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Low-temperature thermoluminescence in $CaGa_2S_4:Eu^{2+}$

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Abstract

In the last years many insulating and semiconducting materials activated with rare-earth elements were found to exhibit phosphorescence and thermoluminescence properties, and are attracting increasing interest due to the variety of application of long-lasting phosphors. In this work we studied the phosphorescence decay and thermoluminescence properties of $CaGa_2S_4:Eu^{2+}$ as a function of temperature in the 9–325 K range. The comparison between spectra recorded as a function of time delay from the excitation pulse at different temperatures indicates that long-lasting emissions peaked at about 2.2 eV occurs at Eu^{2+} sites. Thermoluminescence glow curve is characterized by five components at 69, 98, 145, 185 and 244 K. Experimental data are discussed in the framework of generalized order of kinetic model and allow to estimate the activation energies of trapping defects. The origin of glow components at 69, 98, 145 and 244 K is correlated to trapping defects induced by Eu^{2+} doping, while the component at 185 K is attributed to a continuous distribution of defects.

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1. Introduction

Phoshorescence (PP) or afterglow term generally refers to light emission which lasts for long time (from minutes to hours) after removing the excitation of the sample [1]. PP materials are useful for a variety of applications such as safety indications, traffic signs, luminous paints and light sources [2]. Moreover, these are prospective materials for optical data storage and quantum computing applications [3,4]. In the last years many insulating and semiconducting materials activated with rare-earth elements (REE) were found to exhibit PP and thermoluminescence (TL) properties, and are attracting increasing interest due to the variety of application of long-lasting phosphors. Among the others, many reports were published about PP and TL properties of alluminates, fluorates and silicates compounds doped with REE [5–9]. Long-lasting emission was observed also in calcium thiogallate doped with Eu^{2+} ($CaGa_2S_4:Eu^{2+}$) with TL reported also below room temperature between 100 and 250 K [10,11]. It was found that co-doping with other REE had significant effects on the afterglow properties of $CaGa_2S_4:Eu^{2+}$ [11], and that a suitable choice of co-dopants enhances the brightness and persistence of PP [2].

Calcium thiogallate ($CaGa_2S_4$) doped with REE is a prospective material for optoelectronic and photonic applications [12]. Maximum phonon energy and good optical transmission properties allows to the realization of high-efficiency phosphors [13,14], whose good electrical conduction properties are also promising for electroluminescent displays [15]. $CaGa_2S_4$ doped with erbium exhibits a photoluminescence (PL) emission at 1554 nm, suitable for telecommunication application in the C band [16] while

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doping with Dy and Nd was investigated for laser applications [17,18]. Calcium thiogallate crystallizes in an orthorhombic structure with space group D_{2h}^{24}–Fddd [19] and is characterized by three different crystallographic sites for the calcium ion: two with D_2 point symmetry and one with C_2. The REE substitutes the Ca ions and $CaGa_2S_4:Eu^{2+}$ exhibits PL properties characterized by the emission at about 560 nm due to radiative transitions from the $4f^65d^1$ manifold (fd) to the $^8S_{7/2}$ ground state of Eu^{2+} ions [13–19]. The PL band displays a vibronic nature [19].

In this work we investigated the PP properties of $CaGa_2S_4:Eu^{2+}$ by means of time-resolved PL and PP measurement as a function of temperature and by means of TL measurements.

2. Experimental details

$CaGa_2S_4:Eu^{2+}$ samples (2 mol%) were grown by the solid-state reaction method as previously reported [20,21].

