinds of single crystals, because not all compounds can be acquired as a glass-like material, but the output of optically transparent ceramics was not developed enough yet. Alas, the growing of single crystals is time and labor-consuming, and, for those reasons, also an expensive process. The growing of ZrO_2 single crystals is burdened by the polymorphism of the material – initially a cubic crystal grows, but with the temperature decreasing phase transitions occurs – from cubic to tetragonal and later to monoclinic phase. Pure ZrO_2 single crystal is destroyed by the phase transitions. That is why the search for alternate solutions is on for obtaining optically transparent materials. During the last decade, this research has led to the intense development of several technologies for obtaining transparent ceramics. Some ceramics have been successfully obtained and the optical properties of the resulting material were so excellent that it can be used in the making lasers.

The nanocrystals of the corresponding chemical compound are used as the raw materials for the ceramics sintering. In attempts to sinter the optically transparent ZrO_2 ceramics, positive results have been obtained. This is why the research of the optical properties of ZrO_2 nanocrystals and comparison to the results obtained by studying single crystals and ceramics are essential.

The research papers on ZrO_2 luminescence mention from one to eight luminescence bands observed in the spectra. The interpretation of the luminescence centers varies greatly. Nether information about the induced absorption, which can occur due to the recharging of ZrO_2 defects, was not found in any scientific journals, nor was information about the ZrO_2 luminescence dependence of the oxygen concentration in the material. The solution of these problems is urgent both from the point of view of the basic research and the practical application possibilities of ZrO_2 This is why research that could promote the solving of these problems has been undertaken in this current research paper.

1.1 Motivation

Knowledge about the defects of the material, the formation and properties of the defects as well as the impact of the defects on the transfer of energy and charge and the recombination processes are needed for the development of the application possibilities of the above mentioned ZrO_2 nanocrystals in order to make transparent ceramics and to improve the oxygen sensors. The information found in the scientific literature turns out to be quite deficient and sometimes contradictory. The experiments mentioned in the literature sources were made with different samples of ZrO_2 with different crystalline structures, various stabilizers of the structure and various activators as well as different methods of synthesis. Insufficiencies in the data about the luminescent properties of ZrO_2 and their dependence of thermal processing in gas compositions with different oxygen concentration as well as the comparison of nanocrystals and massive single crystals comprised the main motivation for the research done in this work. It should be noted that while doing the research new questions emerged. For example, while storing the experimental data that the oxygen vacancies in ZrO_2 disturb the transfer of the charge, the question arises whether this could be the cause of the observed induced absorption.

1.2. The aim of this work

The general aim of this work is to obtain new knowledge about the processes, defects and luminescence centers in ZrO_2. Particular goals are:

1. Make a comparison of luminescence properties for zircionia nanocrystal samples produced with different methods.
2. Study the luminescence spectra dependence on the energy of the excitation photons, to determine how many various defects are responsible for the luminescence observed and to gain data, which could be used for the identification of the luminescence centers.
3. Determine the affect of thermal processing of ZrO_2 nanocrystals in gas compositions with different oxygen concentrations on the luminescent properties of ZrO_2 nanocrystals.
4. Verify if the short-lived induced absorption takes place in ZrO_2; try to determine the cause of it and the possible connection with the luminescence centers.
5. Research Eu doped ZrO_2 for the opportunity to state the impact of the structure of the material on the displacement of the luminescence bands of Eu^{3+} in the spectrum which could reveal if Eu^{3+} may be used as the stabilizer of the tetragonal and the cubic structure of ZrO_2.

1.3. Author’s contribution

The contribution of the author in obtaining the data for this research is from multiple sources. The author has taken part in the development of two functional schemes of luminescence research setup and subsequently built them up as well as developed and adapted the software needed for the functioning of the equipment.

The author conducted experiments (except XRD and luminescence study under radiation of synchrotron experiments) which are connected with the obtaining of all the mentioned results and done the processing of the corresponding data.

The discussion and interpretation of the results of the experiments was done collectively with colleagues from the Solid State Radiation physics laboratory. The author has presented the results of the study in multiple international scientific conferences. The author has taken part in preparing publications for several scientific journals and the discussion of them in the laboratory as well as corresponding with the editorial boards of the journals.

1.4. Scientific novelty

The new experimental results were presented, its analyses lead to new knowledge and conclusions about the nature of ZrO_2.

1. For the first time, the comparison between macroscopic single crystals and nanocrystals was made.
   - It is shown that the centers responsible for recombination luminescence in nanocrystals and single crystal are the same
   - Photoluminescence centers excited within band gap are the same in single crystals and nanocrystals, however the concentration differs, and therefore the luminescence spectra also differ.
2. For the first time, systematic research about how the treatment in gases with different oxygen concentration exchanges the luminescence properties was carried out. It is shown that:
   - ZrO_2 nanocrystal luminescence intensity depends on oxygen concentration
   - The defect concentration related to oxygen vacancies changes with the exchange of oxygen vacancies concentration, but these defects responsible for luminescence were not the vacancies themselves
   - Oxygen vacancies act as trapping centers in ZrO_2 nanocrystals.
3. For the first time, the transient absorptions spectra were observed and measured for ZrO_2 single crystal:
   - Transient absorption spectra consist of two overlapping bands
   - Transient absorption decay time strongly differs from that for cathodoluminescence.
4. The Eu doped ZrO_2 nanocrystal luminescence was studied. The relation between Eu concentration and zirconia phase was shown. It is possible to stabilize ZrO_2 cubic phase with Eu ions.

2. Literature review

The three polymorph phases are known for undoped ZrO_2 at atmospheric pressure. It is known that at atmospheric pressure and room temperature undoped ZrO_2 exists at polymorphous phases: monoclinic, tetragonal and cubic. In the temperature region less than 1170 ºC, the stable is monoclinic phase. Therefore, at room temperature and atmospheric pressure only the monoclinic phase is in thermodynamic equilibrium. In the temperature region 1170 ºC − 2370 ºC, the tetragonal phase is stable, but over 2370 ºC the cubic phase is detected [1].

In the course of ZrO_2 growing from melt at normal pressure in melt consideration process the cubic phase ZrO_2 crystals were created. However, during the cooling process, the phase transition occurs – at first the tetragonal phase was created and then monoclinic phase. The structural changes lead to crystal lattice parameters and unit cell volume changes. These are a cause of intrinsic mechanical stresses and, as a result, the ZrO_2 crystal was destroyed into polycrystals. Consequently, it is not possible to obtain large ZrO_2 single crystal from melt at atmospheric pressure. However, it is possible to stabilize ZrO_2 cubic and tetragonal phase by adding different dopands (Y, Ca, Ce, Mg and others).

