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On the correlation between the composition of Pr³⁺ doped garnet type materials and their photoluminescence properties

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ABSTRACT

Lu₃(Al,Ga)₅O₁₂ and (Y,Lu)₃(Al,Mg,Si)₅O₁₂ samples doped with 1% Pr³⁺ were prepared by two aqueous sol–gel chemistry approaches, such as citrate and glycolate methods. All samples were characterised by powder X-ray diffraction (XRD), thermal quenching (TQ), fluorescence lifetime measurements and photoluminescence (PL) techniques. It turned out that the Pr³⁺ emission is very sensitive to the composition of the garnet host lattice. Lu₃Al₅O₁₂:Pr³⁺ samples showed mainly [Xe]4f¹5d¹ → [Xe]4f² broad band emission in UV–blue region, whereas [Xe]4f²–[Xe]4f² line emission of Pr³⁺ dominated in Lu₃Ga₅O₁₂ samples. Modification of garnet crystals with Mg²⁺–Si⁴⁺ pair has led to generation of strong crystal field strength resulting in energy transfer from 5d to 4f orbitals. Y₃AlMg₂Si₂O₁₂ composition generated the strongest crystal field splitting out of all synthesised samples and showed practically only Pr³⁺ [Xe]4f²–[Xe]4f² line emission in the red spectral region.

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1. Introduction

Pr³⁺ is one of the most versatile optically active ions that can luminesce in a very broad spectrum ranging from the deep UV through the visible to the infrared spectral range [1]. Moreover, it was the first ion for which two photon emission after VUV excitation was demonstrated [2]. Therefore, Pr³⁺ activated luminescent materials found application in X-ray detectors, FEDs or excimer discharge lamps [3–7].

The type of luminescence spectrum of Pr³⁺ activated inorganic phosphors and thus its application area is governed by the covalent character of the respective bonds between the activator and the adjacent anions, the crystal field splitting and the Stokes shift. If the host lattice possesses a weak crystal field strength and a wide band gap, then all crystal field states of the [Xe]4f¹5d¹ configuration are located above the ¹S₀ state of the [Xe]4f² configuration, resulting in efficient population of the latter one. In such a case line emission in UV region is usually observed. In addition to that, photon-cascade emission (PCE) as mentioned above resulting in quantum efficiency larger than unity was also observed in fluorides and some oxides [2,8–10]. Stronger crystal fields shift the lowest crystal-field component of the [Xe]4f¹5d¹ excited state configuration below the ¹S₀ level. This leads to UV band emission from the lowest 4f¹5d¹ component to ³H_j and ³F₂ terminal levels of Pr³⁺. Excitation to ³P_j levels gives characteristic

Pr³⁺ line emission with the strongest peak in the cyan spectral region (³P₀ → ³H₄ transition). However, in some compounds an efficient energy transfer from ³P₀ to ¹D₂ levels occurs and only red emission is observed [11,12].

Recently, quite some effort was put into developing Pr³⁺ activated compounds, which possess high chemical and physical stability, for the application in excimer discharge lamps for photochemical and disinfection purposes [3,7]. One of the most stable classes of compounds is garnets, whereby the band gap of 6.5–7.0 eV [13,14] is also sufficiently wide to be applicable as a host for UV emitting ions. Therefore, this paper deals with Pr³⁺ activated garnets and enlightens the relation between the composition of the host lattice and the luminescence processes yielding to UV or visible emission.

2. Experimental section

Lu₃(Al,Ga)₅O₁₂:1%Pr³⁺ samples were synthesised by citric acid method, whereas for synthesis of (Y,Lu)₃(Al,Mg,Si)₅O₁₂:1%Pr³⁺ an aqueous sol–gel method was employed. Samples were prepared from Y₂O₃ (99.99%, Treibacher), Lu₂O₃ (99.99%, Treibacher), Al(NO₃)₃·9H₂O (≥95.0%, Merck), Ga(NO₃)₃·6H₂O (99.9%, AlfaAesar), Mg(NO₃)₂·6H₂O (99%, Merck), Pr(NO₃)₃·6H₂O (99.99%, AlfaAesar), nano-scale SiO₂ (99%, Merck), citric acid monohydrate (99.5%, Merck) and 1,2-ethanediol (≥99.0%, Merck).

