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Temperature dependence spectroscopic study of Ce-doped Cs_3LaCl_6 and Cs_3LaBr_6 scintillators ☆

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ABSTRACT

Single crystals of Ce-doped Cs_3LaCl_6 and Cs_3LaBr_6 show promising scintillation properties in gamma-ray detection. Their thermal response in the range from 40 K to 500 K is discussed in this work. The steady state photoluminescence spectra, photoluminescence decay time, and X-ray excited radioluminescence of Ce-doped and undoped Cs_3LaCl_6 and Cs_3LaBr_6 were studied. The photoluminescence and radioluminescence emission intensity of the Ce-doped crystals decreases less than 25% from 40 K to 500 K. The photoluminescence decay time of Ce^{3+} increases with increasing temperature.

1. Introduction

An ideal scintillator would have fast scintillation decay, good energy resolution, high light yield, high effective atomic number and a favorable emission wavelength [1–3]. For some applications, the temperature stability is also important. For example, in oil well logging, the detectors normally operate in a wide temperature range that varies from room temperature up to 200 °C. Due to the extreme temperature change, the scintillators used as oil well logging tools are expected to be stable with temperature variations in term of light yield, scintillation decay time and emission wavelength [4]. Thus, temperature dependence of scintillation response is an important criterion. In addition, investigation of temperature dependent behavior of scintillation properties can help clarify the scintillation mechanism.

The temperature responses of various scintillators have been reported in previous studies. Boatner et al. [5] reported the light yield of a large group of scintillators from RT up to 480 K. In their work, most halides scintillators experienced light yield loss more than 60% at elevated temperature. Moszynski et al. [6] studied the temperature dependent behavior of $LaBr_3$:Ce, $LaCl_3$:Ce and NaI:T1 in terms of full energy peak position. Yang et al. [7] studied the thermal response of SrI_2:Eu. The photoluminescence emission intensity of SrI_2:Eu drops more than 50% from 40 K to 500 K. Drozdowski and Wojtowicz [8] studied the radiation trapping effect in BaF_2:Ce at elevated temperature. It indicates that temperature dependent re-absorption of Ce^{3+} emission is the key reason of the prolonged photoluminescence decay time. Bessiere et al. [9] compared the scintillation properties of $LaCl_3$:Ce, $LaBr_3$:Ce and LaI_3:Ce. The emission of LaI_3:Ce is completely quenched above 150 K due to its small band gap. Bizarri and Dorenbos . [10] reported the charge carrier and exciton dynamics in $LaBr_3$:Ce in the temperature range from 80 K to 600 K. The energy transfer from self-trapped excitons to cerium ions increases with elevated temperature. The thermal stability of $LaBr_3$:Ce allows its high temperature use.

We previously reported the scintillation properties of Cs_3LaCl_6:Ce and Cs_3LaBr_6:Ce at RT [11]. In this work, we studied the temperature dependence of scintillation properties of both Ce-doped and undoped Cs_3LaCl_6 and Cs_3LaBr_6 single crystals in a wide temperature range from 40 K to 500 K.

2. Experimental

2.1. Synthesis

All the starting materials were 5 N pure anhydrous materials from Sigma Aldrich. Before synthesis, the starting materials were dried in vacuum (10^{-6} Torr) in heating steps of 120 °C, 150 °C and 250 °C. Samples of undoped and Ce-doped Cs_3LaCl_6 and Cs_3LaBr_6 were synthesized in 8 mm diameter quartz ampoules sealed under vacuum. The Ce concentration varies from 0.5% to 40% (atomic

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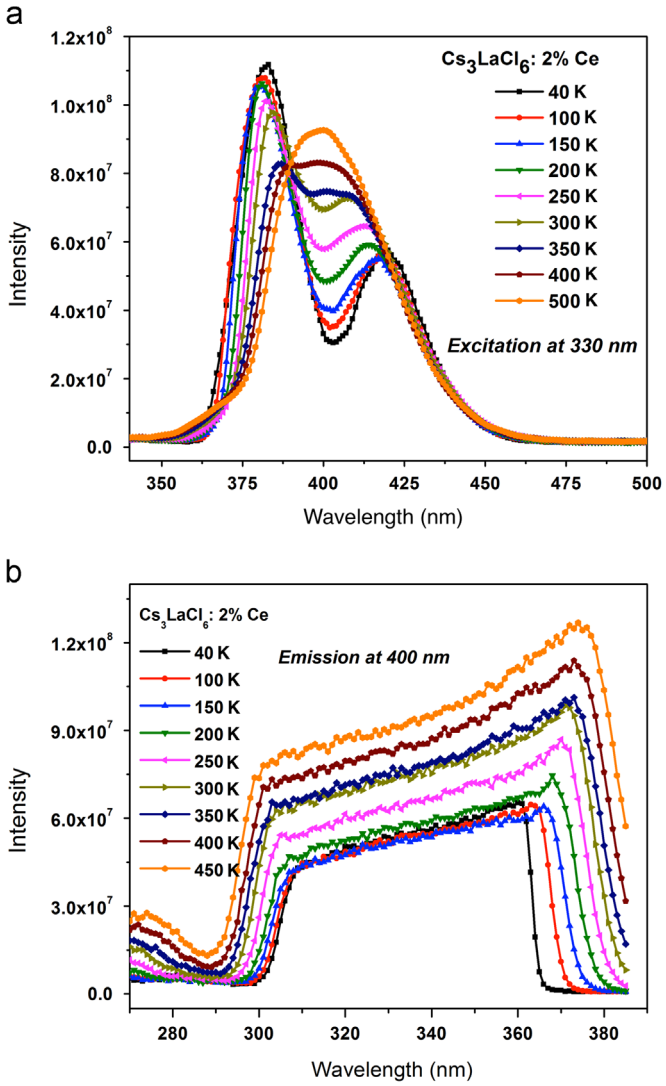

Fig. 1. PL emission (a) and excitation (b) spectra of Cs_3LaCl_6:2% Ce at different temperatures. The emission was recorded with 330 nm excitation, and excitation was recorded with 400 nm emission.

