Synthesis, structural investigation and luminescence spectroscopy of nanocrystalline Gd$_3$Ga$_5$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 Gd$_3$Ga$_5$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 Gd$_2$O$_3$,

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$Ga(NO_3)_3$ and $Ln(NO_3)_3$ (Ln = trivalent lanthanide ion) were dissolved in a HNO_3 solution. The obtained solution was added dropwise to a NH_3 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, Gd_2O_3, $Ga(NO_3)_3$ and the lanthanide nitrate were dissolved in aqueous HNO_3. 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 (Eu^{3+} or Er^{3+}) was 1 at.% with respect to the Gd^{3+} 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° of 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 radiation was dispersed with a half-meter monochromator equipped with a 150 lines/mm grating and detected by an air-cooled CCD device. An Argon pumped Ti-sapphire laser was used to excite the sample at 800 nm wavelength. 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 Eu^{3+}-doped CP and PE nanocrystalline GGG samples. A heat treatment of the Eu^{3+}-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 stoichiometry Gd:Ga = 3:5 [16,17]. The reasons for this behaviour were already discussed in a previous paper [15] 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 $2\theta = 19.93°$ indicates that the off-stoichiometry 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" $Gd_3Ga_5O_{12}$, as testified by the upper pattern of Fig. 1. For the
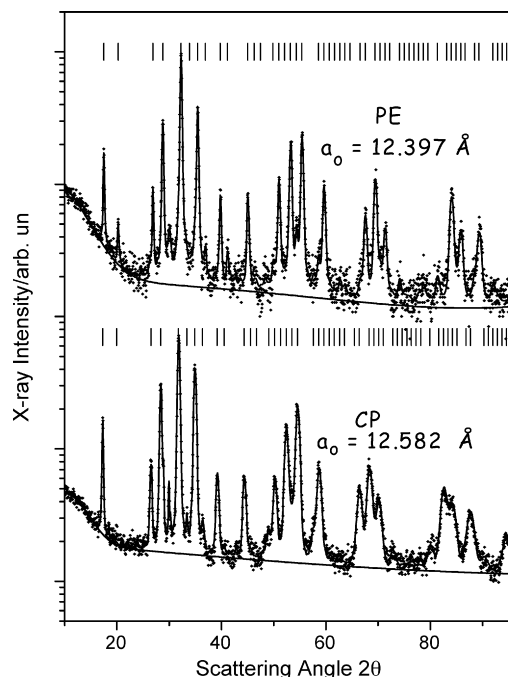

Fig. 1. X-ray diffraction patterns of GGG:Eu^{3+} annealed at 900 °C for 2 h prepared by CP (low pattern) and PE (upper pattern) methods, respectively. The bar sequence marks the expected position of each peak according to the lattice parameter values.

Eu^{3+}-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 $2\theta = 18.45°$, 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 $Gd_4Ga_2O_9$ phase is sometimes observed in our samples doped with RE elements.

