UNIVERSITY OF LATVIA DEPARTMENT OF PHYSICS AND MATHEMATICS



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VACUUM ULTRAVIOLET EXCITATION SPECTROSCOPY OF NANOSTRUCTURED COMPLEX OXIDE PHOSPHORS

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ABSTRACT

The most ambitious and fascinating application of luminescent nanomaterials is probably related to medicine and molecular biology. Here, luminescent nanomaterials are promising tags for optical imaging and fluorescent labelling to allow for novel techniques of non-invasive diagnosis and in vivo observation of complex vital functions. The current work is a summary of the systematic spectroscopic studies of actual nanosized luminescent complex oxides (LaPO₄:Ce,Tb; YVO₄:Eu; Y₃Al₅O₁₂:Ce (YAG:Ce); ZnWO₄; NiWO₄) with an attempt to analyse the electronic relaxation processes performed using energy and time-resolved luminescence spectroscopy. The experiments have been carried out utilising European synchrotron centres: i) The Superlumi endstation of I3 line of DORIS III storage ring at DESY (Hamburg, Germany); ii) The luminescence endstation of the FinEst undulator beamline of MAX III storage ring at MAX IV (Lund, Sweden). The examinations focused on the energy transfer processes within the rare-earth ions leading to the optical transitions. The influence of the different parameters such as temperature, doping concentration, and initial excited state were treated to provide complementary information concerning the electronic structure as well as electronic excitations in nanophosphors. A significant difference in luminescence properties between the nano and macroscopical analogues was found in the current work. The results achieved show that small nanoparticle size and loss centres related to the surface of a nanoparticle are responsible for changes in the luminescence properties of nanosized complex oxides.

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1. INTRODUCTION

1.1. Motivation

Inorganic luminescent materials belong to important luminescent material classes that have intensive application in the lighting of industry, displays, security purposes and high energy physics. Nanosized luminescent materials (nanophosphors) are of interest for all applications of classical bulk luminophores (i.e. fluorescent lamps, light-emitting diodes [1–3], emissive displays [1], tomographs, photostimulable phosphor (PSP) plate detectors). Nanosize luminescent nanoparticles can be implemented in different environments for marking purposes (e.g. advertising or emergency lighting), or as a security feature (e.g. on banknotes, securities, or identification documents) in or on a wide variety of substrates, such as glass [4], plastic, or paper [5]. It is notable however, that nanophosphors have found their most useful application as luminescent markers in molecular biology and medical diagnosis and therapy [6, 7].

The main interest in nanocrystals is related to properties that differ from the properties of the bulk material; otherwise, the value of nanosized particles would be restricted to savings in materials and expenses and with miniaturisation that certainly is very important in the commercial use of nanocrystals. However, reducing particle size to nano can change several properties so that particles with a range of functionalities can be engineered for target applications and this is the main advantage of nanoparticles over bulk analogues.

Nanomaterial properties differ from bulk primarily due to changes in physical attributes (size, shape and specific surface area) and quantum confinement. Due to high surface-to-volume, ratio properties, which in principle are also common to the bulk material, become dominant in nanoparticles. Nanocrystals surface has strong influence on optical, electronic, magnetic and other properties, comparing with bulk materials. Luminescence quantum yield of nanomaterials decrease comparing with macroscopic analogues, as going from macroscopic structures on the microscopic structures sample's morphology plays an important role in the changes of the properties of electrons. The most common reason for a nanoparticle's luminescence quantum yield decrease comparing with its macroscopic analogue is related to surface losses. Therefore, it is important to investigate the impact of the nanocrystalline surface on optical characteristics. Of particular interest is understanding of a fundamental process that affects the luminescence efficiency of nanocrystals. Nowadays, the issue of the day is to find different ways to improve the effectiveness of nanocrystalline luminescence. This can be achieved by increasing the quality of nanocrystals: high-quality crystalline structure, spherical morphology, distribution of luminescent impurities in nanocrystals and their optimal concentration. One of the innovative methods is the use of a core-shell structure [3,8] that allows enhancing luminescence efficiency in nanocrystals while decreasing surface losses.

Solids doped with rare-earth metals or transition metals have proven to be effective nanophosphors. The cause of emission, in this case, is the luminescence of individual elementary or molecular ions [9]. High-quality nanophosphors with different emission colours studied in the present work are LaPO₄:Ce,Tb (green), $Y_3Al_5O_{12}$:Ce (yellow), YVO₄:Eu (red), ZnWO₄ (blue) and NiWO₄ (blue-green). Shielding of the luminescent core with a non-luminescent shell in the form of a core-shell structure is also studied on YVO₄:Eu@YF₃ sample. Taking into account that all materials in this study belong to a class of wide band-gap materials, the excitation in ultraviolet and vacuum ultraviolet spectral range is absolutely necessary for this study.

Therefore, synchrotron radiation facility was employed for luminescence spectroscopy measurements in a wide spectral range, including the vacuum ultraviolet region, which is especially significant for wide band gap solids.

1.2. Aim and Objectives

One of the main challenges of this work is to find opportunities on how to improve the efficiency of nanocrystalline luminescent materials. Therefore, it is important to understand fundamental processes of luminescence centre formation as well as energy transfer processes in nanophosphors. The main goal of the current study is to highlight a comparison of luminescence properties of nanocrystalline complex oxides prepared by different techniques and its macrocrystalline analogues.

The following objectives were established:

- to detail the investigation of luminescence properties of nanosized YVO₄:Eu, LaPO₄:Ce,Tb, Y₃Al₅O₁₂:Ce, ZnWO₄, NiWO₄ and their macroscopic analogues in a wide spectral range using synchrotron radiation;
- to explore impurities excitation, exciton and electron-hole luminescent characteristics and their relaxation processes, exciton formation, and self-trapping processes, as well as radiative/non-radiative relaxation processes;
- to define the influence of reduced particle's size on the electronic structure of the crystal.

1.3. Scientific novelty

Experiments performed in the present work allowed:

- systematic investigation of luminescence properties of nanocrystalline materials (phosphors YVO₄:Eu, LaPO₄:Ce,Tb, Y₃Al₅O₁₂:Ce, ZnWO₄, NiWO₄) in vacuum ultraviolet spectral range utilising synchrotron radiation;
- to identify the impact of the reduced size of the nanoparticle on intrinsic and extrinsic electronic excitations, energy transfer processes and on the multiplication of the electronic excitations.

1.4. Author's contribution

This work was performed at the Institute of Solid State Physics (ISSP), at the University of Latvia (UL). Luminescence measurements in the vacuum-ultraviolet spectral range were performed at HASYLAB (Hamburg, Germany) using synchrotron radiation produced by the DORIS III storage ring of DESY synchrotron and by the MAX III storage ring of MAX IV synchrotron. The author has performed experiments at DESY and MAX IV, participated in luminescence measurements under laser excitation (Laboratory of optical spectroscopy, ISSP, UL). The author has performed all data processing; the analysis of the obtained results was done discussing with the supervisor and colleagues from the Institution.

The results of this work have been presented at international conferences and international schools during 2010–2016. Results have been published in five SCI regular papers.

2. EXPERIMENT

The experiments in the vacuum ultraviolet spectral range involving the present work were carried out at Superlumi experimental station located in Hasylab (Hamburger Synchrotronstrahlungslabor) at DESY (Deutsches Elektronen-Synchrotron) and using a luminescence endstation installed at the FIN-EST branch in the MAX III storage ring at MAX IV laboratory (Lund, Sweden). There are short descriptions of both set-ups given in this chapter. Photons with energies from 3.7 to 40 eV are used for excitation. Three different secondary monochromators coupled with various detectors are available for analysis of the luminescence. Luminescence photons can be detected in the energy range of 1.8–25 eV. The SUPERLUMI set-up and luminescence endstation provide the opportunity to work in a wide temperature range of 4 K to 300 K.

2.1. SUPERLUMI endstation of I beamline

The SUPERLUMI set-up [10] is located above the DORIS III storage ring plane at the beamline I (Fig. 2.1). The circumference of the storage ring is 289.2 m. Due to the relatively long storage circumference, DORIS III has a special time-structure, which is particularly suitable for the time-resolved spectroscopy. DORIS provides light pulses with FWHM 130 ps and a period of 964 ns in single bunch mode. Normally DORIS is filled with five bunches with the same FWHM (130 ps) (multi-bunch mode). The interval between the first and the fifth bunch is 196 ns and between all others is 192 ns.



Fig. 2.1 Beamlines (blue and grey arrows) and buildings (grey areas) of DORIS III storage ring

To illuminate the entrance slit of the primary monochromator, two mirrors are used. The first, a cylindrical water-cooled mirror (M1, located in the plane of the storage ring, unable to see in Fig. 2.2.) accepts 50 mrad of the horizontal and 2.2 mrad of the vertical divergence of the source. Mirror M1 focuses light horizontally to a 10 mm wide image at the entrance slit of the primary monochromator. The second, plane elliptic, mirror (M2, located 3.7 m above the storage ring plane, on the level of the entrance slit) focuses vertically to 0.1 mm at the entrance slit of the primary monochromator. Mirrors M1 and M2 transform the $6 \times 2 \text{ mm}^2$ light source into the $10 \times 0.1 \text{ mm}^2$ light spot on the entrance slit of the primary monochromator. The light is dispersed by the primary monochromator in the vertical direction. A third, rotational-elliptic, mirror (M3, located in the sample chamber) focuses the light onto the sample. As result, the $6 \times 2 \text{ mm}^2$ light source transforms into the $5 \times 0.15 \text{mm}^2$ light spot on the sample.

The SUPERLUMI setup



Fig. 2.2 SUPERLUMI setup of I beamline of DORIS III storage ring at DESY

The SUPERLUMI set-up consists of four monochromators: the primary one, dispersing synchrotron radiation, and other three for analysis of luminescence. Such a combination of spectrometers is especially suitable for wide bandgap materials.

The primary monochromator has a focal length of 2 m, covers the spectral range from 3.7 to 40 eV, and in our experiments, the 1500 μ m wide entrance slit was used. Secondary monochromators include the Pouey monochromator, the VUV monochromator and 0.3 m monochromator in Czerny-Turner mounting (three gratings 300/600/1200 grooves per mm). Czerny-Turner mounting monochromator has two exit arms. One of them serves a liquid nitrogen cooled CCD detector; the other one serves a fast photomultiplier (for time-resolved experiments). The working range of the Czerny-Turner-type monochromator extends from 185 nm to 1150 nm and is limited by the available gratings and detectors. The best achievable resolution (1200 l/mm grating) is 0.16 nm.

The SUPERLUMI working temperature range is from room temperature down to 8-9 K due to liquid helium flow cryostat. Two gratings provide the working region of the primary monochromator (3.7–40 eV): Al-grating (used for the 3.7–20 eV regions) and Pt-grating (for the 15–40 eV region). Each grating has different efficiency distributions; therefore, all spectra should be corrected before analysis. Two filters are used for the Al-grating to eliminate excitation by the second orders: a quartz filter for the energies below 7 eV and an MgF₂ filter for energies 7–9 eV. Due to absorption, the MgF₂ filter seriously reduces the intensity of excitation, significantly reducing the signal to noise ratio. The signal also decreases in the region of 17-20 eV due to the grating inefficiency, which sometimes makes it completely impossible to register anything besides noise. The same difficulty arises in the 36-40 eV region of the Pt-grating. Also, there is gradual decrease over time in the current of synchrotron and, therefore, in the overall intensity of synchrotron radiation between injections.

2.2. Luminescence endstation at FINEST branch of I3 line

A mobile luminescence endstation was installed on the FINEST branch of I3 beamline on the MAX III storage ring [11] (Fig. 2.3). MAX III at MAX IV laboratory was started in 2007 (operated until the end of 2015) and has a circumference of 36 meters and an emittance of 13 nm rad. The electrons are injected with an energy of 400 MeV and are then accelerated up to 700 MeV. The electrons in this energy field are producing synchrotron light in the ultraviolet and infrared area.



