



Mechanism for bifurcation of broadband luminescence spectra from Ce^{3+} ions at dodecahedral sites in garnets $\{\text{CaY}_2\}[\text{M}_2](\text{Al}_2\text{Si})\text{O}_{12}$ ($\text{M} = \text{Al}, \text{Ga}, \text{Sc}$)



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ABSTRACT

Cerium doped $\text{CaY}_2\text{Al}_4\text{SiO}_{12}$, $\text{CaY}_2\text{Ga}_2\text{Al}_2\text{SiO}_{12}$ and $\text{CaY}_2\text{Sc}_2\text{Al}_2\text{SiO}_{12}$ garnet phosphors have been synthesized by using a high temperature solid-state reaction method and studied by optical spectroscopy techniques in the wide temperature range. It has been revealed that the emission spectra from all the synthesized samples can be well represented as the sum of spectral bands due to the 5d - 4f transitions of two optical Ce^{3+} centers having different local environment. It is proposed that these two centers arise due to various types of distortions caused by crystal chemical differences between calcium and yttrium ions located at the dodecahedral crystallographic site in the garnet structure. Such a dual-mode distortion site leads to increasing the Stokes shift of Ce^{3+} emission spectra for the studied garnets in comparison with $\text{YAG}:\text{Ce}^{3+}$. The phosphor $\text{CaY}_2\text{Al}_4\text{SiO}_{12}:\text{Ce}^{3+}$ shows a weak blue shift of Ce^{3+} luminescence compared to $\text{YAG}:\text{Ce}^{3+}$ and demonstrates excellent thermal stability on temperature quenching effects by manifesting the thermal quenching temperature $T_{1/2}$ at 635 K. Substitution of Al^{3+} by larger cations Ga^{3+} or Sc^{3+} has resulted in the additional blue shift of the luminescence spectrum and the appearance of strong thermal quenching.

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1. Introduction

The development of phosphor-converted LEDs (pc-LEDs) emitting “warm” white light is nowadays one of the challenging tasks in the phosphor research (see recent review papers [1–4] and references therein). The typical pc-LED source of white light consists of a blue LED chip and a yellow phosphor, such as Ce^{3+} doped yttrium aluminum garnet $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ ($\text{YAG}:\text{Ce}^{3+}$), which emits a broadband yellow luminescence due to interconfigurational 5d - 4f transitions of Ce^{3+} ions. The white light is generated as a result of mixing blue light from an LED and yellow luminescence excited by blue radiation in a $\text{YAG}:\text{Ce}^{3+}$ phosphor. However, such pc-LEDs emit a bluish “cool” white light with the low color-rendering

index (CRI) and high correlated color temperature (CCT) due to the lack of a sufficient red component in the spectrum. The “warm” white light from pc-LEDs of such a type can be obtained by spectral tuning of Ce^{3+} luminescence from garnet type phosphors using a cationic substitution in the host matrix, which can result in a red shift or/and broadening of the phosphor emission spectrum towards the red spectral region [1].

The crystal chemical formula for the yttrium aluminum garnet can be written as $\{\text{Y}\}_3[\text{Al}]_2(\text{Al})_3\text{O}_{12}$ where the $\{\text{Y}^{3+}\}$ sites are dodecahedrons, the $[\text{Al}^{3+}]$ sites are octahedrons, and the (Al^{3+}) sites are tetrahedrons. The spectral tuning of Ce^{3+} luminescence in garnet-type hosts, in which the Ce^{3+} ions replace Y^{3+} ions at nearly-cubic dodecahedral sites, can be obtained by the substitution of Y^{3+} ions in dodecahedral sites or/and Al^{3+} ions in octahedral and/or tetrahedral sites by the ions with different ionic radii and in some cases with different valence states. Thus the spectral shift of Ce^{3+} luminescence will be due to changes of the crystal field

