Optical Materials 64 (2017) 121–125

Contents lists available at ScienceDirect

Optical Materials

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

Crystal growth and scintillation properties of undoped and Ce^{3+}-doped GdI_3 crystals

Le Ye [a, b], Huanying Li [b], Chao Wang [b], Jian Shi [b], Xiaofeng Chen [b], Zhongqing Wang [c], Yuefeng Huang [c], Jiayue Xu [a, *], Guohao Ren [b, **]

[a] School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai 200235, China
[b] Shanghai Institute of Ceramic, Chinese Academy of Science, Shanghai 200050, China
[c] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

ARTICLE INFO

Article history:
Received 21 September 2016
Received in revised form
23 November 2016
Accepted 28 November 2016

Keywords:
Scintillator
GdI_3
Single crystal growth
Bridgman technique
Ce^{3+} luminescence

ABSTRACT

The growth and scintillation properties of undoped and Ce^{3+}-doped GdI_3 crystals were reported in this paper. These GdI_3:χ%Ce (χ = 0, 1, 2) crystals were grown by the vertical Bridgman growth technique in evacuated quartz crucibles. X-ray excited optical luminescence spectra of GdI_3:Ce exhibit a broad emission band (450 nm–650 nm) peaking at 520 nm corresponding to $5d^1 \rightarrow 4f^1$ transition of Ce^{3+} while the undoped GdI_3 crystal consists of a broad band (400 nm-600 nm) and several sharp lines peaking at 462 nm, 482 nm, 492 nm, 549 nm, 579 nm owing to the impurities ions and defects. The excitation spectra of Ce^{3+} doped GdI_3 consist of two broad bands between 300 nm and 500 nm corresponding to $4f^1 \rightarrow 5d^1$ absorption of Ce^{3+}. The other absorption peaking at 262 nm in the spectrum of GdI_3:2%Ce is assigned to band-to-band exciton transition. The excitation spectrum of undoped GdI_3 contains a flat absorption band from 330 to 370 nm and a broad band between 390 and 450 nm peaking at 414 nm corresponding to the absorption of the unintentionally doped Ce^{3+}, Dy^{3+}, Ho^{3+} impurities and other defects. The emission spectrum of undoped GdI_3 under 332 nm excitation has the identical line peaks with the spectrum measured under X-ray excitation. The emission spectra of GdI_3:2%Ce and GdI_3:1%Ce show a broad band in the range of 450–750 nm with the maximum at 550 nm corresponding to $5d^1 \rightarrow 4f^1$ transitions of Ce^{3+} ion. The GdI_3, GdI_3:1%Ce and GdI_3:2%Ce show fast principle decay time constant 73 ns, 69 ns and 58 ns respectively, besides, the undoped also shows a slow decay constant 325 ns which doesn't appear in Ce^{3+}-doped GdI_3 crystal. The energy resolutions of GdI_3:χ%Ce (χ = 1, 2) measured at 662 KeV are about 3%–5% and the undoped GdI_3 is 13.3%.

1. Introduction

The last decade has been a very fruitful time for iodide scintillators doped with Ce^{3+}. These iodides with the smallest band gap in the halide family of compound could show high light yield in theory [1]. GdI_3:Ce scintillator was first reported in 2006 and grown by Radiation Monitoring Devices using the Bridgman method [2–4]. GdI_3:2%Ce presented a high light output of 58 000 photos/MeV, 5000 photos/thermal neutron interaction, fast decay time constant of 39 ns, 550 nm green emission, high energy resolution 8.7% measured at 662 keV [2]. GdI_3:Ce crystal has the BiI_3-type crystal structure with space group R $\bar{3}$ (148). The crystal lattice parameters of GdI_3 a = b = 7.55 ± 0.01 Å and c = 20.80 ± 0.02 Å. Due to the layer-type structure, the crystal shows a complete cleavage plane. The Gd^{3+} site is coordinated to six I- anions and the coordination can be considered as an octahedron with slight distortions. The GdI_3 crystal has high density of 5.22 g/cm^3, effective atomic number of 56.90 and melting point at 927 °C [5–7]. However, the compound is extremely hygroscopic like other halide materials.