In the present studies the nanocrystalline samples were used. As we see the nanocrystals are particles with sizes in range from a few nanometers up to hundred nanometers and the same crystallographic structure. The ZrO_2 single crystal growing process is expensive and power-consuming since the ZrO_2 has a high melting temperature and phase transitions during the cooling. For practical applications, the alternative to single crystal is ZrO_2 ceramics prepared from micro- and nanopowders. The difference of micro and nano powders is not only in their sizes, but also, for example, in their physical properties.

Lately, the synthesis of nanocrystals and ceramic sintering from them has been of great interest. The nanocrystals were used for transparent ceramic sintering. Optical ceramics are cheaper and easily prepared. It is possible to obtain transparent ceramics for laser application and scintillators [2].

In scientific publications there are many papers devoted to ZrO_2 luminescence studies. Given that for ZrO_2 practical applications the powders are preferable; most studies in the literature are for undoped and doped ZrO_2 powders. The grain sizes of crystallites were different - from some tens of nanometers up to 100 µm. Unfortunately, only a few papers - mainly for the stabilized ZrO_2 single crystal - contain the results of luminescence studies. It is significant that in papers convincing confirmations of luminescence mechanisms are absent. Further, the experimental results and their interpretation in different papers are contradictory.

The spectral region of ZrO_2 transparency is wide; host material electronic transition (fundamental absorption) was excited above 4.2 eV, but in the infrared region the phonon absorption below 600cm^{-1}).

ZrO_2 nano- and microcrystalline powders undoped and doped with different chemical elements have a wide practical application; these materials are easily accessed and the main parts of studies are performed on these samples.

According to band theory [3], the energy of a forbidden band is dependent on material structure since the changing of atom positions lead to changing of the integral of exchange interaction. This is the reason for forbidden band energy dependence on the ZrO2 crystal structure (monoclinic, tetragonal and cubic). The experimentally estimated forbidden gap for monoclinic phase is 4.2 − 5.83 eV, for tetragonal 4.2 − 5.78 and for cubic 4.6 − 6.1 eV [1,4]. The theoretically calculated forbidden gap for monoclinic phase is 4.46 eV, for tetragonal phase is 4.28 eV and for cubic phase is 4.93 eV [1,4].

The experimentally estimated values are different, but the data show that the values for different structures are different. The same regularity was observed in experiments and theoretical simulations: the larger forbidden gap is for the ZrO_2 cubic structure and smallest for tetragonal. It is not known what the is nature of fundamental absorption edge – the exciton excitation or band-to-band transition.

2.2. Literature review of the undoped ZrO_2 luminescence

Summarizing the literature data, one can separate the luminescence band positions into three regions. One region with band peaks below 2 eV, the second region is between 2.0 and 3.5 eV, wheras the third above 4.0 eV.

We do not find data about native defects in ZrO_2 or other type centers with luminescence at < 2.0 eV. Therefore, luminescence bands with peak position < 2.0 eV are assumed as due to dopands (mostly rare earth (RE) ions elements, for example Sm^{3+}, Nd^{3+} , Pr^{3+}) [5]. One of the attendant elements to Zr is Hf and it is difficult to purify the ZrO_2 from this element. The luminescence HfO_2 and ZrO_2 similar overlaps [6,7]. In the literature, the region 2.0 − 3.5 eV was described as native defect luminescence. Often this is related to different F-type centers and other defects due to oxygen vacancies [8,9]. The bands at region > 4.0 eV were interpreted as ZrO_2 excitonic luminescence [6]. Note that the literature data about this spectral region is poor.

The number of luminescence bands described by different authors was from one to eight [10]. A distinguishable number of bands and wide spectral region in which these bands were observed denote that the native defect luminescence studies have no single meaning and considerably the explanation of mechanisms is different. We do not find any literature data about undoped single crystal luminescence, but there are many papers about the luminescence in micro- and nanocrystals. The data concerning luminescence and absorption studies on bulk ZrO_2 is poor for the reasons mentioned above - due to phase transitions - the bulk undoped single crystal is difficult to obtain. Therefore, the primary question concerns the reason for luminescence band position dispersion: dependence on grain sizes, morphology and structure differences, uncontrolled impurities or experimental conditions.

2.3. Literature review of the doped ZrO_2 luminescence

Some addition of dopands does not significantly change the intrinsic defect luminescence intensity, but the dopands with a charge state below Zr^{4+} charge state mostly serve as a phase stabilizer and as a result the defect state distribution is different and significantly the luminescence intensity and spectrum changes.

From the data of the doped ZrO_2 crystal luminescence one can conclude that the dopand luminescence properties are similar to that observed in other materials. It is significant that in many papers it is shown that ZrO_2 is a good material for RE ions incorporation and further application. The RE ions build into ZrO_2 crystal with charge state +3.

Note that the data of luminescence observed for the same ions are different in different papers and it shows again the same as for native defects in $ZrO_{2.}$ For example, it is shown that after annealing at 1400^0C the ZrO_2 doped with RE ions (Gd,Tb,Dy) under electron beam excitation, the dopand luminescence increases but native defect luminescence disappears. Before annealing, the concentration of native defects is high and electronic excitations were trapped at native defects and only a small fraction excite the RE ions [5]. A similar effect was observed under photoexcitation [11]. It is significant that RE ions were used for structure and native defect studies. The ZrO_2 doping and analysis of luminescence data could be used as a method for ZrO_2 quality estimation. It is possible to use RE ions as structure stabilizers; for example, some of RE ions stabilize tetragonal structure even at 2 mol% and higher [12]. Note that ZrO_2 is a good material for “upconversion” effect observation. Often for this process realization the Sm, Tm, Er and Yb dopands were used.

Separately, it is shown that the ZrO_2 doping with nanocrystals is possible, i.e. ZrO_2 was used as matrix material (for inclusion as other material nanoparticles). It will be presented as a composite material [13-15]. This means that in ZrO_2 these particles are not dissolved and together with wide optical transparency region the prospective application is possible. In these systems it is possible to study the quantum confinement effects.

3. Experimental

3.1. Samples

A number of methods are known for nanosized ZrO2 crystal production: sol-gel, hydrothermal, material laser ablation, vaporization-condensation, mechano-chemical, hydrothermal driven by microwaves, etc.

The advantage of any production method can be determined from the necessary properties of the sample obtained. The important properties are the nanocrystal size, distribution of nanocrystal sizes, the crystallinity of sample, the crystalline structure, and purity of sample as well as some other parameters.

The samples produced by five different methods were used in experiments. Therefore, the optical properties and structure dependence on the production method of the samples studied was taken in proper account this allowed the removalof the influence of some accidental effects arising from the sample production method (unexpected impurities, dominance of some kind of intrinsic defects and others).

The nanocrystals for study were produced in the:

1. Institute of High Pressure Physics, Prof. W. Lojkowski, Warsaw, Poland;
2. Institute for Non-Ferrous and Rare Metals, Prof. R. Piticescu, Bucharest, Romania;
3. Institute of Inorganic Chemistry, Technical University of Riga, Prof. J. Grabis, Riga, Latvia.

