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Cathodoluminescence of YAG:Nd optical nanoceramics in the visible and UV ranges

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ABSTRACT

Results of cathodoluminescence studies of optical YAG:Nd nanoceramics with different microstructure are presented. The composition of the samples was studied by the electron-probe microanalysis. The estimation of the average grain size was performed with the use of scanning electron microscopy and based on X-ray diffraction analysis. Local cathodoluminescence technique was used to collect the emission spectra and decays of emission in the UV and visible range. The "memory effect" in YAG:Nd nanoceramics luminescence was noticed and discussed. In particular, it was observed that the initial electron beam irradiation of sample leads to the increase of luminescence efficiency in the visible and UV ranges. It was confirmed also that the observed effect is long-lasting and remains for years. To understand the mechanism of the effect, the estimation of temperature annealing under continuous irradiation by electron beam was done. The model of memory effect involving trap states was proposed and discussed.

1. Introduction

Crystals and optical ceramics of yttrium-aluminium garnet doped with neodymium ions (YAG:Nd) are applied in modern science and technology mainly as laser materials [1]. However, when excited by the electron beam, besides emission in the infrared range, YAG:Nd crystals exhibit an intensive luminescence also in the visible and ultraviolet ranges [2–4]. YAG:Nd ceramics are prospective material that can substitute single crystal in laser and scintillating applications [5]. Moreover, ceramic materials allow to avoid the problem with inhomogeneous doping in large crystals leading to inhomogeneities in optical characteristics. Therefore, particularly the spectroscopic properties of such materials are currently of interest. Recently, the changes of the luminescent asymmetric ratio associated with the change in local symmetry of dopant ions for nanocrystals, nanoceramics and microceramics YAG:Eu were found and discussed for photo- and cathodoluminescence spectra [6]. It was proved that obtained results for nanoceramics composed of nanocrystals may help in better understanding of boundary and grain size effects in commercial ceramics composed of microsized grains.

The present work focuses around unique cathodoluminescent features of YAG:Nd nanoceramics. Its main purpose was to investigate the luminescent properties in visible and UV ranges of YAG:Nd nanoceramics samples synthesized at different conditions and to compare the characteristics of nano material with those of the bulk material. Detailed study of luminescence characteristics of the material in these ranges allows to obtain additional information on the electronic structure of the material, including information on the existence of high-energy defect trap levels, which directly affect the luminescent characteristics also in the infrared range.

2. Samples

Nanocrystalline powders of 1 mol% Nd-doped YAG garnet were prepared by a modified Pechini method described in details elsewhere [7]. The yttrium and neodymium oxide (Stanford Materials Company – 99.999% purity), aluminum chloride (AlfaAesar – 99.9995% purity), ultrapure nitric acid, citric acid (AlfaAesar – 99.5% purity) and ethylene glycol (POCH – 99% purity) were used as starting reagents. Aqueous solutions of yttrium and neodymium were prepared by dissolving Y_2O_3 and Nd_2O_3 with HNO_3. A stoichiometric molar ratio of Y_2O_3, Nd_2O_3 and $AlCl_3$ were dissolved in aqueous citric acid solution under stirring. Then the ethylene glycol

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was added as a cross-linking agent. The solution was stirred for 2 h and then dried at 90 °C for 7 days. The obtained gel was annealed at temperature in 850–1150 °C range for 8 h in air. The samples of 1 mol% YAG:Nd nanoceramics characterized by different grain sizes were prepared from respective powders by high pressure low temperature (HPLT) sintering technique [8]. The samples of diameter of 5 mm pellets were formed by cold pressing under pressure of 50 MPa. Finally the pellets were placed in the toroid-type container and pressed under 8 GPa and the temperature in 450–550 °C range within 1 min.

To compare the properties of YAG:Nd nanoceramics with those of the single crystal the following samples were chosen: the undoped YAG and the YAG:Nd single crystals (Sample 1 and 2, respectively) which were grown by Horizontal Direct Crystallization technique at standard conditions; YAG:Nd nanoceramics samples (Samples 3–6) which were synthesized by High Pressure Low Temperature sintering technique described below at different conditions – the powder preparation temperature was 850 °C (Sample 3 and 4) and 1150 °C (Sample 5 and 6), the sintering temperature was 450 °C (3, 5, 6) and 550 °C (4). Sample 6 was additionally annealed at 600 °C for 4 h in air atmosphere. All obtained samples are listed in Table 1.