Fig. 2.3 Storage rings and beamlines at MaxLab, the I3 line is No.13

The excitation energy of the used endstation can be varied from 4.6 eV to 50 eV and the vertical, horizontal or elliptical polarisation of the incoming radiation can be chosen. Vertical polarisation was used in our measurements. The excitation energy can be varied by using the Eagle primary monochromator equipped with replaceable gratings: MgF_2/Al coated grating for photon

energies from 5 to 11eV, 4300 lines/mm SiC coated grating for energies from 11 to 26 eV, 4300 lines/mm Pt coated grating for photon energies above 26 eV, and a 430 lines/mm Au grating for energies from 5 to 50eV (used in our experiments). The radiation can be focused to an exit slit of the monochromator by using a refocusing mirror (spot size 0.3×0.5 mm). Quartz and LiF filters were attached to the beamline in order to avoid higher orders of excitation. The incoming radiation is focused to the sample holder attached to the luminescence endstation. Ultra high vacuum system (pressure 5.10-9 mbar) and helium-flow cryostat are installed to allow low-temperature measurements up to 7 K. The luminescence signal is collected by fibre optics and directed to a spectrometer. All spectrometers used for this endstation were the same as previously described for Superlumi station - ARC SpectraPro 300i Czerny-Turner-type spectrometer for UV/visible luminescence and ARC spectrometer with two detectors. For collecting a signal during emission spectra measurements a Princeton instruments liquid nitrogen cooled CCD camera (Spec-10) was used, and for excitation measurements, a photomultiplier (Hamamatsu H8259-01), which basically multiplies the current produced by incoming light, was used as a detector.



Fig. 2.4 Optical components and detectors of the setup

2.3. Experimental method

For the investigation of the electronic relaxation of selectively excited nanomaterials, different experimental methods were used:

- An emission or luminescence spectrum represents luminescence intensity as a function of the emitted photon energy. The excitation energy is fixed in these measurements. The curves obtained in this way give the information about radiative channels of relaxation in the materials studied. It is also possible to measure the time-resolved emission spectra.
- During the excitation spectrum measurements, the emitted photon energy is kept constant and corresponding curves display luminescence intensity as a function of exciting photon energy. An excitation spectrum shows different population channels for a given luminescence band. To separate emissions with different lifetimes, time-resolution techniques can be used as well.
- A decay curve reflects the time dependence of radiative relaxation for a certain transition.

2.3.1. Data registration

Data registration was identical for both stations used. Luminescence spectra in the UV and visible range were recorded with a spectrograph SpectraPro-308i (Acton Research Corporation) equipped with a photomultiplier (Hamamatsu R6358P). The spectral resolution of the analysing monochromator was typically 11 nm. Emission spectra were corrected for the spectral response of the detection systems. The excitation spectra were recorded with a spectral resolution of 0.3 nm. The excitation spectra were normalised to equal quantum intensities of synchrotron radiation falling onto the sample by means of sodium salicylate as a reference. The exciting pulse duration is 125 ps, while the instrumental time resolution of the registration system was 1 ns. Emission decay kinetics were measured in 190 nm time window.

2.3.2. Data processing

The raw data are influenced by different properties of the experimental setup, such as spectral resolution, time resolution, the spectral sensitivity of the registration systems, the spectral distribution of the exciting light, time-dependence of the intensity of the exciting light, and the dark pulse rate of detectors.

Due to the energy dependence of the excitation intensity (caused by the light source and the transmission of the beamline and the primary monochromator), it is necessary to correct the excitation and reflection spectra to the incident photon flux. Therefore, it is necessary to measure the intensity as a function of the excitation energy using the luminescence of sodium salicylate. Monochromators usually operate in wavelength units. An equality $E = hc/\lambda$ is used for transforming wavelength (λ) to the energy scale (E). Therefore, all luminescence spectra plotted in energy scale are deformed because $\Delta\lambda \approx -(hc/E^2)\Delta E$ is not linear in energy.

2.4. Samples

2.4.1. LaPO₄:Ce,Tb

Luminescent LaPO₄:Ce,Tb nanocrystals in the form of nanopowders with a particle diameter of 8–10 nm were produced via a microwave-assisted synthesis in ionic liquids [12]. The nanopowders were synthesised at the Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT) (in collaboration with Prof. Claus Feldmann and his peers). The crystallinity of LaPO₄:Ce as prepared, the Tb is proven by the powder x-ray diffraction (PXRD) pattern [12] as well as by the high-resolution transmission electron microscopy (HRTEM). Both types of method show the nanoparticles crystallised with a monazite type of structure. The particle diameter of 8–10 nm is calculated using Scherrer's equation. The dopant concentration is 45 mol. % Ce³⁺ and 15 mol. % Tb³⁺. Commercial macroscopic LaPO₄:Ce,Tb powder with the same dopant level was also used in the current study as reference material in the luminescence measurements. The dopant concentrations of 45 mol% Ce³⁺ and 15 mol% Tb³⁺ are quite common for LaPO₄ phosphors [13, 14]. Due to the similar radii of the trivalent rare earth ions, phase separation does not occur [15, 16].

2.4.2. YVO₄:Eu

 YVO_4 :Eu nanopowder was produced via a microwave-accelerated synthesis in ionic liquids similar to LaPO₄ nanocrystals considered above [8]. The details of the synthesis procedure of YVO_4 :Eu nanopowders, as well as the result of the sample's characterizations by means of electron microscopy, energy loss spectroscopy, infrared spectroscopy, dynamic light scattering (DLS), and x-ray diffraction analysis (XRD), have been reported in [8]. According to electron microscopy, DLS, and XRD, the presence of uniform and highly crystalline particles, 12–15 nm in diameter, is validated. Commercial bulk YVO_4 :Eu powder (with particle size of several microns) from Phillips was also studied for comparison. The dopant level in nanosized YVO_4 :Eu was 15 mol. %, whereas the bulk YVO_4 :Eu was typically doped with 5 mol. %. In order to minimise possible surface-related losses, some of the YVO_4 :Eu nanoparticles have been covered by a non-luminescent YF_3 layer of 1–2 nm in thickness, as was described in [8].

2.4.3. Y₃Al₅O₁₂:Ce

In the present study the luminescence properties of YAG:Ce nanopowders obtained by a modified sol-gel method similar to that used by Pechini, are described in detail elsewhere [17]. YAG:Ce nanocrystals have been produced in Institute of Low Temperature and Structure Research, Polish Academy of Science (in collaboration with Prof. W. Strek). The size of nanoparticles was characterised by means of the Scherrer method, Williamson-Hall method, X-ray powder diffraction and BET methods [18]. The average particle size was estimated to be about 20 nm. Cerium ions concentration was varied from 0.5 % to 5.0 % in YAG: Ce nanopowders. Commercial crystal of YAG:Ce was also studied for comparison.

2.4.4. AWO₄ (A=Zn, Ni)

AWO₄ samples synthesised in Institute of the Solid State Physics University of Latvia (in collaboration with Dr A. Kuzmin). NiWO₄ and ZnWO₄ powders were synthesised using co-precipitation technique [19,20] by mixing two aqueous solutions of Na₂WO₄·2H₂O and Ni(NO₃)₂·6H₂O or ZnSO₄·7H₂O salts in bi-distilled water at room temperature (20 °C). The samples' crystallinity and phase composition (formation of solid solution) were controlled by x-ray powder diffraction (XRD) [20, 21]. Previous structural studies of as-prepared nanocrystals reveal very small particle size – even below 2 nm [20, 21]. Subsequent thermal annealing of nanocrystals leads to the strong agglomeration of nanoparticles, forming microcrystalline (100–200 nm) structures. Such microcrystalline samples of ZnWO₄ and NiWO₄ also have been studied for comparison.

3. THEORETICAL OVERVIEW

3.1. Basics of luminescence

Most phosphors are composed of a transparent microcrystalline host (or a matrix) and an activator, i.e., a small amount of intentionally added impurity atoms distributed in the host crystal. Therefore, the luminescence processes of a phosphor can be divided into two parts: the processes mainly related to the host, and those that occur around and within the activator. In the host lattice with an activator, the activator is directly excited by incoming energy; the electron on it absorbs energy and is raised to an excited state. The excited state returns to the ground state by emission of radiation. When the activator ions show too weak an absorption, a second kind of impurities can be added (sensitizers), which absorb the energy and subsequently transfer the energy to the activators. This process involves transport of energy through the luminescent materials. Generally, the activator ions can be distinguished into two types: in the first type, the activator ions strongly interact with the host lattice. This is the case when 'd' electrons are involved, for example, in Mn^{2+} , Eu^{2+} , and Ce^{3+} as well as for S² ions like Pb²⁺ or Sb³⁺ ions interact with complex anions such as $[MoO_4]^{2-}$ or $[WO_4]^{2-}$. In the second type, the energy levels of the activator ion involved in the emission process show only weak/strong interactions with the host lattice. Based on the type of activators involved, inorganic phosphors can be classified into two main types:

a) self-activated (ZnWO₄, CaWO₄, CaMoO₄, etc);

b) impurity doped (LaPO₄:Ce,Tb, Y₂O₂S:Eu³⁺, YVO₄:Eu³⁺, etc).

The activator ions are doped into the host compound in a smaller concentration, usually a few mole percentages. The activator is responsible for the phosphor action of the host and hence, the appearance of colour. Its type and amount can be precisely controlled; however, sometimes an activator may not be required externally for the host lattice. The lattice itself could turn luminous on exposure to the radiation source. Therefore, these materials are considered to be self-activated.

The observed emission from a luminescent centre is a process of returning to the ground state in a radiative manner. The processes competing with luminescence are the radiative transfer to another ion and the non-radiative transfers such as multiphonon relaxation and cross-relaxation. Fig. 3.1 shows the configurational coordinate model of a broadband emission. Upon excitation, the electron is excited in a broad optical band and brought into a high vibrational level of an excited state. The centre thereafter, relaxes to the lowest vibrational level of the excited state and gives up the excess energy to the surroundings. This relaxation usually occurs in a non-radiative manner. From the lowest vibrational level of the excited state, the electron returns to the ground state (equilibrium distance R' with R' > R) by means of photon emission.



Fig. 3.1 Configurational coordinate model in a luminescent centre [22]

3.2. Luminescence properties of rare-earth ions

In crystals, rare-earth trivalent ions possess very similar optical spectroscopic parameters. Nevertheless, they demonstrate some principal differences associated with the nature of the environment where the ion is located. Like most hosts, the position of the RE³⁺ ion 4*f* energy levels does not vary drastically in the ion from host to host. The levels are not affected much by the environment because 4*f* electrons are shielded from external electric fields by the outer $5s^2$ and $5p^6$ electrons [16]. Luminescence originating from electronic transitions between 4*f* levels is predominantly due to an electric dipole or magnetic dipole interactions. Electric dipole *f*–*f* transitions in free 4*f* ions are parity-forbidden but become partially allowed by mixing with orbitals having different parity because of an odd crystal field component.

In addition to the discrete 4*f* levels, there are other levels present. The broad bands can be split into two groups. In the first group, one of the of 4*f* electrons

is raised to the higher 5*d* levels. Transitions from configuration $4f^n$ to $4f^{n-1}$ are allowed. The second group of bands, charge-transfer processes, corresponds to the promotion of an electron from one of the surrounding ions to the 4*f* orbit of the central ion [22].

In the energy region spanned by 4f levels, one finds two additional kinds of electronic states with different characters from those levels. They are the $4f^{n-1}5d^1$ states and the charge-transfer states (CTS) [16]. In the former, one of the 4f electron(s) is transferred to a 5d orbital and, in the latter case, electrons in the neighbouring anions are transferred to a 4f orbital. Both of these processes are allowed and result in strong optical absorptions. The energies of the $4f^{n-1}5d^1$ and CTSs are more dependent on their environments than the energies of 4f states, but the relative order of energies of these states are found to be the same for the whole series of rare-earth ions in any host materials. They can interact with 4f levels, leading to $f \rightarrow f$ emissions. In the event that the energy levels of these states are lower than those of 4f transitions in Ce^{3+} , Pr^{3+} , and Eu^{2+} . Spectra of this luminescence vary as a result of crystal field splitting in host crystals.