In Fig. 2 the SEM images of the Er^{3+}-doped CP and Eu^{3+}-doped PE nanocrystalline samples are shown. The morphology of the Er^{3+}-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 Eu^{3+}-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 XRD, 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 Er^{3+}-doped CP sample, obtained upon excitation at 488 nm, is composed of the $(^2H_{11/2}, {}^4S_{3/2}) \rightarrow {}^4I_{15/2}$ (550 nm), ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ (670 nm) and $(^2H_{11/2}, {}^4S_{3/2}) \rightarrow {}^4I_{13/2}$ (860 nm) emission transitions (Fig. 3). The spectrum is closely similar to that found for a GGG:Er^{3+} nanocrystalline sample of the same composition
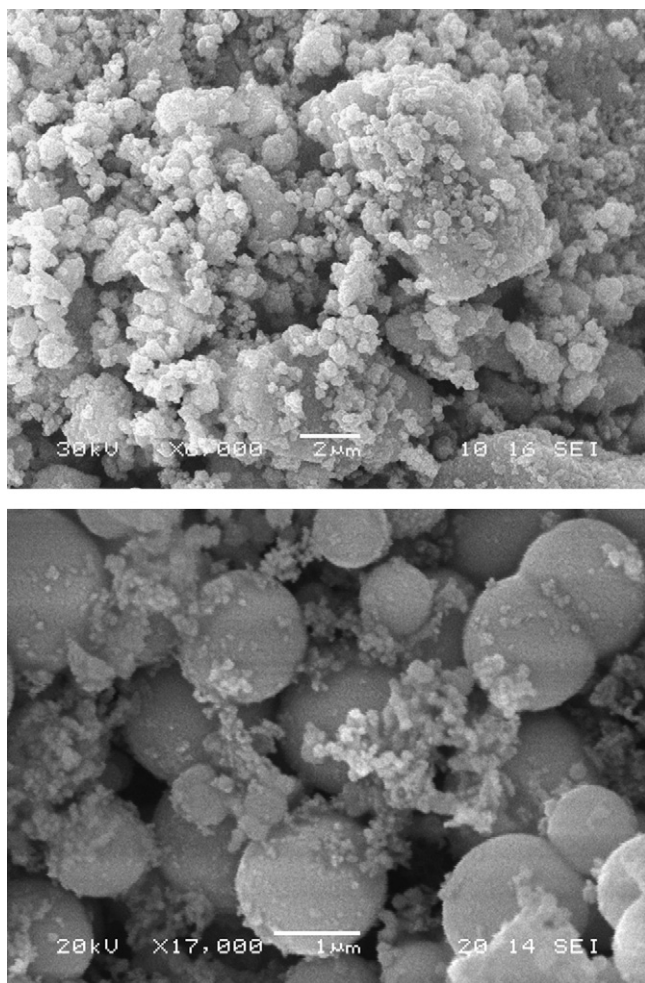
Fig. 2. SEM images of GGG:Er^{3+} nanocrystalline powders prepared by the coprecipitation method (upper panel) and GGG:Eu^{3+} nanocrystalline powders prepared by the Pechini method (lower panel).
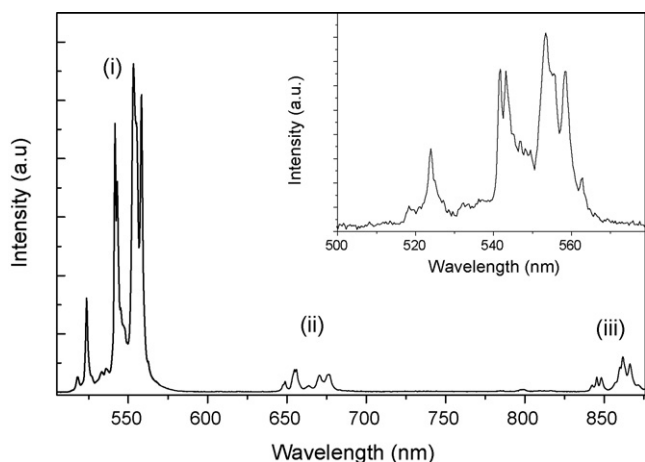

Fig. 3. Luminescence spectrum of GGG:Er^{3+} prepared by the coprecipitation method ($\lambda_{exc} = 488$ nm) showing the following transitions: (i) ($^2H_{11/2}$, $^4S_{3/2}$) → $^4I_{15/2}$, (ii) $^4F_{9/2}$ → $^4I_{15/2}$, and (iii) ($^2H_{11/2}$,$S_{3/2}$) → $^4I_{13/2}$. Inset: upconversion spectrum of the GGG:Er^{3+} sample prepared by the coprecipitation method ($\lambda_{exc} = 800$ nm).

prepared by a combustion synthesis [10]. The room temperature decay curve (not shown) of the thermalised $^2H_{11/2}$, $^4S_{3/2}$ levels shows a non-exponential behaviour. The average decay time τ_{avg} is evaluated from the equation [11]:

