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Preparation and luminescence properties of $Gd_3Ga_5O_{12}$ nanocrystalline garnet

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Nanocrystalline $Gd_3Ga_5O_{12}$ and $Gd_3Ga_5O_{12}$:Tb^{3+} phosphors were obtained by sintering precursors, which had been prepared by the co-precipitation method. X-ray diffraction (XRD), atomic force microscopy (AFM), and X-ray luminescence spectra were used to characterize the synthesized nanocrystalline garnet. The XRD results revealed that the samples begin to crystallize at 750°C and a fully crystallized pure $Gd_3Ga_5O_{12}$ phase could be obtained at 850°C. The AFM images indicate that the phosphor powders contain aggregates of grain-like particles. Under X-ray excitation the $Gd_3Ga_5O_{12}$:Tb^{3+} phosphor showed the characteristic green emissions of Tb^{3+} ($^5D_4 \rightarrow {}^7F_{6,5,4,3}$ transitions). A comparison between X-ray luminescence spectra of pure and Tb^{3+}-doped $Gd_3Ga_5O_{12}$ samples prepared by solid-state reaction and by the co-precipitation method was made.

Nanocrystalline garnet $Gd_3Ga_5O_{12}$ / Co-precipitation / Rare-earth ion / X-ray luminescence

1. Introduction

Rare-earth doped gadolinium gallium garnet ($Gd_3Ga_5O_{12}$, GGG) has attracted much attention as an important material for application in many optical devices. However, high-quality large-sized $Gd_3Ga_5O_{12}$ crystals are hard to grow because of the serious decomposition and evaporation of Ga_2O_3 encountered during single crystal growth by the Czochralski method. Therefore, many efforts have been made to synthesize polycrystalline $Gd_3Ga_5O_{12}$ powders and ceramics, which are typically prepared by solid-state reaction. This method usually requires high calcination temperature and long holding time. As a result, a wide distribution of grain sizes and irregular morphology are obtained [1,2]. To correct these drawbacks of the solid-state reaction method, different wet-chemical processes have been applied with the purpose to produce nanopowders for optical applications [3-6]. Among these processes the co-precipitation method is one of the most important techniques for the synthesis of nanocrystalline functional materials. The co-precipitation method allows preparing polycrystalline materials at a lower sintering temperature and with a shorter annealing time. Nanostructure materials are also considered to be potentially useful for technological application in biomedicine, because such materials display novel, often enhanced properties compared to the corresponding traditional bulk compounds.

In this paper we report on the preparation of pure and Tb^{3+}-doped $Gd_3Ga_5O_{12}$ garnet by the co-precipitation method using aqueous ammonia as the precipitator and a polyethylene glycol as cross-linking agent. Powders sintered at various temperatures were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and X-ray luminescence spectroscopy. A comparative analysis of the luminescence spectra of micro- and nanosamples was also performed to study the influence of the particle size on luminescence characteristics.

2. Experimental details

2.1. Samples

Pure and Tb^{3+}-doped microceramic $Gd_3Ga_5O_{12}$ samples were prepared by standard ceramic technology, described in detail in [2,7]. Briefly, appropriate quantities of Ga_2O_3 and Gd_2O_3 powders (analytical purity on a cation basis) were used as initial materials. The oxide powders were mechanically mixed in an agate mortar till a homogeneous mass was obtained. Pellets were formed by uniaxially pressing of the powders in a steel die (8 mm in diameter) at 150 kg/cm^2 and heated for 10-12 h at temperatures above 1200°C.

Nanopowders of pure and Tb^{3+}-doped $Gd_3Ga_5O_{12}$ were prepared by the co-precipitation method in a polyethylene glycol (PEG) assisted process. Stoichiometric quantities of Ga_2O_3 and Gd_2O_3 oxide powders were dissolved in an aqueous nitric acid (HNO_3) solution. The amount of Tb^{3+} rare-earth ions was 1 and 0.1 mol.% with respect to Gd^{3+}. Then a suitable amount of PEG (molecular weight 300, 400 g/mol) was added to the solution as a cross-linking agent. The PEG concentration was $C_{PEG} \sim$ 70 mg/ml. A chemical reaction took place between the obtained nitrates and the polyethylene glycol. An aqueous ammonia solution was then added dropwise into the solution. During this process the pH of the solution was monitored (pH ~ 10). The obtained solution was continuously stirred by using a magnetic agitator. The resulting nanoparticles were separated by centrifugation, filtration and washing with distilled water several times, and finally dried in vacuum at 60°C for 1 day in order to produce fine dry powders. The samples were heat-treated at 400°C in air for 24 h to thermally decompose the hydroxide and reaction products, and subsequently ball-milled for 40 min. Finally, the powders were sintered for 6 h at 750-950°C. Nanoceramic pellets were formed by uniaxially pressing the powders in a steel die (8 mm in diameter) at 150 kg/cm^2.

