Journal of Luminescence 198 (2018) 314–319

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Composition dependent spectral shift of Mn^{4+} luminescence in silicate garnet hosts $CaY_2M_2Al_2SiO_{12}$ (M = Al, Ga, Sc)

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ARTICLE INFO

Keywords:
Garnets
Photoluminescence
Mn^{4+} phosphors
White LED
Thermal quenching

ABSTRACT

Multi-component silicate garnet ceramics $CaY_2M_2Al_2SiO_{12}$ having different cations M = Al, Ga or Sc at octahedral sites doped with Mn^{4+} ions have been synthesized and studied as possible red-emitting phosphors for warm white pc-LED applications. The short-wavelength shift of Mn^{4+} emission spectrum has been obtained with increasing the radius of the cation at octahedral sites as a result of decreasing the covalence of the "Mn^{4+}-ligand" bonding, which leads to an increase of the energy of the emitting Mn^{4+} ^2E_g level. However, simultaneously, stronger thermal quenching of Mn^{4+} luminescence is observed with the increase of the cation radius because of decreasing the energy of the $^4T_{2g}$ level as well as the O^{2-} – Mn^{4+} CT state, leading to the decrease of activation barrier for thermal quenching due to non-radiative relaxation from the emitting Mn^{4+} ^2E_g level to the Mn^{4+} ground state. All studied phosphors demonstrate rather poor thermal stability of Mn^{4+} luminescence with thermal quenching temperatures $T_{1/2} < 240$ K.

1. Introduction

Phosphor-converted light emitting diodes (pc-LEDs) have presently no alternatives as light sources for general lighting due to their superior performances compared to any other kinds of white light sources [1]. Most of commercially available white pc-LEDs are based on the simplest and cost efficient scheme consisting of a blue LED chip and a yellow-emitting phosphor, such as the Ce^{3+} doped garnet $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce). However, the main drawbacks of such white-light sources are a low color-rendering index (CRI) and a high correlated color temperature (CCT) due to the lack of a sufficient red component in the spectrum, which makes white light from such sources bluish, or "cold", i.e. uncomfortable for human eyes. Accordingly, nowadays one of the challenging tasks in general lighting is the development of pc-LEDs emitting "warm" white light. This problem can be optimally resolved by adding to the above scheme of white pc-LED a red-emitting phosphor efficiently excited by blue LED chip radiation.

Thus, the development of red emitting phosphors is of tremendous importance for the further optimization of solid-state light sources for indoor illumination applications. To achieve the optimum balance between high CRI and efficacy in white pc-LED devices, it is needed to explore narrow-band red-emitting phosphors, which strongly absorb blue light and efficiently emit in red spectral range of 610–650 nm. In contrast to commercial red-emitting phosphors, which typically possess a broad emission band from Eu^{2+} ions [2], Mn^{4+} doped phosphors can exhibit an emission spectrum consisting of narrow lines only in the red spectral range, without a useless tail to longer (NIR) wavelengths, where human eyes are not sensitive. Since Mn^{4+} can be stabilized only in octahedral coordination the energy levels of Mn^{4+} are given by the Tanabe-Sugano diagram for the d^3 electron configuration in an octahedral crystal field [3]. Accordingly, Mn^{4+} ions in crystal hosts have broad absorption bands in the blue and UV spectral ranges due to relatively strong spin-allowed transitions $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^4T_1$, respectively, and narrow-line emission due to spin-forbidden transition $^2E_g \rightarrow {}^4A_{2g}$.