The commercial samples for study:

1. The single crystal ZrO_2+9,5 mol% Y2O3 platelet, size 10x10x1 mm, <100> oriented, (obtained from Alfa Aesar), Surfaces were polished for stationary and induced absorption measurements.
2. The micro sized powder of ZrO_2, purity 99,7%, reduced concentration of Hafnium Hf <75 ppm (obtained from Alfa Aesar).
3. The micro sized powder of ZrO_2:Ca, 4 mol% Ca purity 99,7%, reduced concentration of Hafnium (obtained from Alfa Aesar).

3.2. Equipment

The luminescence study was the primary topic within the present investigation; however, the measurements of FTIR and UV – VIS stationary absorption as well as induced absorption were also carried out. The testing of other ZrO_2 properties was completed within a separate set of measurements: grain size (BET, SEM, XRD), structure (XRD), analysis of chemical composition and impurities (EDAX).

Most of the luminescence measurements were conducted using similar equipment. This equipment provided the ability to record the kinetics and the spectra of luminescence as well as the excitation spectra of luminescence. The experiments were conducted using five setups with differnt technical parameters. The main functional units were in all five setups: (a) Excitation source; (b) Optical and mechanical part; (c) Registration unit.

(a) The excitation sources were: (I) ArF laser PSX-100-2, the energy of photons 6,42 eV; (II) YAG laser supplied with 4-th harmonic generator, 4.66 eV; (III) Nitrogen laser LG-21, 3,67 eV; (IV) X-ray tube with Tungsten target, 40 kV, 10 mA; (V) Solid state tuning laser NT342/3UV (EKSPLA), which was used for the study of luminescence dependence on excitation photon energy and (VI) Electron accelerator (270 keV acceleration voltage, density of excitation 10^{12} el/cm^2 per pulse, puse length 10 ns).

(b) The cryostat cooled by liquid Nitrogen as well as a closed cycle Helium refrigerator was used. The temperatures were possible within 85 K- 700 K for liquid Nitrogen cryostat and within 10 K – 400 K for the closed cycle Helium refrigerator. The special case was the sample holder with heater for up to 1000 K.

(c) The registration of signal was: (I) by spectrometer Andor Shamrock 303i-B supplied with CCD (Andor DU-401A-BV) camera at exit port. This spectrometer has the possibility to use the PMT at the secondary exit port also. (II) Using monochromators MDR2 or MDR3 with PMT at exit ports. (III) More frequently photon counting heads H8259 or H259-02 and PMT-115 and PMT-85 for the analog signal detection were used.

4. Results and discussion

4.1. Luminescence of undoped ZrO_2

The electron beam created in the material high energy excitations and relaxation of these excitations resulted in the appearance of electrons in the conductivity band and holes in the valence band. This result of relaxation is similar to that obtained under band-to-band excitation. It was expected that under electron beam excitation most of luminescence centers can be observed; thus, the luminescence spectra recorded under electron beam excitation serve as some basis for further study. The wide luminescence band within 2 – 4 eV peaking at 2.9 eV (Fig.1) in ZrO_2 was observed at room temperature (RT) under electron beam excitation. The peak position of this band was temperature dependent.

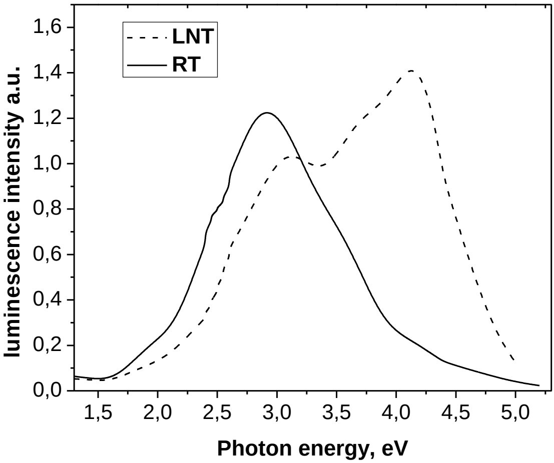

Fig. 1

Luminescence spectra of undoped nanocrystalline ZrO_2 sample under electron beam excitation (the solid line –at RT, the dashed line - at liquid Nitrogen temperature).

Similar luminescence spectra were observed for all samples studied. The presence of a wide band indicated that more than one type of luminescence centers could be involved. The high probability for this is that the intrinsic defects are responsible for luminescence band observed since possible unexpected impurities such as Hf, Er, Dy ions (to purify the ZrO_2 from these ions is difficult [16]) have the narrow excitation and luminescence lines and the narrow lines were not in the recorded spectrum.

The additional luminescence band peaking at 4.15 eV and having a shoulder at 3.7 eV appeared in the luminescence spectrum at a liquid nitrogen temperature (LNT) under electron beam excitation. The luminescence band peaking at 4.2 - 4.35 eV, according to the literature, was for self-trapped excitons. The difference of peak position in the spectrum of our study and the peak position described in the literature was negligible and this difference arises due to different temperature measurements as well as due to differences in phase content or simply due to measurement scatter.

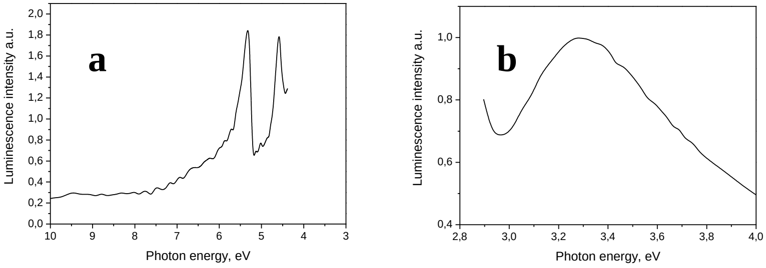

Fig. 2

Luminescence excitation spectra for: a) 4.2 eV band; b) for 2.9 eV band.

The origin of the luminescence band could be cleared up by study of corresponding excitation spectra. The excitation spectra were obtained using the synchrotron UV radiation at DESY, Germany (the author is thankful to V.Pankratov and L.Grigorjeva for the exciton excitation spectra measurements). The excitation spectrum for 4.2 eV luminescence at liquid Helium temperature reveals two well separated bands (Fig.2, spectrum a) peaking at 4.6 and 5.3 eV. Both bands are at photon energies close to the band gap energy. The band at 4.6 eV corresponds to the excitation of excitons in tetragonal structure ZrO_2. The band at 5.3 eV might be the same for monoclinic structure ZrO_2, since the sample used in these experiments was a mixture from ZrO_2 monoclinic and tetragonal phase nanocrystals. Since we found only a few papers studying the excitons in ZrO_2 there is a need for additional study for a stronger interpretation.