Apart from the $f \rightarrow d$ allowed transitions and the CTS bands, strong excitation can often be achieved by the energy transfer. The excitation residing in an ion can migrate to another ion of the same species that is in the ground state as a result of resonant energy transfer when they are located close to each other. The ionic separation where the luminescence and energy transfer probabilities become comparable is in the vicinity of several Angstroms. Energy migration processes increase the probability that the optical excitation is trapped at defects or impurity sites, enhancing non-radiative relaxation. This causes concentration quenching because an increase in the activator concentration encourages such non-radiative processes. As a result, that excitation energy diffuses from ion to ion before it is trapped and leads to emission. On the other hand, a decrease in the activator concentration decreases the energy stored by the ions.

The characteristic energy levels of 4*f* electrons of trivalent lanthanide ions have been precisely investigated by Dieke and co-workers [23]. While the energy of the *f*-levels is more or less independent of the host lattice, the luminescence of rare-earth ions can be understood based on transitions between atomic eigenstates shown in the Dieke diagram (Fig. 3.2). The levels were determined experimentally by considering the optical spectra of individual ions incorporated in LaCl₃ crystals; this diagram is applicable to ions in almost any environment because the maximum variation of the energy levels is, at most, of the order of several hundred cm⁻¹. As a consequence, certain $f \rightarrow f$ transitions always show characteristic luminescence, such as the red emission of Eu³⁺ in LaPO₄:Eu, YVO₄:Eu, Y₂O₃:Eu or YBO₄:Eu.



Fig. 3.2 Dieke diagram showing the energy levels of the trivalent rare-earth ions [23]

4. LITERATURE OVERVIEW

4.1. Cerium and terbium codoped lanthanum phosphate

Basic physical-chemical properties of $LaPO_4$ will be described in chapter 4.1.1. Luminescence properties of $LaPO_4$:Ce,Tb are summarised in 4.1.2.

4.1.1. Lanthanum phosphate single crystal

Lanthanum phosphate (LaPO₄), also known as monazite, is considered as a technologically potential material for corrosion and thermal barrier applications by virtue of its thermal stability, high thermal expansion coefficient, and low thermal conductivity. LaPO4 has been widely used as a phosphor and proton conductor as well as in sensors, lasers, ceramic materials, catalysts and heat-resistant materials. This is due to its interesting properties of very low solubility in water, high thermal stability, a high index of refraction, very high melting temperature (2000 K), and high chemical stability [9, 24–27]. LaPO₄ is reported to have good corrosion resistance in environments containing sulphur and vanadium salts and is reported to be non-reactive with many molten metals [28–30]. It has also been used for thermal insulation, catalytic, and sensor applications [31]. Its resistance to radiation damage and relative stability as a mineral over billions of years has led to the identification of monazite as a candidate material for the immobilisation of radioactive waste elements by incorporation into the monazite crystal lattice [32]. Lanthanum phosphate as host matrices exhibits quite a good ionising and particle radiation as well as photochemical stability. LaPO₄ belongs to a class of wide band-gap materials and its experimental band gap was reported to be around 8.0 eV [33, 34].

The structure of bulk LaPO₄ is shown in Fig. 4.1. It is a monoclinic orthophosphate (space group $P2_1/n$, Z = 4) composed of LaO₉ polyhedra and PO₄ tetrahedra. Lanthanum ions are surrounded by nine oxygen ones. Each oxygen ion is positioned at a different distance (between 2.484 Å and 2.813 Å). Although recently it was described that the crystalline structure of nanosized LaPO₄ doped with Ln ions (Ln=Pr³⁺, Eu³⁺) was changing according to nanoparticle size [35]. For particles with mean size of about 8 nm, a hexagonal phase with the structural type of CePO₄ (space group $P6_222$) was detected; but for LaPO₄:Ln samples with a grain size in the range of 35-90 nm, a monoclinic phase with structural type CePO₄ (a space group $P2_1/c$) was observed.



Fig. 4.1 The structure of bulk LaPO₄ [36]

Some basic physical properties of $\rm LaPO_4$ monocrystal summarised in Table 4.1.

Lattice type	Monoclinic monazite (space group $P2_1/n$, Z = 4)	[37]
Density	5.13 g/cm ³	[38]
Dielectric constant, ε	14	[39]
Melting point	1 797 °C / 2070 K	[40]
Coefficient of thermal expansion	10.5·10 ⁻⁶ K ⁻¹ (1273K)	[41]
Hardness (Mohs scale)	5	[42]
Thermal conductivity (973 K)	1.8 W/mK	[41]
Refractive index	1.85	[43]
Band gap, Eg	8.5 eV	[33]

Table 4.1 Basic physical properties of LaPO₄

4.1.2. Luminescence properties of LaPO₄:Ce,Tb crystals

LaPO₄ has been shown to be a useful host lattice for lanthanide ions to produce phosphors that emit in a broad range of colours [9, 24, 44–46]. Even in 1963, it was already known that LaPO₄: $0.01Ce^{3+}$ was a "short luminescence delay time phosphor", and emits ultraviolet light, which peaks spectrally at about 340 nm when excited with cathode rays, and its luminescence decay time was about 24 nsec [47]. Doping with different types of rare earth ions (Eu³⁺, Ce³⁺, Tb³⁺, Nd³⁺, Er³⁺, Pr³⁺, Ho³⁺, Yb³⁺, Tm³⁺) in macro- as well as nanosized LaPO₄ have been frequently reported in the literature. Among all these phosphate-type phosphors, trivalent cerium (Ce³⁺) and terbium (Tb³⁺) co-activated LaPO₄ (LaPO₄:Ce,Tb) bulk powder is known as the most efficient because of the high-efficiency energy transfer between Ce³⁺ and Tb³⁺ [9, 24, 44–46]. Therefore, bulk LaPO₄:Ce,Tb is intensively used even as an excellent green emitting phosphor for fluorescent lamps [9, 15, and 16]. Nowadays nanocrystalline LaPO₄:Ce,Tb is known as one of the most promising highly luminescent green phosphors, which is one of the best candidates for biomedical applications such as fluorescence resonance energy transfer (FRET) assays, biolabelling, optical imaging, or phototherapy [48–50] where green emission from Tb³⁺ is highly important.

Under UV excitation (for instance under 254 nm radiation of mercury discharge lamps) only forbidden f-f transitions of Tb³⁺ in LaPO₄ could be excited and, therefore, the Tb³⁺ emission is not efficient. On the other hand, allowed an f-d transition in Tb³⁺ ion lays at much higher energies, i.e. at VUV spectral range. Therefore, in order to effectively absorb relatively low energy UV light, a sensitizer should be used. In LaPO₄ phosphor, Ce^{3+} ions with effective 4f-5dabsorption behave as the sensitizer, whereas Tb³⁺ ions act as the luminescent centre. Indeed, under UV excitation of Ce³⁺ ion a $4f^1 \rightarrow 4f^05d^1$ transition occurs. After energy transfer from Ce³⁺ to Tb³⁺ a green Tb³⁺ emission resulting from ${}^{5}D_{4}-{}^{7}F_{1}$ relaxation takes place. Generally speaking, energy transfer plays a major role in most luminescent and laser processes and the appropriate mechanisms for some double-doped crystalline materials that have been perfectly established [9, 15, and 16]. A resonant energy transfer from Ce³⁺ to Tb³⁺ was tentatively suggested. On the other hand, in many cases for the successful realisation of a resonant energy transfer, it is necessary that the spectral dependence of the excitability of Tb³⁺ overlap strongly with a Ce³⁺ decay. According to literature data [44], the Ce³⁺ emission band does not overlap with the $4f^8 \rightarrow 4f^8$ absorption of the Tb³⁺ in LaPO₄ and, therefore, resonant energy transfer processes seem improbable. The typical emission spectrum of bulk LaPO₄, exciting Ce³⁺ ions, consist of two main well-distinguished parts: a broad $4f^1 \rightarrow 4f^05d^1$ C³⁺ emission band peaking at ~350 nm and sharp Tb³⁺ lines (that corresponds to ${}^{5}D_{4} \rightarrow {}^{7}F_{I}$ and ${}^{5}D_{3} \rightarrow {}^{7}F_{I}$ transitions) in the green to the red spectral range [12, 44, 51, 52]. Despite luminescence properties of bulk LaPO₄:Ce,Tb as well as energy transfer processes between Ce³⁺ and Tb³⁺ ions, which have been intensively studied [13, 15, 51–53], it was recently suggested an alternative mechanism of energy transfer in nanosized LaPO₄:Ce,Tb [54].

Absorption spectrum of LaPO₄:Ce,Tb consist of intense and broad $4f^05d^1 \rightarrow 4f^1$ Ce³⁺ band (240–320 nm) peaking at 256 nm and 276 nm [55]. Excitation in the Ce³⁺ band at 276 nm gives both the emission of cerium (3.4–4.13 eV) and that of terbium (1.77–3.35 eV), due to energy transfer from cerium to terbium. The excitation spectrum of Tb³⁺ emission in bulk

LaPO₄:Ce,Tb described in [31] consists of two parts – 4.0–5.6 eV and 5.6–7.7 eV. Part of the excitation spectrum of Tb³⁺ emission in 4.0–5.6 eV is very close to the excitation spectrum of Ce³⁺ emission. Taking in account that f-f transitions of Tb³⁺ occur in this spectral range and that these transitions are not effective, the intensive Tb³⁺ excitation band (in 4.0–5.6 eV) is due to energy transfer from Ce³⁺ to Tb³⁺. The excitation spectrum of Tb³⁺ emission at energies higher than 5.6 eV represents f-d transitions of the Tb³⁺ ions. The abundant structure of this part of the Tb³⁺ excitation spectrum is explained by the spin-allowed and spin-forbidden f-d transitions from the ground $^{7}F(4f^{3})$ state to the lowest ^{7}D ($4f^{7}5d$) and to the lowest $^{9}D(4f^{7}5d)$ terms. In sum, ten bands could be resolved in the excitation spectrum of Tb³⁺ emission in LaPO₄:Ce,Tb in the 5.6–7.7 eV range, which is described in detail in [33] for terbium-doped LaPO₄. The broad excitation band peaked at 7.9 eV is reported to be due to near-activator exciton by analogy to the near-activator exciton bands in the Ce³⁺ excitation spectrum [31].

Decay curve of Ce^{3+} emission in LaPO₄:Ce,Tb single crystal is exponential with a characteristic time of about 16–18 ns [56]. Tb³⁺ luminescence decay is in the millisecond range due to spin and parity forbidden *f*–*f* transition and is about 3.2 ms for macroscopic samples [13]. Ce³⁺ and Tb³⁺ luminescence decay kinetics of nanocrystalline LaPO₄:Ce,Tb do not obey the single-exponential law, it can be approximated by the sum of two exponents – "fast" and "slow". For Ce³⁺ emission characteristic times are ~4–5 ns and 15–20 ns, for Tb³⁺ emission ~1 ns and 4 ns. Similar non-exponential decay was already observed for Tb³⁺ emission in nanosized LaPO₄. CePO₄:Tb³⁺, and nanosized LaPO₄:Tb³⁺. The deviation from an exponential law of Ce³⁺ emission decay in nanomaterials also has been observed recently in some other nanocrystalline materials.

4.2. Europium-doped yttrium vanadate

Physical-chemical properties of the YVO_4 single crystal will be described in 4.2.1. Also, luminescence properties of europium doped YVO_4 are summarised in chapter 4.2.2.

4.2.1. Yttrium vanadate single crystal

 $\rm YVO_4$ is one of the most promising inorganic luminescent materials, which possess zirconia-type tetragonal structure and a wide range of practical applications in many display devices. $\rm YVO_4$ compound has sparked a great interest in the fields of solid-state chemistry, material science, and technology. Yttrium vanadate crystals have a good thermal stability, large birefringence, and very wide transparency range. Due to such physical properties, it is an interesting synthetic alternate for conventional crystals for the fabrication of several optical devices.

