Growth, optical and scintillation properties of Gd3+ doped Bi4Si3O12 single crystals

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Received January 16, 2020; revised March 24, 2020; accepted April 7, 2020; published online April 24, 2020

Pure Bi4Si3O12(BSO) and Bi4Si3O12:Gd (BSO:Gd) crystals with nominal concentrate of 1.0–6.0 mol% Gd2O3 were grown by the modified vertical Bridgman method. The X-ray powder diffraction, transmission and fluorescence spectra have been investigated on BSO:Gd crystals. Scintillation properties of Gd3+ doped Bi4Si3O12 single crystals have been investigated. Doped with small amount of Gd2O3(1.0–6.0 mol%), the relative light yield and energy resolution of BSO crystals were improved significantly. The experimental data indicates that the sensitization effect of a small amount of Gd3+ doping enables the intrinsic defects reduce, and improve the light yield and a large amount of Gd3+ doping can cause the new crystal field distortion and further affect the intrinsic luminescence of BSO. These results indicate that BSO:Gd crystals could be one of the promising candidates for replacing BGO in some applications such as electromagnetic calorimeter and dual readout in nuclear or high energy physics. © 2020 The Japan Society of Applied Physics

1. Introduction

Scintillating crystals are materials that emit pulses of fluorescence by absorbing high-energy particles or rays, used in X-rays, gamma rays, detection of neutrons and other energetic particles. Scintillating crystals are the important key materials of detector and imaging technology in high-energy physics, nuclear medicine, safety inspection, industrial nondestructive inspection, space physics and nuclear prospecting.1–10) Bi4Si3O12(BSO) crystal has high hardness, short decay time, the advantages of low cost, good mechanical properties, stable chemical properties and good photoelectric performance that is a kind of new excellent scintillation material.11,12) Compared with the same structure of famous scintillator Bi4Ge3O12(BGO) crystal, the decay time of BSO crystal is about a third of BGO crystal and has better ability to resist radiation. BSO and BGO crystals are characterized by high density (6.80 g cm−3 and 7.13 g cm−3, respectively), short radiation length (1.15 cm and 1.12 cm, respectively), and high effective atomic number, which are considered as high quality scintillating crystals.11–17) It is considered one of the best candidate crystals for dual-readout calorimeters and homogenous hadron calorimeter with its ability of better separating the Cherenkov and scintillation light and collecting Cherenkov light signal effectively because of the short ultraviolet absorption edge for BSO crystal. Especially its low price advantage of BSO crystal for the applications in future large high energy lepton colliders about one hundred cubic meters has be unmatched for other crystals.12,18,19)

One of the important factors limiting its application of BSO crystal is the low light output, which is only about a fifth of that of a BGO crystal. So BSO crystal will be widely used to replace the expensive BGO crystal if the light output can be improved.20) Doping with rare earth elements is used to improve the scintillation properties of scintillation crystals. The properties of Ce3+, Nd3+, Eu3+, Yb3+, Dy3+, Cr3+, Eu3+, Sm3+, Ho3+, Tb3+, and Fe3+ doped BSO crystals have been investigated by many researchers.21–26) The relative light yield can be further improved with low concentration Dy3+ doped BSO crystals.27) The absorption edge moves in the short-wave direction for Eu3+ doped BSO crystal, that is typical for Eu-doped oxide materials is due to the charge transfer of Eu–O, which facilitates the efficient separation of the the Cherenkov and scintillation light.26) Therefore, rare-earth ion doping can improve the properties of BSO crystals to varying degrees. In this paper, pure BSO and BSO:Gd single crystals were grown in the same condition and the scintillation properties were investigated.

2. Experiment and methods

2.1. Synthesis and crystal growth

Pure BSO and BSO:Gd crystals with nominal concentrate of 1.0–6.0 mol% Gd2O3 were grown by the modified vertical Bridgman method. High purity Gd2O3(>4 N), SiO2(>4 N) and B2O3 (>5 N) were used as starting materials, as shown in Table 1. These starting materials were dried at 300 °C for 3 h before weighing accurately. These starting materials were weighed according to stoichiometric equation ratio of B2O3:SiO2 and doping concentrations of Gd2O3 (0, 1.0, 2.0, 4.0 and 6.0 mol%) and then mixed in a ball mill coated with polyethylene for 8 h. The mixture was then held at 800 °C for 8 h in SXW-1200 °C box-type furnace by Shanghai shiyian electric furnace co., Ltd. After sintering, it was ground to powder and mixed again in the FOCUSY F-P2000E ball mill

| Oxide | Quantity (g) | Gd3+ (mol%) | B2O3 (g) | SiO2 (g) |
|-------|--------------|-------------|----------|----------|
| Gd2O3(4 N) | 0.9574 g | 1.0 | 252.3787 | 47.6213 |
| 1.9149 g | 2.0 | 252.3787 | 47.6213 |
| 3.8298 g | 4.0 | 252.3787 | 47.6213 |
| 5.7447 g | 6.0 | 252.3787 | 47.6213 |

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Fig. 1. (Color online) The cut and polished BSO:Gd(1.0 mol%) crystals for optical properties testing.

