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The time-resolved luminescence characteristics of Ce and Ce/Pr doped YAG ceramics obtained by high pressure technique

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ABSTRACT

Transparent Ce and Ce/Pr doped YAG ceramics were prepared under high pressures (up to 8 GPa) and relative low temperature (450 °C). Grain size of the ceramics is less than 50 nm. However unknown defects or disorders strains on grain boundaries caused the additional absorption in these ceramics. The luminescence intensity, spectra and the decay time dependence on pressure applied during ceramic preparation were studied. Concentration of some intrinsic point defect was reduced under the high pressure applied for sintering process.

It is shown that formation time of the excited state of Ce luminescence depends on the pressure applied during ceramic sintering.

1. Introduction

Recently progress has been achieved on transparent laser ceramics preparation by means of the high temperature vacuum sintering technology. Starting powders are tens of nanometer grain size [1,2]. Average grain size of the ceramic is ~3 μm, width of grain boundary is narrow and transparency is more than 80% [3]. However, sintering time is long and sintering temperature is high (up to 1800 °C).

The sintering under high pressures (2–8 GPa) at relatively low temperature (450 °C) is an alternative method for preparation of transparent ceramic. The ceramic fabrication method under high pressure at low temperature (HPLT) was described in [4–6]. Optical properties of HPLT YAG ceramics doped with Nd and Ce were studied [5–7]. Transparency of the obtained ceramics at 1064 nm for a 1.16 mm thick sample is 52% [5] which is lower than that for the ceramics prepared by high temperature vacuum sintering. Density of ceramics depends on the pressure used during preparation and the highest achieved density is up to 99% of theoretical density of the YAG [5]. Main differences in absorption spectra of HPLT ceramics and YAG:Ce single crystal were detected in spectral region of 400–250 nm [6]. So, the absorption coefficient equal to 100 cm^{-1} is at 200 nm for the crystal and at 397 nm for the ceramic. This large red shift of the absorption edge shows that in HPLT ceramics some unknown types of defect states exist and possible reasons of the observed shift are not clear and are under discussion up to now.

SEM images of the HPLT ceramics show that the grain size of ceramics are close to an average grain size of the starting nanopowders [5,6]. According to the XRD results the ceramics show only cubic structure of YAG [5,9]. It is concluded in [9,10] that the average grain sizes decrease from 40 nm down to 24 nm when the pressure up to 8 GPa is applied however the suggestion is under discussion up to now. The relative residual micro-strains calculated from XRD [5,10] increase with the pressure applied during sintering.

The Ce doped ceramics is known as a promising material for fast scintillators. In the present work special attention is given to the time-resolved luminescence in nanosecond time range of Ce and Ce/Pr doped transparent ceramics prepared by HPLT method.

2. Experimental

2.1. Equipments

The time-resolved luminescence was measured at 300 K (RT) by using two experimental setups. In one of them a pulsed nitrogen laser (337 nm, 8 ns pulse duration) was used for photoluminescence excitation. Luminescence measurements were carried out with a photon counting head (HAMAMATSU H8259) and photon counting board FastComTech module P 7887 with 500 channels and minimal time beans 250 ps. Spectra were accumulated in time gate 125 ns. In the second setup a wavelength-tunable picosecond

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(30 ps) solid state laser was used for luminescence excitation. The excitation wavelength was 287 nm. The luminescence spectra and decay kinetics were measured with the Streak-scope C4334 (HAMAMATSU).

Radioluminescence was excited by steady state X-rays (40 kV; 10 mA) and the CCD camera ANDOR iDUS DU401A-BV with monochromator SHAMROC303 was used for spectra registration.

Optical absorption spectra were measured by a spectrometer LABOMED UVS-2800.

2.2. Samples

YAG ceramics doped with Ce (0.9 mol%) and Ce/Pr (0.5/0.5 mol%) were prepared using HPLT sintering methods described in [4,5]. The ceramics were fabricated at different applied pressures (2–8 GPa) at temperature of 450 °C. Starting nanopowders were prepared by the modified Pechini method. The powder synthesis is described in [8]. Average grain size of the starting nanopowder was ~35 nm as was estimated from SEM images. Several ceramics were annealed at 1000 °C for 1 h. Views of the studied ceramics are shown in the Fig. 1.

3. Results and discussion

The absorption spectra of HPLT ceramics are shown in Fig. 2. Two different absorption mechanisms are suggested from the absorption spectra of studied ceramics: (1) absorption coefficients in spectral region <400 nm are higher for the ceramics prepared under higher pressure and correlate with relative concentration of residual micro-strains; a similar result was obtained in [6] for the HPLT YAG:Ce ceramics; (2) in spectral region of 495–1100 nm absorption coefficient is lower for the ceramics prepared at higher pressure and it correlates with the average grain size, porosity and density of the ceramic.