Some physical properties of the YVO_4 single crystal are presented in Table 4.2.

Lattice type	Zircon tetragonal, space group D4h	[57]
Density	4.22 g/cm ³	[58]
Dielectric constant, ε	9.3	[59]
Melting point	1810-1940 °C	[58]
Coefficient of thermal expansion	$a_{axic} = 4.43 \cdot 10^{-6} \mathrm{K}^{-1}, c_{axis} = 11.37 \cdot 10^{-6} \mathrm{K}^{-1}$	[57]
Hardness (Mohs scale)	5	[57]
Thermal conductivity (300 K)	a_{axis} -8.9 W/mK, c_{axis} -12.1 W/mK	[60]
Refractive index	1.9504 pie λ = 1550 nm	[61]
Band gap, Eg	3.5 eV	[62]
Transparency range	400-5000 nm	[59]

Table 4.2 Basic physical properties of YVO₄

It is well known that the crystalline form of YVO_4 compound is tetragonal, with a space group of $D_{19}^{4h}I_{41}$ /amd, which is related to tetragonal zircon. The crystal structure of YVO_4 compound is shown in Fig. 4.2. The YVO_4 consist of two kinds of polyhedral: VO_4 tetrahedron and YO_8 triangular dodecahedron. Each V⁵⁺ site is surrounded by four oxygen atoms with a separation of 1.71 Å between V and O, and each Y is surrounded by eight O atoms with a Y–O distance of either 2.29 Å (for four of the eight Y–O bonds) or 2.44 Å (for the remaining four Y–O bonds), the point symmetry of Y³⁺ is D2d without an inversion center. The shortest V–V, Y–Y, O–O, and V–Y distances are about 3.9, 3.9, 2.6, and 3.1 Å, respectively. The space between the isolated VO_4 tetrahedral units is occupied by Y³⁺ ions. Along the z-axis, alternating tetrahedral and dodecahedra share edges [63].



Fig. 4.2 YVO₄ structure [64]

 YVO_4 is one of the best candidates with high luminescence efficiency for doping the rare earth ions. It provides a wide band gap and suitable Y³⁺ sites where trivalent rare-earth ions can be easily substituted without additional charge compensation. Due to its unique electronic structure and well-defined transition modes, rare-earth ions entrapped in the YVO₄ matrix constitute an essential domain of the lanthanide-based nanostructure families. Europium-doped yttrium vanadate is widely used as an efficient red emitting phosphor in displays and fluorescent lamps, X-ray detectors, and cathode ray tubes [9, 15, 16, and 65]. Moreover, doped YVO₄ crystal has a low generation threshold, good mechanical and chemical properties [66]. Recent studies show that nanosized europium doped YVO₄ is relevant for plasma display panels [67], and additional interest is related to labelling, signalling, and biomedical purposes [49].

Since Levine and Palilla [68] in 1964 developed the Eu^{3+} doped YVO_4 as a red phosphor for the commercial applications in colour television cathode ray tube displays and high-pressure mercury lamps, there has been an extensive study on this material doped with different lanthanide ions such as Er^{3+} , Sm^{3+} , and Dy^{3+} .

4.2.2. Luminescence properties of YVO₄:Eu crystals

Luminescence properties of YVO₄:Eu crystals have been studied for more than 40 years [65, 68–76]. In the excitation spectra of YVO₄, broad bands ranging from 220 to 350 nm corresponds to absorption of vanadate bands resulting from a charge transfer from the excited ligands to the central vanadium atom inside the VO_4^{3-} ions [77]. The absorption transition involved is a charge transfer from oxygen 2p to the vanadium 3d states. Pure YVO₄ does not show luminescence at room temperature, but at temperatures below 200 K, it shows blue emission centred at 420 nm with ultraviolet excitation [16]. The emission and excitation are due to the ${}^{3}T_{1} \leftrightarrow {}^{1}A_{1}$ transition, luminescence takes place from the lowest level of the excited states manifold after radiationless relaxation from higher excited states and lattice relaxation in the lowest level [78]. This results in a significant Stokes shift. Once the vanadate centre is excited, it can either emit the absorbed energy as luminescence or it can transfer the energy to a dopant, which can subsequently emit its own characteristic radiation. The decay behaviour of the VO4³⁻ molecular complex exciting at 265–310 nm is complicated and consist of an initial rise and a subsequent decay [65, 79]. The YVO₄:Eu³⁺ shows strong red emission under UV illumination due to efficient energy transfer from excited VO₄³⁻ complex anions to Eu³⁺ activator ions; quantum yields as high as 70% are reported for the bulk material, as provides that YVO₄:Eu³⁺ is one of the most important phosphor compounds [80].

The emission spectra of YVO_4 :Eu³⁺ consist of emission bands ranging from 550 nm to 700 nm that are assigned to electronic transitions of europium ion

 $({}^{5}D_{0}-{}^{7}F_{J=1,2,3,4})$. The emission spectrum is dominated by the Eu³⁺ ${}^{5}D_{0}-{}^{7}F_{2}$ (at 619 nm) transition that is hypersensitive to chemical bonds in the vicinity of the Eu³⁺ ions, which is because the Eu³⁺ is located at a low symmetry local site (D_{2d} , without inversion center) in the YVO₄ host lattices [81]. On the other hand, the band at 595 nm (${}^{5}D_{0}-{}^{7}F_{1}$) is a magnetic dipole one and it hardly varies with the crystal field strength around Eu³⁺ ion [82]. The presence of emission lines from higher excited states of Eu³⁺ (${}^{5}D_{1}$, ${}^{5}D_{2}$, ${}^{5}D_{3}$) is attributed to the low vibration energy of VO₄³⁻ groups (823 cm⁻¹). As it was described by Blasse and Grabmaier [15] the multiphoton relaxation of VO₄³⁻ is not able completely to bridge the gaps between the higher energy levels and grown level of Eu³⁺, as result, there are weak emissions from ${}^{5}D_{1}$, ${}^{5}D_{2}$, ${}^{5}D_{3}$ levels.

The decay behaviour of Eu³⁺ luminescence in YVO₄ crystal strongly depends on excitation. For the ${}^{5}D_{0}-{}^{7}F_{2}$ emission (618 nm) under excitation into the Eu³⁺ *f*-*f* transition at 395 nm decay curve can be well fitted by a single exponential function. A lifetime of Eu³⁺ obtained for the bulk is 0.525 ms [68] and 0.740 ms for nanocrystalline YVO₄:Eu [65].

4.3. Cerium-doped yttrium aluminium garnet

In chapter 4.3.1, a summary of some physical-chemical properties of YAG:Ce single crystal and luminescence properties of cerium doped YAG crystals will be put forth and further described in 4.3.2.

4.3.1. Yttrium aluminium garnet single crystal

Yttrium Aluminium Garnet (YAG) is a synthetic crystalline material of the garnet group. Pure YAG is colourless, non-hygroscopic, chemically inert crystal with body-centered cubic lattice. YAG has emerged as the most widely produced laser gain host and has enjoyed recent popularity as a promising material for optical, electronic and structural applications [83, 84]. The YAG host is a stable compound, mechanically robust, physically hard, optically isotropic, and transparent from below 300 nm to beyond 4 microns. Optical YAG crystals are suitable for use in UV and IR optics. Products from YAG can be used as optical elements in the broad spectral range from 250 nm to 5000 nm. YAG mechanical and chemical properties are close to sapphire, but YAG do not exhibit double refraction like sapphire and is much easier to polish comparing with Sapphire. In contrast to glass, YAG has very low absorption in the 2–3 micron range where glasses usually have a high absorption due to strong bonds of water molecules. YAG is also a candidate for applications of high-temperature structural materials due to its low creep rate and high thermal stability and good chemical resistance [85, 86]. Some physical properties of YAG are presented in Table 4.3.

Lattice type	Body centered cubic (space group Ia3 <i>d</i>)	[87]
Density	4.56 g/cm ³	[87]
Dielectric constant, ε	11.7	[87]
Melting point	1970 °C / 2273 K	[88]
Coefficient of thermal expansion	$8.9 \cdot 10^{-6} \mathrm{K}^{-1}$	[87]
Hardness (Mohs scale)	8.5	[89]
Thermal conductivity (300 K)	10.1 W/mK	[60]
Refractive index	1.81 pie $\lambda = 1050$ nm	[90]
Band gap, Eg	7.9 eV	[91]
Transparency range	0.21 to 5.5 μm	[87]

Table 4.3 Basic physical properties of YAG:Ce.

It has a body-centered cubic structure (space group Ia3*d* or O_h^{10}) with 160 (80) atoms in the cubic (primitive) cell. The Y ions (A atom) occupy the 24(c) sites and each is dodecahedral coordinated to eight O. The O atoms occupy the 96(h) sites whose exact locations depend on three structural parameters x, y, and z and are different for different garnet oxides. There are two different sites for Al, Al_{oct} (B' atom) occupy the 16(a) site with an octahedral point symmetry (C_{3i}) and Al_{tet} (B") atoms occupy the 24(d) sites with a tetrahedral point symmetry (S_4). The garnet structure can be viewed as interconnected octahedrons, tetrahedrons, and dodecahedrons with shared O atoms at the corners [92]. YAG structure is depicted in Fig. 4.3.



Fig. 4.3 YAG structure

Due to its interesting physical properties, YAG is widely used as a host material for rare-earth ions that usually replace Y ions, due to similar radii. The most popular dopants for YAG are Yb³⁺, Ce³⁺, Eu³⁺, Nd³⁺, Pr³⁺, or other rare

earth elements. In many cases, rare-earth ion spectra consist of lines whose existence can be described with forbidden transitions in the 4f shell.

4.3.2. Luminescence properties of YAG:Ce crystals

Cerium doped YAG (YAG:Ce) is an important and well-known luminescent material that had been studied more than 40 years. YAG:Ce is one of the most popular materials among others because of its efficient yellow-green luminescence, when subjected to blue or ultraviolet light, or to x-ray light [93]. It is used in white light-emitting diodes, the phosphor in cathode ray tubes; it is suitable for use in photomultipliers. Moreover YAG:Ce is one of the most perspective scintillator material, for application in Positron Emission Tomography (PET) scanners, high-energy gamma radiation and charged particle detectors, and high-resolution imaging screens for gamma, x-rays, beta radiation and ultraviolet radiation [94, 95].

Cerium ion is the simplest rare-earth activator because of an unpaired electron on 4f orbital. Among the lanthanide ions, the $4f \rightarrow 5d$ transition energy is the lowest in Ce³⁺. In contrast to other rare-earth ions, the luminescence of Ce³⁺ ions consists of bands that are described with allowed transition of several 4f-5d configurations. As for luminescence in Ce³⁺ are responsible allowed transitions, a lifetime of excited electrons is short, so the decay time of the Ce³⁺ emission is 10^{-7} to 10^{-8} s [16]. The position of luminescence band in spectrum depends on the crystal structure of material.

Increasing crystalline field, increase also splitting of 5d- state, maximums of luminescence bands tends to long-wavelength part of the spectrum and increase bandwidth that corresponds to electron transition from 5d state to two levels of 4f- shell. Splitting of 4f- level into ${}^{2}F_{5/2}$ un ${}^{2}F_{7/2}$ states gives two luminescence bands of Ce³⁺ in most cerium doped phosphors.

YAG:Ce³⁺ luminescence, excitation and absorption spectra in single crystals are described in many papers [96–102]. Absorption spectra of bulk YAG:Ce consist of several bands, three of them with maximums at 460, 340 and 220 nm, that corresponds to 4f-5d transitions in Ce³⁺ are reported in many papers [98–103], although there are differences in the assignments of the remaining two bands. The band at 372 nm described in [96] was not observed in other absorption spectra. The band at 261 nm [102] was not observed in some other excitation and absorption spectra and a lattice defect band at 270 nm in the absorption spectrum of YAG is absent in ceramic samples of YAG:Ce³⁺ [98].