By now a rather large number of Mn^{4+} red phosphors have been developed [4–9], which are based mainly on fluoride hosts because of relatively simple and efficient fabrication process of such phosphors and due to the fact that Mn^{4+} emission in fluorides is located close to optimal wavelength for the red phosphor near 630 nm. However, the stability of fluoride phosphors is not as good as oxide phosphors which generally have a better resistance to external conditions such as high temperature, high humidity, and high excitation density provided by high-power LEDs, i.e. in many cases fluoride phosphors are not suitable

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https://doi.org/10.1016/j.jlumin.2018.02.054
Received 30 November 2017; Received in revised form 9 February 2018; Accepted 20 February 2018

for practical applications. Mn^{4+} activated oxides are much more stable but their emission wavelengths are too long compared to optimal red emission. So far, the shortest peak wavelengths of temperature stable Mn^{4+} emission in oxide materials have been obtained for $Mg_{14}Ge_5O_{24}$:Mn^{4+} (659 nm), $Y_2Mg_3Ge_3O_{12}$:Mn^{4+} (658 nm), $CaAl_{12}O_{19}$:Mn^{4+} (656 nm), $SrAl_{12}O_{19}$:Mn^{4+} (655 nm), and $Sr_4Al_{14}O_{25}$:Mn^{4+} (654 nm) [9–13]. Hence, the currently known Mn^{4+} activated oxide phosphors are unsuitable for general lighting applications.

It is commonly accepted that the energy of the Mn^{4+} ^2E_g emitting level does not depend on the strength of the crystal field (CF) and is determined by the effect of delocalization of the outer d orbitals of Mn^{4+} ions because of formation of chemical bonds with ligands (nephelauxetic effect). The Mn^{4+} emission energy is inversely correlated with the Mn^{4+} - ligand delocalization degree, i.e. it is higher for more ionic bonding and is lower for more covalent bonding. As a result, the host materials allowing longer Mn^{4+} - ligand distance can provide blue shifted Mn^{4+} emission. Thus, one can expect that by increasing the ionic radius of the host cation at the octahedral site in a series of isostructural multicomponent compounds, i.e. by increasing the interionic distance between Mn^{4+} ions and ligands it will be possible to tune the Mn^{4+} emission spectrum to shorter wavelengths, which is required for developing narrow-band red-emitting phosphors for new generation of white pc-LEDs.

In the present work a series of multi-component silicate garnet ceramics with different cations in octahedral sites of $CaY_2M_2Al_2SiO_{12}$ (M = Al, Ga, Sc) doped with Mn^{4+} ions has been synthesized and studied as possible red phosphors for pc-LED applications.

2. Experimental

Ceramic samples of $CaY_2M_2Al_2SiO_{12}$ (M = Al, Ga, Sc) doped with Mn^{4+} were obtained under thermal treatment in ambient air atmosphere by using precursors synthesized under hydrothermal conditions. For hydrothermal synthesis of undoped samples copper-insert lined autoclaves with a volume of ~40 cm^3 were utilized. Grinded mixtures of oxides for appropriate stoichiometries were subjected to hydrothermal treatment during 100 h in a 0.1 mol% NaOH aqueous solution under autogenous pressure at ~ 450 °C, with a filling degree of 50%.

The resulting precursors were washed with distilled water and ethanol and thereafter oven-dried at 1000 °C for 4 h in air. The hydrothermal garnet powders were mixed with $KMnO_4$ (1.5–0.1 mol%) and the compensative oxides (e.g. MgO) by taking into account that Mn^{4+} ions occupy the octahedral site in the garnet structure, namely $M^{3+} + M^{3+} \rightarrow Mg^{2+} + Mn^{4+}$, and K^+ ions will be removed as a result of the following multi-stage thermal treatment as described below. The blends were uniaxially pressed into pellets with a diameter of 10 mm and a thickness of 3 – 5 mm to promote intimate contact and the pellets were heated at 500 °C for 24 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 air. Eventually, pellets of synthesized ceramic phosphors were polished for later characterization.

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. EVA software (Bruker). Unit cell parameters were determined with an accuracy of around 0.001 Å.

Photoluminescence (PL) as well as PL excitation (PLE) spectra were recorded on an Edinburgh Instruments FLS920 spectrometer equipped with a Xenon arc lamp (450 W) and a cooled (− 20 °C) single-photon counting photomultiplier (Hamamatsu R2658P). Spectral resolution for the PL and PLE spectra measurements was typically set to value of 0.1 nm. The recorded PL spectra were corrected by applying a spectral sensitivity function obtained from a tungsten incandescent lamp certified by the National Physics Laboratory, UK.