2.2. Measurements

X-ray studies were carried out on a diffractometer STOE STADI P (Cu K_α-radiation). Phase analysis was made using the program package STOE WinXPOW. The morphologies were observed with an atomic force microscope (ASM) Solver P47H-PRO. To investigate the X-ray luminescence a home-made setup based on an SF-4A quartz monochromator was used. X-ray excitation was performed by a microfocused X-ray tube (45 kV, 0.3 mA) with a copper anticathode through a beryllium window mounted on the cryostat. The luminescence studies were carried out at room temperature.

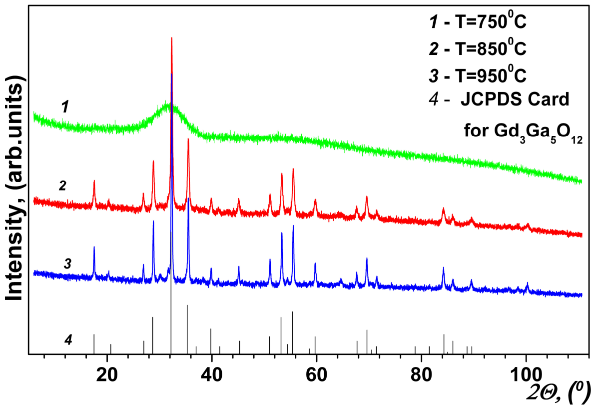

Fig. 1 X-ray diffraction patterns of nanocrystalline $Gd_3Ga_5O_{12}$ powders calcined at various temperatures.

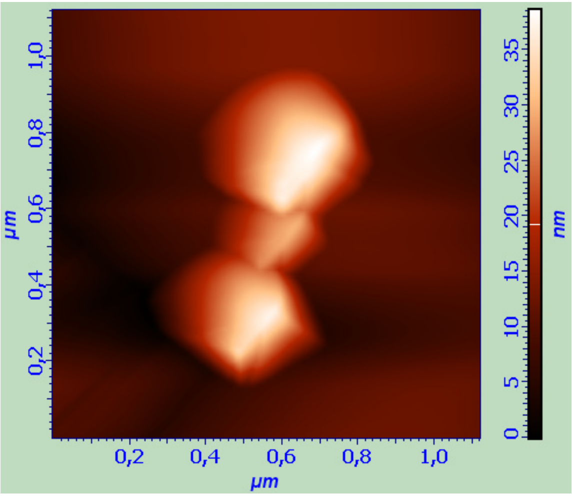

Fig. 2 2D AFM image of $Gd_3Ga_5O_{12}$ nanopowder calcined at 850°C.

3. Results and discussion

Fig 1 shows representative X-ray diffraction (XRD) patterns of the $Gd_3Ga_5O_{12}$ nanopowders obtained by the co-precipitation method with a polyethylene glycol (PEG with molecular weight 400 g/mol) and annealed at different temperatures (curves 1-3). A broad peak at $2\theta = 32.3°$ appears for the calcination temperature 750°C. It indicates that at this temperature a garnet phase has begun to crystallize. Analysis of the other diffractograms showed that the minimum calcination temperature that allowed obtaining a single garnet phase was $T \sim$ 800°C. All the diffraction peaks observed in the XRD patterns for the calcination temperatures 850 and 950°C are in complete agreement with those of the JCPDS Card No. 13-0493 for $Gd_3Ga_5O_{12}$ (curve 4). Table 1 shows the full width at half maximum (FWHM) of the strongest X-ray diffraction peaks at 32.3° of samples sintered at various temperatures. It can be seen that FWHM becomes narrower with increasing temperature. The crystallite size was estimated from the X-ray diffraction patterns using the Scherrer formula $D = 0.89{\cdot}\lambda/\beta{\cdot}\cos\theta$, where D is the average grain size, λ the wavelength of the X-rays (0.154 nm), θ the diffraction angle and β the full-width at half-maximum (FWHM) of the peak at 32.3°. The average crystallite size of the nanopowders (see Table 1) varies from 20 nm to 37 nm, becoming larger with increasing calcination temperature, which is in agreement with [5,6].

