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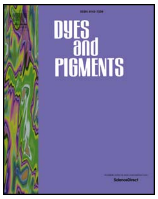

Luminescence peculiarities of Eu^{3+} ions in multicomponent $Ca_2YSc_2GaSi_2O_{12}$ garnet

Pavel Loiko[a,*], Nicholas Khaidukov[b], Anna Volokitina[a], Inga Zhidkova[b], Elena Vilejshikova[c], Artyom Novichkov[a], Vladimir Aseev[a], Josep Maria Serres[d], Xavier Mateos[d], Konstantin Yumashev[c]

[a] ITMO University, Kronverkskiy Pr., 49, 197101 St. Petersburg, Russia
[b] N.S. Kurnakov Institute of General and Inorganic Chemistry, 31 Leninskii Prospekt, 119991 Moscow, Russia
[c] Center for Optical Materials and Technologies (COMT), Belarusian National Technical University, 65/17 Nezavisimosti Ave., 220013 Minsk, Belarus
[d] Física I Cristal·lografia de Materials I Nanomaterials (FiCMA-FiCNA)-EMaS, Dept. Química Física I Inòrganica, Universitat Rovira I Virgili (URV), Campus Sescelades, E-43007 Tarragona, Spain

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ABSTRACT

Novel multicomponent garnet phosphors, $Ca_2Y_{1-x}Eu_xSc_2GaSi_2O_{12}$ (x = 0, 0.05, 0.1, 0.25 and 0.5), have been synthesized by a high-temperature solid-state reaction method using the precursors obtained under hydrothermal conditions. Their structures, morphology and vibronic properties have been studied by XRD, SEM methods and Raman spectroscopy. It has been found that ceramic phosphor pellets consist of microcrystals having a narrow size distribution and a mean size of 1 μm with a maximum phonon energy of 864 cm^{-1} for the crystal lattice of these compositions. Under UV and blue excitation, $Eu^{3+}:Ca_2YSc_2GaSi_2O_{12}$ phosphors exhibit red f-f luminescence of Eu^{3+} ions at the distorted D_2 site of the garnet structure and broadband blue and red emissions centered at ~417 nm, 600 nm and 770 nm as ascribed to the defects of the garnet host. The quantum yield of luminescence reaches 26% for $Ca_2Y_{0.75}Eu_{0.25}Sc_2GaSi_2O_{12}$. The spectroscopic properties of Eu^{3+} ions have been characterized with the Judd-Ofelt (J-O) theory and luminescence decay studies. The J-O parameters are Ω_2 = 2.212, Ω_4 = 2.888, and Ω_6 = 2.259 [10^{-20} cm^2] and the luminescence quantum efficiency for Eu^{3+} ions η_q is 83% in $Ca_2Y_{0.95}Eu_{0.05}Sc_2GaSi_2O_{12}$. The developed materials are promising as color-tunable phosphors.

1. Introduction

Trivalent europium ions (Eu^{3+}) possess an electron configuration [Xe]$4f^6$ with the corresponding energy-level scheme of 4f levels featuring a metastable $^5D_0$ state separated by a large energy-gap (~12000 cm^{-1}) from the lowest ^7F_J (J = 0 … 6) multiplet with the $^7F_0$ ground-state [1]. This results in multiple visible emissions according to the $^5D_0 \rightarrow {}^7F_J$ 4f-4f transitions, of which the $^5D_0 \rightarrow {}^7F_2$ one is typically dominant in the spectrum leading to intense red (~610 nm) luminescence of high color purity [2]. The above-mentioned energy-gap underlies a weak non-radiative (NR) relaxation leading to long emission lifetimes from hundreds of μs to a few ms and high luminescence quantum efficiency. These features are widely used for developing red phosphors based on different compounds doped with Eu^{3+} ions, e.g. commercial $Eu^{3+}:Y_2O_3S$ phosphors.

To date, Eu^{3+} doped dielectric inorganic materials synthesized in the shape of nanocrystals [3–6], ceramics and glass-ceramics [7–9], thin films [10] and single-crystals [11], have prospects for various applications in the fields of solid-state lighting [12,13], bio-imaging [14], fluorescence labelling [15] and deep-red (~703 nm) lasers [16]. In addition, as the purely electric-dipole (ED) $^5D_0 \rightarrow {}^7F_2$ transition is hyper-sensitive to the symmetry of the local crystal field [17], Eu^{3+} ions can be used as local structural probes [18]. In other words, searching for novel Eu^{3+}-doped materials and the routes of their synthesis for tailoring their luminescent properties to the specific needs remains one of the ongoing challenges of materials engineering.