Fig. 2. (Color online) The cut and polished BSO:Gd crystals for scintillation properties testing.

for 3 h. The samples were then put into the aluminum oxide crucible and held at 850 °C for 12 h in SXW-1200 °C box-type furnace to prepare pure BSO and BSO:Gd polycrystalline materials. The feed materials were then loaded into the Pt crucible to grow single crystal in Bridgman furnace. In this work, the polycrystalline powders were melted at 1075 °C which is about 50 °C higher than the melting point of BSO crystal for about 12 h to ensure complete melting. The lowing rate of the crucibles was 0.2–0.5 mm h\(^{-1}\). The orientation of the seed crystal was chosen to be (001) in all our growth runs.\(^{23,25,26}\) The crystal growth is performed by a self-made crucible furnace that is heated by electric resistance, and the furnace temperature is controlled by a DWT-702 precision temperature controller.

2.2. Optical properties measurement

In order to verify the phase purity of BSO crystal, a small section of the grown sample was hand-milled in an agate mortar for the X-ray diffraction analysis (XRD). The XRD analysis was carried out in the 2\(\theta\) range from 10° to 80° by using the Philips XPERT-MED X-ray diffractometer with a conventional CuK\(\alpha\) radiation. The grown single crystals were cut along the growth axis and polished into wafers of 2 mm thickness for the measurements of optical properties. The sample with the dimensions of 10 mm \(\times\) 10 mm \(\times\) 2 mm was cut and polished from the ingot for the study of optical properties, as shown in Fig. 1. The transmittance spectra of BSO:Gd crystals were measured by a double-beam ultra-violet-infrared spectrophotometer (Agilent Cary5000) from 200 to 900 nm at room temperature. The emission and excitation spectra of BSO:Gd crystals were measured by a fluorescence spectrometer (FLS-980).

2.3. Scintillation properties measurement

To compare the light output of BSO:Gd with that of CsI(Tl), a standard CsI (Tl) sample 10 mm \(\times\) 10 mm \(\times\) 8 mm in size was also measured under the same experimental conditions, and the Fig. 2 is the BSO:Gd samples. The relative light yield of BSO:Gd samples irradiated with a 137Cs \(\gamma\)-rays source (662 keV) in units of photoelectron numbers per MeV of energy deposition was measured by using a Hamamatsu CR105 photomultiplier tube (PMT) at room temperature. The crystals were air-coupled on one end to the PMT with bialkali photocathode. The output of the photomultiplier was shaped by a preamplifier and analyzed by a pulse height analyzer operated in the peak voltage mode. The energy resolution of BSO:Gd crystals was determined by using the same equipment excited with 662 keV \(\gamma\)-rays from a 137Cs source. The crystals were wrapped with Teflon tape and viewed on one end by a PMT (CR105) with optical grease. The yield of the photomultiplier was analyzed by a multichannel analyzer (DV4096). In all these measurements one end of the sample was coupled to the PMT with Dow Corning 200 fluid. A 137Cs source was employed to excite the samples.

3. Results and discussion

3.1. X-ray powder diffraction

Figure 3 is the XRD patterns of BSO:Gd crystals. There are additional peaks in the XRD patterns of BSO:Gd single crystals compared to PDF#33-0215-BSO in the Fig. 3. There is a peak around 27.5° next to the large diffraction peak and the intensity of the peak increased with increasing Gd\(^{3+}\) concentration. This diffraction peak is considered to be the diffraction peak of Gd\(^{3+}\) ions. There are some small diffraction peaks between 35 and 40° due to the impurities. In general, the diffraction peak does not change significantly with the increase of Gd\(^{3+}\) ions concentration, and it is basically the same as the XRD pattern of the unadulterated BSO crystal, indicating that the introduction of Gd\(^{3+}\) ions fails to significantly change the structure of the BSO crystal. The lattice parameters were calculated according to the XRD patterns, as shown in Table II. The lattice constants show a decreasing trend with the increase of concentration of Gd\(^{3+}\) ions. This indicates that a certain amount of Gd\(^{3+}\) ions enter the lattice of the BSO crystal. It is considered as Gd\(^{3+}\) ions replaces Bi\(^{3+}\) ions in the BSO crystal on the basis of the valence and ionic radius of Bi\(^{3+}\), Gd\(^{3+}\) and Si\(^{4+}\) ions in the crystal field because the rare earth ions are more likely to replace the ions with a similar radius. The lattice constants will decrease because the ionic radius of Gd\(^{3+}\) (0.091 nm) is less than Bi\(^{3+}\) (0.096 nm)\(^{29}\).