Fig. 2 shows a 2D ASM image of GGG powder (PEG with molecular weight 400 g/mol) calcined at 850°C for 6 h. Analysis of the AFM image indicates that the phosphor powders are composed of agglomerates with characteristic polyhedral morphology and an average diameter of 100-160 nm. The AFM microscopy results for powders calcined at various temperatures clearly show that the particle size

Table 1 Full-width at half-maximum (β) and grain size (D), calculated from the reflection at 2θ = 32.3° in XRD patterns of $Gd_3Ga_5O_{12}$ samples calcined at different temperatures.

T_{calc} (°C)	β (°)	D (nm)
800	0.42	20
850	0.32	25.4
950	0.22	37

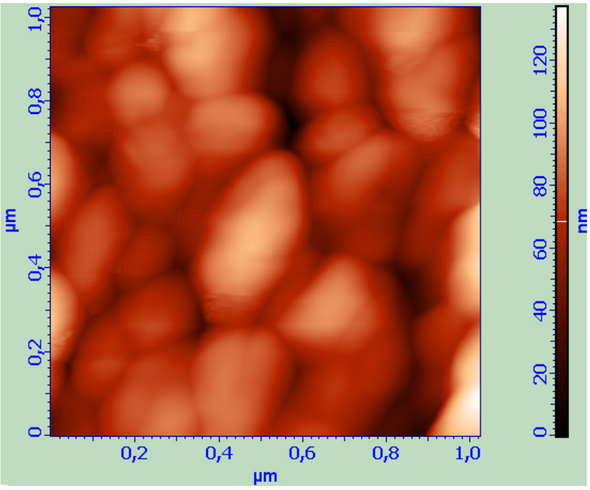

Fig. 3 2D AFM image of a $Gd_3Ga_5O_{12}$ nanoceramic calcined at 850°C.

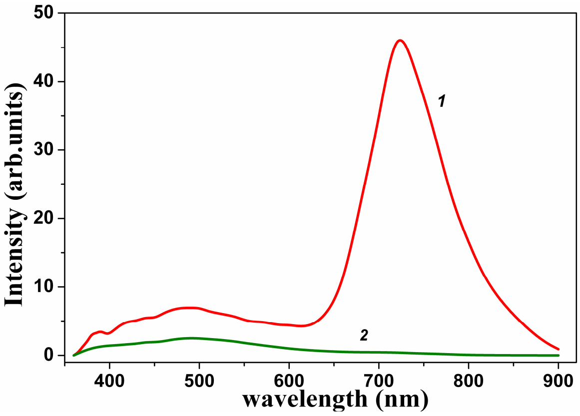

Fig. 4 X-ray luminescence of nominally pure $Gd_3Ga_5O_{12}$ micro- (red, curve 1) and nanoceramics (green, curve 2) at room temperature.

becomes larger with increasing sintering temperature, which is in agreement with what was calculated using the Scherrer formula. Fig. 3 shows a 2D ASM image of GGG nanoceramics. From this image we can conclude that the nanoceramics consist of aggregated particles, which are dispersed uniformly, with an average grain size as estimated using Scherrer's formula.

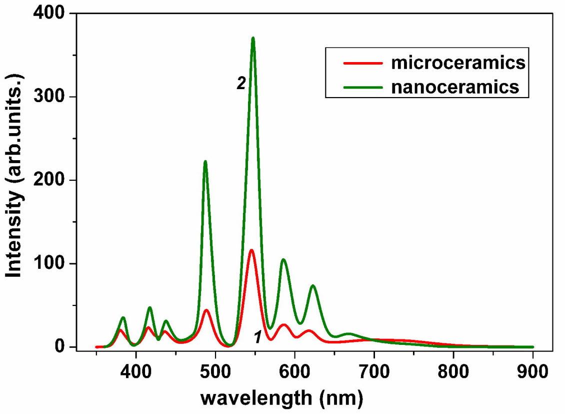

Fig. 5 X-ray luminescence of Tb^{3+}-doped $Gd_3Ga_5O_{12}$ (1 mol.% Tb^{3+}) micro- (red, curve 1) and nanoceramics (green, curve 2) at room temperature.

