

Luminescence characteristics of doubly doped KLuS₂:Eu, RE (RE = Pr, Sm, Ce)



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ABSTRACT

KLuS₂ single crystals doped with divalent europium and co-doped with trivalent praseodymium, samarium or cerium were synthesized in the form of crystalline hexagonal platelets as interesting candidates for white LED solid state lighting. Luminescence characteristics in UV/Vis, including radioluminescence, photoluminescence excitation and emission spectra and photoluminescence decays, were measured in the broad concentration and temperature interval revealing presence of thermally stable emission features of both Eu²⁺ and co-dopants in a single KLuS₂ host. Energy transfer from Eu²⁺ to Pr³⁺, Sm³⁺ and Ce³⁺ is identified. CIE xy-coordinates are used to compare effects of dopants on resulting spectrum. The application potential in white LEDs phosphors is discussed.

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1. Introduction

Ternary sulfides AB₂S₄ (A = Ca, Sr, Ba; B = Al, Ga, Y) doped with rare earth (RE) ions (RE = Ce, Pr, Sm, Eu) have been investigated in recent history as interesting materials for application in the field emission displays (FED) [1] and mainly SrGa₂S₄ doped by Ce³⁺ or Eu²⁺ received an attention [2,3]. Recently, such compounds, either singly or doubly doped with RE or transition metal ions have been proposed for new applications such as solid-state lighting in white LEDs sources [4] using near-ultraviolet or blue excitation LEDs. Various sulfidic hosts as potentially interesting for such purposes were also recently reviewed in [5]. In particular, alkali earth sulfide phosphors doped with Eu²⁺ and Ce³⁺ attracted an attention in this field [6]. Proposals of circadian light sources with a tunable spectrum for better adaptation to the day light cycle and human perception, based on two LEDs emitting in the near-UV and blue spectral regions, and with a tailored multi-color glass phosphor in front of them, can also be found [7]. Great number of different chemical compositions for above mentioned phosphor application are reviewed in [8] and sulfides doped by either RE or transition metal ions as electroluminescent powders, lamp, CRT, thin film electroluminescence, color conversion and persistent and storage phosphors are documented in a review article [9]. More than thirty different Eu²⁺-doped sulfide hosts, either binary or those of a general A^{II}B₂₍₄₎^{III,IV}S₄₍₇₎ formula (A = Sr, Ba, Ca, Mg,

Zn; B = Si, Al, Ga, In), and their basic spectroscopic properties are summarized in [10].

Ternary sulfides of general formula ALnS₂ (A = Rb, K; Ln = La, Gd, Lu) doped by rare-earth ions have recently become of interest due to their encouraging application potential in the field of X-ray phosphors and white LED solid state lighting as well [11–17]. In the pioneer paper [11] basic optical properties and intrinsic material advantages of RbLaS₂:RE (RE = Eu, Ce, Pr, Sm, Tb) were addressed. A work focusing on RbLuS₂:RE followed, where a temperature dependence of Pr³⁺ emission is shown and charge transfer (CT) transitions from S²⁻ to Pr³⁺ or Sm³⁺ were introduced as a new interesting way of excitation in near UV/blue region [12]. Thermally induced ionization of the Ce³⁺ activator in such sulfide host is discussed for the first time in [13] where the temperature and concentration dependences of Pr and Ce emission features are studied as well. Ce³⁺ emission due to the 5d–4f transition in RbGdS₂ host is peaking at 715 nm with the lowest energy absorption band at 485 nm (given by the 4f–5d¹ transition). A surprising presence of divalent europium in KLuS₂ host was revealed in [14] and optical properties of such material were reported. Its main emission band given by the 5d–4f transition of Eu²⁺ is situated at 515–520 nm with the lowest energy absorption band (4f–5d¹ transition) at 390 nm and room temperature (RT) decay time of around 450 ns. Thermal stability of the Eu²⁺ emission is confirmed up to 200 °C. Fundamental RT luminescence characteristics of KLnS₂ (Ln = La, Gd, Lu) both undoped and doped by Pr³⁺, Sm³⁺, Tb³⁺ and Tm³⁺ were investigated in [15]. Detailed study of cerium doped KLuS₂ [16] provided temperature and concentration dependences