In this paper, GdI_3:χ%Ce (χ = 0, 1, 2) ingots were grown with Bridgman technique and characterized with X-ray emission spectrum and photoluminescence spectrometers. Their energy resolution and scintillation decay time are presented to be better than those reported in previous literature.

2. Experimental

Single crystal of GdI_3, GdI_3:1%Ce and GdI_3:2%Ce were grown

* Corresponding author.
** Corresponding author.
E-mail addresses: xujiayue@sit.edu.cn (J. Xu), rgh@mail.sic.ac.cn (G. Ren).

http://dx.doi.org/10.1016/j.optmat.2016.11.048
0925-3467/

using the vertical Bridgman method, and the silica glass tubes with size of Φ15 mm were used as crucibles. Ultra-dry, high purity GdI_3 (99.98% purity) and CeI_3 (99.99% purity) powders were used as starting materials without further purification. Since the starting materials and final products are strongly hygroscopic, more careful handling was necessary. It's prohibited to exposure the raw materials or crystal to air and humid environment during synthesis, samples manufacturing and test. So all starting raw materials were handled in a glove box in where both H_2O and O_2 levels were less than 0.1 ppm through a nitrogen environment and then the ingot handling was taken in a drying compartment.

The crucibles were evacuated by connecting them to a vacuum pump to remove the remaining moisture and then sealed with oxyhydrogen flame. Bridgman furnace was divided into two-zones, the high temperature zone of the furnace was set 1020 °C, higher than its melting point of 927 °C, and the low temperature zone was lower than 750 °C. The temperature gradient of interface between solid and melt was kept about 40 °C ± 5 °C/cm. The melt began to solidify at the capillary tip, which acted as a seed to get single crystalline and its diameter was 2 mm. A solidification rate of 0.4 mm/h and a cooling rate of 7 °C/h [8,9]. GdI_3:Ce single crystal with a diameter of 15 mm and a length of 40 mm was successfully grown and the crystal ingot were cut into several parts and shown in Fig. 1. The grown ingots are yellow, transparent and include some little black particles in the top region. They were polished and encapsulated into samples in the drying compartment where the dewpoint temperature of H_2O was set at −50 °C. The samples without crack and inclusion were sealed inside quartz cells and then sealed into aluminum tube which filled with magnesia powder stuffing and covered with a quartz glass as a window. Fig. 2 shows the samples of GdI_3:Ce before and after encapsulation. In this way, the samples can be tested in atmosphere and deposit for few months without damage. The X-ray diffraction pattern for the grown crystal has confirmed that the samples are single crystal with a hexagonal structure.

