Crystal growth and scintillation properties of undoped and Ce³⁺-doped GdI₃ crystals

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Abstract

The growth and scintillation properties of undoped and Ce³⁺-doped GdI₃ crystals were reported in this paper. These GdI₃: $\chi\%$ Ce($\chi=0, 1, 2$) crystals were grown by the vertical Bridgman growth technique in evacuated quartz crucibles. X-ray excited optical luminescence spectra of GdI₃:Ce exhibit a broad emission band (450nm-650nm) peaking at 520nm corresponding to 5d¹→4f¹ transition of Ce³⁺ while the undoped GdI₃ crystal consists of a broad band (400nm-600nm) and several sharp lines peaking at 462nm, 482nm, 492nm, 549nm, 579nm owing to the impurities ions and defects. The excitation spectra of Ce³⁺ doped GdI₃ consist of two broad bands between 300nm and 500nm corresponding to 4f¹→5d¹ absorption of Ce³⁺. The other absorption peaking at 262nm in the spectrum of GdI₃:2%Ce is assigned to band-to-band exciton transition. The excitation spectrum of undoped GdI₃ contains a flat absorption band from 330 to 370nm and a broad band between 390 and 450nm peaking at 414nm corresponding to the absorption of the unintentionally doped Ce³⁺, Dy³⁺, Ho³⁺ impurities and other defects. The emission spectrum of undoped GdI₃ under 332nm excitation has the identical line peaks with the spectrum measured under X-ray excitation. The emission spectra of GdI₃:2%Ce and GdI₃:1%Ce show a broad band in the range of 450 to 750nm with the maximum at 550nm corresponding to 5d¹→4f¹ transitions of Ce³⁺ ion. The GdI₃, GdI₃:1%Ce and GdI₃:2%Ce show fast principle decay time constant 73ns, 69ns and 58ns respectively, besides, the undoped also shows a slow decay constant 325ns which doesn't appear in Ce³⁺-doped GdI₃ crystal. The energy resolutions of GdI₃: $\chi\%$ Ce($\chi=1, 2$) measured at 662 KeV are about 3% to 5% and the undoped GdI₃ is 13.3%.

Keywords:

Scintillator; GdI₃; Single crystal growth; Bridgman technique; Ce³⁺ luminescence

1.Introduction

The last decade has been a very fruitful time for iodide scintillators doped with Ce³⁺. These iodides with

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the smallest band gap in the halide family of compound could show high light yield in theory[1]. GdI₃:Ce scintillator was first reported in 2006 and grown by Radiation Monitoring Devices using the Bridgman method[2-4]. GdI₃:2%Ce presented a high light output of 58 000 photos/MeV , 5 000 photos/thermal neutron interaction, fast decay time constant of 39ns, 550nm green emission, high energy resolution 8.7% measured at 662keV[2]. GdI₃:Ce crystal has the BiI₃-type crystal structure with space group $R\bar{3}(148)$. The crystal lattice parameters of GdI₃ $a = b = 7.55 \pm 0.01 \text{ \AA}$ and $c = 20.80 \pm 0.02 \text{ \AA}$. Due to the layer-type structure, the crystal shows a complete cleavage plane. The Gd³⁺ site is coordinated to six I- anions and the coordination can be considered as an octahedron with slight distortions. The GdI₃ crystal has high density of 5.22 g/cm³, 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, GdI₃: χ %Ce($\chi=0, 1, 2$) 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 GdI₃, GdI₃:1%Ce and GdI₃:2%Ce were grown using the vertical Bridgman method, and the silica glass tubes with size of $\Phi 15\text{mm}$ were used as crucibles. Ultra-dry, high purity GdI₃(99.98% purity) and CeI₃(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 H₂O and O₂ levels were less than 0.1 ppm through an 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 $\pm$ 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 2mm. A solidification rate of 0.4 mm/h and a cooling rate of 7 °C/h [8,9].GdI₃: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 H₂O 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 GdI₃: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.