3. EPMA, SEM and XRD characterization

The characterization of samples was performed with the use of the following techniques on relevant equipment: electron-probe microanalysis (EPMA, CAMEBAX electron-probe x-ray microanalyzer); scanning electron microscopy (SEM, JEOL-JSM-7001A JEOL Ltd., scanning electron microscope); and X-Ray Diffraction (XRD, Bruker D2 Phaser X-Ray Diffractometer with LYNXEYE detector).

The EPMA study of samples showed that all samples were homogeneous in Nd^{3+} distribution and did not show any presence of other phase inclusions. The concentration of ~0.1 at. % Nd^{3+} in all YAG:Nd samples (see Table 1) is considered to be optimal for the maximum luminescence intensity because of the lowest probability of nonradiative excitation energy transfer between neodymium ions in YAG host [9].

To characterize the grain size in YAG:Nd nanoceramics samples, the SEM studies were performed for Samples 3 and 5. To etch the polished surface of the samples, the mixture of acids (hydrofluoric and orthophosphoric in correlation 1:5, respectively) was prepared and the samples were immerged into this solution for several minutes with no heating. As the samples are dielectric, it is required to cover their surface with conducting material to provide a stable charge runoff during electron-probe investigations; therefore a thin layer of carbon was evaporated on the surface of samples, saving the area for study uncovered to include the carbon on the visualization of sample surface. Fig. 1 represents SEM image of Sample 5 received in secondary electron mode, accelerating voltage U = 5 kV. The average grain size of Sample 5 is 40 nm, but the distribution by grain sizes for this sample is rather wide (Fig. 2).

The Samples 3, 4 and 5 were also characterized by XRD. The analysis of XRD curves showed that the coherent-scattering region for these samples is 21 nm, 20 nm and 40 nm, respectively, the estimation error was 10%.

4. CL study

4.1. CL spectra

The CL measurements were performed on Camebax electron-probe microanalyzer equipped with optical spectrometers of original construction for different spectral ranges [10]. CL properties of the samples were measured under the following conditions: electron beam accelerating voltage was 15 kV, electron beam current

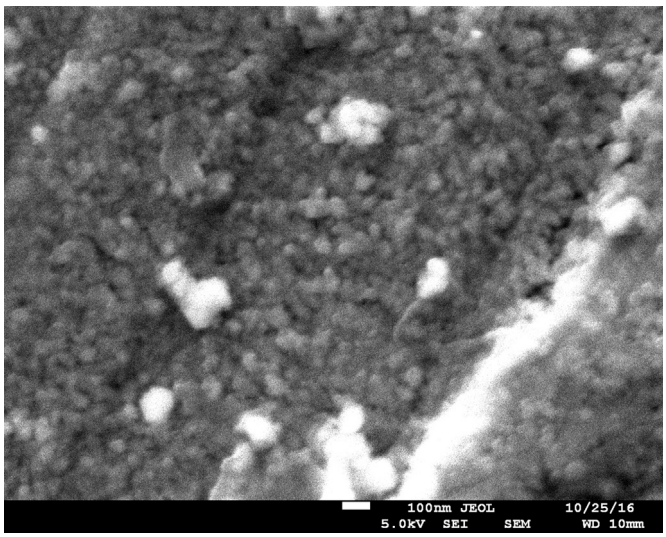

Fig. 1. SEM image of Sample 5.

Table 1
The description of samples.

	Sample no	Nd concentration, at. %	Synthesis technology	Conditions
YAG undoped single crystal	1	0	Horizontal Direct Crystallization (HDC)	–
YAG:Nd single crystal	2	0.15 ± 0.2	HDC	–
YAG:Nd nanoceramics	3	0.11 ± 0.2	High Pressure Low Temperature sinter (HPLT)	Powder preparation T = 850 °C Sintering T = 450°C Pressure – 8 GPa Annealing – no
	4	0.11 ± 0.2	HPLT	Powder preparation T = 850 °C Sintering T = 550 °C Pressure – 8 GPa Annealing – no
	5	0.11 ± 0.2	HPLT	Powder preparation T = 1150 °C Sintering T = 450 °C Pressure – 8 GPa Annealing – no
	6	0.11 ± 0.2	HPLT	Powder preparation T = 1150 °C Sintering T = 450 °C Pressure – 8 GPa Annealing 600 °C/4 h

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