The excitation spectrum for 2.9 eV luminescence band is a wide excitation band peaking at 3.3 eV; thus the, excitation is within band gap. This is strong evidence that the luminescence was from intrinsic defects and this is in agreement with descriptions in the literature. Hence, the two kinds of ZrO_2 luminescence are the luminescence of the self trapped excitons observed in the tetragonal, and possibly in the monoclinic structure $ZrO_{2,}$ and the luminescence of defects - probably from intrinsic defects.

4.2. Defect luminescence of ZrO_2

4.2.1. Comparison of ZrO_2 different samples

The different band positions of ZrO_2 luminescence and various number of luminescence bands observed by different authors (as described in the review chapter of this study) led to ambiguity of interpretation. The origin of differences mentioned could be the polymorphism of ZrO_2 (different phase content of samples), different size nanocrystals, unexpected as well as possible technological impurities or other reasons.

The experiments were carried out in the present study to clarify this problem. The first experiment was the ZrO_2 luminescence spectra study under YAG laser 4-th harmonic (4.66 eV) excitation of samples produced by different methods. The luminescence spectra were recorded for five samples: (I) Yttrium stabilized ZrO_2 single crystal; (II) Commercial ZrO_2 powder; (III) Yttrium stabilized ZrO_2

nanocrystals; (IV) Undoped ZrO_2 nanocrystals produced by microwave driven hydrothermal method; (V) Undoped ZrO_2 nanocrystals produced by plasma synthesis. The luminescence spectra recorded at RT is in Fig.3.

The luminescence spectra in Fig. 3 differ significantly and the experiment did not yield information as to why. However, it will be noted that the peak position of luminescence band is at higher energies for smaller size nanocrystals as well as for Y doped nanocrystals. One can see that the luminescence spectra differ even for undoped samples – for the commercial ZrO_2 powder and for nanocrystals obtained by two different methods. Thus, the photoluminescence under the same excitation (YAG laser) was different for undoped ZrO_2 samples and this is a possible reason why the results obtained by different authors on ZrO_2 luminescence study were not the same.

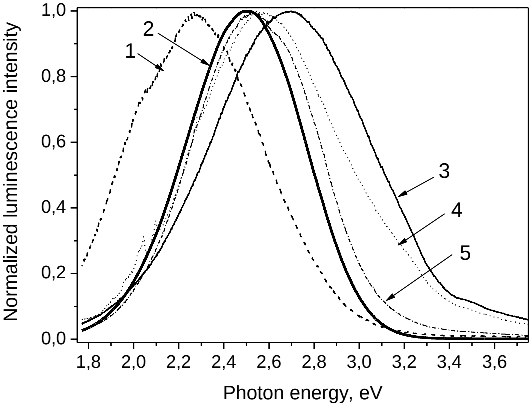

Fig. 3

Photoluminescence of different ZrO_2 samples under YAG laser 4-th harmonic (4.66 eV) excitation: (1) Y stabilized ZrO_2 single crystal; (2) Y stabilized ZrO_2 nanocrystals produced by hydrothermal method (3) Commercial ZrO_2 powder; (4) Undoped ZrO_2 nanocrystals produced by hydrothermal method; (5) Undoped ZrO_2 nanocrystals produced by plasma synthesis.

The luminescence spectra excited by X-ray showed a band peaking at ~ 2.5 eV and these spectra were very similar for all samples under study; therefore only spectra for two samples, Y stabilized single crystal and undoped ZrO_2 nanocrystals obtained by hydrothermal method, were displayed on Fig.4. The luminescence spectra of all ZrO_2 samples were similar under electron beam excitation also.

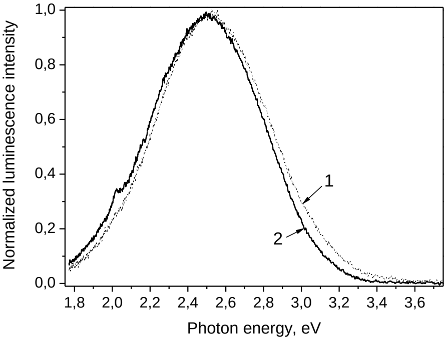

Fig. 4

The luminescence spectra at RT under X-ray excitation for (1) for undoped ZrO_2 nanocrystals and (2) Y stabilized ZrO_2 single crystal.

Since the final stage of excitation relaxation is electron and hole recombination for both excitation sources – X-ray and electron beam – one can draw out that the centers responsible for radiative recombination are the same in all samples. This result led to the hypothesis that the defects are the same in all ZrO_2 samples but the concentrations of different defects vary. It will be emphasized that the excitation of the same ZrO_2 sample by different lasers (different photon energy) led to the rather different luminescence spectra (Fig.5), indicating that a number of different defects were involved.

The luminescence spectra under different energy photon excitation differ for all samples studied nanocrystals, microcrystals, Y stabilized and undoped. Note the difference is not only in the band position, the spectra shape differs also, e.g. the spectrum 2 in Fig.5 cannot be obtained from any combination of spectrum 1 and 3.

The analysis showed that even the spectra in Fig. 4 were not elementary – for the approximation more than one Gaussian is necessary.

4.2.2. Dependence on nanocrystal grain size

One of the experiments at the early stage of this research was the recording of luminescence spectra at RT for different size ZrO_2 nanocrystals under X-ray excitation. The wide luminescence band extending from 1,8 to 3.2 eV was observed for different size undoped ZrO_2 nanocrystals obtained by the microwave driven hydrothermal method. The samples before the experiment were annealed (all simultaneously) in the air, the grain sizes were determined after annealing and then the luminescence spectra were recorded. The intensity of luminescence was grain size dependent (Fig. 6).

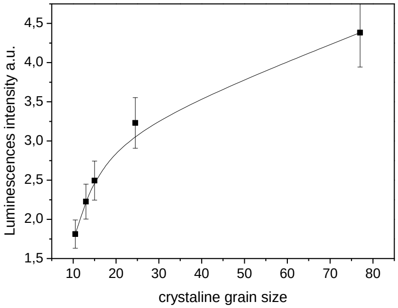

Fig.6

The luminescence intensity dependence on nanocrystal grain size.

The luminescence intensity increases for larger grain size nanocrystals and similar dependence was also observed under selective photo excitation. This dependence was observed for intrinsic defects luminescence and for dopant luminescence also.

The relation surface-to-volume increases if the grain size decreases; thus, the relative contribution from surface defects increases for smaller size nanocrystals. Hence, if the surface defects could be the luminescence centers the dependence in

Fig.6 must be opposite. Therefore, the luminescence intensity dependence on nanocrystal grain size indicates that the surface defects act as non-radiative recombination centers. However, we have no futher strong evidence at the present stage of investigation.

