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Infrared laser stimulated broadband white emission of Yb^{3+}:YAG nanoceramics

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ABSTRACT

The infrared (IR) stimulated broad band anti-Stokes white emission of Yb^{3+} doped YAG nanoceramics was observed. It occurred under a focused beam of incident IR laser diode in vacuum. This intensity of white emission has decreased with increasing ambient atmosphere pressure. The power dependence of white emission has demonstrated the threshold behaviour characteristic to the avalanche effect. It was shown that the intensity of white emission increased with Yb^{3+} concentration. The white emission was observed in normal ambient atmosphere only for fully concentrated YbAG nanoceramic.

1. Introduction

Recently, the intense anti-Stokes white emission (ASWE) in highly concentrated rare earth (RE) oxides was reported by Tanner et al. [1,2] under excitation with a focused beam of infrared (IR) laser diode (LD) in vacuum. This upconversion emission was characterized by a high efficiency close to 10% and relatively low emission temperature. The anti-Stokes white emission that occurred at ambient atmosphere was quite recently observed by us in $LiYbP_4O_{12}$ and $NdAlO_3$ nanocrystals [3,4]. The emission rise times were very slow and emission intensity has increased by more than two orders of magnitude in vacuum. The dependence of ASWE intensity on LD excitation power demonstrated the threshold dependence characteristic to avalanche process [5].

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) is very well known compound, widely applied as a matrix for lanthanide based phosphors [6–11]. Great interest of this compound is a result of its special properties such as good thermal and chemical stability, a high thermal conductivity etc. Relatively large energy gap (6.5 eV) makes this material a good electric insulator. Trivalent ytterbium ions posses only two energy levels within the 4f subshell – the ground $^2F_{7/2}$ and excited $^2F_{5/2}$ states separated by 1.3 eV. In the YAG ground state of Yb^{3+} ion is located about 3 eV below the top of valence band [12].

In the present work the IR LD induced anti-Stokes white emission (ASWE) of Yb^{3+} doped YAG nanoceramics was investigated. In particularly, the effect of Yb^{3+} concentration on the white emission was investigated.

2. Experimental

The YAG:Yb nanocrystalline powders have been prepared using modified Pecchini method [13] described previously elsewhere [14]. The high purity yttrium oxide (Y_2O_3), ytterbium oxide (Yb_2O_3), aluminum nitrate hydrate ($Al(NO_3)\cdot 9H_2O$), citric acid nonhydrate ($C_6H_8O_7$) and ethylene glycol ($C_2H_6O_2$) have been used as a starting compounds. Appropriate amount of oxides have been diluted in ultrapure nitric acid to produce nitrates. Afterwards aqueous solutions of nitrates have been mixed together with nonhydrate citric acid and ethylene glycol for 1 h. In the next stage obtained solution was heated for 1 week at 90 °C until the resin was formed. Finally the resin was calcinated at 900 °C in air for 16 h. To characterize influence of dopant concentration on luminescence properties of YAG:Yb four samples with a different Yb concentrations have been prepared (1%; 5%; 20%; 100%). The X-ray diffraction pattern (XRD) recorded for obtained powder samples are presented in Fig. 1a. Average grain size calculated from the Scherrer equation [15] was ~35 nm and it is in a good agreement with a value obtained from transmission electron microscopy (TEM) measurements (see Fig. 1b). The X-ray diffraction data of nanocrystalline ceramic are presented in Fig. 1d. The higher level of background associated with a broad band observed in XRD patterns is a confirmation of presence of amorphous phase reported previously in nanocrystalline ceramics [16,17].

Fabrication of nanoceramics was performed using the low temperature high pressure (LTHP) method [16] at 8 GPa and heating for 1 min at 450 °C. The emission spectra were measured using 976 nm CW laser diode (LD) as an excitation source and AVS-USB2000 Spectrometer (Avantes). The build-up of up-conversion emission intensity was recorded using the oscilloscope LeCroy WaveSurfer 400 with mechanical chopper. The 1931 2° CIE

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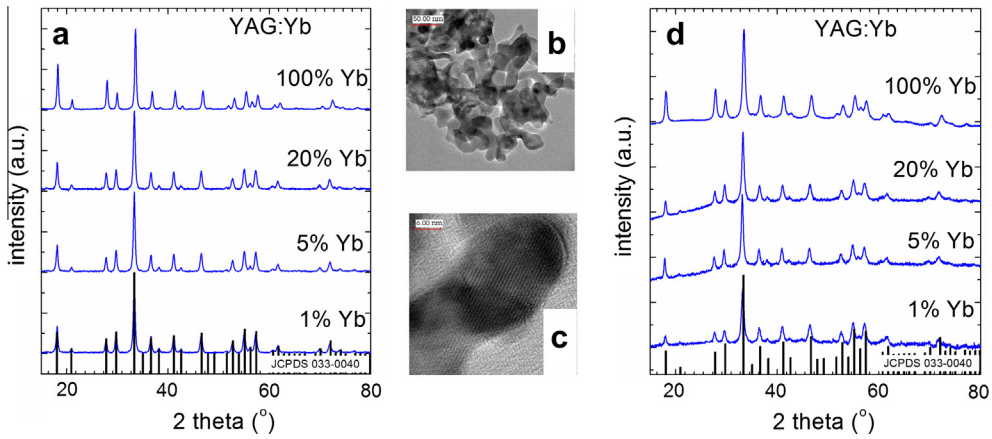