$$\tau_{avg} = \frac{\int tI(t)\,dt}{\int I(t)\,dt}$$

and it results to be 100 μs, similar to that found for a GGG:Er^{3+} nanocrystalline sample of the same composition prepared by a combustion synthesis (122 μs) [6]. The radiative lifetime of the emitting states, estimated from a Judd–Ofelt analysis for a Er^{3+}-doped GGG single crystal, is 200–220 μs [19]. Therefore, the quantum efficiency of the emission in the green region at 550 nm for the Er^{3+}-doped CP nanocrystalline sample turns out to be about 45%. The non-exponential shape of the decay curve is presumably due to cross-relaxation processes and/or to the presence of more than one site in which the Er^{3+} ions could be accommodated in the garnet crystal lattice [20]. However, the non-exponential behaviour of the decay curve could also be due to the presence of a notable amount of disorder affecting the sites in which the lanthanide ions are accommodated. In fact, due to the large surface to volume ratio typical of nanostructured systems, a significant percentage of lanthanide ions lies on the surface of the nanoparticle in distorted sites. Strong green ($^2H_{11/2}$, $^4S_{3/2}$) → $^4I_{15/2}$ emission can be obtained at room temperature upon excitation at 800 nm (200 mW) of the $^4I_{9/2}$ level in the CP nanocrystalline GGG:Er^{3+} (Fig. 3, inset). The upconversion process can be tentatively assigned to the usual mechanism commonly reported in the literature for Er^{3+}-doped materials [6]. It is worth to remark that the upconversion emission for the Er^{3+} CP sample in the red region (around 650 nm, not shown) was very weak. Power studies are in progress to investigate the nature of the upconversion mechanism.

4. Conclusions

Lanthanide-doped GGG nanocrystalline samples have been obtained using coprecipitation and Pechini preparation methods. After a suitable heat treatment, single phase cubic GGG nanopowders have been obtained. The CP and PE samples show different morphologies. The CP samples are composed by irregular agglomerations of small crystallites, forming building blocks quite irregular in shape. Differently, the particles of the PE nanopowders show a spherical shape and have a large size distribution range. The Er^{3+}-doped CP nanopowders 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. Efficient green upconversion is observed upon excitation in the near IR.

Acknowledgements

References

[1] Y. Guyot, H. Canibano, C. Goutadier, A. Novoselov, A. Yoshikawa, T. Fukuda, G. Boulon, Opt. Mater. 28 (2006) 1.
[2] S. Chenais, F. Balembois, F. Druon, G. Lucas-Leclin, P. Georges, IEEE J. Quantum Electron. 40 (2004) 1235.
[3] R. Gerhardt, J. Kleine-Borger, L. Beilschmidt, M. Frommeyer, H. Dotsch, B. Gather, Appl. Phys. Lett. 75 (1999) 1210.
[4] B.M. Tissue, Chem. Mater. 10 (1998) 2837.
[5] D.K. Williams, H. Yuan, B.M. Tissue, J. Lumin. 83/84 (1999) 297.
[6] F. Vetrone, J.-C. Boyer, J.A. Capobianco, A. Speghini, M. Bettinelli, J. Phys. Chem. B 107 (2003) 10747.
[7] R. Naccache, F. Vetrone, J.C. Boyer, J.A. Capobianco, A. Speghini, M. Bettinelli, J. Nanosci. Nanotechnol. 4 (2004) 1025.
[8] D. Sun, Q. Zhang, Z. Wang, J. Su, C. Gu, A. Wang, S. Yin, Mater. Sci. Eng. A 392 (2005) 278.
[9] M. Pang, J. Lin, J. Cryst. Growth 284 (2005) 262.
[10] R. Krsmanovic, S. Polizzi, P. Canton, Mater. Sci. Forum 494 (2005) 143.
[11] M. Daldosso, D. Falcomer, A. Speghini, P. Ghigna, M. Bettinelli, Opt. Mater., in press.
[12] R.A. Young (Ed.), The Rietveld Method, University Press, Oxford, 1993.
[13] L. Lutterotti, S. Gialanella, Acta Mater. 46 (1998) 101.
[14] C. Cannas, A. Musinu, G. Piccaluga, C. Deidda, F. Serra, M. Bazzoni, S. Enzo, J. Solid State Chem. 178 (2005) 1526.
[15] M. Bazzoni, M. Bettinelli, M. Daldosso, S. Enzo, F. Serra, A. Speghini, J. Solid State Chem. 178 (2005) 2301.
[16] C.D. Brandle, A.J. Valentino, J. Cryst. Growth 12 (1972) 3.
[17] S. Geller, G.P. Espinoza, L.D. Fullmer, P.B. Grandell, Mater. Res. Bull. 7 (1960) 814.
[18] M. Allibert, C. Chatillon, J. Mareschal, F. Lissalde, J. Cryst. Growth 23 (1974) 289.
[19] D.K. Sardar, W.M. Bradley, J.J. Perez, J.B. Gruber, B. Zandi, J.A. Hutchinson, C.W. Trussel, M.R. Kokta, J. Appl. Phys. 93 (2003) 2602.
[20] V. Lupei, Opt. Mater. 19 (2002) 95.