The luminescence spectrum of bulk YAG:Ce consists of two main parts: cerium related and intrinsic emissions. Cerium-related emission arises due to transition from the lowest 5*d* excited state to a 4*f* ground state of Ce ion. Splitting of 4*f*- level into ${}^{2}F_{5/2}$ un ${}^{2}F_{7/2}$ states gives two luminescence bands of Ce³⁺ in YAG:Ce at low temperatures [104]. Two types of centres are responsible for

the intrinsic luminescence in bulk YAG: self-trapped exciton (STE) and *antisite* centre [91, 105–108]. Exciting YAG single crystal in exciton absorption range (about 7.0 eV) two overlapped emission bands appears in range of 3.0 eV – 6.0 eV [107, 109, 110]. High energy band with a maximum around 4.7 eV is responsible for self-trapped excitons emission, but the band in the range 3.95–4.2 eV is attributed to Y^{3+}_{Al} (antisite defects) luminescence. High-energy emission band is more dominant at low temperatures because the lifetime of the excited state is longer due to low possibility of non-radiative transitions at low temperatures.

The decay of Ce³⁺ in YAG single crystal can be expressed as a single exponent with a time constant to the range of 63–80 ns [91, 111]. Decay kinetics of cerium emission in nanocrystalline YAG:Ce may be approximated by two exponents with decay times 9 ns and 47 ns, and the contribution of the fast component of luminescence decay is about 33% [91].

4.4. Wolframite-type tungstates crystals

In this chapter will be summarised some physical-chemical properties of wolframite-type tungstates crystal and described luminescence properties of it.

4.4.1. AWO₄ (A=Zn, Ni) single crystals

AWO₄ compounds and name tungstates, are interesting materials for applications such as scintillation detectors, laser-active hosts, optical fibers, sensors, and phase-change optical recording media [92, 112, 113]. A self-activated zinc tungstate ($ZnWO_4$) and nickel tungstate (NiWO₄) possess good properties such as high chemical stability, high average refractive index, high X-ray absorption coefficient, high light yield, short decay time and low afterglow. These two tungstates are very promising host materials since they are nonhygroscopic and nontoxic, and they exhibit intrinsic photoluminescence properties. ZnWO₄ has application in scintillator [114], Raman laser converters [115], high-temperature solid lubricant [116], magnetic and luminescent materials [117], laser hosts [118], optical fibers [119], and gas-sensing systems [120]. The compound has recently attracted a lot of attention due to its promising role in the searches for the weakly interacting massive particle. ZnWO₄ further exhibits considerable photocatalytic and photoelectrocatalytic properties in the mineralisation of organic compounds [121]. The properties of $ZnWO_4$ have been found to be closely related to its crystallinity, particle size distribution, and morphology and hence, depend on its method of synthesis [122]. NiWO₄ finds applications in catalysis [123], as humidity and gas sensor [124, 125], a photoanode in the photovoltaic electrochemical cell [126], a pigment [127] and in the microwave [128] and electrochromic devices [129].

The type of the tungstate structure can be scheelite or wolframite and depends crucially on the ionic radius of the A^{2+} cation [130]: for small A^{2+} cations (A = Co, Cd, Fe, Mg, Ni, & Zn) the wolframite structure is preferable, but in the case of bigger A^{2+} cations (A=Ba, Ca, Eu, Pb, & Sr) the scheelite structure becomes favorable.

In the present work, $ZnWO_4$ and $NiWO_4$, are examined, which have the monoclinic wolframite-type structure of the space group P2/c or C_{2h}^4 . The primitive cell contains 2 formula units, i.e. it contains 12 atoms in a unit cell. In the structure of wolframite AWO₄, both cations A and W have octahedral oxygen coordination and each octahedron shares 2 corners with its neighbours [131]. The structure is shown in the Fig. 4.4. The presence of two non-equivalent oxygen atoms is responsible for three pairs of A–O and W–O bonds, having different lengths. EXAFS data analysis of ZnWO₄ and NiWO₄ [132] prove that WO6 octahedra in this two tungstates are distorted with four short (1.84 Å) and two long (2.13 Å) W–O distances. Thus, both A and W atoms are surrounded by six oxygen ions, forming distorted octahedral coordination.



Fig. 4.4 Crystal structure monoclinic (P2/c) AWO₄ [133]

ZnWO₄, mineral name sanmartinite, have the lattice parameters a = 4.7 Å, b = 5.7 Å, c = 4.9 Å and $\beta = 90^{\circ}6'$ [130], but lattice parameters of NiWO₄ are a = 4.6 Å, b = 5.7 Å, c = 4.9 Å, and $\beta = 90.03^{\circ}$ [134].

Basic properties of ZWO_4 are listed in Table 4.4. Unfortunately, it was impossible to find in literature the same data for NiWO₄, but we suppose that NiWO₄ properties are quite close to ZnWO₄.

Lattice type	Monoclinic structure, space group <i>P2/c</i>	[131]
Density	7.8 g/cm ³	[135]
Dielectric constant, ε	20.7	[136]
Melting point	1200 °C / 2098 K	[137]
Coefficient of thermal expansion	7.9·10 ⁻⁶ K ⁻¹	[138]
Hardness (Mohs scale)	4-4.5	[119]
Thermal conductivity (300 K)	4.54 W/mK	[139]
Refractive index	2.32 at $\lambda = 490$ nm	[140]
Band gap, Eg	4.6 eV	[114]

Table 4.4 Basic physical properties of ZnWO₄

4.4.2. AWO₄ (A=Zn, Ni) luminescence

The optical and luminescent properties of wolframite-type $ZnWO_4$ and NiWO₄ crystals have been widely studied in the past more than once [20, 114, 141–148].



Fig. 4.5 Schematic energy level diagram (not to scale) for the luminescence processes in the (WO₄)²⁻ complex in scheelite structure (a) and the (WO₆)⁶⁻ complex in wolframite structure (b). The full arrows indicate allowed absorption and emission transitions. The broken lines arrows indicate forbidden transitions [141]. A schematic representation of energy levels responsible for radiative transitions in wolframites is shown in Fig. 4.5. Molecular orbital calculations were done in the $(WO_6)^{6-}$ complex in O_h point symmetry for obtaining this diagram [149]. It was described before [141, 143, 150] that for the intrinsic luminescence component in AWO₄ crystals is responsible electronic transition ${}^{3}T_{1u} \rightarrow {}^{1}A_{1}$ between O^{2-} and W^{6+} ions within the octahedral $(WO_6)^{6-}$ molecular complexes. Absorption by the $(WO_6)^{6-}$ complex is assigned to the ${}^{1}A_{e1} \rightarrow {}^{1}T_{1u}$ transitions.

Absorption spectra of NiWO₄ consist of 4-5 bands in UV and visible range from 1 eV to 3.5 eV [127, 142, 151]. Some authors [146] by analogy with NiO [152, 153] attribute these bands to the transitions from the ground state ${}^{3}A_{2}$ to excited states ${}^{3}T_{2}$, ${}^{1}E$, ${}^{3}T_{1}$, ${}^{1}T_{2}$ and ${}^{3}T_{1}$. In [127] and [151] have a similar explanation to observed absorbance bands. The band at 2.97 eV is attributed to the charge-transfer transition in the WO₆ matrix. Bands at 1.67 and 2.74 eV are assigned to the forbidden electronic transition from ${}^{2}A_{2g}$ to ${}^{1}E_{g}$ and ${}^{1}T_{2g}$, respectively. The band at 1.48 eV is assigned to the presence of Ni²⁺O₄ indicating that Frenkel defects are present in NiWO₄ with the dislocation of Ni²⁺ from octahedral to tetrahedral sites. Absorbance band at 3.7 eV observed in [127] may be related to charge transfer transitions.

Excitation spectra of few anisotropic tungstate crystals with scheelite and wolframite structure type were described by Kolobanov et al [114]. The excitation spectrum of intrinsic emission in the ZnWO₄ single crystal consists of the threshold at 3.8 eV that corresponds to the region of fundamental absorption edge (Urbach tail), a band with a maximum around 4 eV is due to the direct creation of excitons [114, 143]. Significant luminescence intensity decreased in the region from 4.2 to 10 eV is characteristic for the excitonic type of energy transfer to the emission centres [144]. In the energy region above 11 eV, the rise of the intensity in the excitation spectra is observed, which is caused by the beginning of the multiplication of electronic excitation processes. Further increase of intensity exhausts at excitation energy corresponding to the participation in the multiplication of electronic excitation processes of the electrons from the bottom of the valence band [114, 143]. There is no information available in literature about NiWO₄ excitation spectra. However, taking into account that it has the same structure as ZnWO₄ and all processes are within [WO₆]⁶⁻ molecular complex, moreover, it was described by Kolobanov et al that excitation of different tungstens are similar, we suppose that excitation spectrum of NiWO₄ can be analyzed by analogy with ZnWO₄.

It has been reported by G. Blasse [154] that metal tungstates exhibit blue luminescence spectra, which is based on the radiative transition within the tetrahedral. In particular, the intrinsic blue luminescence bands at room temperature at about 2.5 eV for $ZnWO_4$ [114, 141, 143, 147, 148] and 2.06 eV for NiWO_4 [151], are observed. Emission band of $ZnWO_4$ shifts to the low-energy region and becomes narrower with cooling of the samples that is due to

the interaction of STE with phonons [141]. Although previously it has been confirmed by studies of the emission and excitation spectra that only a single, broad blue emission band exists in pure single crystals of ZnWO₄ and other tungstates that have been assigned to radiative electron transition within [WO₆]⁶⁻ molecular complex [114, 143], emission bands were reported in literature, ascribed to some impurities and different structural defects. The emission spectrum for the ZnWO₄ film was deconvoluted into three narrower emission bands: a strong intrinsic emission peaked at 2.51 eV (495 nm) and two weak emissions in higher energy range of 2.80 eV (444 nm) and in lower energy range of 2.30 eV (540 nm) [117]. By analogy with CdWO₄ that have the same wolframite structure as ZnWO₄ and NiWO₄, higher energy and intrinsic emissions are explained with the intrinsic WO_6^{6-} complex with a double emission from one and the same center $({}^{3}T_{1\mu} - {}^{1}A_{1\rho})$, whereas the lower energy emission is due to recombination of e-h pairs localized at oxygen atom deficient tungstate ions [155, 156]. However, Ovechkin [150] ascribed the higher energy band to the self-trapped exciton in tungstenite crystals with strong electron-phonon coupling, and main intrinsic emission and lower energy bands to the transitions of T_{2u} - T_{2g} and T_{1g} - T_{2g} in the WO₆⁶⁻ complex

5. EXPERIMENTAL RESULTS AND DISCUSSION

5.1. LaPO₄:Ce,Tb luminescence

In luminescence spectra of Tb³⁺ emission for both bulk and nanosized samples the characteristic Tb³⁺ lines resulting from ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ transitions occur. The fine structure of the Tb³⁺ lines is significantly smoothened in the case of the nanopowder comparing to the commercial bulk material (inset in Fig. 5.1). A characteristic duplex structure of the Ce³⁺ emission band in the 300–360 nm range caused by splitting 4*f* ground level is well resolved in the bulk sample, whereas this duplex structure is almost absent in the spectrum of the nanopowder. Maximum of Ce³⁺ emission band is slightly shifted to the low energy side in the nanosized sample.