Fig. 1. The structure and morphology of YAG:Yb nanocrystalline powder and ceramic: X-ray diffraction data of powders (a); and transmission electron microscopy images of powders (b) and (c); and X-ray diffraction data of nanoceramic (d) .

coordinates have been calculated using color matching functions. The emission spectra recorded at a low pressure condition were performed using the vacuum cell supplied with Turbomolecular Drag Pump TMH071 P and electronic drive unit TC 600 (Pfeiffer). The comparison of emission intensities of ceramics for different dopant contents were performed with providing constant excitation density. Presented spectra were normalized to the excitation peak. The experiment was performed repeatedly in order to eliminate errors.

3. Results and discussion

Emission properties of Yb^{3+}:YAG nanoceramic were measured using 976 nm laser diode (LD) as the excitation line. The emission spectra were measured under atmospheric pressure conditions (1000 mbar) and at reduced (0.01 mbar) pressure conditions. A bright yellowish-white emission observed in vacuum conditions under IR excitation laser beam focused onto the YbAG nanocrystalline ceramic is shown in Fig. 2a. A broad upconversion emission for fully concentrated sample YbAG nanoceramic was found in the visible range. The intensity of anti-Stokes white (ASWE) emission was strongly dependent on the incident excitation power. The effect of excitation laser power on the intensity of white emission is illustrated in Fig. 2b. One can see, that the intensity is centered at 650 nm with two characteristic peaks at 624 nm and 672 nm.

The power dependence of ASWE emission shown in Fig. 2c demonstrates the characteristic threshold ($P_{th} \sim 0.9$ W) behavior. This dependence is may be discussed in terms of the power law expression $I_{em} \sim P^N$ [16] with a small order parameter $N = 1.37$. Above the threshold point in a range 0.9–1.3 W there is observed the fast increase of intensity with $N = 9.13$. Above 1.35 W there is observed the saturation region. Such behavior is characteristic to the photon avalanche process [5]. From comparison of emission spectra of nanocrystalline powder and ceramic a small blue shift of emission was observed for the nanoceramic. The explanation of origin of observed behavior needs further studies.

The dependence of anti-Stokes white emission of Yb:YAG nanoceramic on concentration of Yb^{3+} ions is illustrated in Fig. 3a. One can find that with increasing dopant ions the maximum of emission band shifts to lower energies therefore the color of emitted light can be tuned by the dopant concentration (see Fig. 3b). Moreover the white emission in atmospheric pressure could be observed only for fully concentrated sample.

Previously presented results of the ASWE emission [1–4] depicted tremendous influence of surrounding pressure on emission intensity. The effect of pressure on upconversion emission of YbAG nanocrystalline ceramic under IR excitation is presented in Fig. 3c. It has been found that for all of investigated samples a overall intensity increased over two orders of magnitude with lowering the surrounding pressure from the atmospheric one to 5 mbar. However, the ASWE emission in atmospheric pressure condition was observed only for a fully concentrated sample. The significant impact of pressure on the emission intensity was noticed even for samples with a lower dopant content. In case of nanoceramics with a concentration of Yb^{3+} ions in the range 1–20%, the white emission occurs in lower pressure conditions and with a further lowering of pressure the ASWE intensity increases about 2 orders of magnitude. Further decrease of pressure below 5 mbar does not affect the emission intensity and some kind of saturation can be observed. Wang et al. [1,2] proposed the heat dissipation model that complies a reduced thermal convection responsible for enhancement of emission intensity in reduced pressure conditions. Moreover, a small grain size of nanocrystalline ceramic has adverse impact of its thermal properties. According to the thermal dissipation model the intensity of emission can be expressed as a function of surrounding pressure:

$$I_{em} = I_0 \exp(-P/P_0) \quad (1)$$

where P_0 represents a critical magnitude of pressure of ambient atmosphere above which the emission intensity begins to decrease and I_0 is the initial intensity.

A comparison of emission spectra recorded in range from 10 K to 300 K temperature is shown in Fig. 3d. One can note that intensity of emission band decreases over 10 times with lowering the temperature to 10 K. For temperatures below 230 K the temperature has small influence on emission intensity while above this value emission band rises significantly with temperature.

The influence of dopant concentration on anti-Stokes emission intensity of Yb^{3+}:YAG nanocrystalline ceramic is presented in Fig. 4. The emission spectra were normalized to the intensity of excitation beam and overall integral intensity is shown in the plot. One can see that with increase of Yb^{3+} ions content the emission increase significantly (over two orders of magnitude). Presented dependence exhibits a nonlinear profile and could be fitted by an exponential function. This aberration from a linear profile suggests occurrence of some damping effect that takes place. The images presented as a inset in Fig. 4 illustrate the color of emitted light.

For Yb^{3+} doped samples the charge transfer emission could be responsible for a broadband emission. van Pieterson et al. [18] have reported a broadband emission of oxides, phosphates and fluorides