Synthesis, structural investigation and luminescence spectroscopy of nanocrystalline \( \text{Gd}_3\text{Ga}_5\text{O}_{12} \) doped with lanthanide ions

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Dedicated to Professor Mauro Graziani on his 70th birthday.

Abstract

Gadolinium gallium garnet (GGG) nanocrystalline powder doped with lanthanide ions (Eu\(^{3+}\) and Er\(^{3+}\)) have been obtained using two different methods (coprecipitation and Pechini). The X-ray diffraction results show that single phase cubic GGG nanopowders have been obtained for both preparation methods. The samples prepared by the two procedures show different morphologies, as revealed by scanning electron microscopy images. The Er\(^{3+}\)-doped nanopowders obtained with the coprecipitation method show strong luminescence upon 488.0 nm excitation. The emission spectrum is similar to the one of the single crystal and of nanopowders of the same composition prepared by a combustion synthesis. The Er\(^{3+}\)-doped GGG nanopowders obtained by the coprecipitation method show efficient upconversion in the green region (around 550 nm) upon excitation in the near IR at a wavelength of 800 nm.

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1. Introduction

Garnets are among the most important hosts for luminescent active centers, such as lanthanide and transition metal ions. Single crystals of Nd\(^{3+}\)- and Yb\(^{3+}\)-doped gadolinium gallium garnet \( \text{Gd}_3\text{Ga}_5\text{O}_{12} \) (GGG) have been studied for their possible application as active elements for diode pumped lasers [1–3]. On the other hand, lanthanide-doped nanostructured materials have gained importance for possible applications as imaging or display devices in which the resolution is inversely related to the particle size [4,5]. The luminescence properties have been investigated for Pr\(^{3+}\), Ho\(^{3+}\) - and Er\(^{3+}\)-doped GGG nanocrystalline powders prepared by a combustion synthesis [6,7]; these materials appear to show efficient visible upconversion emission after excitation with IR radiation. To the best of our knowledge, only a few papers have been published on the preparation and optical properties of lanthanide-doped nanocrystalline GGG powders and thin films, obtained using a coprecipitation or Pechini sol–gel process [8,9].

In the present communication, we report on the synthesis of Ln\(^{3+}\)-doped (Ln = Eu, Er) nanocrystalline GGG powders using two preparation methods (coprecipitation and Pechini). After a suitable heat treatment, the obtained powders result to be single phase with a garnet structure. Size distributions and morphological properties of the nanocrystalline samples are obtained from scanning electron microscopy (SEM) images and compared with previous results obtained for GGG nanocrystalline powders prepared by combustion synthesis [10] or other methods. Laser excited Stokes and upconversion emission spectra have been measured and discussed.

2. Experimental details

2.1. Preparation procedure

The coprecipitation and Pechini methods employed for the preparation of the nanocrystalline GGG powders are described in detail in a separate paper [11]. Briefly, for the coprecipitation method, stoichiometric quantities of \( \text{Gd}_2\text{O}_3 \)
Ga(NO₃)₃ and Ln(NO₃)₃ (Ln = trivalent lanthanide ion) were dissolved in a HNO₃ solution. The obtained solution was added dropwise to a NH₃ aqueous solution and the precipitate was filtered and then dried at 60 °C. The samples were heat treated at 500 °C for 30 h, ball milled for 30 min and finally heat treated at 900 °C for 2 h. The samples prepared by the coprecipitation method will be denoted hereafter as CP samples. For the Pechini method, Gd₂O₃, Ga(NO₃)₃ and the lanthanide nitrate were dissolved in aqueous HNO₃. A suitable quantity of citric acid, corresponding to a 3:1 molar ratio amount with respect to the gadolinium nitrate, was subsequently dissolved in the solution under stirring and heating (80–100 °C). Then, a quantity of polyethylene glycol (PEG) corresponding to two times the mass amount of citric acid was added to the solution. The sol samples were heat treated at 90 °C for 2 days and then at 800 °C for 16 h. The samples prepared by the Pechini method will be denoted hereafter as PE samples. The amount of the dopant lanthanide ions (Eu³⁺ or Er³⁺) was 1 at.% with respect to the Gd³⁺ ions for both the CP and PE samples.

2.2. Instrumental details

2.2.1. X-ray diffraction

The X-ray diffraction (XRD) patterns were recorded overnight using a Bruker D8 diffractometer in the Bragg–Brentano geometry with Cu Kα radiation (λ = 1.54178 Å). The goniometer was equipped with a graphite monochromator in the diffracted beam and the patterns were collected with 0.05° step size.

The powder patterns were analysed according to the Rietveld method [12] using the programme MAUD [13]. Full discussions on capabilities and limitations of the Rietveld refinement from powder diffraction data have been previously reported [14,15].

2.2.2. Scanning electron microscopy

SEM images were taken with a Jeol (Tokyo, Japan) JSM 5600. Samples were coated with a Au thin film, in order to avoid charging effects.