Fig. 5.1 Emission spectra of Tb³⁺ and Ce³⁺ ions (inset) in the macroscopic and nanosized LaPO₄:Ce,Tb under excitation in the Ce³⁺ absorption band (250 nm) at 10 K

Comparison of excitation spectra of Ce^{3+} and Tb^{3+} in bulk and nanosized samples are depicted in Fig. 5.2. The excitation spectrum of the Ce^{3+} emission (Fig. 5.2(a)) in the 4.0–6.5 eV range of the bulk sample shows 4f-5d transition of Ce^{3+} ion in the LaPO₄ matrix. This spectrum is composed of five bands peaking at 4.46, 4.76, 5.2, 5.8 and 6.05 eV, which are due to the transition from the ground state ${}^{2}F_{5/2}(4f^{1})$ to the five crystal-field split levels of ${}^{2}D(5d^{1})$ excited state in LaPO₄ lattice. The excitation spectrum for Ce³⁺ emission in the nanosized sample has intensive bands in the 3.5–6.5 eV spectral range, which are qualitatively similar to the corresponding excitation bands obtained for the bulk material. However, the fine structure due to the crystal-field splitting is poorly resolved for the nanomaterial. The intensive excitation band peaking at 4.0 eV (300 nm) is observed for the nanomaterial and is absent in the excitation spectrum of bulk LaPO₄:Ce,Tb. It is supposed that the redshift of the excitation spectra is due to perturbation of 5d levels of Ce³⁺ ions in nanosized LaPO₄:Ce,Tb. As a result of such perturbation, the 5d excited state is slightly shifted and Ce³⁺ excitation spectrum in nano LaPO₄:Ce,Tb is shifted to the low energy side, comparing with the corresponding spectrum for the bulk sample.

The low energy part of the excitation spectrum of Tb^{3+} emission for the bulk sample, where the f-f transition in Tb^{3+} occurs is very close to the excitation spectrum of Ce^{3+} emission. This intensive excitation appears due to energy transfer from Ce^{3+} to Tb^{3+} , as f-f transitions of Tb^{3+} emission are not effective in the terbium-doped LaPO₄ [33]. The excitation spectrum of Tb^{3+} emission at energies higher than 5.6 eV represents f-d transitions of the Tb^{3+} ion. The abundant structure of this part of the Tb^{3+} excitation spectrum is explained by the spin-allowed and the spin-forbidden f-d transition from the ground $^{7}F(4f^{3})$ state to the lowest $^{7}D(4f^{7}5d)$ and to the lowest $^{9}D(4f^{7}5d)$ terms.



Fig. 5.2 Comparison of excitation spectra of Ce³⁺ (340 nm) (a) and Tb³⁺ (542 nm) (b) emissions for bulk and nanosized LaPO₄:Ce₇Tb at 10K in 3.5–10 eV spectral range

The excitation spectrum of Tb^{3+} emission in LaPO₄:Ce,Tb nanopowder have similar intensive peaks in 3.5–5.6 eV range as a bulk sample that arises due to energy transfer from Ce³⁺ ions to Tb^{3+} ions. However, the part of the excitation spectrum due to *f*–*d* transitions on Tb^{3+} (5.6 eV and higher) is significantly suppressed in the nanomaterial, meaning that Tb^{3+} cannot be directly excited in nanosized LaPO₄:Ce,Tb, but could be excited after energy transfer from Ce³⁺ only. We suggest that due to the small nanoparticle size and a high impurity concentration, Tb^{3+} and Ce³⁺ ions are closely distributed. Since the cerium concentration is in three times higher than for terbium, Ce³⁺ ions "shield" Tb^{3+} ions and Ce³⁺ excitation is much more probable.

Spectral range from 6.5 to 8.5 eV in both bulk and nano LaPO₄:Ce,Tb could belong to excitonic excitation bands (including self-trapped and/or bound excitons), as band gap energy of LaPO₄ is 8 eV. The excitation bands of the bound exciton near Ce³⁺ are well resolved in the 6.5-8.0 eV range in bulk LaPO₄:Ce,Tb, whereas these bands are significantly smoothed and suppressed in the nanopowder (Fig. 5.2(a)), obviously due to surface influence, as optical properties of excitons are extremely sensitive to nanoparticle size with increased role of surface effects.



Fig. 5.3 Comparison of excitation spectra of Ce³⁺ (340 nm) (a) and Tb³⁺ (542 nm) (b) emissions for bulk and nanosized LaPO₄:Ce,Tb at 10 K in wide spectral range (3.45-40 eV). Black arrows point out the initial stage of MEE processes

Comparing excitation spectra at energies higher than 8eV it is clearly seen that both Ce^{3+} and Tb^{3+} emissions practically could not be excited in the nanopowders if the excitation energy exceeds the band gap energy of LaPO₄ (Fig. 5.3). This fact clearly indicates that there is no energy transfer from the LaPO₄ matrix to the Ce^{3+} and Tb^{3+} ions in nanoparticles. In the bulk sample, after some relaxations, electrons and holes are trapped by dopants, forming excited Ce^{3+} and Tb^{3+} ions, and their radiative relaxation leads to Ce^{3+} and Tb^{3+} emissions. On the other hand, electrons and holes in the nanoparticles could be easily trapped by surface defects, where their non-radiative relaxation occurs. Such surface related loss processes are the main reason of luminescence vanishing under high energy excitations in nanosized LaPO₄:Ce,Tb.

Also it worth mentioning the multiplication of electronic excitations (MEE) that takes place under high energies. MEE processes' creation means that two or more luminescence centres are created per one absorbed photon. It is clearly seen from Fig. 5.3 that for bulk LaPO₄:Ce,Tb, the rise of the excitation intensity for both Ce³⁺ and Tb³⁺ emissions starts at about 15–17 eV. This value is very close to the value of $2E_g$, keeping in mind that E_g in LaPO₄ is 8 eV.

5.2. YVO₄: Eu luminescence

5.2.1. YVO₄:Eu luminescence under synchrotron radiation



Fig. 5.4 Comparison of fine structure of Eu³⁺ emission in YVO₄:Eu under 300 nm excitation

Emission spectra for bulk and two nano (as-grown and YF₃ covered) YVO₄:Eu samples reveal the characteristic Eu³⁺ emission lines (Fig. 5.4) which are well known in the literature [8, 65, 76]. These spectra do not depend on excitation energy wavelength and are identical under any excitations in the 3.7-40 eV energy range observed on both synchrotron-based endstations. The luminescence intensity of Eu³⁺ drops down in the nanocrystalline sample comparing with the bulk material; even though the luminescence intensity significantly recovered after surface passivation by YF3 core-shell layer. The band gap of YVO4 is comparably small ($E_g \approx 3.4$ eV), meaning that even under comparably low 300 nm excitation, europium luminescence could be excited only after energy transfer from YVO_4 matrix to Eu^{3+} ions with subsequent f-f radiative relaxation $({}^{5}D_{0} \rightarrow {}^{7}F_{I}$ transitions). Therefore, Eu³⁺ emission should very sensitive to surface related losses in YVO4 nanoparticles. Surface related losses mean that electronic excitations are trapped by surface defects and/or imperfections with subsequent non-radiative annihilation. Under band-to-band excitation, the excited intrinsic molecular complex $(VO_4)^{3-}$ is created. The energy transfer from $(VO_4)^{3-}$ complex to activator ion leads to characteristic Eu³⁺ emission. However, electrons and holes during their thermalization could be efficiently trapped by surface loss centres instead of the formation of excited $(VO_4)^{3-}$ complex with subsequent energy transfer to Eu³⁺ ions. Therefore, a non-radiative relaxation on the surface of a nanoparticle could be considered as one of the competing relaxation channels in nanoparticles. Obviously, surface passivating of YVO4 nanoparticles by yttrium fluoride layer leads to the suppressing of some surface loss centres and increases the efficiency of Eu³⁺ emission.



Fig. 5.5 Luminescence spectra of intrinsic emission in bulk, nano, and core-shelled nano YVO₄:Eu under UV excitation at 10 K. Emission lines of Eu³⁺ are measured with low spectral resolution

Another competing relaxation process is a radiative relaxation of excited (VO₄)³⁻ molecular complex that itself is an efficient, intrinsic luminescence centre in YVO₄ and this intrinsic emission stems from ${}^{3}T_{1} - {}^{1}A_{1}$ radiation [16]. Additionally to the Eu³⁺ emission lines shown with a high resolution in Fig. 5.4, the broad, intrinsic luminescence has also been detected for bulk and nano YVO₄:Eu in the blue spectral range (Fig. 5.5). This relatively wide emission band at about 450 nm has been observed in the bulk and nanocrystalline samples, while this intrinsic emission is negligibly small or even absent in the emission spectrum of the YVO₄:Eu@YF₃.

Temperature dependencies of the intrinsic emission bands in bulk and nanocrystalline YVO₄:Eu under UV excitation is presented in Fig. 5.6. The position and shape of the intrinsic emission bands in the bulk and nanocrystals are the same at low temperature, although it changes as the temperature increases. In the case of nanocrystals, the intrinsic emission band tends to be shifted toward the low energy side if temperature increases, whereas the position of the corresponding band in the bulk remains the same at any temperature. Similar red shift of the emission band is known for other complex oxide compounds taking the form of ABO_4 with A standing for a monovalent alkaline, divalent alkaline earth, or trivalent lanthanide metal ion, and B for W, Mo, V, or P. According to the literature [157–159] the red-shifted emission band in ABO_4 materials is related to perturbed or defected metal-oxide molecular complex. This means that the red-shifted broad emission band in the nanocrystalline sample stems from the $(VO_4)^{3-}$ molecular complex, which is close to the surface of a nanoparticle.



Fig. 5.6 Temperature dependencies of the intrinsic emission bands in bulk and nanocrystalline YVO₄:Eu under UV excitation

We have applied Mott and Seitz equation to the temperature dependence and evaluated activation energies for thermal quenching of intrinsic emission in bulk and nanocrystalline YVO₄:Eu by analogy how it was described in [160]. Activation energies obtained for bulk and nano are equal with 59 meV and 35 meV respectively. Such a difference in activation energies also confirms that emission centres responsible for blue intrinsic emission in bulk and nanocrystals are different: the regular and surface related (VO₄)^{3–} complex in bulk and nano, correspondingly.

The intensity of the broad blue emission in respect of the intensity Eu³⁺ lines is highest in non-covered nanocrystals, while it is absent in YVO₄:Eu@YF₃ nanocrystals. This means that YF₃ protection layer around YVO₄:Eu nanoparticle increases the intensity of Eu³⁺ emission not only due to a passivation of surface loss centres but also because of switching off one of competing relaxation channels – luminescence of $(VO_4)^{3-}$. We suggest the following scenario explaining the behaviour of intrinsic emission in nanosized YVO4:Eu and YVO4:Eu@ YF₃ samples. Excited $(VO_4)^{3-}$ molecular complex tends to have a quick energy transfer to neighbouring activator ions. Taking into account that $(VO_4)^{3-}$ molecular complex is a part of the host lattice, obviously, its concentration, in any case, is higher than the concentration of Eu^{3+} . Furthermore, since a radiative f-ftransition in Eu³⁺ is forbidden it is a relatively slow (please see the decay kinetics below) and each Eu³⁺ ion cannot accept energy again while it is not relaxed, there are some residual amount of excited (VO₄)³⁻ complexes, which relax radiatively in the bulk sample producing blue intrinsic emission band (Fig. 5.5). On the other hand, energy transfers from $(VO_4)^{3-}$ complexes to Eu³⁺ ions are restricted by nanoparticle size of nanopowders. Some amount of excited (VO₄)³⁻ centres is able to transfer energy to nearest Eu³⁺ ions only, whereas a long-distance energy transfer is restricted by nanoparticle size. The energy transfer occurs via similar $(VO_4)^{3-}$ complexes, however, surface related $(VO_4)^{3-}$ complexes are perturbed by surface and therefore they are distinguished from the corresponding volume complexes. Therefore, surface $(VO_4)^{3-}$ complexes are terminate stage of energy transfer, i.e. reaching the surface $(VO_4)^{3-}$ complexes the radiative decay takes place producing the broad blue emission band (Fig. 5.5). The energy transfer via VO₄ centres is quick but nanoparticle size is small, meaning that the probability of energy transfer to Eu³⁺ or to the surface of a nanoparticle is very similar. Therefore, the intensities of the Eu³⁺ and blue emissions depicted in Fig. 5.5 are comparable. The absence of the intrinsic emission band in YVO₄:Eu@YF₃ sample can be explained by the equivalency between a surface and a volume (VO₄)³⁻ centres in core-shell layered YVO₄:Eu@YF₃ nanoparticles. This means that excited $(VO_4)^{3-}$ centre near core surface is not the last stop of energy transfer anymore and it can transfer energy back to the next vanadate-oxygen complexes in volume of nanoparticle until a non-excited Eu³⁺ ion is found. Since nanoparticles' size is small, the probability of energy transfer to

 Eu^{3+} ions in such conditions is very high. Our model successfully explains the absence of the blue intrinsic emission with simultaneous increase of the intensity of Eu^{3+} in the emission spectrum of core-shell layered YVO₄: $Eu@YF_3$ depicted in Fig. 5.5.