4.2.3. Comparison of single crystal and nanocrystal luminescence

The luminescence spectra of different ZrO_2 samples are described in Chapter 4.2.1. The more detailed comparisons for Y stabilized ZrO_2 single crystal and Y stabilized ZrO_2 nanocrystals are presented below.

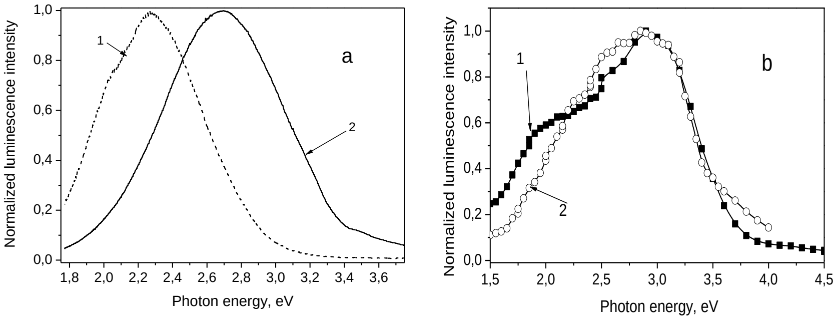

Fig. 7

Luminescence spectra under laser (a) and electron beam (b) excitation, for Y stabilized ZrO_2 single crystal (1) and Y stabilized nanocrystals (2)

It was noted that the luminescence spectra of ZrO_2 single crystal and nanocrystals were similar under X-ray excitation as well as under electron beam excitation Fig.7 b. The possible reason for the different luminescence spectra of these samples under 4.66 eV laser beam excitation was mentioned as the different concentrations of various type intrinsic defects. The additional information can be shown from the luminescence decay kinetics. The analysis of these kinetics showed that the three decay components can be drawn out for both single crystal and nanocrystal luminescence. The first component has a decay time ~50ns, the second ~ 3µs and the third extends over a milliseconds or even seconds range. The first and second components seem to be the exponents, whereas the third not. Thus, the analysis of luminescence decay is not simple; however, one can draw out that the processes responsible for luminescence were similar in both samples and differences arise due to contributions from various type defects in luminescence. Moreover the defect types could be the same, whereas contributions from them in luminescence differ due to different concentration.

It was observed that the luminescence spectrum of a sample strongly depends on excitation photon energy (Fig.5.). This dependence indicates that the number of luminescence bands could be larger. Therefore, an experiment was carried out for the investigation of the luminescence band peak position dependence on excitation photon energy. The tunable OPO laser was used for luminescence excitation. The step by step excitation with 1 nm step was completed. The luminescence spectrum was recorded at each excitation step and thus the family or luminescence spectra were obtained. The luminescence peak position was determined for each spectrum and the dependence of this position on excitation photon energy was built up (Fig.8).

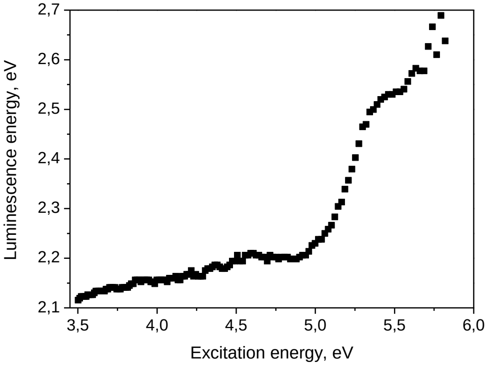

Fig. 8

Luminescence band position dependence on excitation photon energy for Y stabilized ZrO_2 single crystal.

The continuous shift of luminescence band position versus excitation photon energy was obtained. This dependence shows two regions: the first one with excitation photon energy below 5 eV and the second one above 5 eV. Within the first region the luminescence band position dependence on excitation photon energy was less expressed than in second. This difference was possibly due to different energy transfer. The direct excitation of defects takes place below 5 eV, whereas above 5 eV the energy is close to the band gap and the energy transfer can be related to excitonic and /or electrons and holes processes.

4.3. Treatment in gases

The ZrO_2 nanocrystals annealed at different partial pressures of oxygen were studied to highlight the role of oxygen vacancies in luminescence. The annealing of ZrO_2 samples in gas mixtures with different oxygen and nitrogen (or some another gas) content leads to luminescence change. This method allows the possibility of changing the oxygen concentration in ZrO_2 nanocrystals.

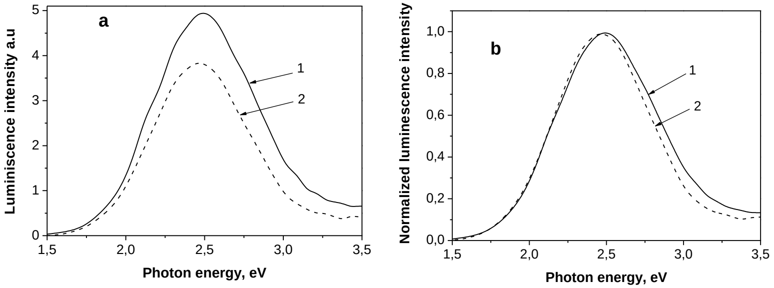

Fig. 9

Photoluminescence dependence on oxygen treatment for undoped ZrO_2 nanocrystals (1) 2%O_2 content in gas mixture ; (2) 21% O_2 content in gas mixture. (a) Luminescence's intensity and (b) spectral distribution change.

It was found that the luminescence intensity under excitation within band gap increases for ZrO_2 nanocrystals annealed at low partial oxygen pressure, whereas under band-to-band excitation luminescence intensity of the same samples decreases. The effect depends on oxygen partial pressure during nanocrystals annealing – less partial pressure higher luminescence intensity under excitation within band gap. (Fig. 9a). This shows the intrinsic defects responsible for luminescence are oxygen vacancy related; however, most of these defects were not oxygen vacancies themselves. The oxygen vacancies act as charge traps and suppress the charge (possibly also energy) transfer. This result also shows that these centers are not the oxygen atoms or ions in interstate position. Additionally, not only the luminescence intensity changes, but also the luminescence spectra changes Fig. 9b. Annealing in low oxygen concentrations leads to luminescence band shift to higher energies.

This luminescence band shift is in good agreement with previous conclusions about luminescence spectral dependence on the ZrO_2 phase. For samples with tetragonal structure the luminescence bands are peaking at higher energies than for monoclinic samples. The oxygen vacancies also are involved in tetragonal phase stabilization. In samples with tetragonal phase there are more vacancies than for samples with monoclinic phase.

The luminescence intensity dependence on treatment in gases with different oxygen concentration is shown in Fig.10. Under electron beam excitation with increase of oxygen vacancies concentration the luminescence intensity decreases, but under laser excitation within the band gap the luminescence intensity increases Fig. 10.