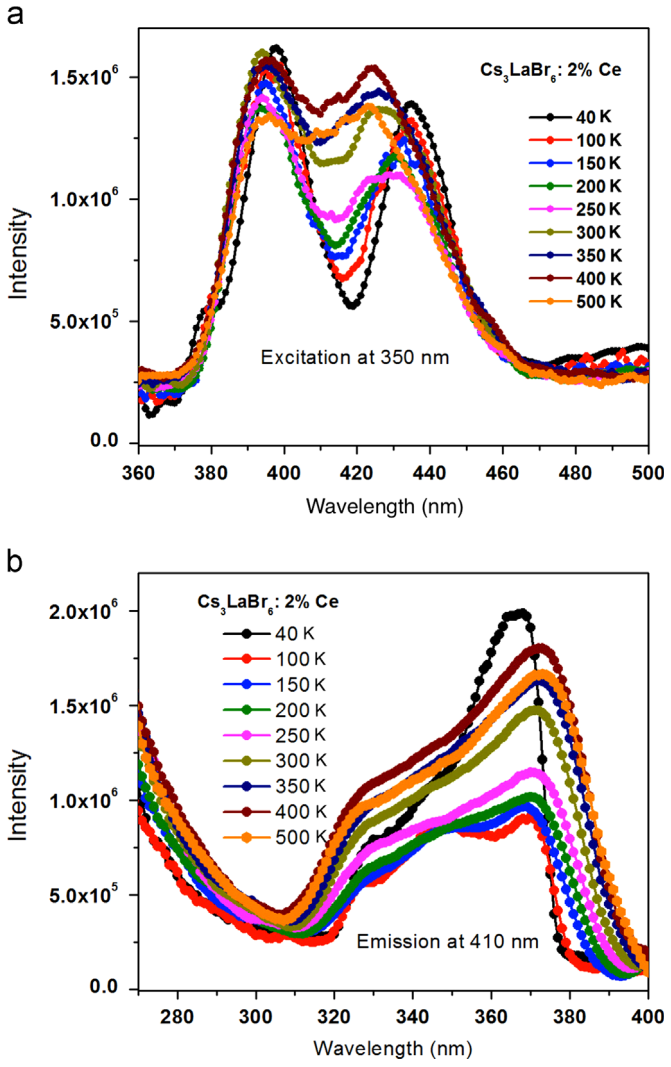

Fig. 2. PL emission (a) and excitation (b) spectra of Cs_3LaBr_6:2% Ce at different temperatures. The emission was recorded with 350 nm excitation, and excitation was recorded with 410 nm emission.

percentage). The samples were melted and mixed by a Multiple Alternating Direction (MAD) method, and detailed procedures can be found elsewhere [11,12]. Then the synthesized polycrystalline boule was translated in a Bridgman furnace with a thermal gradient. The translation rate was 3–5 mm/h, and cooling rate was 5 °C/h.

2.2. Photoluminescence (PL) spectra and PL decay time

Steady state PL emission and excitation spectra were measured with a Horiba Jobin Yvon Fluorolog 3 Spectrofluorometer equipped with a 450 W Xe lamp. A closed cycle compressed helium cryostat (Advanced Research Systems, DE-202) was used to cool and heat the sample from 40 K to 500 K under vacuum ($<10^{-3}$ Torr). A Hamamatsu R928 PMT was used to record the emission as a function of wavelength.

The PL decay time was measured with the same Spectrofluorometer, equipped with a Horiba NanoLED light source. The repetition rate of the LED was set to 1 MHz.

2.3. Radioluminescence (RL) spectra

The RL spectra were recorded from 40 K to 500 K under vacuum ($<10^{-3}$ Torr). The sample was mounted on a copper cold finger on an Advanced Research System DE-202 closed cycle compressed helium cryostat. X-rays were generated from a CMX-003 X-ray generator. The voltage and current of the X-ray tube was, respectively 35 kV and 0.1 mA. The emission spectra were recorded with a 150 mm focal length monochromator (PI ACTON SpectraPro SP-2155 m) over a wavelength range from 200 nm to 800 nm. In order to check for thermal lag, two heating-cooling cycles from low to high temperature, and high to low temperature was recorded for each sample. The thermal-induced emission from shallow traps is trivial [13]. For emission intensity comparison, the intensity is integrated area below the peak (290–640 nm) and whole scan range (200–800 nm). The background was subtracted to exclude the effect of noise.

3. Results

3.1. PL emission/excitation spectra

The PL emission and excitation spectra of Ce-doped and undoped Cs_3LaCl_6 and Cs_3LaBr_6 were measured. Fig.1(a) and (b) shows the emission and excitation spectra of Cs_3LaCl_6:2% Ce at different temperatures. In the emission spectra, the splitting of $4f(^2F_{5/2})$ and $4f(^2F_{7/2})$