3.2. Transmission spectra

The transmittance spectra of pure and BSO:Gd(1.0 mol%) crystal samples have been measured in the range of 200–900 nm, as shown in Fig. 4. The transmittance spectra is a smooth curve. It shows that no absorption peaks appears. The main reason for this result is that the 4f sublayer of Gd\(^{3+}\) ions is semi-filled and has a closed shell structure. Typically, Gd\(^{3+}\) only shows 4f–4f transition in oxide materials in UV range. Furthermore, the absorption of 4f–4f transition of Gd\(^{3+}\) appears around 270 nm, and it is below the bandgap of BSO. The transmittance in the range from 300 to 350 nm is slightly improved because of Gd\(^{3+}\) doping. It may be that Gd\(^{3+}\) ions transfer energy to the BSO matrix because of the UV type B emission of Gd\(^{3+}\) around 312 nm due to \(^6P_{7/2} \rightarrow ^6S_{7/2}\) transitions increases noticeably, which increases the fluorescence performance and thus improves the ultraviolet transmittance of the material.\(^{30}\) The samples keep near 80% transmittance in the range from 350 to 900 nm. So the transmittance of BSO crystal does not almost change for a small amount of Gd\(^{3+}\) doped.
3.3. Emission and excitation spectra

The excitation wavelength of the emission spectrum is 280 nm. Figure 5(left) shows the luminous band of BSO crystal was modulated by the doped Gd\(^{3+}\) ions and the luminous intensity of BSO crystal slightly improves in doping 1\%mol Gd\(^{3+}\). With the increase of doping concentration, the excitation peak of BSO crystals decreased to different degrees, indicating that the scintillation performance of BSO crystals was expected to be improved by low-dose Gd\(^{3+}\) doping. The excitation wavelength of excitation spectrum is 480 nm. Figure 5 (right) shows that there are three luminous peaks in the excitation spectrum, all belonging to the excitation band of Gd\(^{3+}\), which are 276 nm, 291 nm and 312 nm, respectively, corresponding to \(^8S_{7/2} \rightarrow ^6I_{7/2}\), \(^8S_{7/2} \rightarrow ^6P_{3/2}\), \(^8S_{7/2} \rightarrow ^6P_{7/2}\) transitions. Among them, the intensity of \(^8S_{7/2} \rightarrow ^6I_{7/2}\) and \(^8S_{7/2} \rightarrow ^6P_{3/2}\) excitation bands increased with the decrease of Gd\(^{3+}\) doping concentration. Gd\(^{3+}\) ions transfer energy to the BSO matrix due to \(^6P_{3/2} \rightarrow ^8S_{7/2}\) transitions of Gd\(^{3+}\) ions increases noticeably, which increases the fluorescence performance and thus improves the ultraviolet transmittance of the material.

3.4. Relative light yield and energy resolution

Figure 6 (left) is the pulse height spectrum of 662 keV \(\gamma\)-rays from a \(^{137}\)Cs source with 600 V high voltage. The spectrum peak position corresponding to channel numbers of 1.0 mol% Gd\(^{3+}\) doped BSO crystal is slightly higher than the pure BSO crystal. However, the spectrum peak position corresponding to channels of 2.0 mol%, 4.0 mol% and 6.0 mol% Gd\(^{3+}\) doped BSO crystal are less than the pure BSO crystal. The relative light yields of BSO crystals decrease obviously with the increasing of Gd\(^{3+}\) content. It shows that the relative light yield increases with a small amount of Gd\(^{3+}\) doped BSO crystal. The relative light yield of BSO:Gd crystals are found to be 5.0\%, 5.1\%, 4.7\%, 4.0\% and 3.5\% of CsI(Tl) crystal for pure BSO, 1.0 mol%, 2.0 mol%, 4.0 mol% and 6.0 mol% Gd\(^{3+}\) doped BSO crystals, respectively. The scintillation properties of pure BSO and BSO:Gd crystals, as shown in Table III.