Micro-strains were created under high pressure applied during the fabrication of the ceramics [5,10]. Presence of the micro-strains stimulates changes in the local symmetry for some of the atoms on grain surfaces of nanocrystals, especially of dopant atoms since the majority of the dopant ions are located in vicinity of grain boundaries [11]. It is suggested in [9,12] that under high pressure a partial amorphous phase is created in intergrains area. However, XRD, FTIR and Raman spectra do not show additional phase or phonon modes in the HPLT ceramics [9].

In the present work the luminescence was excited either at 337 nm (Ce^{3+} absorption band or at 287 nm (both Ce^{3+} and Pr^{3+} ions are excited [13]). However, it must not be ruled out that absorption of some YAG lattice defects overlaps with Ce^{3+} absorption especially since the absorption coefficient of HPLT ceramic in this region is high (Fig. 2).

The luminescence spectra of YAG:Ce/Pr ceramics (Fig. 3) are close to those observed in [13] for YAG:Ce/Pr nanopowders – the wide band with the maxima at 530 nm (electron transition from Ce^{3+} $\mathbf{5d^1}$ to $\mathbf{4f^1}$ states) and superimposed narrow lines due to transitions in the Pr ion at 488 nm and 608 nm ($^3\boldsymbol{P_0}$ and $^1\boldsymbol{D_2}$ to $^3\boldsymbol{H_4}$ states, accordingly).

Bandwidth of the Ce luminescence under the 337 nm excitation was enhanced with the pressure applied during the sintering process. We suggest that Ce electronic states are perturbed by some defects and concentration of these defects depends on the sintering pressure. After annealing of the ceramics at 1000 °C the bandwidth decreases due to the partial annealing of the defects created under high pressure applied during the sintering. The intensity of Ce^{3+} luminescence depends on the sintering pressure and is the lowest for 8 GPa ceramics. Luminescence intensity significantly increases after the annealing. For example, the luminescence intensity at 520 nm for YAG:Ce/Pr ceramics fabricated at 4 GPa after the annealing is twenty times higher. However, the annealed ceramics are not transparent. It is known [14,15] that the luminescence due to native defects – antisite yttrium (Y_{Al}) and F^+ appears in YAG single crystals and nanopowders in spectral region of 350–450 nm. Luminescence in this spectral region was registered in HPLT ceramics and its intensity depends on the sintering pressure. Higher intensity was detected for ceramics sintered at lower pressure. Decay time of defect luminescence depends on the sintering pressure and the faster decay is detected for the ceramics prepared at 8 GPa. The fast decay time and the high absorption coefficient in spectral region <450 nm are the reasons why luminescence intensity is lower for the ceramics prepared at the higher pressure. The luminescence due to the transitions in Ce ion is important for scintillation applications and for white LED development [13,16]. The luminescence decay time is very important parameter for the material characterization since the decay time depends not only on Ce concentration but also on the local crystal field of the luminescence center.

Luminescence decay kinetics under 511 keV photon excitation for YAG:Ce single crystal and optical ceramics (Baikowski, Japan Ltd.) were compared in [17]. Estimated decay time is 119 ns and 85 ns for a single crystal and for the ceramic respectively. In Fig. 4 luminescence decay kinetics for YAG:Ce and YAG:Ce/Pr HPLT ceramics prepared under the same pressure are displayed. The luminescence was excited by 337 nm and 8 ns laser pulses.

Decay kinetics fitting by a double exponential function is also shown in Fig. 4. The decay time of the slow component for YAG:Ce is slightly below that reported [17] for the YAG:Ce ceramic prepared by high temperature vacuum sintering. The difference is due to different average grain sizes of these two ceramics, defects on the grain surfaces as well as some additional defects in the HPLT ceramics. The HPLT YAG:Ce/Pr ceramic shows lower Ce luminescence decay time relatively to YAG:Ce ceramic (37 ns and 54 ns, in accordance to the fitting results, see Fig. 4). However, the decay times do not significantly depend on the pressure applied during sintering process.

In this case at least two additional to 30–60 ns processes must be pointed out: the fast decay component ($\leqslant$8 ns) and the rise front of the luminescence pulse. In Fig. 5 the initial stage of the luminescence kinetic is shown. The luminescence was excited at 287 nm and 30 ps laser pulses.

