Emerging Blue-UV Luminescence in Cerium Doped YAG Nanocrystals

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Time-resolved luminescence properties in of Ce^{3+} doped $Y_3Al_5O_{12}$ (YAG) nanocrystals have been studied by means of vacuum-ultraviolet excitation spectroscopy. It was discovered that additionally to the regular Ce^{3+} yellow-green emission which is well-known luminescence in YAG, new emission covering broad spectral range from 2.7 eV to 3.5 eV was revealed in the luminescence spectra for all YAG:Ce nanocrystals studied. This blue-UV emission has fast decay time about 7 ns as well as intensive well-resolved excitation band peaking at 5.9 eV and, in contrast to green Ce^{3+} emission, practically is not excited at higher energies. The origin of the blue-UV emission is tentatively suggested and discussed.

Bulk cerium doped $Y_3Al_5O_{12}$ (YAG:Ce) is an important and well-known luminescent material that had been studied more than 40 years. This compound became as one of the most popular materials among others because of its high radiation and chemical stability as well as efficient yellow-green luminescence [1, 2 and references therein]. Luminescent nanocrystals or nanophosphors (including YAG:Ce) recently received increased attention because of their potential application in medicine and biophysics (labeling, signaling, and biomedical purpose) [3]. Generally, nanophosphors of various inorganic compounds in form of nanopowders and nanoceramics have been successfully synthesized during the last decade all over the world thanks to rapidly developed nanotechnologies. It was reported that YAG:Ce nanopowders have been successfully synthesized by means of many technique, which include co-precipitation method [4], hydrothermal process [5], Pechini method [6], sol-gel method [7]. Resent researches of YAG:Ce are mostly focused on the synthesis, characterization and applications of YAG:Ce in form of nanopowders [8, 9], nanoceramics [10-13] and single crystalline films [14, 15].

The main goal of the current investigation is a study of the luminescence properties of nanosized YAG:Ce under high energy excitations including vacuum ultraviolet (VUV) range, which is important for biolabelling, radiation therapy applications and scintillators. In our study we applied synchrotron radiation, which has significant advantages over the radiation of ordinary sources. The main advantages of synchrotron radiation is the extended wavelength range attained, that gives broad and continuous spectrum. In recent works it was shown how important is to use synchrotron radiation in investigation of optical and luminescence properties of wide band gap insulators [9, 16–20] as well as of nanocrystalline and two-dimensional semiconductors [21, 22].

The luminescence measurements was carried out using pulsed synchrotron radiation at the Superlumi station at Photon Science (DESY, Hamburg) [23]. 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 spectral resolution of 0.3 nm. The excitation spectra were normalized to equal quantum intensities of synchrotron radiation falling onto sample by means of sodium salicylate as reference. The exciting pulse duration is 125 ps, while the instrumental time resolution of the registration system was 1 ns. Emission decay kinetics have been measured in 196 nm time window.

YAG:Ce nanopowders have been synthesized by means of a modified sol–gel method similar to that used by Pechini, which described in details elsewhere [24]. The nanopowders were characterized by means of Scherrer method, Williamson-Hall method, X-ray powder diffraction and BET methods [10]. The average particle size was estimated to be about 20 nm. Cerium ions concentration in YAG:Ce nanopowders was varied from 0.5 % to 5.0 %.

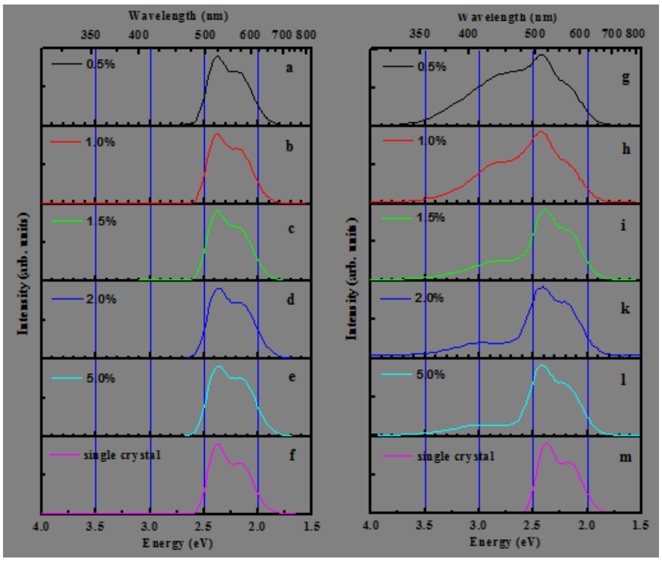

Figure 1 Emission spectra of YAG:Ce nanopowders having different Ce^{3+} content under 115 nm (10.78 eV) (a-e) and 210 nm (5.9 eV) (g-l) excitations. The luminescence spectra of the YAG:Ce single crystal under corresponding excitations are given for comparison (f, m). All spectra are scaled at 520 nm (2.4 eV).