PL, PP and TL measurements were performed as a function of temperature from 9 up to 325 K, by means of a closed-cycle He cryogenerator in cold finger configuration. Sample excitation was provided by the emission at 260 nm (4.77 eV) of an optical parametric oscillator with frequency doubler device (Spectra Physics MOPO), seeded by the third harmonic of a pulsed Nd-YAG laser (Spectra Physics QuantaRay PRO-270). The excitation pulse energy was ≈1 μJ/pulse and pulse-width at half-maximum was 10 ns with 10 Hz repetition rate. PL, PP and TL measurements were performed in 90° geometry, focusing the emitted light signal onto the entrance slit of a triple grating monochromator (ARC Spectra Pro 300i) with spectral bandwidth of 0.1 eV. The signal was detected by a gatable intensified CCD (Princeton Instruments PIMAX). Depending on PL bands under examination different time delays from excitation pulse and time gates were used. PP measurements were performed at constant temperature after excitation of the sample for 10 min. TL measurements were performed after irradiation of the samples for 10 min at 35 K. Samples were heated with a linear heating program at rate of 0.1 K/s. Spectra recording were synchronized with the heating rate in order to have a resolution of 0.2 K/spectrum. If compared to TL measurements performed with photomultiplier tubes, the use of the CCD allows to record the spectral distribution of the thermally stimulated emission at each point of the glow curve.

All spectra were corrected for the spectral response of the optical system.

3. Results

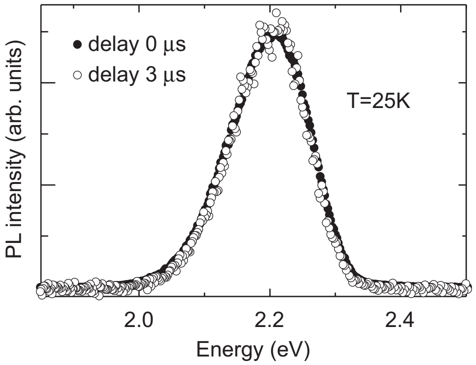

Fig. 1. Time-resolved PL spectra recorded at 25 K with excitation at 260 nm. Spectra were collected in the μs time domain with 1 μs of gate width at two different delays from the excitation pulse.

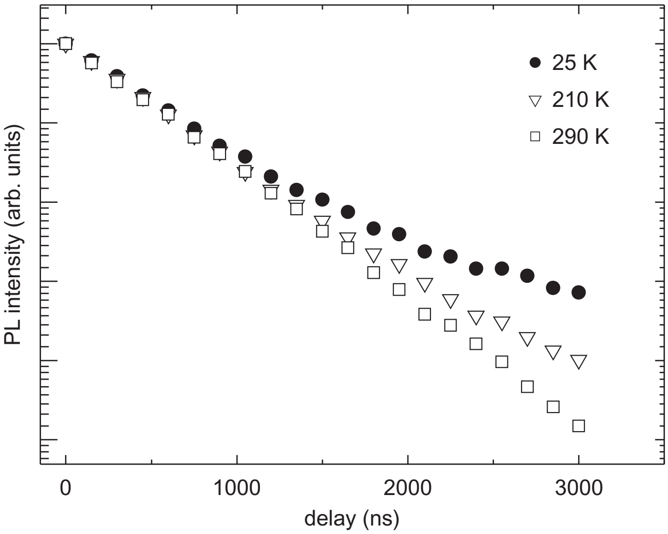

Fig. 2. PL intensity time decay measurements at three different temperatures: PL lifetime of 670 ± 20 ns was measured at 290 K by assuming a single-exponential decay. Below 290 K fluorescence decay is interested by a non-exponential tail.

Time-resolved PL spectra recorded at 25 K are shown in Fig. 1 as a function of the time delay from excitation pulse. The characteristic Eu^{2+} radiative transition from $4f^65d^1$ state to the ground state [13–19] is observed at 2.2 eV (564 nm). By comparison between PL spectra recorded at different delays from excitation pulse, no variation in the band shape of the PL is observed with increasing delay from excitation. PL time decays recorded at different temperatures are shown in Fig. 2 in a semi-log plot. Experimental data show that at temperature below 290 K, fluorescence decay is interested by a non-exponential tail whose contribution increases with decreasing temperature. PL lifetime of 670 ± 20 ns was measured at 290 K by assuming a single-exponential decay. The analysis of the decay curves at lower temperature performed in the 0–1 μs delay range, where single-exponential decay is observed, indicates that the PL lifetime does not depends on the temperature.

PP decay measured at 9 K in the 0–10^3 s time domain is shown in Fig. 3. Experimental data can be fitted with a first-order exponential decay with an estimated decay constant of 420 s. PP spectrum recorded 1 min after the excitation pulse reported in the inset of Fig. 3 shows that