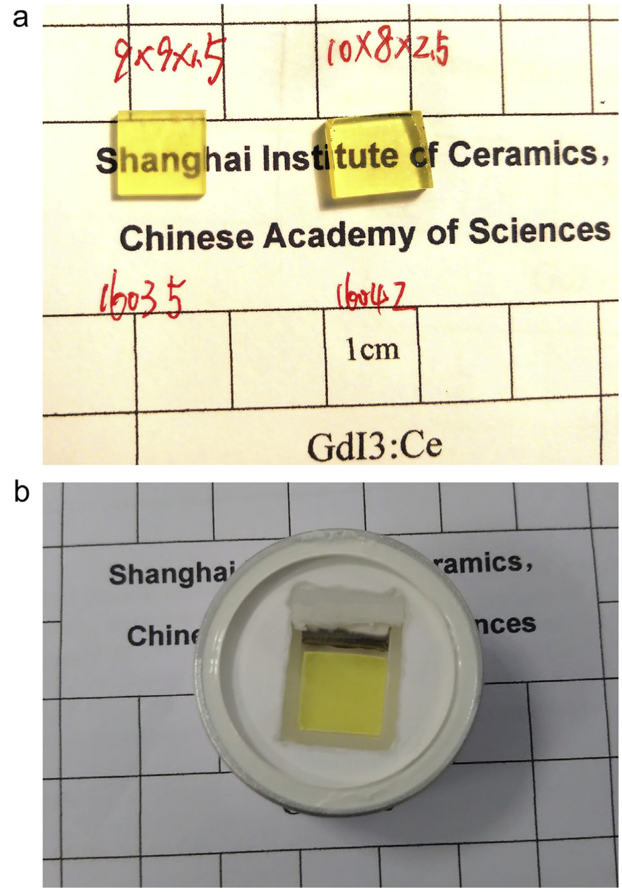

Fig. 2. The samples of GdI_3:Ce crystal; (a)without encapsulation, (b) after encapsulation.

3. Result and discussion

3.1. Radioluminescence

The radioluminescence spectra of GdI_3, GdI_3:1%Ce and GdI_3:2% Ce were conducted on an X-ray excited luminescence (XEL) spectrometer assembled at Shanghai Institute of Ceramics with a Hamamatsu photomultiplier tube (PMT) R456. The X-ray tube equipped with Cu-anode was operated at 65 kV and 3 mA and the high voltage of PMT was set 700 V for GdI_3:Ce while 900 V for the undoped GdI_3. It must be pointed out that the luminescence intensity of undoped GdI_3 excited by X-ray is quite lower than Ce-doped GdI_3.

Fig. 3 displays the radioluminescence spectrum of GdI_3, GdI_3:1% Ce and GdI_3:2%Ce. The GdI_3 doped with Ce^{3+} consists of a broad emission from 450 nm to 650 nm which are attributed to Ce^{3+} $5d^1 \rightarrow 4f^1$ transition peaking at 520 nm. The curve of undoped GdI_3 consists of a broad emission band from 400 nm to 600 nm and

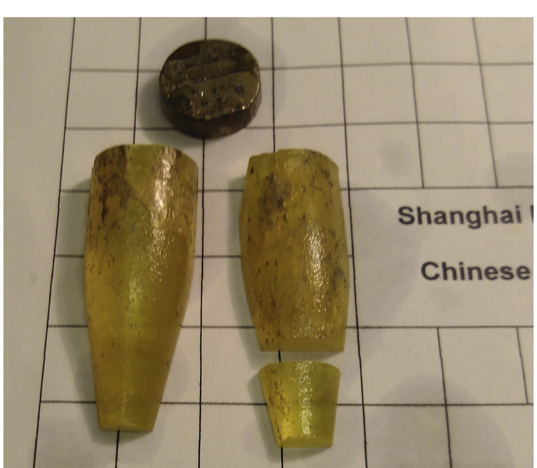

Fig. 1. The grown ingots of GdI_3:2%Ce.

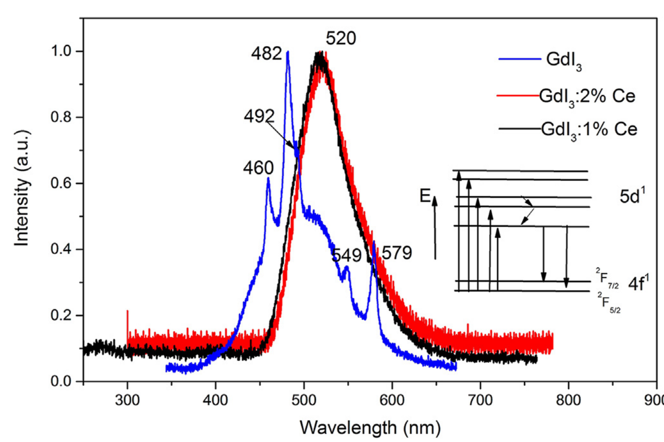

Fig. 3. Radioluminescence spectra of GdI_3, GdI_3:2%Ce and GdI_3:1%Ce.