A comparative analysis of the luminescence properties of nanopowders and nanoceramics with respect to those of microceramics was made. A luminescence spectrum for a nominally pure $Gd_3Ga_5O_{12}$ microceramic under X-ray excitation is presented in Fig. 4 (curve 1). The maximum intensity of X-ray luminescence is observed in the spectral region 700-760 nm at room temperature. This wide luminescence band, which is typical for Cr^{3+} ions in octahedral position of the garnet structure, can be attributed to $^4T_2 \rightarrow {}^4A_2$ emission transitions [7]. Besides the band with λ_m = 730 nm, a weak broad band at about 490 nm, which corresponds to matrix luminescence, is observed in the emission spectra of $Gd_3Ga_5O_{12}$ microceramics under X-ray excitation. Only the matrix luminescence at λ_m = 490 nm was observed for the nanoceramic (Fig. 4, curve 2). Moreover, the total intensity of this luminescence decreases by a factor of more than 2 with respect to the band at λ_m = 490 nm for the microceramic.

X-ray luminescence spectra of Tb^{3+}-doped nanocrystalline $Gd_3Ga_5O_{12}$ powders are represented on Fig. 5. The activated samples reveal relatively high light yield. Characteristic strong lines assigned to the $^5D_3 \rightarrow {}^7F_j$ and $^5D_4 \rightarrow {}^7F_j$ (j = 6, 5, 4, 3) transitions of the Tb^{3+} ions are observed. The total luminescence intensity increases with increasing Tb^{3+} activator concentration from 0.1 to 1.0 mol.%. The spectrum of emission lines due to Tb^{3+} can be separated into two groups. The blue emission below 480 nm is from $^5D_3 \rightarrow {}^7F_i$ transitions, while the green emission above 480 nm is from $^5D_4 \rightarrow {}^7F_i$ transitions. The intensity of the blue emission (Fig. 5, curves 1, 2) is much weaker than that of the green emission. It was shown in [8], in the case of $Y_{3-x}Al_5O_{12}$:Tb_x powders, that the spectral energy distribution of Tb^{3+} emission is strongly dependent on the Tb concentration. The blue emission ($^5D_3 \rightarrow {}^7F_j$) dominates for very low Tb concentrations (< 0.1 %) and disappears for concentrations above

~2 %. For X-ray excitation of nano- and microceramics $Gd_3Ga_5O_{12}$ with activator concentrations of about 1 mol.% Tb^{3+} (Fig. 5) the luminescence transition $^5D_4 \rightarrow {}^7F_j$ (green emission) dominates. There is no appreciable difference in the shape or band position of the activator photoluminescence curve of the nanocrystalline garnet (1) with respect to that of the ceramics prepared by a solid state reaction (2). However, a luminescence band in the spectral region 700-760 nm, attributed to uncontrolled chromium impurities, was observed for the nominally pure and Tb^{3+}-doped microceramic samples. Note that the activator emission is enhanced by approximately a factor 3 in the case of nano-sized $Gd_3Ga_5O_{12}:Tb^{3+}$ with respect to the corresponding microceramic. The increase of activator ions is due to the lower content of defects and uncontrolled impurities in the nanosized materials.

4. Conclusions

Using the co-precipitation method with aqueous ammonia as precipitator and PEG as cross-linking agent, polycrystalline pure and Tb^{3+}-doped $Gd_3Ga_5O_{12}$ garnet phases have been prepared by sintering at the relatively low temperature 850°C for 6 h. Analysis of the XRD patterns showed that the particle size of the polycrystalline materials synthesized in the temperature range 800-950°C varied within 20-37 nm. The particle size of $Gd_3Ga_5O_{12}$ garnet increases with increasing temperature. The AFM images indicate that the phosphor powders are composites of agglomerates with characteristic polyhedral morphology. The nanosized materials were found to be more stoichiometric and had a lower content of defects and uncontrolled impurities than the microceramics and single crystals. This led to enhanced intensity of the Tb^{3+} activator characteristic emission for the nanocrystalline $Gd_3Ga_5O_{12}$ compounds.

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