The luminescence spectra of YAG:Ce nanopowders under high energy excitation (exceeding band gap energy of YAG) are shown in Fig. 1(a-e). In this figures one can see that all spectra demonstrate only yellow-green emission of regular Ce^{3+} in YAG. There are no significant differences in the spectra shapes depending on Ce^{3+} concentration. The emission spectrum for the single crystal given for comparison (Fig. 1(f)) also does not reveals any principle distinguishes with the emission spectra of the nanopowders. 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 Ce^{3+} (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. 1(g-l)). The intensity of the blue-UV depends on Ce^{3+} concentration in YAG nanopowders. One can see that this emission can reach up to 75% of intensity of the regular Ce^{3+} emission in 0.5% doped nanopowder and it supresses strongly if 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 maximum at 2.4 eV (520 nm) was detected for single crystal under any excitations.

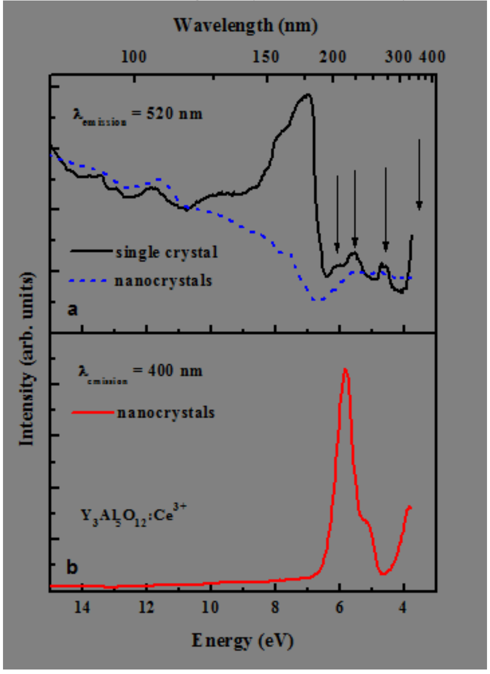

Figure 2 The excitation spectra of the regular Ce^{3+} emission in YAG:Ce single crystal and one of nanopowders (0.5%) (a). The excitation spectrum of the blue-UV emission band in one of the YAG:Ce nanocrystalline samples (0.5%) (b). The arrows in (a) indicate the spectral position of regular Ce^{3+} excitation peaks known in literature for bulk YAG:Ce (see details in the text).

The excitation spectra for the regular yellow-green Ce^{3+} emission in one of YAG:Ce nanopowders (0.5% Ce^{3+} concentration) as well as in the single crystal are shown in Fig. 2(a), while Fig. 2(b) depicts the excitation spectrum of the blue-UV (at 400 nm) emission observed in one of the nanopowdered samples (also 0.5% Ce^{3+} concentration). Note, the excitation spectra in Fig. 2 are typical for all nanopowders studied and their shapes are poorly cerium concentration dependent. The excitation spectrum of the regular Ce^{3+} emission in the single crystal reveals several excitation bands in the transparency region of YAG (Fig. 2(a)): ~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 2(a)). These excitation bands in YAG:Ce^{3+} have been reported in many studies before and the peak maxima, which depend to some extent upon temperature and the concentration of Ce^{3+} are analyzed in details in [9, 25-27]. These excitation peaks stem from the splitting of $5d^1$ excited state of Ce^{3+} in the crystalline field of D_2 symmetry, when Ce^{3+} ion is incorporated into the YAG lattice substituting Y^{3+} ion. The same excitation peaks can be also resolved in the excitation spectrum of regular Ce^{3+} emission in nanopowdered samples (Fig 2(a)) despite of 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 2(a)) that excitonic excitations are strongly suppressed in nanocrystalline sample. This fact was already observed and discussed in details elsewhere [9]. The excitation curves at energies higher than 8 eV are identical for the single crystal and nanopowders. The excitation spectrum of Ce^{3+} emission in YAG in 8-40 eV spectral range has been studied in details in [28] where the rise of Ce^{3+} intensity at energies exceeding 8 eV was explained by the direct impact excitation of Ce^{3+} centers by hot photoelectrons as well as by the multiplications of electronic excitation processes.