Among the dielectric compounds capable of hosting rare-earth (RE) dopants, the cubic garnet compositions are rather widespread. These compounds have the general crystal chemical formula $\{A_3\}[B_2](C_3)O_{12}$ (the full unit cell contains eight formula units) where {A}, [B] and (C) indicate the dodecahedral (D_2), octahedral (C_{3i}) and tetrahedral (S_4) sites, respectively, and, in particular, A = RE^{3+}, Ca^{2+} or Mg^{2+}, B = Mg^{2+}, Sc^{3+}, Ga^{3+} or Al^{3+}, and C = Ga^{3+}, Al^{3+} or Si^{4+} [19]. The garnet crystals feature good chemical stability, high mechanical and

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[*] Corresponding author.

E-mail addresses: kinetic@tut.by, pavel_loiko@corp.ifmo.ru (P. Loiko).

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thermal properties, large refractive index, long lifetimes of the emitting states of the RE^{3+} ions and high maximum phonon frequencies, $h\nu_{ph}$ ~800-900 cm^{-1} [20].

By combining the above ions of different valence at various crystallographic sites, a significant number of different compositions can be obtained without changing the garnet structure. Although the structure type does not change, the local coordination structure of the sites can be changed largely depending on a garnet composition and, as a result, the crystal field parameters and crystal-field strengths for optically active ions at the garnet sites can vary considerably. For example, under excitation in the blue spectral range, Ce^{3+} doped $\{Y_3\}[Al_2](Al_3)O_{12}$ (YAG) has broad emission with a maximum at 540 nm and for Ce^{3+}:$\{Ca_3\}[Sc_2](Si_3)O_{12}$, emission occurs at 505 nm as well as the temperature quenching luminescence for this material is less than that for Ce^{3+}:YAG [21]. There are several reviews on the crystal chemical features of garnets $\{Ca,RE\}_3[Mg,Sc,Ga,Al]_2(Ga,Al,Si)_3O_{12}$ and the effect of these features on spectroscopic properties of Ce^{3+}, for example [22–24]. Recent research concerning garnets $\{Ca_2RE\}[ScB](CSi_2)O_{12}$ (RE = Lu, Y or Gd; B = Sc or Ga, C = Ga or Al) doped with Ce^{3+} should be also noted [25]. However, there are only few papers concerning luminescence properties of Eu^{3+} in multicomponent garnets $\{Ca,RE\}_3[Mg,Sc,Ga,Al]_2(Ga,Al,Si)_3O_{12}$, for example Eu^{3+}:$Ca_3Sc_2Si_3O_{12}$ [26].

In the present work, phosphors based on multicomponent garnet $\{Ca_2Y\}[Sc_2](GaSi_2)O_{12}$ doped with Eu^{3+} ions have been synthesized as well as their structural, vibronic and spectroscopic properties have been characterized.

2. Synthesis of phosphors

Ceramic samples of $\{Ca_2Y_{1-x}Eu_x\}[Sc_2](GaSi_2)O_{12}$, where x = 0, 0.05, 0.1, 0.25 or 0.5 is the atomic fraction of Y^{3+} substituted by Eu^{3+}, were obtained by a high-temperature annealing in air using the precursors synthesized under hydrothermal conditions [27]. For the hydrothermal synthesis, copper-insert lined autoclaves with a volume of ~40 mL were used. Finely ground and mixed oxides CaO (99.9% purity), Y_2O_3 (99.99%), Eu_2O_3 (99.99%), Sc_2O_3 (99.9%), Ga_2O_3 (99.99%) and SiO_2 (99.9%) having appropriate ratios were subjected to hydrothermal treatment at 450 °C for 100 h in a 0.1 mol % NaOH aqueous solution under autogenous pressure and a filling degree of 50%. The resulting precursors were washed with distilled water and ethanol. Then, the compositions were dried in an oven at 800 °C for 4 h in air. The hydrothermal powders were uniaxially pressed in a steel press at 150–200 MPa into pellets with a 10 mm diameter and a thickness of ~1 mm. The obtained pellets were annealed at 1000–1300 °C for 10 h in air. The annealed white pellets were faintly translucent.

3. Experimental

The structure and the phase purity of the samples were characterized with powder X-ray diffraction (XRD) using a Bruker D8 Advance X-Ray diffractometer with a Cu K_α sealed tube (1.54184 Å). The structure refinement was performed by the Rietveld method using the HighScore Plus software. The morphology of the polycrystalline samples was studied with an Environmental Scanning Electron Microscope (ESEM, model FEI QUANTA 600) equipped with an Inca Analyzer (INCAx-sight, OXFORD Instruments) for Energy-Dispersive X-ray (EDX) spectroscopy. The size distribution was determined with the ImageJ software.