In citric acid method preparation of Lu₃(Al,Ga)₅O₁₂:1%Pr³⁺ lutetium oxide was first dissolved in a hot (≈75 °C) diluted nitric acid. Then stoichiometric amounts of praseodymium, aluminium and/or gallium nitrates were added. Subsequently, citric acid

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monohydrate with the molar ratio to all metal cations (2:1) was added. The resulting solution was stirred for 1 h at the same temperature. Then the beaker was transferred to the drying oven (150 °C) and left overnight. The brownish sponge-like gel was obtained. It was crushed and ground to fine powder, which was first annealed at 1000 °C for 2 h in air for decomposing the organic compounds and phase formation, followed by sintering at 1500 °C for 4 h in air for improvement of crystallinity.

In glycolate sol–gel preparation of $(Y,Lu)_3(Al,Mg,Si)_5O_{12}:1\%Pr^{3+}$ samples yttrium and/or lutetium oxides were dissolved in hot diluted nitric acid. The solution was evaporated till dryness to remove the excess of nitric acid. Dry residue was again dissolved in distilled water and appropriate amounts of aluminium, magnesium, praseodymium nitrates and silicon dioxide were added. The resulting mixtures were stirred for 1 h at temperatures between 70–80 °C. Then 1,2-ethanediol was added with the molar ratio of 2:1 to all metal ions and mixtures were stirred for an additional hour at the same temperature. Subsequently, after concentrating the solutions by slow evaporation under stirring the $(Y,Lu,Pr)-Al-Mg-Si-O$ nitrate glycolate sols turned into transparent gels. The oven dried (150 °C) gels became brownish due to initial decomposition of nitrates. The gel powders were powderized in an agate mortar and preheated for 2 h at 1000 °C in air followed by sintering at 1600 and 1550 °C for 4 h in air for $(Y,Lu)_3Al_3MgSiO_{12}:1\%Pr^{3+}$ and $(Y,Lu)_3AlMg_2Si_2O_{12}:1\%Pr^{3+}$, respectively.

XRD data were collected from $2\theta = 15\text{--}60^\circ$ (step width 0.02° and integration time 1 s) using Ni-filtered $Cu K_\alpha$ radiation on Rigaku MiniFlex II diffractometer working in Bragg–Brentano ($\theta/2\theta$) geometry.

Reflection spectra were recorded on Edinburgh Instruments FS900 spectrometer equipped with a 450W Xe arc lamp, cooled single-photon counting photomultiplier (Hamamatsu R928) and an integration sphere coated with barium sulphate. $BaSO_4$ (99% Sigma-Aldrich) was used as a reflectance standard.

Excitation and emission spectra were recorded on Edinburgh Instruments FSL900 fluorescence spectrometer equipped with 450 W Xe arc lamp, mirror optics for powder samples and cooled ($-20^\circ C$) single-photon counting photomultiplier (Hamamatsu R2658P). The

photoluminescence emission spectra were corrected by correction file obtained from tungsten incandescent lamp certified by NPL (National Physics Laboratory, UK). For PL decay kinetics studies a 265 nm picosecond pulsed light emitting diode from Edinburgh Instruments (model—EPLD265) was used as an excitation source. For thermal quenching measurements a cryostat “MicrostatN” from Oxford Instruments has been applied to the present spectrometer. Measurements were carried out from 100 to 500 K in 50 K steps.