The excitation spectrum of blue-UV emission (400 nm) depicted in Fig. 2(b) drastically differs from the excitation spectra of the regular Ce^{3+} emission shown in Fig. 2(a). The excitation spectrum of the blue-UV 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 shown Fig 2(b) 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 (Fig. 2(a)). Therefore, the excitation spectrum of the blue-UV emission can’t be simply explained in term of crystal field splitting of $5d^1$ state of the regular Ce^{3+} ion.

Another remarkable feature of the excitation spectra of the blue-UV emission (Fig. 2(b)) is that this emission can’t be effectively excited at energies higher than band gap energy in YAG (8 eV). This experimental result shows that there is extremely weak energy transfer efficiency from YAG lattice to the emission center responsible for the blue-UV emission band in YAG:Ce nanocrystals.

Emission decay kinetics of both regular yellow-green and the blue-UV emissions in YAG:Ce nanocrystals are shown in Fig. 3. The decay kinetic of the regular Ce^{3+} emission observed in the single crystal is shown also in Fig. 3(a) for comparison. It is known that the Ce^{3+} emission in YAG single crystal has a characteristic decay time constant about 80 ns [8]. On the other hand, the decay time constant in nanocrystals usually is faster than in bulk due to non-radiative relaxation induced by surface loss centers which always occur in nanoparticles’ surface [8, 29, 30]. Obviously, total decay time of the regular Ce^{3+} emission in the single crystal as well as in the most of nanocrystals (Fig. 3(a)) is much slower than the time window of the registration system. Nevertheless, one can see that there is a strong decay time dependence on Ce^{3+} concentration in YAG:Ce nanocrystals studied: emission decay is faster in those YAG:Ce nanocrystals having a higher Ce^{3+} concentration. This dependence in Fig. 3(a) indicates that increasing Ce^{3+} concentration ions leads to increased number of Ce^{3+} ions on surface sites of nanoparticles where influence of surface loss centers is strong.

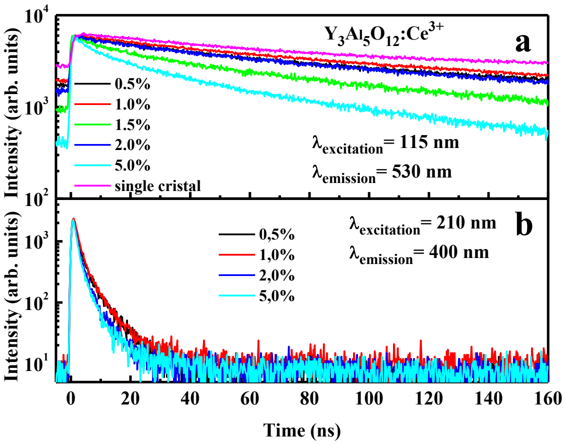

Figure 3 Decay kinetics of the regular yellow-green (a) and the blue-UV (b) emissions for YAG:Ce nanocrystals having different Ce^{3+} concentration. The decay kinetic of the regular yellow-green emission band for the single crystal is given for comparison in (a).

The decay kinetics of the blue-UV emission (Fig. 3(b)) have a completely distinguished behavior. First, the blue-UV emission decays 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. Secondly, there is no any significant dependency of the decay curves displayed in Fig 3(b) on the Ce^{3+} concentration in the nanocrystals examined.

Distinguished emission and excitation spectra as well as emission decay kinetics observed in YAG:Ce nanocrystals for the yellow-green and the blue-UV emission bands indicate that these emissions belong to the different emission centers. The origin of the yellow-green emission is evident – the regular Ce^{3+} ion substituting Y^{3+} site (Ce^{3+}_Y). Luminescence properties of this center in the nanocrystalline samples can be described and explained adhering to the analogy with the bulk YAG:Ce. On the other hand, the origin of the blue-UV emission center is debatable.