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of the material emission features, phenomenological modelling and light yield determination. EPR study aiming to understand the divalent europium incorporation and stabilization in KLuS_2 has been reported very recently [17]. Crystal structures of KLaS_2 , KPrS_2 , KEuS_2 , KGdS_2 , KLuS_2 , KYS_2 , RbYS_2 , NaLaS_2 were determined in [18] and crystal structure redeterminations of NaGdS_2 , NaLuS_2 , NaYS_2 were also performed [19].

In this work we study the optical properties of co-doped (Ce, Pr, Sm) KLuS_2 :Eu single crystalline platelets. The main idea is to enrich the Eu^{2+} emission at 515–520 nm by different activators in the red part of the optical spectrum to produce a broad spectral phosphor for white LED source in a single host. Furthermore, the occurrence of the $\text{Eu}^{2+} \rightarrow \text{RE}^{3+}$ energy transfer and its concentration dependence are discussed.

2. Experimental setup

Crystalline samples of doubly doped KLuS_2 were prepared by the chemical reaction of H_2S (99.5%) with a mixture of lanthanide oxides (Lu_2O_3 99.999%, Eu_2O_3 99.99%, Pr_6O_{11} 99.999%, Sm_2O_3 99.99%, CeO_2 99.95%) and an excess of K_2CO_3 (99.997%). Details of preparation were described in [11,18]. The X-ray single-crystal structure determination of KLuS_2 was performed [18]. Absorption spectra were measured using UV/VIS Spectrophotometer Shimadzu UV-1601. Photoluminescence (PL) spectra and decay curves were measured by the custom made Spectrofluorometer 5000 M, Horiba Jobin Yvon, using the steady state deuterium lamp (photoluminescence excitation (PLE) and PL spectra in the 190–500 nm and 200–800 nm spectral regions, respectively), Seifert X-ray tube (radioluminescence (RL) spectra within 200–800 nm), microsecond xenon-filled lamp and nanosecond pulsed LED diodes (PL decay curves) as the excitation sources. Spectra were corrected for instrumental effects and a convolution procedure was applied to the decay curves to determine true decay times (SpectraSolve software package, Ames Photonics). RT luminescence properties of KLuS_2 :Eu, RE crystalline platelets were studied without powdering the samples.

3. Results and discussion

3.1. Optical properties

Normalized RT RL spectra of doubly doped KLuS_2 with different activators and their concentrations (see legends) are displayed in Fig. 1. Each spectrum features already known broad emission band at 510–520 nm given by the partially allowed $5d-4f$ transition of Eu^{2+} ion in KLuS_2 host [14]. While co-doped with Pr^{3+} , see Fig. 1a, this band is overlapped with a characteristic Pr^{3+} $4f-4f$

transition from the 3P_0 level at 498 nm. More $4f-4f$ emission lines from different levels of Pr^{3+} (1D_2) are, however, present in the 600–800 nm region enriching the emission spectrum of the Eu^{2+} in the red part of the optical spectrum. Their relative intensity is increasing with increasing Pr^{3+} concentration. When the Sm^{3+} ions are used as co-dopants, see Fig. 1b, characteristic well resolved intense $4f-4f$ emission lines from $^4G_{5/2}$ level are present in the yellow/red part of the spectrum (550–750 nm) accompanying and enriching the Eu^{2+} emission. With increasing Sm^{3+} concentration, its relative emission intensity is enhanced. Finally, co-doping with the Ce^{3+} activator (in Fig. 1c) results in the presence of additional broad band peaking at around 600 nm and 650 nm due to $5d-4f$ transition of the Ce^{3+} ion [16]. As in previous cases, relative intensity of the Ce^{3+} emission is increasing with higher cerium content. It is to be noted that co-dopants do not quench each other and emission bands of both of them are well visible in the emission spectra under the X-ray excitation.