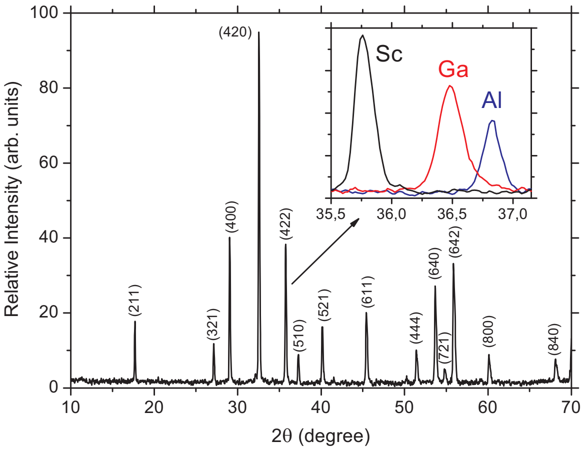

Fig. 1. XRD pattern of $CaY_2Sc_2Al_2SiO_{12}$:Mn^{4+}; numbers on the graph represent the Miller indices, (*hkl*). In the insertion the peak positions of XRD (422) reflexes for studied garnets $CaY_2Al_2Al_2SiO_{12}$:Mn^{4+} (1), $CaY_2Ga_2Al_2SiO_{12}$:Mn^{4+} (2) and $CaY_2Sc_2Al_2SiO_{12}$:Mn^{4+} (3) are shown in an extended scale.

Temperature dependent PL measurements from 80 to 500 K were performed using an Oxford Instruments cryostat MicrostatN2, where liquid nitrogen was applied as the cooling agent. Typical temperature stabilization time was 60 s and accuracy of maintaining temperature was ± 3 K. PL measurements at 3 K were performed in a closed cycle cryocooler Optistat AC-V12 from Oxford Instruments, where helium was used as the cooling agent.

3. Results and discussion

The XRD patterns have proved that synthesized samples have the garnet crystal structure without traces of any impurity phases (Fig. 1). With increasing ionic radius of the cation at the octahedral site the diffraction reflexes shift to smaller angles, and the unit cell volume as well as the interionic distance in the octahedral site increase, as expected (see Table 1).

Synthesized Mn^{4+} doped garnet phosphors possess typical Mn^{4+} PL spectrum in the red spectral range, which is dominated by the Stokes vibronic sidebands of the $^2E_g \rightarrow {}^4A_{2g}$ transition of the Mn^{4+} ion (Fig. 2). The peak wavelength of Mn^{4+} PL spectrum shifts to shorter wavelengths with the increase of the octahedral cation size, as predicted (Table 2), and at 300 K the shortest peak wavelength obtained for Sc-based compound is 658 nm, still in rather deep red region. Simultaneously, the long-wavelength shift of excitation bands due to spin-allowed Mn^{4+} transitions as well as owing to the O^{2-} – Mn^{4+} charge transfer (CT) transition occurs.

At low temperature, the PL spectrum of the $CaY_2Al_4SiO_{12}$:Mn^{4+} phosphor shows well-resolved fine structure (Fig. 3a) with a zero-phonon line (ZPL) corresponding to pure electronic transition $^2E_g \rightarrow {}^4A_{2g}$ and a set of Stokes vibronic sidebands. Also the bands in the PLE spectrum (Fig. 3b) corresponding to the second spin-allowed Mn^{4+} transition $^4A_2 \rightarrow {}^4T_1$ and the O^{2-} – Mn^{4+} CT transition are much better resolved.

Table 1
Lattice parameters of garnets $CaY_2M_2Al_2SiO_{12}$ (M = Al, Ga, Sc).

Compound	a (Å)	V (Å^3)	R_{M3+} (Å) (CN = 6)	R(M^{3+}-O^{2-}) (Å)
$CaY_2Al_2Al_2SiO_{12}$	11.959	1710.3	0.535	1.922
$CaY_2Ga_2Al_2SiO_{12}$	12.053	1751.0	0.620	1.939
$CaY_2Sc_2Al_2SiO_{12}$	12.302	1861.8	0.745	1.975