To our knowledge the blue-UV luminescence observed in the current study for the YAG:Ce nanocrystals is not reported in literature before. Taking into account that the XRD analysis did not reveal any difference in structure of the nanocrystals and bulk YAG [10, 11] we suggest that the blue-UV emission occurs due to reduced size of the nanoparticles. The nanoparticle’s size is about 20 nm and it definitely such nanoparticles can’t induce quantum confinement effects in the nanocrystals studied. However, the contribution of surface drastically increases in nanoparticles having such particle size. Therefore, the nanoparticles can have a significant numbers of specific centers related to the nanoparticle’s surface (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 Ce^{3+} concentration (Fig. 1(g-l)) we suggest that the center responsible for the blue-UV emission is Ce^{3+} ion in some specific site of YAG lattice. This specific site for Ce^{3+} ion should be unusual for bulk YAG:Ce because we did not detect the blue-UV emission in the crystal under any excitations (Fig. 1(f, m)). It is suggested that without any charge compensation Ce^{3+} ion can successfully substitute Al^{3+} site in YAG forming $Ce^{3+}{}_{Al}$ center. It is known, that Al^{3+} sites in YAG have the nearest surroundings of two types: tetrahedral and octahedral. If the Ce^{3+} replaces the Al^{3+} ions, that are located in octahedral positions, it has 6-coordinated nearest surroundings, while tetrahedral $Ce^{3+}{}_{Al}$ is 4-coordinated. In any case $Ce^{3+}{}_{Al}$ ion has another symmetry because regular $Ce^{3+}{}_{Y}$ ion nearest surroundings is 12-coordinated. It means that there is absolutely different crystal field splitting of 5d excited state for $Ce^{3+}{}_{Al}$ and $Ce^{3+}{}_{Y}$ centers. Hence, $Ce^{3+}{}_{Al}$ and $Ce^{3+}{}_{Y}$ centers have spectrally different emission bands: the blue-UV and yellow-green, respectively. The difference in the crystal field splitting for $Ce^{3+}{}_{Al}$ and $Ce^{3+}{}_{Y}$ centers is confirmed also by their excitation spectra (Fig. 2), which are absolutely different for different emission centers. The existence of two types of non-equivalent Al^{3+} sites in YAG means that there are two types of $Ce^{3+}{}_{Al}$ centers 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 nanoparticle's surface. Surface origin of $Ce^{3+}{}_{Al}$ in YAG:Ce nanocrystals is also confirmed by the following experimental facts: i) there is a strong concentration quenching of the intensity of the blue-UV emission (Fig. 1(g-l)); ii) there are unusual fast decay kinetics of the blue-UV emission (Fig. 3(b)) comparing with the regular yellow-green luminescence (Fig. 3(a)). Indeed, increasing Ce^{3+} concentration leads to the high concentration of $Ce^{3+}{}_{Al}$ ions in restricted surface area creating favorable conditions for non-radiative cross-relaxation processes resulting to the degradation of the blue-UV emission band (see evolution in Fig. 1(g-l). Furthermore, nanopartical's surface always has some amount of surface loss centers, which significantly increase the probability of non-radiative processes shortening emission decay time. Obviously, the influence of surface loss centers is stronger if luminescence centers are close to the nanoparticle's surface. Since the decay time of the blue-UV emission is much faster than the yellow-green one, we conclude that $Ce^{3+}{}_{Al}$ centers stem from surface site or in the close vicinity of nanoparticle's surface. Note, the decay kinetics of the blue-UV emission do not contain any slow decay component similar to the decay time of the regular Ce^{3+} emission. In means that there are no $Ce^{3+}{}_{Al}$ centers in volume of nanoparticles.

In conclusion, the intensive blue-UV emission have been discovered in nanocrystalline YAG:Ce. Analyzing time-resolved luminescence characteristics obtained in wide spectral range we suggested that Ce^{3+} ions substituting Al^{3+} in nanoparticle's surface are responsible for the blue-UV emission observed in YAG:Ce nanocrystals. Depending on Ce^{3+} concentration the intensity of the blue-UV emission can reach up to 75 % of intensity of the regular yellow-green emission in YAG:Ce nanocrystals. Both blue-UV and yellow-green emissions in nanocrystalline YAG:Ce cover spectral range from 350 nm to 650 nm providing unique opportunity for fabrication of new type of white phosphors based on one type of impurity ion only.

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