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strength induced on Ce^{3+} ions at dodecahedral sites and variation of cubic symmetry distortion at the Ce^{3+} ion site [5] caused by changes of interionic distances in Ce^{3+} dodecahedron and neighbor polyhedrons after cationic substitution. On the other hand, the composition modification can worsen the thermal stability of phosphor luminescence which is also one of the main parameters of LED phosphors. Unfortunately, the complex influence of various parameters such as crystal field splitting, covalence, the Stokes shift, lattice distortion, lattice defects, etc. does not allow predicting theoretically the exact spectral and thermal properties of any phosphor based on a particular garnet composition. Accordingly, the phosphor properties should be studied experimentally. In the present study a number of Ce^{3+} doped garnet phosphors, namely $\text{CaY}_2\text{Al}_4\text{SiO}_{12}$, $\text{CaY}_2\text{Ga}_2\text{Al}_2\text{SiO}_{12}$ and $\text{CaY}_2\text{Sc}_2\text{Al}_2\text{SiO}_{12}$, have been synthesized and their spectroscopic properties have been characterized.

2. Experimental

Ceramic samples of $\text{CaY}_2\text{Al}_4\text{SiO}_{12}$, $\text{CaY}_2\text{Ga}_2\text{Al}_2\text{SiO}_{12}$ and $\text{CaY}_2\text{Sc}_2\text{Al}_2\text{SiO}_{12}$ doped with 1 mol % Ce^{3+} (or 0.33 at %) were obtained under thermal treatment at 1300 °C for 10 h in a CO-containing reducing atmosphere by using precursors synthesized under hydrothermal conditions [6]. For hydrothermal synthesis copper-insert lined autoclaves with a volume of ~40 cm³ were utilized. Grinded mixtures of oxides for appropriate stoichiometries were subjected to hydrothermal treatment for 100 h in a 0.1 mol % NaOH aqueous solution under autogenous pressure, a filling degree of 50% and a temperature of ~450 °C.

The resulting precursors were washed with distilled water and ethanol as well as, then, they were oven-dried at 800 °C for 4 h in air. The hydrothermal powders were uniaxially pressed into tablets with a diameter of 10 mm and a thickness of 3–5 mm to promote intimate contact and the tablets were heated at 1000 C for 8 h in air. Subsequently, the samples were thoroughly ground, re-pelletized and sintered at 1150 C for 8 h in air. Finally, the samples were again ground into finely dispersed powders, re-pelletized and sintered at 1300 °C for 8 h in a CO-containing reducing atmosphere provided by activated charcoal. Eventually, pellets of synthesized ceramic phosphors were polished for later characterization. Prepared samples were light yellow in color caused by Ce^{3+} 4f → 5d absorption in the blue spectral region.

The structure type and phase purity of the synthesized samples were characterized with conventional powder X-ray diffraction (XRD) technique and powder XRD patterns were obtained by using a Bruker D8 Advance X-Ray powder diffractometer with Cu K_α radiation. Identification of synthesized compounds, indexing of X-ray powder diffraction patterns and refinement of unit cell parameters were performed with the Diffrac. Suite.EVAsoftware (Bruker). Unit cell parameters were determined with an accuracy of around 0.001 Å.

The excitation spectra, emission spectra and the temperature-dependent (77–500 K) emission spectra were measured by a Hitachi F7000 spectrofluorometer. The luminescence decay curves were measured by a FLS920-Combined Fluorescence Lifetime and Steady State Spectrometer (Edinburgh Instruments).

3. Results and discussion

The X-ray phase analysis has confirmed that all the synthesized compounds are single-phase samples containing only the garnet phases and no XRD reflections corresponding to any impurity have been detected. XRD patterns of garnets $\{\text{CaY}_2\}[\text{M}_2](\text{Al}_2\text{Si})\text{O}_{12}$ (M = Sc, Ga, Al) are shown in Fig. 1. All the XRD patterns of synthesized samples have been indexed for a cubic unit cell with the