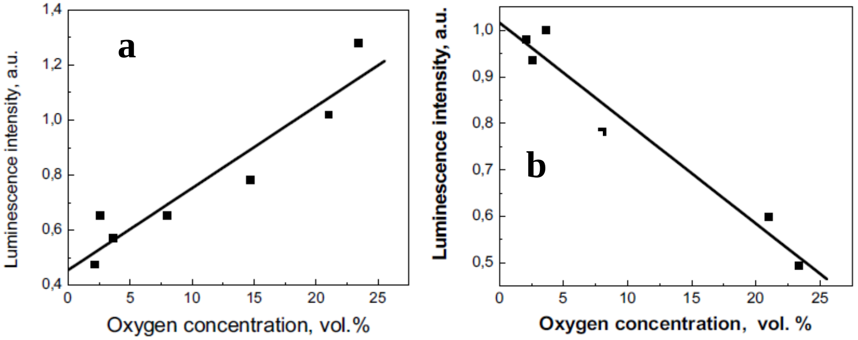

Fig. 10

Zirconia nanocrysal luminescence intensity dependence on annealing in gases with different oxygen concentrations. Under electron beam excitation (a) and under laser excitation within the band gap (b)

In case of photoluminescence excited within the band gap, the defects are excited directly; whereas under electron beam excitation, the electrons and holes are created and the energy and/or charge transfer process takes place. Luminescence intensity decreases under electron excitation show that additional oxygen vacancies disturb the energy transfer to the defects responsible for luminescence. Possibly, the oxygen vacancies acts as charge traps, thereby decreasing the number of electrons. But with increase of oxygen vacancies concentration the possibility of F-center creation increases. This is possible to check by transient absorption measurements.

4.4. Transient absorption

The transient absorption was registered in ZrO_2:Y single crystal at RTunder pulsed electron beam excitation. Transient absorption spectrum overlap with cathodoluminescence spectra; however, there is the possibility to separate these spectra.

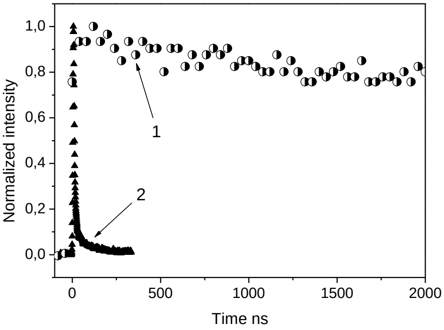

Fig. 11

Transient absorption kinetic (1) and luminescence kinetic under electron beam excitation (2) measured at 2.5 eV

The time resolved absorption studies reveal two absorption bands with maxima at 1.7 eV and 2.6 eV. Comparing the luminescence decay under electron beam excitation and transient absorption decay the strong difference in decay times was found (Fig.11). The transient absorption decay time is long lasting whereas the luminescence decay is measured in nanoseconds. That means that the centers responsible for luminescence and transient absorption are not the same. It is not excluded that the centers responsible for transient absorption are involved in processes accounting for the ZrO_2 long lasting luminescence described in [17].

4.5. Eu doped zirconia luminescence

The luminescence of ZrO_2 doped with rare earth (RE) ions has been studied by a number of researchers. The luminescence of Eu^{3+} is sensitive to the ion surrounding symmetry; therefore, this luminescence is a probe for the crystal structure.

The Eu ions substitute Zr^{4+} ions in ZrO_2 and since the Eu ion is inovalent (the charge state 2+ or 3+), the oxygen vacancy is involved for charge compensation. Therefore, it is expected that the ZrO_2 doped with Eu^{3+} could result in tetragonal and cubic phase stabilization.

The incorporation of Eu^{3+} in ZrO_2 is expected; however, under some kind of excitation the electron could be trapped by Eu^{3+} and it was anticipated that the Eu^{2+} excited state would be formed. Since it is well known that the Eu^{2+} luminescence is within 390 - 520 nm range, this region was monitored under two kinds of excitation: (I) selective using OPO for the excitation scanning within 220 – 300 nm with the step 1nm; and (II) non-selective using electron beam pulses. The second kind of excitation led to the creation of electrons and holes and the estimated density of charge carriers in the bands was close to 10^{19} cm^{-3}. The range of expected Eu^{2+} luminescence overlaps with ZrO_2 intrinsic defects luminescence. These two kinds of luminescence can be separated using the time resolved technique since the Eu^{2+} luminescence decay is within microseconds; whereas ZrO_2 luminescence decay does not exceed 50 ns. The luminescence of Eu^{2+} was not detected under either kind of excitation even for a sample containing 10 at.% Eu. It was concluded that the trapping of the electron by Eu^{3+} and formation of the Eu^{2+} excited state in ZrO_2:Eu is not efficient. This result is in good agreement with incorporation mechanisms described in [18].

4.5.1. Luminescence dependence on Eu concentration

The more intense luminescence bands correspond to the $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole) and $^5D_0 \rightarrow {}^7F_2$ (electric dipole) transitions; corresponding bands usually peak at 570-600 nm and 600-640 nm. The much weaker luminescence comes from

$^5D_0 \rightarrow {}^7F_3$ transitions peaking at the 640-660nm region. The luminescence from $^5D_0 \rightarrow {}^7F_2$ transition in monoclinic ZrO_2 split in three bands. In order to ascertain the luminescence intensity dependence on the Eu^{3+} concentration, the intensity of luminescence at 613 nm was measured for ZrO_2:Eu samples with different Eu contents within the range of 0,1 – 5 at.% (Fig.12). Similar luminescence intensity dependence from Eu concentration is for bands 620-640nm because these bands have the same origin as for bands peaking at 613 nm. The luminescence intensity measured at this wavelength tend to saturate above 2 at.%,

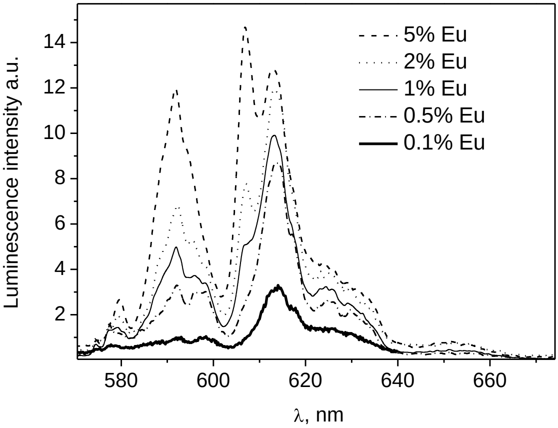

Fig.12

Luminescence spectra of ZrO_2, containing different Eu concentration. The band peaking at 607 nm was resolved for samples containing Eu above 1 at. %;

However, the luminescence spectra for these samples were different – for samples containing Eu above 1 at.% the additional luminescence band centred at 607 nm appears. The intensity of the 607 nm band became most intense at Eu content of 5 at.%. Similar observations of the 607 nm band are described also [19, 20, 21].