Fig. 5.7 Excitation spectra of Eu^{3+} emission in the bulk, nanosized and nanosized YF_3 -covered YVO_4 :Eu at 10 K in the 3.5-10 eV (a) and 3.5-40 eV (b) spectral ranges

Excitation spectra for Eu^{3+} emission for three samples studied are depicted in Fig. 5.7. Spectra are normalised for better comparison. At least three peaks could be resolved in the excitation spectra for all samples studied: at 4 eV, 5 eV, and 6 eV. Taking into account that similar excitation spectra are observed for YVO_4 :Eu samples which were produced by different methods we can conclude that the structure of the excitation spectra in 3.5–7.0 eV spectral range has intrinsic nature. For instance, we suppose that density of states in vanadate bands is responsible for the structure of the excitation spectra.

The most significant distinction in the excitation spectra between bulk and nano YVO_4 :Eu is observed in the high energy part. The excitation spectrum for bulk YVO_4 :Eu has a strong rise at energies higher than 10 eV reaching maximum at 30 eV. It is necessary to note that the intensity of the excitation peak at 30 eV is very close to most intensive peak at 4 eV. Such strong intensive excitation of Eu³⁺ emission with photons with energies near 25 eV could have

practical application. For instance, in helium discharge lamps taking into account the first ionisation potential 24.581 eV of helium gas.

Exploring excitation spectra for nanosized YVO_4 :Eu and nanosized coreshell covered YVO_4 :Eu we can conclude that multiplications of electronic excitations processes are strongly suppressed there. Indeed, the intensity of the excitation peak at 30 eV in nanosized YVO_4 :Eu is about 30% but in nanosized YVO_4 :Eu@YF is about 10% comparing with the bulk sample. The degradation of the excitation spectrum in nano YVO_4 :Eu could be explained by surface trapping of hot electrons that were excited from yttrium and vanadium core orbitals to the conduction band. The surface passivation by nanoparticle covering in the YVO_4 :Eu@YF sample does not help to increase the intensity of the excitation peak in 12–45 eV range. Since band gap energy of the shell YF₃ is about 11 eV [161] it is supposed that YF₃ layer around YVO_4 :Eu nanoparticles works as "shield" absorbing partially excitation energy intended for the YVO_4 :Eu core.



Fig. 5.8 The comparison of the excitation spectra of Eu³⁺ and intrinsic emissions in bulk and nanocrystalline YVO₄:Eu³⁺

By comparing excitation spectra of impurity (Eu³⁺) and intrinsic (blue) emissions in bulk and nanocrystalline YVO_4 :Eu³⁺ it is clearly seen than the excitation spectra for two emissions in bulk sample are identical (Fig. 5.8). Whereas in the nanosized sample, the efficiency of Eu³⁺ emission is significantly less than the efficiency of the intrinsic one. The most prominent difference between the efficiency of Eu³⁺ and intrinsic emissions is observed in 10–40 eV spectral range. The Fig. 5.9 shows the intensity ratio spectrum for the emission Eu³⁺ and the intrinsic emission. The ratio I_(Eu)/I_(intrinsic) drops down below 0.5 in the spectral range 10-40 eV. This is the additional argument, which demonstrates that electrons and holes in the nanoparticles under high-energy excitation tend to be trapped by a surface with subsequent relaxation via radiative recombination within $(VO_4)^{3-}$ complex. Such process is a competing relaxation channel, comparing with the radiative relaxation of Eu^{3+} ions and, therefore, it leads to the degradation of Eu^{3+} emission under high-energy excitations.



Fig. 5.9 The ratio of excitation spectra of Eu³⁺ and intrinsic emissions in nanocrystalline YVO₄:Eu³⁺

5.2.2. YVO₄:Eu luminescence under laser excitation

To gain more information about luminescence properties in macrocrystalline and nanocrystalline YVO_4 :Eu powders we have measured the luminescence decay kinetics for both intrinsic emission and Eu³⁺ emissions under 266 nm laser excitation. Time-resolved luminescence characteristics have been carried out under excitation of tunable pulsed solid-state laser PG401/SH pumped by PL2143/Pre-T laser (pulse duration ~30 ps) from Ekspla and using Bruker Optics SPEC 250IS/SM monochromator/spectrometer coupled to a Streak Scope C4334 (time resolution better than 30 ps) from Hamamatsu.

Temperature dependence of normalised decay kinetics of the intrinsic emissions for macroscopic and nanosized YVO_4 :Eu are depicted in Figs. 5.10(a) and 5.10(b), respectively. These decay kinetics are non-exponential at any temperature. This result contradicts to the data for YVO_4 single crystals where intrinsic luminescence has a single exponential decay in wide temperature range [162]. A deviation from a single exponential decay law means that both bulk and nanosized samples have non-radiative relaxation centres. Increasing temperature the probability of non-radiative transitions increases and decay kinetics of intrinsic luminescence become faster. However, it is clearly seen from Figs. 5.10(a) and 5.10(b) that the temperature quenching is much more pronounced in the nanocrystalline sample where the decay kinetics shortening starts already at a temperature higher than 50 K, whereas the threshold for the temperature quenching for the bulk YVO_4 :Eu is higher than 100 K. This means that non-radiative relaxation centres (most likely surface related centres) play a more significant role in the intrinsic luminescence band degradation in the nanocrystalline sample rather than in the bulk one. If the blue intrinsic emission in nanocrystals stems from $(VO_4)^{3-}$ complexes from nanoparticles' surface, then the behaviour of decay kinetics of nanocrystalline YVO_4 :Eu is cogent.



Fig. 5.10 Temperature dependence of intrinsic emission decay kinetics in macroscopic and nanosized YVO₄:Eu under 266 nm excitation

The comparison of the decay kinetics of Eu³⁺ emission at room temperature for the bulk, nanocrystalline and core-shell layered nanocrystalline YVO4:Eu is given in Fig. 5.11. It is necessary to note, the decay kinetics of Eu³⁺ luminescence do not depend on the temperature in the contrast to the decay kinetics of intrinsic emission. The decay kinetic for the bulk sample (Fig. 5.11) is exponential with a decay time constant about 1 ms that is typical for Eu³⁺ luminescence [16]. On the other hand, the decay kinetics of Eu³⁺ luminescence for both uncoated and core-shell layered nanocrystalline samples does not obey the single exponential low. These two decay kinetics (red and green lines in Fig. 5.11) are identical and significantly faster than the corresponding decay kinetic for the bulk YVO₄:Eu. This can be explained by energy transfer from the excited state of europium to quencher centres as discussed before for many nanophosphors [54, 65, 163]. The origin and the exact nature of these quenchers are not yet understood. However, due to the similarity of the decay kinetics of Eu³⁺ emission for the uncoated and the coated YVO4:Eu nanoparticles we can suppose that YF3 core-shell layer cannot remove quencher centres responsible for the decay kinetics shortening. This means that the recovery of Eu³⁺ emission intensity in coreshell layered nanoparticles is achieved at the expense of the suppression of the intrinsic emission but not due to the passivation of surface loss centres.



Fig. 5.11 Decay kinetics of Eu^{3+} emission in macroscopic, nanosized and nanosized YF₃ covered YVO₄:Eu under 266 nm excitation at 300 K

5.3. Y₃Al₅O₁₂:Ce luminescence

Luminescence spectra of all YAG:Ce nanopowders in the present study were investigated under two excitations - 115 nm (11 eV) high-energy excitation (exceeding band gap energy of YAG) and 210 nm (6 eV) energy (below than band gap energy of YAG). The luminescence spectra of YAG:Ce nanopowders under high-energy excitation at room temperature are shown in Fig. 5.12(a-e). In this figures, one can see that all spectra demonstrate only yellow-green emission of regular Ce³⁺ in YAG. There are no significant differences in the spectra shapes depending on Ce³⁺ concentration. The emission spectrum for the single crystal given for comparison (Fig. 5.12(f)) also does not reveal any principle distinguishes with the emission spectra of the nanopowders. It is known, that the regular Ce³⁺ emission in YAG arises due to transition from 5d excited state to a 4f ground state of Ce³⁺ ions. The ground state of Ce³⁺ ion consists of two levels: ${}^{2}F_{7/2}$ and ${}^{2}F_{5/2}$, and therefore, the Ce³⁺ emission band is split [103,164] showing a double structure of the emission spectra observed in Fig. 5.12(a-f). On the other hand, the emission spectra of YAG:Ce nanopowders are drastically changed if excitation energy is below than band gap energy of YAG. In this case, additionally to the yellow-green emission of the regular Ce³⁺ (peaking at 520 nm) the intensive emission in the blue-UV spectral range was observed in all nanopowders studied under 210 nm (5.9 eV) excitation (Fig. 5.12(g-l)). Note that intensity of the blue-UV depends on Ce³⁺ concentration in YAG nanopowders. One can see that this emission can reach up to 75% of the intensity of the regular Ce³⁺

emission in 0.5% doped nanopowder and it suppresses strongly if the Ce^{3+} concentration in nanopowders increases from 0.5% to 5%. It is important to note that in contrast to nanopowders, only regular Ce^{3+} emission band with a maximum at 2.4 eV (520 nm) was detected for single crystal under any excitations.



Fig. 5.12 Emission spectra of YAG: Ce nanopowders having different Ce³⁺
 content under 115 nm (10.78 eV) (a-e) and 210 nm (5.9 eV) (g-l) excitations.
 The luminescence spectra of the YAG:Ce single crystal under corresponding excitations are given for comparison (f, m)

The excitation spectra of nanosized Ce³⁺ doped YAG (0.5 % concentration) samples for both emissions – yellow-green Ce³⁺ emission and UV differs from ones of YAG:Ce single crystal (Fig. 5.13). The excitation spectrum of the regular Ce³⁺ emission in the single crystal reveals several excitation bands in the transparency region of YAG: ~340 nm (3.7 eV), 270 nm (4.59 eV), 220 nm (5.6 eV), and 205 nm (6.05 eV) (see arrows in Fig 5.13(a)) due to splitting of $5d^1$ excited state of Ce³⁺ in the crystalline field of D₂ symmetry, when Ce³⁺ ion is incorporated into the YAG lattice substituting Y³⁺ ion. The same excitation peaks can

be also resolved in the excitation spectrum of regular Ce^{3+} emission in nanopowder samples despite their relatively low intensity and increased broadening. Additionally to the excitation bands due to 4f-5d transitions the strong excitation is observed in the excitonic spectral range in YAG:Ce single crystal just below band gap energy of YAG (8 eV). It is clearly seen (Fig 5.13(a)) that excitonic excitations are strongly suppressed in the nanocrystalline sample [165]. The excitation curves at energies higher than 8 eV are identical for the single crystal and nanopowders. The rise of Ce^{3+} intensity at energies exceeding 8 eV was explained by the direct impact excitation of Ce^{3+} centres by hot photoelectrons as well as by the multiplications of electronic excitation processes [107].



Fig. 5.13 Comparison of excitation spectra of green (2.3 eV) (a) and blue (3.0 eV) (b) emission for one of YAG nanopowder at 10 K

The excitation spectrum of the 400 nm emission contains the strong main peak at 210 nm (5.9 eV) with the well-resolved shoulder at 240 nm (5.17 eV) and the low energy peak at about 330 nm. The result showed Fig 5.13 indicates that the excitation spectrum of the blue-UV emission is incomparable with the excitation bands of the regular Ce^{3+} emission observed for both single and

nanocrystalline samples in 4-8 eV spectral range. Therefore, the excitation spectrum of the blue-UV emission cannot be simply explained in term of crystal field splitting of the $5d^1$ state of the regular Ce³⁺ ion. The excitation spectrum of the blue-UV emission shows that this emission cannot be effectively excited at energies higher than band gap energy in YAG (8 eV), probably there is extremely weak energy transfer efficiency from YAG lattice to the emission centre responsible for the blue-UV emission band in YAG:Ce nanocrystals.