The VUV spectrometer (Edinburgh Instruments FS920) was used for exciting phosphor samples at 160 nm. Spectrometer was equipped with VUV monochromator VM504 from Acton Research Corporation (ARC) and deuterium lamp as an excitation source. Sample chamber was flushed with dried nitrogen in order to prevent absorption of VUV radiation by water and oxygen. Excitation and emission spectra were recorded in the ranges of 150–350 and 250–800 nm, respectively. The emission spectra were corrected by correction file obtained from tungsten incandescent lamp certified by NPL. The relative VUV excitation intensities of the samples were corrected by dividing the measured excitation spectra of the samples with the excitation spectrum of sodium salicylate ($o\text{-}C_6H_4OHCOONa$) under the same excitation conditions. For measuring reflection spectra in the range of 150–350 nm an integration sphere coated with $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM:Eu) was applied to the spectrometer. The reflection spectra were obtained as follows: first an excitation spectrum of BAM:Eu was recorded ($\lambda_{em}=451$ nm), then excitation spectrum of the sample was recorded monitoring the same emission wavelength under the same conditions (i.e. emission and excitation slit sizes, step size, integration time, etc.). Subsequently, excitation spectrum of the sample was divided by excitation spectrum of BAM:Eu giving reflection spectrum of the sample.

All measurements were performed at room temperature and ambient pressure in air unless mentioned otherwise.

3. Results and discussion

XRD patterns of $Lu_3(Al,Ga)_5O_{12}$ and $(Y,Lu)_3(Al,Mg,Si)_5O_{12}$ doped with 1% Pr^{3+} are depicted in Fig. 1a and b, respectively,

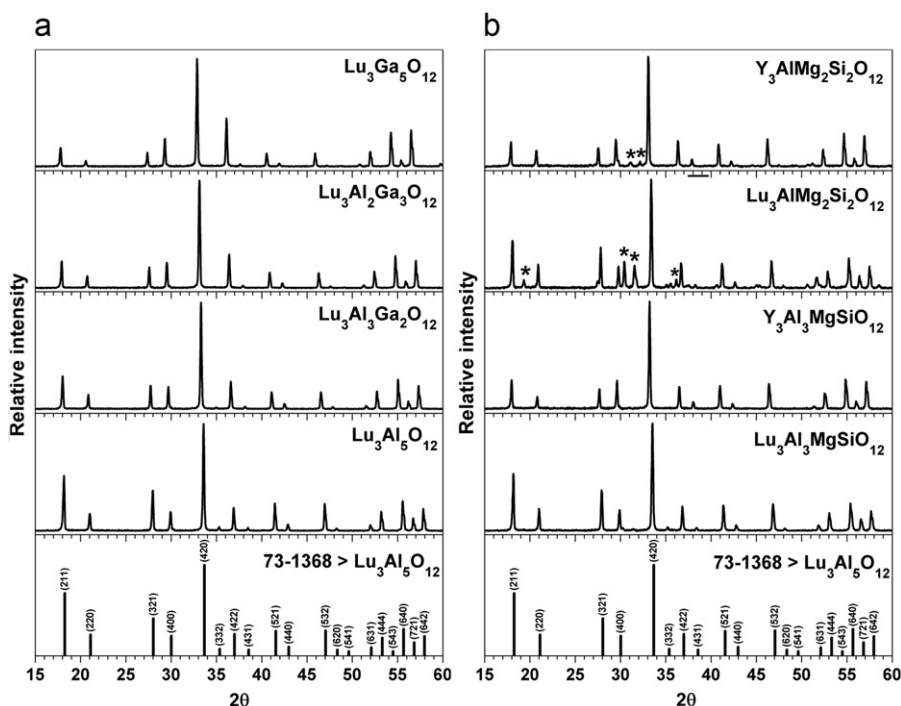


Fig. 1. XRD patterns of: (a) $Lu_3(Al,Ga)_5O_{12}$ and (b) $(Y,Lu)_3(Al,Mg,Si)_5O_{12}$ doped with 1% Pr^{3+} .

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