3.Result and discussion

3.1. Radioluminescence

The radioluminescence spectra of GdI_3 , $\text{GdI}_3\text{:1\%Ce}$ and $\text{GdI}_3\text{:2\%Ce}$ 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 700V for $\text{GdI}_3\text{:Ce}$ while 900V 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 , $\text{GdI}_3\text{:1\%Ce}$ and $\text{GdI}_3\text{:2\%Ce}$. The GdI_3 doped with Ce^{3+} consists of a broad emission from 450nm to 650nm which are attributed to $\text{Ce}^{3+} 5d^1 \rightarrow 4f^1$ transition peaking at 520nm. The curve of undoped GdI_3 consists of a broad emission band from 400nm to 600nm and several line spectrum peaking at 460, 482, 492, 549, 579nm. And the energy diagram of Ce^{3+} is also represented in Fig.3. Ce^{3+} has a $4f^1$ electronic configuration. The ground state is split by the spin-orbit coupling into two components, $^2F_{5/2}$ and $^2F_{7/2}$, separated by 0.3 eV. The first excited configuration $5d^1$ is split by the crystal field into five components. Ions excited in a 5d state rapidly relax to the lower 5d level, from which luminescence occurs.[10]

The Inductive Coupled Plasma Emission Spectrometer test of raw material with PerkinElmer Optical 8300 shows that the trace trivalent rare earth impurities still remain even though the purity of the starting materials GdI_3 is as high as 99.98%. And these trace impurities do have strong influence on the spectra of undoped GdI_3 . The line peaks and the broad band from 400 to 600nm are conjectured to result from the unintentionally doped Ce^{3+} , Ho^{3+} , Dy^{3+} and other ions or defects in the starting material GdI_3 . The broad band is attributed to $\text{Ce}^{3+} 5d^1 \rightarrow 4f^1$ transition. The peaks at 579nm is due to the unwanted impurity $\text{Dy}^{3+} {}^4F_{9/2} \rightarrow {}^6H_{13/2}$ [11]. The peak at 482, 490nm are due to the emission of $\text{Ho}^{3+} {}^5F_2 + {}^5F_3 \rightarrow {}^5I_8$ and 549nm is due to ${}^5F_4 + {}^5S_2 \rightarrow {}^5I_8$ [12]. The line peak 460nm is probably induced by other impurity ion or defects in the crystal. The emission line peaking at 312nm of $\text{Gd}^{3+} {}^6P_J \rightarrow {}^8S_{7/2}$ was not observed because of the energy transfer from Gd^{3+} to Ce^{3+} , Dy^{3+} , Ho^{3+} and other defects[13]. Compared with $\text{GdI}_3\text{:Ce}$, these emission lines existing in the undoped GdI_3 have completely disappeared in the spectrum of Ce^{3+} -doped GdI_3 due to energy transfer from the luminescence center of undoped GdI_3 to Ce^{3+} [14]. And it must be pointed out that the luminescent intensity of undoped GdI_3 is much weaker than $\text{GdI}_3\text{:Ce}$.

3.2.Photoluminescence excitation and emission measurements

The photoluminescence excitation and emission spectrum of GdI_3 , $\text{GdI}_3\text{:1\%Ce}$ and $\text{GdI}_3\text{:2\%Ce}$ were obtained using a FLS980 Spectrometer produced by Edinburgh Instruments with Xe lamp at room temperature.

Fig.4 presents the photoluminescence excitation spectra of three crystal samples with the emission monochromator set to 550nm. In the excitation spectrum(curve a, b, c), two broad bands are observed locating between 300nm and 500nm. The excitation bands from 330nm to 440nm in the spectra of $\text{GdI}_3\text{:2\%Ce}$ and $\text{GdI}_3\text{:1\%Ce}$ are due to $\text{Ce}^{3+} 4f^1 \rightarrow 5d^1$ absorption. The another absorption peaking at 262nm in the spectrum of $\text{GdI}_3\text{:2\%Ce}$ is assigned to band-to-band exciton transition[2]. And the excitonic absorption locating at 262nm is quite weak and difficult to detect in curve a, b. The excitation spectrum of GdI_3 consists of a flat absorption band from 330 to 370nm and a broad band between 390 and 450 peaking at 414nm corresponding to the absorption of the unintentionally doped Ce^{3+} impurities. The absorption of Dy^{3+} , Ho^{3+} and other defects which are covered by the flat absorption band from 330 to 370nm is the reason that causes the excitation spectrum of

GdI₃ slightly different from Ce³⁺ doped GdI₃. The absorption bands are overlapping with the emission of Gd³⁺ 312nm that causes the energy transfer from Gd³⁺ to impurities[15,16].