Fig. 5.14 Decay kinetics of the regular yellow-green (a) and the blue-UV (b) emissions for YAG:Ce nanocrystals having different Ce³⁺ concentration. The decay kinetic of the regular yellow-green emission band for the single crystal is given for comparison in (a)

Emission decay kinetics of both regular yellow-green and the blue-UV emissions in YAG:Ce nanocrystals are shown in Fig. 5.14. The decay kinetic of the regular Ce³⁺ emission observed in the single crystal is added for comparison in Fig. 5.14(a). Observed decay kinetics in nanocrystals is faster comparing with decay kinetics of bulk due to non-radiative relaxation induced by surface loss centres that always occur in nanoparticles' surface [46, 54, 91]. Increasing Ce³⁺ concentration ions leads to increased number of Ce³⁺ ions on surface sites of nanoparticles where the influence on surface loss centres is strong. Describing decay kinetics of blue-UV emission (Fig. 5.14(b)) we see that they are much faster than the yellow-green one: the decay time constant of the blue-UV emission can be roughly estimated as about 6-8 ns. It is clearly seen that blue-UV emission band kinetics is no any significant dependency from Ce³⁺ concentration in the nanocrystals examined.

Different excitation spectra and difference in emission decay kinetics obtained for yellow-green and blue-UV emission bands indicate that this emission arises from the different emission centres. The origin of the yellow-green emission is evident – the regular Ce³⁺ ion substituting Y³⁺ site (Ce³⁺_Y). Luminescence properties of this centre in the nanocrystalline samples can be described and explained by analogy with the bulk YAG:Ce.

Taking into account that the XRD analysis did not reveal any difference in the structure of the nanocrystals and bulk YAG [18, 167] we suggest that the blue-UV emission occurs due to the reduced size of the nanoparticles. The size of a nanoparticle is about 20 nm and it definitely cannot induce quantum confinement effects in the nanocrystals studied. However, the contribution of surface drastically increases in nanoparticles having such particle size. Therefore, such nanoparticles can have significant numbers of specific centres related to the surface of the nanoparticle (or located close to the surface), which are not typical for the corresponding bulk material. Furthermore, since the intensity of blue-UV emission depends strongly on the Ce³⁺ concentration (Fig. 5.12(g-l)) we suggest that the centre responsible for the blue-UV emission is Ce³⁺ ion in some specific site of YAG lattice. This specific site for Ce³⁺ ion should be unusual for bulk YAG:Ce because we did not detect the blue-UV emission in the crystal under any excitations (Fig. 5.12(f,m)). It is suggested that without any charge compensation Ce3+ ion can successfully substitute Al3+ site in YAG forming the Ce³⁺_{Al} centre. It is known that Al³⁺ sites in YAG have the nearest surroundings of two types: tetrahedral and octahedral. If the Ce³⁺ replaces the Al³⁺ ions that are located in octahedral positions, it has 6-coordinated nearest surroundings while tetrahedral Ce³⁺_{Al} is 4-coordinated. In any case, Ce³⁺_{Al} ion has another symmetry because regular Ce³⁺, ion nearest surroundings are 12-coordinated. This means that there is an absolutely different crystal field splitting of 5d excited state for Ce³⁺_{Al} and Ce³⁺_Y centres. Hence, Ce³⁺_{Al} and Ce³⁺_Y centres have spectrally different emission bands: the blue-UV and yellow-green, respectively. The difference in the crystal field splitting for Ce^{3+}_{Al} and Ce^{3+}_{Y} centres is confirmed also by their excitation spectra (Fig. 5.13). The existence of two types of non-equivalent Al³⁺ sites in YAG means that most likely there are two types of Ce³⁺_{Al} centres in nanocrystals. It explains unusual broadening the blue-UV emission.

Since ionic radii of the aluminium and cerium are different (1.15 Å for Ce^{3+} and 0.675 Å for Al^{3+}) the formation of $Ce^{3+}{}_{Al}$ in bulk YAG:Ce is impossible. However, in contrast to bulk YAG:Ce nanoparticles have a big surface area where a relatively large Ce^{3+} ion can successfully substitute Al^{3+} site on surface of the nanoparticle. Surface origin of $Ce^{3+}{}_{Al}$ in YAG:Ce nanocrystals are confirmed by the following: i) the strong concentration quenching of the intensity of the blue-UV emission (Fig. 5.12(g-l)); ii) unusual fast decay kinetics of the blue-UV emission (Fig. 5.14(b)). Indeed, increasing Ce^{3+} concentration leads to the high concentration of $Ce^{3+}{}_{Al}$ ions in the restricted surface area creating favourable conditions for non-radiative cross-relaxation processes resulting in the degradation of the blue-UV emission band (see evolution in Fig. 5.12(g-l)). Furthermore, nanoparticle's surface always has some amount of surface loss

centres, which significantly increase the probability of non-radiative processes shortening emission decay time. Obviously, the influence of surface loss centres is stronger if luminescence centres are close to the surface of the nanoparticle. Since the decay time of the blue-UV emission is much faster than the yellow-green one, we conclude that Ce^{3+}_{Al} centres stem from the surface site or in the close vicinity of surface of the nanoparticle.

5.4. AWO₄ (A=Zn, Ni) luminescence

Luminescence spectra of micro and nanosized $ZnWO_4$ and $NiWO_4$ registered under 90 nm excitation at low temperature presented in Fig. 5.15. Note that the photoluminescence spectra in Fig. 5.15 have been normalised at the band maximum, and their intensity should not be compared.



Fig. 5.15 Luminescence spectra of microcrystalline NiWO₄ and ZnWO₄ crystals (a) Luminescence spectra of nanocrystalline ZnWO₄ and NiWO₄ (b). All spectra were recorded under 90 nm excitation at low temperatures (10 K for ZnWO₄ and 80 K for NiWO₄)

The photoluminescence spectrum of microcrystalline $ZnWO_4$ powders spans from 1.5 eV to 3.5 eV and has its intensity maximum around 2.5 eV. The origin of the band has been previously assigned to radiative electron transitions within the $[WO_6]^{6-}$ molecular complex [114, 143]. Luminescence spectra of microcrystalline NiWO₄ also span from 1.5 eV to 3.5 eV, but have its maximum at 2.25 eV and have a shoulder at 2.5 eV. The irregular asymmetric shape of the emission band in microcrystalline NiWO₄ is close to that which was observed previously in solid solutions $Zn_cNi_{1-c}WO_4$ [159], as for $Zn_cNi_{1-c}WO_4$ the emission band at 2.26 eV was also observed. The origin of such band shape can be attributed to the self-absorption effect, i.e. to a modulation of optical absorption by the intense intraion transition within Ni²⁺(³d₈) ions from the ground state ${}^{3}A_{2g}$ to the excited state ${}^{3}T_1$ [167]. Comparing luminescence spectra on nanocrystalline $ZnWO_4$ and $NiWO_4$ we can see that the maximum of the photoluminescence band in nano-NiWO₄ is shifted by 0.32 eV to higher energy compared to nano- $ZnWO_4$ and is located at 2.7 eV. Such a blue-shift can be explained by a difference in the relaxation of WO₆ octahedra in the two tungstates, which is directly evidenced by W L3-edge EXAFS data described in [168].



Fig. 5.16 Excitation spectra of microcrystalline ZnWO₄ for 560 nm emission at room temperature

The excitation spectra of microcrystalline ZnWO₄ (annealed at 400 °C and 900 °C) for intrinsic luminescence is depicted in Fig. 5.16. The excitation spectrum of micro ZnWO₄ consists of a strong band at 4 eV having the excitation origin. The intensity of the excitation spectra of both ZnWO₄ starts to grow in the energy region above ~ 11 eV due to the beginning of the multiplication of electronic excitation (MEE) process. In this process, a secondary electron-hole (e-h) pair is created due to the inelastic scattering of a sufficiently "hot" photoelectron, having an energy results in deeper valence electrons starting to participate in MEE process. When the photon energy reaches ~ 17 eV, i.e. ≈ 2Eg + Ev, where $Eg \approx 4.6-4.9$ is the band gap energy and $Ev \approx 7.5$ eV is the valence band for ZnWO₄, the electron from the bottom of the valence band participate in the MEE process, and the intensity of the excitation spectra exhausts.

The broad bands in excitation spectra of microcrystalline $ZnWO_4$ at 5–6 eV, 8–10 eV, 12 eV, 13.5 eV, 15 eV and 16 eV are due to the one-electron transitions from the top of the valence band.



Fig. 5.17 Excitation spectra of nanocrystalline ZnWO₄ at 400 and 650 nm emission at room temperature

The excitation spectra of nanocrystalline $ZnWO_4$ detected at 400 nm and 650 nm emission wavelength are depicted in Fig. 5.17 and are close to that from microcrystalline samples. However, a strong band of the excitonic origin in na-no-ZnWO₄ is shifted to smaller energies below 4.0 eV. A set of peaks observed at 6, 9, 12 and 16 eV for nano ZnWO₄ is suggested to be attributed to the one-electron transitions from the top of the valence band to quasi-localized states.

Excitation spectra of both micro and nanocrystalline NiWO₄ detected at 450 nm are presented in Fig. 5.18. The excitation spectra of microcrystalline NiWO₄ show some temperature dependence in the range from 7 to 80 K due to the lattice expansion Difference in excitation spectra of NiWO₄ and ZnWO₄ is due to the difference of about 1eV in the band gaps: Eg = 3.6 eV [142] for NiWO₄, but Eg = 4.6 eV for ZnWO₄ [114]. As a result, the strong excitonic band clearly visible in ZnWO₄ is not observed in present data for NiWO₄ due to the spectrometer range resolutions – the excitonic band is expected to be located below 3.7 eV.



Fig. 5.18 Excitation spectra of micro- and nanocrystalline NiWO₄

The excitation spectra of nanocrystalline NiWO₄ detected at 450 nm emission wavelength are close to that of microcrystalline samples. Similarly to $ZnWO_4$ the broad bands at 5–6 eV, 8–10 eV, 12 eV, 13.5 eV and 16 eV are due to the one-electron transitions from the top of the valence band. These transitions are even more pronounced in the case of nano-NiWO₄ due to quasi-localized nature of the involved electronic states. This suggestion about the one-electron transitions from the top of the valence band to quasi-localized states was proved theoretically with (LCAO) calculations in [133].

6. THESES

- 1. In contrast to the macrocrystalline analogue, effective excitation of Tb³⁺ luminescence in nanosized LaPO₄:Ce,Tb in the VUV spectral range is possible after an energy transfer from Ce³⁺ only.
- 2. Degradation of the emission as well as excitation spectra in a VUV range in nanosized LaPO₄:Ce,Tb and YVO₄:Eu phosphors could be explained by charge carriers trapping during their thermalisation by surface defects with subsequent non-radiative relaxation.
- 3. The main reason of Eu^{3+} luminescence intensity recovery in YF₃ core-shell layered nanocrystalline YVO₄:Eu is explained by switching off a strong competing relaxation channel intrinsic emission, but not due to a passivation of the surface.
- 4. New blue-UV emission band has been discovered in Y₃Al₅O₁₂:Ce nanocrystals. It is suggested that Ce³⁺ ion substituting Al³⁺ is the emission centre of this blue-UV luminescence.
- 5. In nanosized ZnWO₄ and NiWO₄, a number of bands are observed in the excitation spectra. It is suggested that bands are connected with one-electron transitions from the top of the valence band to quasi-localized states.

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8. AUTHOR'S LIST OF PUBLICATIONS

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9. PARTICIPATION IN CONFERENCES

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- 14. L. Shirmane, Luminescence and vacuum ultraviolet excitation spectroscopy of nanocrystalline oxides, *1st NFFA-Europe Summer School*, 2016, Barcelona, Spain

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