Figure 6(right) is the energy resolution of pure BSO and BSO:Gd crystals were determined by using the same equipment excited with 662 keV \(\gamma\)-rays from a \(^{137}\)Cs source with 850 V high voltage. The FWHM is almost the same for BSO:Gd crystals, but the peak position corresponding to channel numbers are different and the channel numbers of Gd\(^{3+}\) doped BSO crystal decrease with the increase of concentration obviously. The energy resolution is closely associated with the relative light yield. The small value of the energy resolution means better scintillation property. Table III indicates a decrease of the energy resolution with the

| Lattice constants | BSO | BSO:Gd (1.0 mol%) | BSO:Gd (2.0 mol%) | BSO:Gd (4.0 mol%) | BSO:Gd (6.0 mol%) |
|------------------|-----|-----------------|-----------------|-----------------|-----------------|
| \(a = b = c\) (nm) | 1.028 699 | 1.026 314 | 1.025 275 | 1.025 152 | 1.028 18 |
| esd | 0.000475 | 0.002 073 | 0.002 894 | 0.002 614 | 0.00098 |
| Vol (nm\(^3\)) | 1.088 59 | 1.081 04 | 1.077 76 | 1.077 37 | 1.086 94 |
decreasing of Gd$^{3+}$ content. However, the energy resolution of 1.0 mol% Gd$^{3+}$ doped BSO is better than pure BSO crystal. So the ability to distinguish between particles will be improved for BSO crystal with a small amount of Gd$^{3+}$ doped.

### 3.5. Luminescent mechanism

The relative light yield is improved and the energy resolution is reduced with a small amount of Gd$^{3+}$ doped BSO crystal. The scintillation properties have different degrees lowered with a large number of Gd$^{3+}$ doped. The reason is that the BSO crystal is intrinsic luminescent scintillator and the luminescence mechanism depends on the Bi$^{3+}$.\(^{31}\) The Bi$^{3+}$ is in the distortion of the octahedron with six ligand oxygen ions in the BSO crystal. The scintillation properties of BSO crystal are weakened because of its intrinsic defects.\(^{26}\) The sensitization effect of a small amount of Gd$^{3+}$ doping enables the intrinsic defects reduce, and improve the light yield. A large amount of Gd$^{3+}$ doping can cause the new crystal field distortion and further affect the intrinsic luminescence of Bi$^{3+}$.

### 4. Conclusions

BSO:Gd crystals were grown by the modified vertical Bridgeman method. The introduction of Gd$^{3+}$ ions fails to significantly change the structure of the BSO crystal. The transmittance in the range from 300 to 350 nm is slightly improved because of Gd$^{3+}$ doping. The luminous band of BSO crystal was modulated by the doped Gd$^{3+}$ ions and the luminous intensity of BSO crystal slightly improves in doping 1% mol Gd$^{3+}$. There are three luminous peaks in
the excitation spectrum, all belonging to the excitation band of Gd$^{3+}$ corresponding to $^8S_7/2 \rightarrow ^6I_{7/2}$, $^8S_7/2 \rightarrow ^6P_{3/2}$, $^8S_7/2 \rightarrow ^6P_{5/2}$ transitions. Under irradiation by $\gamma$-ray, the light yield of BSO doping with small doses of Gd$^{3+}$ increased obviously and the energy resolution improved significantly compared to pure BSO. The experimental data indicates that the sensitization effect of a small amount of Gd$^{3+}$ doping enables the intrinsic defects reduce, and improve the light yield and a large amount of Gd$^{3+}$ doping can cause the new crystal field distortion and further affect the intrinsic luminescence of Bi$^{3+}$. The improved light yield and energy resolution in the small doses of BSO:Gd crystals are considered as impressing achievement in the optimization of this good scintillator in some applications such as dual-readout calorimeters and homogeneous hadron calorimeter.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (61965001 and 61461001), the Ningxia Province Key Research and Development Program (2018BEE03015) and the Natural Science Foundation of Ningxia (2019AAC03103), the Ningxia first-class discipline and scientific research projects (electronic science and technology, No. NXYLXK2017A07). The authors thank Beijing Hamamatsu Photon Techniques INC. for scintillation light yield measurement, the Key Laboratory of North Minzu University (Physics and Photoelectric Information Functional Materials Sciences and Technology), the Ningxia advanced intelligent perception control innovation team, the Ningxia acoustooptic-crystals industrialization Innovation team and the Ningxia new solid electronic materials and Devices research and development innovation team.

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Table III. Presents the scintillation properties of pure BSO and BSO:Gd crystals.

| Crystal     | Gd$^{3+}$ | Relative light yield | Energy resolution |
|-------------|-----------|----------------------|-------------------|
| CsI(Tl)     | 100.0%    | —                    | —                 |
| BSO         | 5.0%      | 23.9%                | —                 |
| BSO:Gd      | 1.0 mol%  | 5.1%                 | 23.6%             |
|             | 2.0 mol%  | 4.7%                 | 24.9%             |
|             | 4.0 mol%  | 4.0%                 | 25.1%             |
|             | 6.0 mol%  | 3.5%                 | 29.5%             |

Fig. 6. (Color online) Pulse height spectra of BSO:Gd crystal samples excited with 662 keV $\gamma$-rays from 137Cs source (left, relative light yield and right, energy resolution).