Therefore, it was assumed that a better characteristic for the luminescence intensity dependence on concentration can be the light sum of $^5D_0 \rightarrow {}^7F_2$ transitions peaks in different surroundings. This light sum is proportional to the area under the 607nm and 613nm bands. The area was determined as an integral of the spectrum over 600 – 640 nm range. This integral intensity of luminescence did not show saturation even up to 5 at.% of Eu content (Fig.13) indicating that the mutual interaction between Eu^{3+} ions in ZrO_2 is weak and the concentration quenching of luminescence was not noticeable for this concentration. The concentration quenching is expected to be at approximately 10 at.% Eu. The two luminescence bands for the same electron transition in Eu^{3+} are evidence that ion was incorporated in two different symmetry sites.

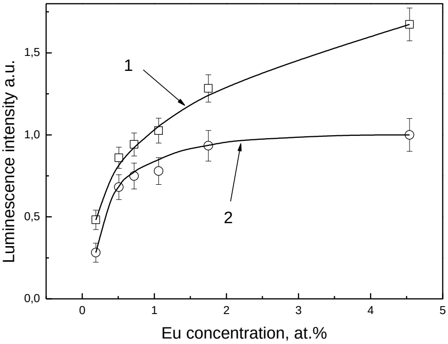

Fig.13

Luminescence intensity dependence on Eu concentration, open circles – intensity of 613 nm band, open squares – integral intensity within range 600-640 nm, the scale for integral intensity was reduced.

The probability of $^5D_0 \rightarrow ^7F_2$ (electric dipole) transition strongly depends on the Eu^{3+} surrounding symmetry, whereas probability of $^5D_0 \rightarrow ^7F_1$ (magnetic dipole) transition is nearly independent of the Eu^{3+} surrounding symmetry. Therefore the relation of luminescence intensities of corresponding bands ($I_{el.dip.}/I_{magn.dip.}$) is the Eu^{3+} surrounding symmetry characteristics [22]. This relation is known as the asymmetry ratio and the larger asymmetry ratio is for the lower surrounding symmetry of Eu^{3+}. The values were estimated calculating integral light sum from 570-600nm for magnetic dipole transition and light sum from 600-640 nm for electric dipole transition; the asymmetry ratios are 2.7 and 2.2 for samples containing 0.1 at.% and 5 at.% Eu, respectively. Hence, the Eu^{3+} surrounding symmetry was higher for the sample containing 5 at. % Eu, than in sample doped with 0.1 at.% Eu. The asymmetry ratio of this sample was compared with that for the Y stabilized and the Eu doped tetragonal phase $Zr_{0.94}Y_{0.06}O_2$:Eu nanocrystals containing 0.05 at.% Eu. The luminescence spectrum of this sample is at Fig.14 and the estimated asymmetry factor is 1.3.

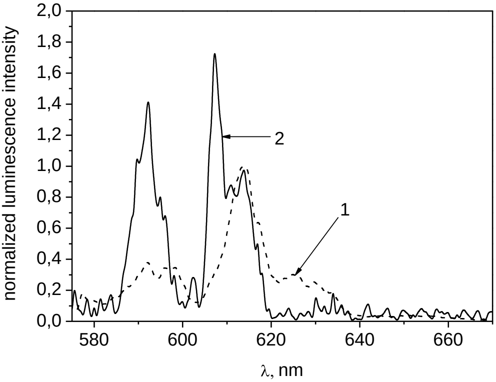

Fig.14

The luminescence spectrum of ZrO_2 with 0.5at% Eu (1) and tetragonal structureY stabilized ZrO_2:Eu containing 0.05 at % Eu (2), the luminescence band peaking at 607 nm is dominant.

Another parameter sensitive to the symmetry is Eu^{3+} luminescence decay time. Luminescence decay measured in the band peaking at 607 nm was slower than for the 613 nm band (Fig.15.). This is additional evidence that the Eu^{3+} surrounding symmetry is higher for the sample containing 5 at.% Eu.

Therefore, it is suggested from the results that the symmetry is higher for heavily doped ZrO_2:Eu nanocrystals because these nanocrystals have the tetragonal or even cubic crystalline structure. This suggestion was checked by XRD analysis. The XRD patterns (Fig.16.) clearly showed that the sample containing 0.1 at.% Eu was monoclinic and the sample containing 5 at.% Eu was a mixture from tetragonal and monoclinic phase nanocrystals.

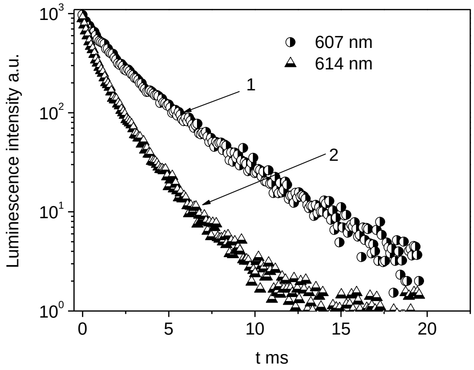

Fig. 15

Luminescence decay kinetics for sample with 5 at.% Eu

The conclusion ascertained was that both luminescence bands at 613 nm and at 607 nm correspond to $^5D_0 \rightarrow {}^7F_2$ transition in Eu^{3+} ion, the first one in the monoclinic phase and the second one in the tetragonal and also cubic phase ZrO_2: Eu nanocrystals. The result of XRD experiments show that the Eu^{3+} can stabilize the ZrO_2 tetragonal and cubic phases. The XRD for the sample containing large amounts (10 at.%) of Eu was quite similar to that for the sample (5 at%) with ZrO_2 monoclinic and tetragonal phase mixture (Fig.16) . It should be noted that the XRD reflex peaks of the tetragonal and cubic phase ZrO_2 seem similar; however, some differences are present. The peak position and peak intensities for tetragonal and cubic phase ZrO_2 differ. Therefore, it is possible to conclude that the ZrO_2:Eu sample containing 10 at.% Eu (Fig.16) is cubic and Eu stabilizes the ZrO_2 cubic phase. The etalons with references 01-080-2155 and 01-081-1551 [23] were used to determine the tetragonal and cubic phases.

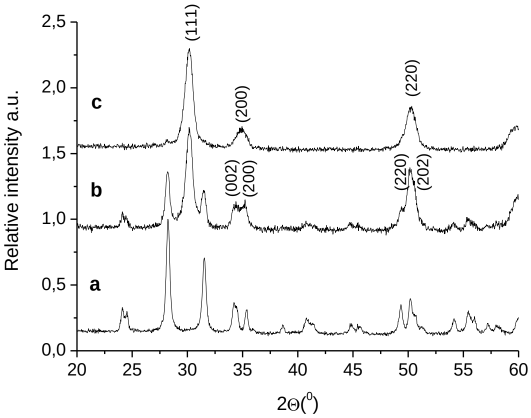

Fig. 16

XRD patterns for samples ZrO_2:Eu containing 0.1 at.% Eu sample with dominant monoclinic phase (a); 5 at. % Eu tetragonal sample with admixture of monoclinic phase (b) and 10 at.% Eu sample with dominant cubic phase (c).