Raman spectra were measured using a Renishaw inVia confocal Raman microscope using a Leica ×50 objective (N.A. = 0.75) and an edge filter. The excitation wavelength λ_{exc} was 488 nm (an Ar^+ laser line).

Lumunescence spectra for λ_{exc} = 465 nm were measured using the same confocal Raman microscope. Luminescence spectra for λ_{exc} = 365 nm, excitation spectra and absolute luminescence quantum yield (QY) were measured using a Hamamatsu C9920-02G spectrometer. The setup comprised an excitation light source, a monochromator, an integrating sphere and a CCD spectrometer for detecting the complete spectral range simultaneously. The QY was defined as a ratio of the number of photons emitted from the sample ($N_{h\nu}{}^{em}$) to the number of those absorbed by the sample ($N_{h\nu}{}^{abs}$). The $N_{h\nu}{}^{abs}$ value was determined with respect to a reference sample. Luminescence spectra for λ_{exc} = 265 nm were measured using an UV lamp and a compact spectrum analyzer (model C10027-01, Hamamatsu). For luminescence decay studies, a fluorescence spectrophotometer (Cary Eclipse, Agilent Technologies) was used providing λ_{exc} = 390 nm and λ_{lum} = 610 nm.

All spectroscopic studies were performed at room temperature (293 K).

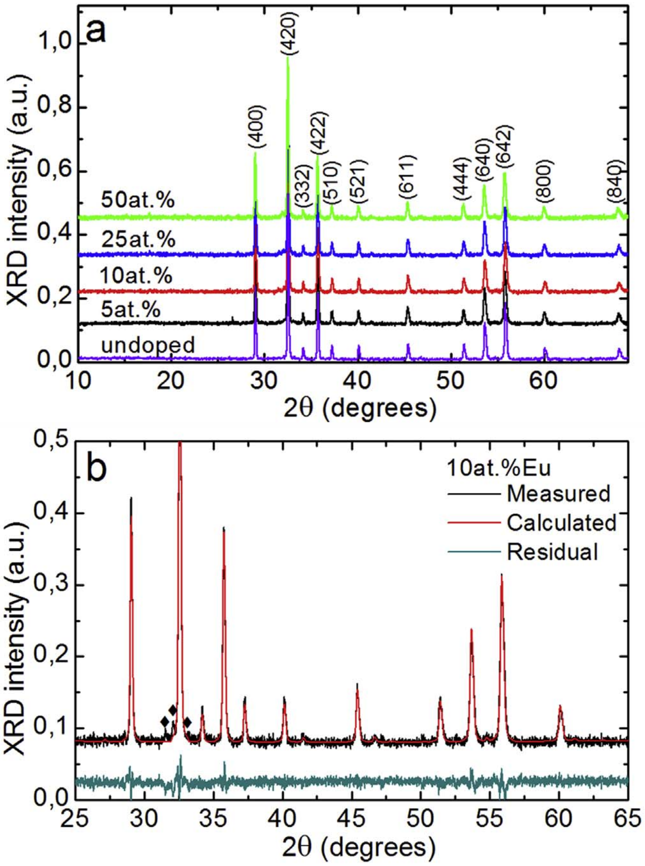

Fig. 1. (a) X-ray diffraction (XRD) patterns of the synthesized garnet samples undoped and doped with 5, 10, 25 and 50 at.% Eu^{3+}, the numbers denote the Miller's indices; (b) Example of the Rietveld refinement plot for a 10 at.% Eu^{3+} doped sample. ◆ indicates reflexes of an apatite phase.

4. Results and discussion

4.1. Structure

The measured powder XRD patterns for the synthesized samples are shown in Fig. 1(a). They have been analyzed with the Rietveld refinement method, as shown in Fig. 1(b) for the 10 at.% Eu doped sample (i.e., for x = 0.1), the reduced chi-squared value of $\chi^2 = (R_{wp}/R_{exp})^2$ for this sample is 1.91. All the obtained compositions crystallize in the cubic garnet structure (sp. gr. O_h^{10} - $Ia\bar{3}d$, No. 230); their lattice parameter a, unit-cell volume V and calculated density ρ_{calc} are listed in Table 1. In particular, for the 10 at.% Eu^{3+} doped sample, a = 12.3306 Å, V = 1874.8 $Å^3$ (Z = 8) and ρ_{calc} = 4.12 g/cm^3. As the Eu^{3+} concentration increases, the lattice parameter and the density also increase. To analyze this, one need to consider the mechanism of