The correct estimation of the decay time of the fast component is not done, since (1) the time response of the equipment is close to this decay time; (2) it is necessary to take into account the rising

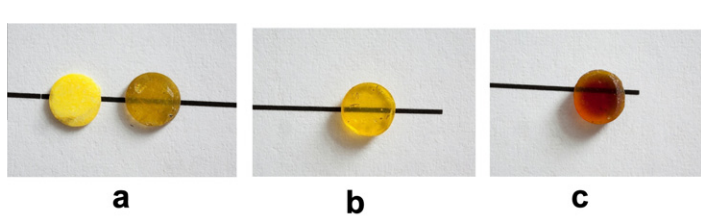

Fig. 1. The view of HPLT ceramics: a – YAG:Ce (0.9 mol%), 4 GPa annealed at 1000 °C and as prepared; b – YAG:Ce (0.9 mol%), 8 GPa; c – YAG:Ce/Pr (0.5/0.5 mol%) 8 GPa.

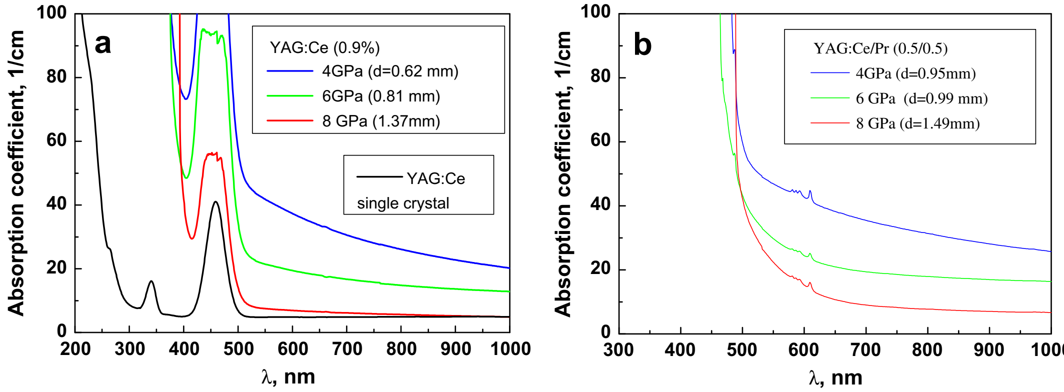

Fig. 2. Absorption spectra of YAG:Ce (a) and YAG:Ce/Pr (b). The samples thickness are given.

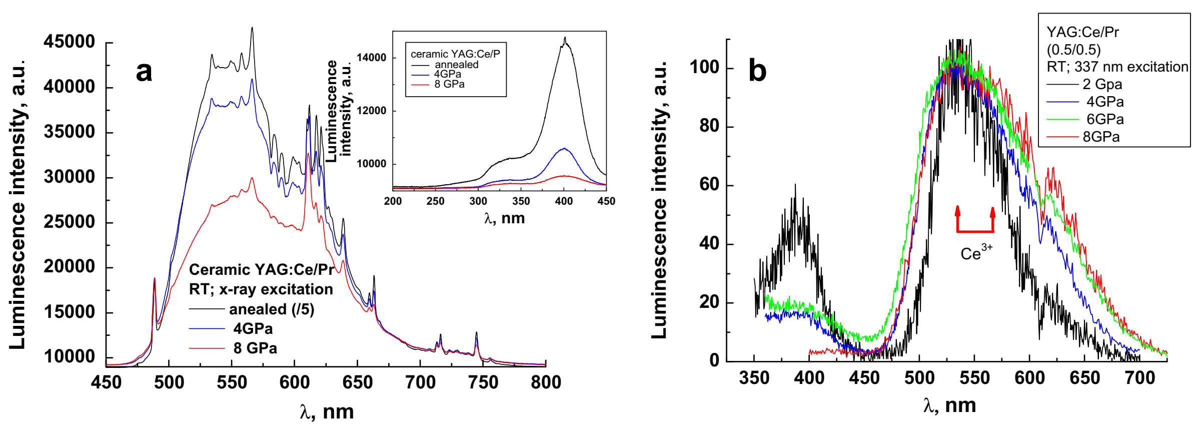

Fig. 3. Luminescence spectra of the YAG:Ce/Pr ceramics under X-ray excitation (a) and under photoexcitation in Ce absorption band (b). In the inset: the luminescence due to native defects is shown.