Fig. 2 shows PLE and PL spectra of doubly doped KLuS_2 , for different excitation and emission wavelengths (see legends). In all presented PLE spectra, the band edge of KLuS_2 situated at 304 nm and the Eu^{2+} absorption band ($4f-5d$ transition) situated at 390 nm are present, consistently with the earlier reported data [14,15]. CT transition from S^{2-} to Pr^{3+} (see Fig. 2a) or Sm^{3+} (see Fig. 2b) are located at 341 nm and 307 nm, respectively [11,12,15]. Only the onset of the $4f-5d$ absorption band of Ce^{3+} is noted at 460–490 nm [16] (see Fig. 2c) as the PLE spectra in the 440–500 nm region are partially distorted due to a very weak excitation source (deuterium steady state lamp) and strong correction curve influence. In all presented PL spectra, the known band due to Eu^{2+} $5d-4f$ transition is situated at 510–520 nm [14], whose position well coincide with the one from RL spectra. Furthermore, it is accompanied by characteristic $4f-4f$ transitions of Pr^{3+} and Sm^{3+} present in the 600–800 nm (see Fig. 2a) and 560–800 nm (see Fig. 2b) region, respectively. Ce^{3+} emission given by the $5d-4f$ transition is present at 580–700 nm region overlapping with that of Eu^{2+} . The PL amplitude ratio between Eu^{2+} and co-dopant depends on the excitation wavelength, see Fig. 2a–c. For white LED sources, excitation wavelengths at 395 nm and 455 nm are of a great importance due to easily available excitation diodes. As an example, PL spectrum of KLuS_2 :Eu, Sm under the 455 nm excitation (see Fig. 2b) exhibits the presence of both Eu^{2+} and Sm^{3+} emission at comparable relative intensity.

3.2. $\text{Eu}^{2+} \rightarrow \text{RE}^{3+}$ energy transfer

Fig. 3a demonstrates the occurrence of the efficient $\text{Eu}^{2+} \rightarrow \text{Ce}^{3+}$ energy transfer thanks to the 520 nm Eu^{2+} emission and 490 nm

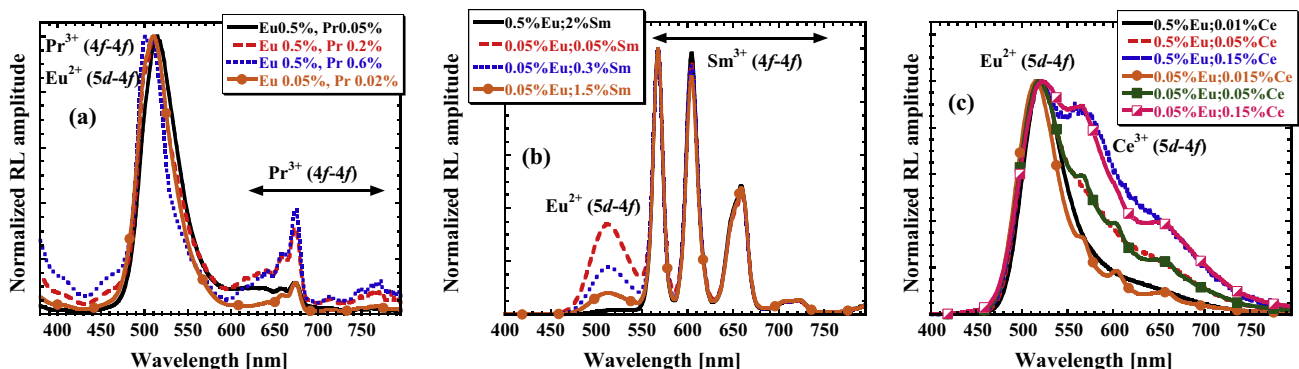


Fig. 1. Normalized RT X-ray excited (40 kV, 15 mA) emission spectra of KLuS_2 :Eu co-doped with Pr^{3+} (a), Sm^{3+} (b) and Ce^{3+} (c) with different concentrations (see legends).

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