Fig.5 displays the Photoluminescence emission spectra. Fig.5 (a) is the spectra of undoped GdI₃ under 332nm and 418nm excitation. The spectra of GdI₃ excited under UV 332nm and 418nm both present a broad band from 450 to 700nm corresponding to 5d¹→4f¹ transition of the unintentionally doped Ce³⁺. Compared to the radioluminescence spectra, the photoluminescence spectrum of GdI₃ excited under UV 332nm has many line peaks which are similar to the spectrum measured under X-ray excitation. The peaks at 578nm is due to the unwanted impurity Dy³⁺ ⁴F_{9/2}→⁶H_{13/2}. The peak at 481, 549, 666nm are due to the emission of Ho³⁺ ⁵F₂+⁵F₃→⁵I₈, ⁵F₄+⁵S₂→⁵I₈, ⁵F₅→⁵I₈, respectively. The line peak 458, 756nm are probably induced by other impurity ion or defects in the crystal.

Fig.5 (b) shows the comparison of different concentration Ce-doped GdI₃:χ%Ce(χ=0, 1, 2) crystal. Because the emission spectra of undoped GdI₃ under 418nm excitation, GdI₃:2%Ce under 332, 450nm excitation, GdI₃:1%Ce under 332nm excitation are the similar to the GdI₃:1%Ce spectrum measured under 450nm excitation due to the 5d¹→4f¹ Ce³⁺ emission, so only several typical curves have been listed. From the Fig.5(b,c), the emission line peaks existing in the undoped GdI₃ completely disappeared in the emission spectrum of GdI₃:Ce under 332, 450nm excitation, but it is easy to notice that the peaks at 342, 420, 480nm in the emission spectrum of GdI₃:2%Ce excited at 262nm. The situation is caused by the incomplete energy transfer from other luminescence centers to Ce³⁺ [17]. The luminescence intensity excited at 262nm is much weaker than that excited at 335,450nm, just few energy level transitions of impurities are excited when the sample excited by 262nm, and then the incomplete energy transfer to Ce³⁺ happens. The peak at 420, 480nm is probably due to the emission of Ho³⁺ ⁵G₅→⁵I₈, Dy³⁺ ⁴F_{9/2}→⁶H_{15/2} respectively.[11,12]

3.3. Pulse height measurements

The pulse height spectra of GdI₃, GdI₃:1%Ce and GdI₃:2%Ce samples excited with γ-rays of 662 keV from a ¹³⁷Cs source, recorded with a shaping time of 3 μs are shown in Fig.6. And a calibrated CsI:Tl sample crystal is used to calibrate the instrument. The measurement was evaluated with using Hamamatsu R594 PMT at room temperature. The detailed data of samples are presented in Table I.

The pulse height spectra have been fitted by Gauss model, and the energy resolution of the samples have been figured out. The energy resolution of undoped GdI₃ is 13.3% which is due to its bad surface quality. The best energy resolution of GdI₃:1%Ce and GdI₃:2%Ce are estimated to be 4.1%, 3.4% at 662keV respectively, which are much better than the previous report [2,6] (about 8 mm³ value(8.7%) at a larger size).

3.4. Scintillation decay

The scintillation decay curves of GdI₃:χ%Ce(χ=0, 1, 2) samples excited with 662keV γ-rays from a ¹³⁷Cs source are shown in Fig.7. The decay curves of GdI₃:1%Ce and GdI₃:2%Ce samples could be well fitted by one-exponential function. The equation is shown below:

$$y = y_0 + A_1 e^{-x/t_1}$$

where y₀ is the baseline offset originating of random coincidences, A₁ is the amplitude of curve, t₁ is the component of the decay time. The fitting decay curves of GdI₃:1%Ce and GdI₃:2%Ce samples both present one decay time constant 69ns and 58ns respectively, which is slower than 39ns reported by J.Glodo[2]. But there is no other slower decay component from the fitting result which is different from the previous report [2,3,6]. The possible reasons are sample quality, defects concentration and testing method.

The curve of undoped GdI₃ can be well fitted by a sum of two-exponential function. The decay constants from the fitting results are composed of two components, 73ns and 324ns. Their relative intensity is 51% and

49%, respectively. The faster component 73ns is due to the unintentionally doped Ce^{3+} contamination. The slower component 324ns is typically due to exciton based energy transfer.