The luminescence integral intensity dependence on Eu concentration showed that mutual interaction between the Eu^{3+} ions is weak in ZrO_2 nanocrystals up to a 5 at.% concentration where the aggregation of dopant ions did not take place. The position of a luminescence band corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition in the Eu^{3+} ion and peaks at ~613 nm for the monoclinic phase and at ~ 607 nm for the tetragonal and cubic phase ZrO_2. The monoclinic phase ZrO_2:Eu nanocrystals were dominant up to 1 at.% dopant concentration while at larger concentrations there is a tetragonal phase nanocrystals admixture. The XRD data and FT –IR spectra are strong evidence that the Eu^{3+} ion changes the structure of ZrO_2 nanocrystals. At the same time, the Eu^{3+} ion is also the luminescence centre and with structural changes the luminescence spectra changes. High concentrations of Eu ions in zirconia lead to stabilization of the cubic phase.

4.5.1. Zirconia intrinsic defects and Eu luminescence

As described previously, there is the possibility to change the oxygen vacancy concentration in ZrO_2 nanocrystals. In a vacuum a fraction of the oxygen leaves the nanocrystals and the oxygen vacancy concentration increases. Luminescence spectra for ZrO_2:Eu (Eu dopant concentration 1 at.%) nanocrystal samples under YAG laser excitation at atmospheric pressure and in a vacuum are showed at Fig. 17. Luminescence intensity in a vacuum from Eu ions in zirconia decreases, but intrinsic defect luminescence intensity increases. The decrease of oxygen concentration in the host decreases the energy transfer to Eu ions; therefore, Eu luminescence intensity decreases but oxygen vacancies related to intrinsic defect luminescence increases.

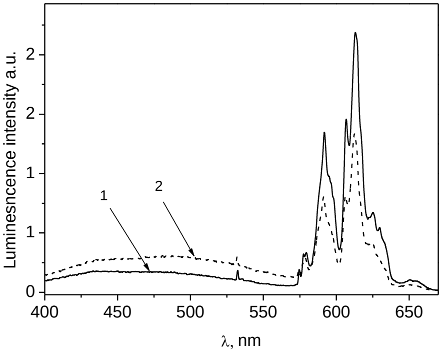

Fig. 17

Luminescence under laser excitation (4.66 eV) for ZrO_2 with Eu 1at% , at normal atmospheric pressure (1) and at vacuum (2).

Under YAG laser 4th harmonic excitation (266 nm) the samples are excited in ZrO2:Eu charge transfer band. The excitation maximum is at 250 nm. If the excitation in Eu absorption lines takes place, then the Eu luminescence intensity is independent from the oxygen vacancy concentration in nanocrystals.

5. Conclusions and theses

5.1. Main results

To better understand the processes related to ZrO_2 luminescence properties I conducted a literature overview. The literature studies were not limited to articles about optical properties studies, but also included literature about ionic conductivity, synthesis, treatment, structural properties and theoretical calculations. This approach provides a complete outlook about physical processes in ZrO_2 nanocrystals. After summarizing the literature, it was possible to construct a hypothesis about luminescence processes in zirconia.

The research practical portion is divided in three parts: experimental, data processing and analysis. The main factor needed to make correct experiments is having the correct equipment and the choice of appropriate methodology. I conducted all of the experiments presented in this work except the excitation spectra made using synchrotron radiation and the XRD measurements. Because of different results described in literature, I made a check of these results. A part of the presented results is in agreement with results described in literature. My original results provide an explanation to the previous contradictious results found in literature.

I made upgrades to the experimental setup and also built two new aparatus. This allows for more research possibilities. I also worked on automatisation software solutions to make the equipment more efficient and to increase user safety.

Data analyses and hypotheses and planning were made in discussions with my supervisor and colleagues.

For the first time, a comparison of luminescence properties for zirconia nanocrystals and single crystals was made. The common and different results were analyzed and presented in scientific papers {1, 5, 8}. Different results for photo luminescence spectra became excited with energies below band gap, but similar results under electron beam or X- ray excitations were observed. For the first time, the transient absorption for ZrO_2 was measured.The spectrum reveals two transient absorption bands {1, 8}.

Unique luminescence dependence on oxygen concentration was presented {3}. A dependence on oxygen concentration in luminescence was revealed. The treatment changes the oxygen concentration in ZrO_2 nanocrystals.

The dopand luminescence properties were studied and the possibility to stabilize the ZrO_2 cubic phase with Eu was presented.

5.2. Main theses

− Luminescence intensity dependence on ZrO_2 nanocrystal grains size is related to the electronic excitation nonradiative recombination on grain surfaces; therefore, nanocrystals with smaller grain sizes have less intense luminescence.

− Annealing in gas mixtures, with different oxygen and nitrogen ratios, leads to intrinsic defect luminescence change. This luminescence intensity change is related to oxygen vacancies concentration in ZrO_2, but the oxygen vacancies are not the main luminescence centers.

− The radiative recombination centers are the same in pure ZrO_2 nanocrystals, Y stabilized nanocrystals and Y stabilized single crystal, but these center concentration ratios vary. The lattice cells distorted by oxygen vacancy form a quasi – continuous energy spectrum within band gap and these distorted lattice cells are intrinsic defects responsible for ZrO_2 luminescence within the wide spectral region.

− The presence of oxygen vacancies in ZrO_2 suppresses charge transfer. Additionally, electron trapping in vacancies is related to long lasting induced absorption.

− Eu ions incorporate in ZrO_2 in Zr site as Eu^{3+}. The position of luminescence band corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition in the Eu^{3+} ion and peak at ~613 nm for the monoclinic phase, and at ~ 607 nm, for tetragonal and cubic phase ZrO_2. High concentration of Eu leads to stabilization of cubic phase of nanocrystalline ZrO_2.

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Participation in conferences

The scientific results were presented and discussed in more than 20 conferences. I was a coauthor for more than 30 conference reports. I made oral presentations in several international conferences like: ICDIM’2008 and FMNT, and with poster presentations, in numerous other conferences: EMRS FALL MEETING, LUMDETR 2009, 10th International Conference and Exhibition of the European Ceramic Society Estrel Convention Center, SCINT 2007, NTNE 2007, EURODIM’2006, NANOVED, ECO- NET 2006 Workshop, DOP-2005 and ISSP UL scientific conferences.

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