2.2.3. Luminescence spectroscopy

The room temperature Stokes emission spectrum was measured exciting with the 488 nm line of an Argon laser. The emission intensity was dispersed with a half-meter monochromator equipped with a 150 lines/mm grating and detected by a cooled CCD device. The emission decay curves were measured using as the excitation source the second harmonic (at 532 nm) of the fundamental radiation of a pulsed Nd:YAG laser, a GaAs photomultiplier and a digital oscilloscope.

3. Results and discussion

Fig. 1 shows selected powder X-ray diffraction patterns of Eu³⁺-doped CP and PE nanocrystalline GGG samples. A heat treatment of the Eu³⁺-doped CP powders at 900 °C for 2 h produces almost entirely a GGG cubic phase (see Fig. 1). The lattice parameter of this phase is 12.582(±3) Å, considerably larger than the values of 12.377 and 12.383 Å reported for single crystals of precise stoichiometric Gd₃Ga₅O₁₂ [15]. The reasons for this behaviour were already discussed in a previous paper [16] and are related essentially to the Gd:Ga off-stoichiometric ratio. An accurate analysis of the relative intensity of the (2 2 0) peak at 2θ = 19.93° indicates that the off-stoichiometric ratio Gd:Ga can be around 3.7:4.3 after assuming that the excess Gd atoms replace for the octahedral sites of Ga [18]. From a full pattern analysis of the peak broadening it is possible to determine the average coherent diffraction domain size to be around 40 nm, with simultaneous presence of lattice microstrain of about 0.1%. On the other hand, the Pechini method seems to be a viable alternative synthesis for “stoichiometric correct” Gd₃Ga₅O₁₂, as testified by the upper pattern of Fig. 1.

Eu³⁺-doped PE nanocrystalline GGG samples, the lattice parameter a = 12.397 Å turns out to be very close to those reported for GGG single crystals. The (2 2 0) peak intensity is correctly accounted for by the Rietveld model (full line) at 2θ = 18.45°, which suggests a formally correct stoichiometric ratio of the two cationic species. The average crystallite size is attested at 50 nm and the lattice strain is now 0.2%, confirming the nanocrystalline structure of these materials. It should be noted that up to 3.0 wt% of the monoclinic Gd₃Ga₅O₁₂ phase is sometimes observed in our samples doped with RE elements.

In Fig. 2 the SEM images of the Er³⁺-doped CP and Eu³⁺-doped PE nanocrystalline samples are shown. The morphology of the Er³⁺-doped CP samples is an irregular agglomeration of small crystallites, as indicated by the X-ray diffraction results. These agglomerates can reach a very large size whose building blocks are themselves quite irregular in shape. Differently, the particles of the Eu³⁺-doped PE nanopowders show a spherical shape. Such regular spheres have a large size distribution, and the smallest spheres could coincide with the dimension of single crystallites, as indicated by XRZD, whereas the largest ones are in the micrometer range. The morphologies of both the CP and PE nanocrystalline samples are different from the porous, sponge-like one found for nanocrystalline GGG samples prepared by a combustion synthesis [10].

The room temperature luminescence spectrum of Er³⁺-doped CP sample, obtained upon excitation at 488 nm, is composed of the 4I15/2 → 4I11/2 (550 nm), 4F9/2 → 4I15/2 (670 nm) and 4I15/2 → 4I13/2 (860 nm) emission transitions (Fig. 3). The spectrum is closely similar to that found for a GGG:Er³⁺ nanocrystalline sample of the same composition:
Fig. 2. SEM images of GGG:Er\(^{3+}\) nanocrystalline powders prepared by the coprecipitation method (upper panel) and GGG:Eu\(^{3+}\) nanocrystalline powders prepared by the Pechini method (lower panel).

Fig. 3. Luminescence spectrum of GGG:Er\(^{3+}\) prepared by the coprecipitation method (\(\lambda_{\text{exc}} = 488\) nm) showing the following transitions: (i) \(^{2}\text{H}_{11/2},\ 4\text{S}_{3/2} \rightarrow 4\text{I}_{15/2}\), (ii) \(4\text{F}_{9/2} \rightarrow 4\text{I}_{15/2}\), and (iii) \(^{2}\text{H}_{11/2},\ 4\text{S}_{3/2} \rightarrow 4\text{I}_{13/2}\). Inset: upconversion spectrum of the GGG:Er\(^{3+}\) sample prepared by the coprecipitation method (\(\lambda_{\text{exc}} = 800\) nm).

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Figure 2 and Figure 3 images accompany the text, illustrating the SEM images of the nanocrystalline powders and the luminescence spectrum of GGG:Er\(^{3+}\). The text provides detailed descriptions of the experimental methods, results, and implications.
(http://www.ing.unitn.it/~luttero/) for making available a copy of the programme MAUD running on a personal computer.

References