4. Conclusion

In this paper the transparent ingots of $\text{GdI}_3:\chi\%\text{Ce}$ ($\chi=0,1,2$) with a diameter of 15 mm and a length of 40 mm have been grown by the vertical Bridgman technique in evacuated quartz crucibles. The radioluminescence spectra and photoluminescence emission spectra of undoped GdI_3 exhibit identical emission lines peaking at 460, 482, 492, 549, 579nm owing to the Ho^{3+} , Dy^{3+} impurities ions existing in the raw materials and then these lines peaks disappear in the spectrum of Ce^{3+} -doped GdI_3 due to energy transfer to Ce^{3+} . The broad band from 450 to 750nm in radioluminescence spectra and photoluminescence emission spectra of GdI_3 are attributed to the unintentionally doped Ce^{3+} $5d^1 \rightarrow 4f^1$ transition. Two broad bands between 300nm and 500nm in the excitation spectra of $\text{GdI}_3:1\%\text{Ce}$ and $\text{GdI}_3:2\%\text{Ce}$ are assigned to the optical absorption of Ce^{3+} ions. GdI_3 , $\text{GdI}_3:1\%\text{Ce}$ and $\text{GdI}_3:2\%\text{Ce}$ samples show fast principle decay time constant 73, 69 and 58ns respectively. And the fast principle decay constant of Ce^{3+} doped GdI_3 are slower than 39ns reported previously, the possible reasons are sample quality, defects concentration and testing method. The energy resolution excited with 662 keV γ -rays from a ^{137}Cs source are estimated to be 4.1%, 3.4% for $\text{GdI}_3:1\%\text{Ce}$ and $\text{GdI}_3:2\%\text{Ce}$ respectively, which are better than the value(8.7%) reported previously at a larger size sample.

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Fig.1 The grown ingots of $\text{GdI}_3:2\%\text{Ce}$

Fig.2 The samples of $\text{GdI}_3:\text{Ce}$ crystal; (a)without encapsulation , (b) after encapsulation

Fig.3 Radioluminescence spectra of GdI_3 , $\text{GdI}_3:2\%\text{Ce}$ and $\text{GdI}_3:1\%\text{Ce}$

Fig.4 Photoluminescence excitation spectra of GdI_3 , $\text{GdI}_3:1\%\text{Ce}$ and $\text{GdI}_3:2\%\text{Ce}$ crystal monitored at 550nm

Fig.5-a Photoluminescence emission spectra of undoped GdI_3 crystal

Fig.5-b Photoluminescence emission spectra of Ce-doped GdI_3 crystal

Fig.5-c Photoluminescence emission spectra of $\text{GdI}_3:2\%\text{Ce}$ crystal

Fig.6 Pulse height spectrum of GdI_3 , $\text{GdI}_3:1\%\text{Ce}$, $\text{GdI}_3:2\%\text{Ce}$ and CsI:Tl excited with of 662 keV from a ^{137}Cs source, recorded with a shaping time of 3 μs .

Fig.7. Scintillation decay curves and their fitted lines of GdI_3 , $\text{GdI}_3:1\%\text{Ce}$, $\text{GdI}_3:2\%\text{Ce}$ excited with 662 keV γ -rays from a ^{137}Cs source.

Table I. Pulse height spectra of $\text{GdI}_3:\chi\%\text{Ce}(\chi=0, 1, 2)$ with CsI:Tl crystal for comparison

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Table I. Pulse height spectra of $\text{GdI}_3:\chi\%\text{Ce}(\chi=0, 1, 2)$ with CsI:Tl crystal for comparison

Sample	PMT HV(volts)	Size/mm	Dead time	Channel number	FWHM	E.R%
GdI_3	-1500	13×8×2	2%	196.62	26.15	13.3
$\text{GdI}_3:1\%\text{Ce}$	-1500	10×8×2	4.0%	294.52	12.01	4.1
$\text{GdI}_3:2\%\text{Ce}$	-1500	11×8×2.5	≤4%	303.20	10.25	3.4
CsI:Tl	-1500	Φ25.4×25.4	≤13%	489.16	38.25	7.8