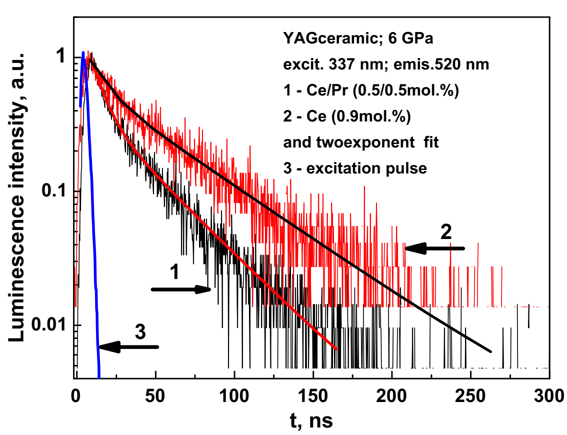

Fig. 4. Luminescence decay kinetics and two exponent fitting: for YAG:Ce/Pr (1) $I = 1.8 * \exp(-t/8\ \text{ns}) + 0.5 * \exp(-t/37\ \text{ns}) + 8 \times 10^{-4}$ and for YAG:Ce (2) $I = 0.8 * \exp(-t/10\ \text{ns}) + 0.7\exp(-t/54\ \text{ns}) + 1 \times 10^{-3}$.

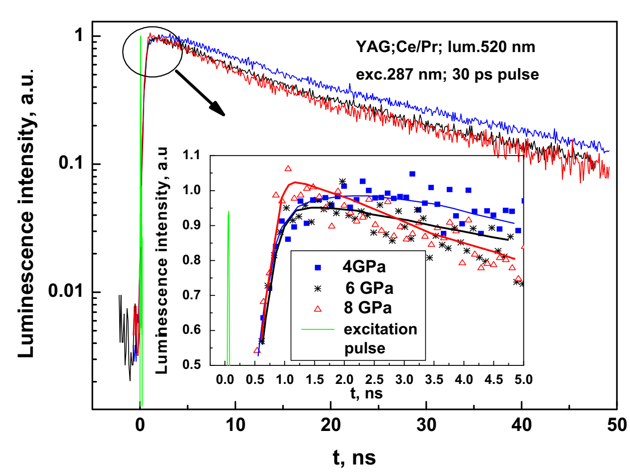

Fig. 5. Luminescence kinetic of YAG:Ce/Pr ceramics prepared at different sintering pressure. In the inset the rising front of luminescence kinetics is shown.

front as well as the duration of the excitation pulse and to perform a deconvolution procedure. However, it is clear that the luminescence rising front depends on the pressure applied during fabrication of the ceramics (Fig. 5, inset) – a faster rise was observed for the ceramic prepared at 8 GPa. So the formation time of luminescence center excited state depends on the sintering pressure.

In [18] the photoacoustic spectroscopy was applied for the analyses of the YAG:Ce single crystal Ce excited states. It is shown that at least four different excited states ***d*** exist in Ce^{3+} configuration coordinates depending on the local lattice vibration in various symmetry. Thus the configuration of excited states must be different for ceramics prepared at different pressures since the Ce^{3+} local symmetry depends on the defects in grain boundaries of ceramics. The luminescence rising front is due to the energy transfer between the different **5*d*** excited states.

4. Conclusions

The luminescence intensity decreases in line for the ceramics samples sintered at 2–8 GPa. The annealing of the sintering ceramics at 1000 °C leads to a considerable increase of the luminescence intensity. Concentration of some intrinsic point defect (Y_{Al}; F-type) was reduced under the high pressure applied for the sintering process of ceramic. However the annealing at 1000 °C introduces additional point defects. The luminescence decay time for the band related to the intrinsic point defects depends on the applied pressure–faster decay and lower luminescence intensity was observed for the ceramics sintered under a higher pressure.

Ce^{3+} luminescence decay in the time region 50–300 ns is similar for all studied ceramics and it does not depend on sintering pressure. Compared to Ce doped ceramics the Ce/Pr doping decreases the luminescence decay time. The slow decay component (decay time ~30–40 ns for Ce/Pr doped ceramics) of Ce emission does not depend on the sintering pressure.

The initial stage of the luminescence kinetics shows the rising front; the rising time depends on the sintering pressure. The defects in Ce^{3+} neighbor sites change the configurations of the $\boldsymbol{5d^1}$ excited state, correspondingly changing the electron relaxation process between different $\boldsymbol{d}$ states and modifying the luminescence center excited state formation time.

We suggest that the observed effects are due to the small grains in the nanostructured ceramics, luminescence quenching on the grain boundaries and additional interface stress fields which depend on the sintering pressure.

Acknowledgments

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