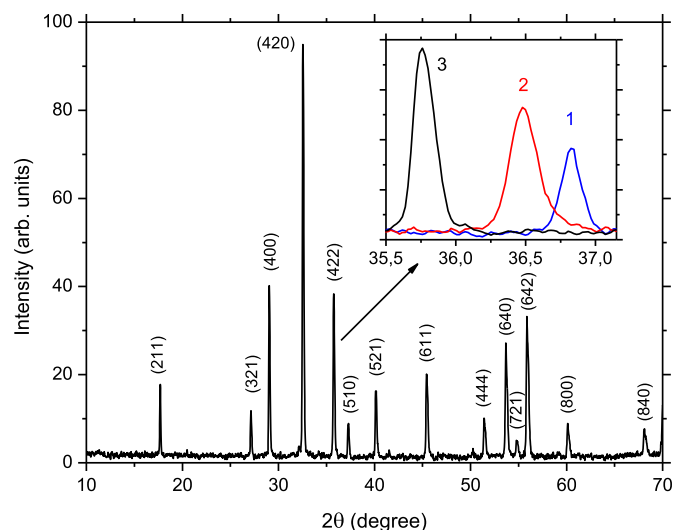


Fig. 1. XRD pattern of $\text{CaY}_2\text{Sc}_2\text{Al}_2\text{SiO}_{12}:\text{Ce}^{3+}$; numbers on the graph represent the Miller indices, (hkl) . In the insertion the peak positions of XRD (422) reflexes for garnets $\text{CaY}_2\text{Al}_2\text{Al}_2\text{SiO}_{12}:\text{Ce}^{3+}$ (1), $\text{CaY}_2\text{Ga}_2\text{Al}_2\text{SiO}_{12}:\text{Ce}^{3+}$ (2) and $\text{CaY}_2\text{Sc}_2\text{Al}_2\text{SiO}_{12}:\text{Ce}^{3+}$ (3) are shown in an extended scale.

lattice constants summarized in Table 1 in comparison with the constant for $\text{YAG}:\text{Ce}^{3+}$ [5]. It should be noted that coupled heterovalent substitution $\text{Ca}^{2+} + \text{Si}^{4+} \rightarrow \text{Y}^{3+} + \text{Al}^{3+}$ on the two sites leads to only some insignificant change of the parameter for $\text{CaY}_2\text{Al}_2\text{Al}_2\text{SiO}_{12}$ and $\text{CaY}_2\text{Ga}_2\text{Al}_2\text{SiO}_{12}$ compared to $\text{Y}_3\text{Al}_2\text{Al}_3\text{O}_{12}$. Also it can be seen that there is an increase of the unit cell parameter with the ionic radius of the cations according to the relation $\text{Al}^{3+} < \text{Ga}^{3+} < \text{Sc}^{3+}$.

Upon excitation in the blue spectral region all the Ce^{3+} doped garnet compounds show a characteristic broadband luminescence due to the Ce^{3+} 5d - 4f transitions (Fig. 2). The respective excitation bands (Fig. 2) correspond to transitions from the $4f^2$ $F_{5/2}$ ground state to two lowest-energy 5d levels of Ce^{3+} : 5d₁ and 5d₂. The spectral parameters of these broadband emissions from the doped garnets are summarized in Table 1 in comparison with the luminescence parameters of $\text{YAG}:\text{Ce}^{3+}$ taken from Ref. [7] for an identical Ce^{3+} concentration of 0.33 at %. The wavelengths of emission (λ_{em}) and excitation (λ_{ex}) indicated in the Table correspond to the maxima in the intensity of luminescence for the observed experimental emission and excitation bands. The Stokes shifts of the emissions from Ce^{3+} in these garnets and the values of the full width at half maximum (FWHM) for emission bands are also presented in Table 1. Actually the shape and position of the maxima of emission (excitation) spectra of all the garnet phosphors studied here are dependent of the excitation (emission) wavelength. In other words, there is a shift of the emission band depending on the excitation wavelength and a shift of the excitation band depending on the monitoring emission wavelength, namely: longer-wavelength excitation (into both the 5d₁ and the 5d₂ excitation band) corresponds to longer-wavelength emission and vice versa. This situation is shown in Fig. 3 for the $\text{CaY}_2\text{Ga}_2\text{Al}_2\text{SiO}_{12}:\text{Ce}^{3+}$ phosphor as an example.

As a matter of fact, all the emission bands demonstrate the complex patterns which consist of, at least, two narrower bands overlapping each other, in particular, see Fig. 3 for the phosphor $\text{CaY}_2\text{Ga}_2\text{Al}_2\text{SiO}_{12}:\text{Ce}^{3+}$. Accordingly, emission spectra from all the phosphors have been decomposed into individual bands assuming that this bifurcation is a consequence of two optical Ce^{3+} centers having different local environment and accordingly different crystal-field splitting of the Ce^{3+} 5d manifold, which leads, in

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