Growth and scintillation properties of Tm^{3+} doped Bi$_4$Si$_3$O$_{12}$ single crystals

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Doping with Tm^{3+} of 0.5mol%, 1.0mol%, 2.0mol% in the Bi$_4$Si$_3$O$_{12}$ (BSO) crystals were grown by the modified vertical Bridgman method, respectively. The Bi$_4$Si$_3$O$_{12}$:Tm(BSO:Tm) polycrystalline powders are prepared of using two step sintering method, namely sintered 12h at 800℃, cool to room temperature, after grinded, then sintered 8~12h at 850℃, used for crystal growth. The transmittance of Bi$_4$Si$_3$O$_{12}$:Tm(BSO:Tm) crystals is about 80% and the optical quality of the crystal is same as the pure BSO crystal. The scintillation properties of BSO:Tm crystals are tested and analyzed. Pulse height measurements under γ-ray irradiation show that doping with 0.5 mol% Tm$_2$O$_3$ can increase the relative light yield of BSO from 5.0% to 5.2% of the CsI(Tl) crystal, consequently improving the ability to distinguish between particles. These results indicate that BSO:Tm crystals could be a promising candidate in some applications, such as electromagnetic and dual-readout calorimeters in nuclear or high energy physics.

1. Introduction

Bi$_4$Si$_3$O$_{12}$ (BSO) crystal is an excellent new scintillation material that has good mechanical properties, stable chemical properties, and good photoelectric performance [1,2]. It has aroused attention in recent years as a scintillation material because of its high hardness, short decay time, and low cost. Although the BSO crystal is a multifunctional crystal with excellent comprehensive performance, the crystal has not been applied yet. Due to the large difference in melting point and density of Bi$_2$O$_3$ and SiO$_2$, the phase relationship of BSO near the melting point is very complicated and component segregation is easily generated, which brings certain difficulties to the growth of large-sized BSO crystals. In recent years, BSO crystals are usually grown by the Czochralski and Bridgman methods. Although the researchers have separately prepared BSO crystals of large size and higher quality by two methods, there was still a gap the length of 230 mm crystals used in the standard calorimeter. The fundamental reason is that it is difficult to control the components segregation of the BSO crystal during crystal growth, resulting in low crystal yield. Therefore, in order to truly realize the application of BSO crystals, the preparation methods such as Czochralski and Bridgman methods also need to break through some technical barriers [3-9].

Another reason for limiting the application of BSO crystals is their low light output, which is only one-fifth of that of Bi$_4$Ge$_3$O$_{12}$ (BGO) crystals. Rare earth doping is the main way to increase crystal light output. The rare earth ion doping such as Eu^{3+}, Yb^{3+} and Dy^{3+} can improve the light output of BSO crystal to a certain extent, and the low-dose doping Dy^{3+} improves obviously the scintillation performance of BSO crystal [10-19]. Therefore, to clarify the reason why the intrinsic luminescence of Bi^{3+} in BSO crystal is low, it is possible to control the distortion of BSO crystal structure by specific rare earth ion doping and it is expected to comprehensively improve the scintillation performance of BSO crystal. So far, the scintillation properties of BSO crystals doped with Tm^{3+} have not been reported. In this paper, pure BSO and BSO:Tm single crystals were grown under the same conditions using the vertical Bridgman method. Transmission spectra and scintillation properties were investigated.

2. Experimental

2.1. Materials synthesis and crystal growth

High purity Tm$_2$O$_3$, SiO$_2$, and Bi$_2$O$_3$ were used as starting materials, as shown in Table 1. The BSO:Tm polycrystalline powders are prepared of using two step sintering method, namely sintered 12h at 800℃, cool to room temperature, after grinded, then sintered 8~12h at 850℃ in SXW-1200 ℃ box-type furnace by Shanghai shiyan electric furnace co., LTD., used for crystal growth.

The BSO and BSO:Tm crystals with nominal concentrate of 0.5–2.0 mol% Tm_2O_3 were grown by the modified vertical Bridgman method. The growth of BSO:Tm crystals use Pt crucible, resistance heating, temperature to 1070℃, stay a few hours, and then cooling at a rate of about 0.2 to 0.5 ℃/h, BSO melt namely in the direction of the crystallography seed into a single crystal. 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. Acording to the [19,20], the Tm ions will replace the position of Bi^{3+} in BSO crystals, therefore, the stoichiometric ratio of ingredients is according to $(Bi_{1-x}Tm_x)_4Si_3O_{12}$(x=0, 0.005, 0.01 and 0.02) in this experiment. The specific process of crystal growth for BSO and BSO:Tm can be referenced [17-19]. The BSO:Tm crystals were grown by the modified vertical Bridgman method, as shown in Fig.1 for BSO:Tm(1%).

2.2. Characterizations and methods

The XRD analysis was carried out in the 2θ range of 10–80°, using a Philips XPERT-MED X-ray diffractometer with conventional CuKα radiation with a small grown sample. The samples with the dimensions of 10mm×10mm×2mm and 10 mm × 10 mm × 8 mm were prepared respectively for the study of optical properties and scintillation properties, as shown in Fig. 2 and Fig. 3. Transmittance spectra of BSO:Tm crystals was measured by a double-beam ultraviolet–infrared spectrophotometer (Agilent Cary5000) from 200 to 900 nm at room temperature.

The relative light yield spectrum ,energy resolution and decay time spectrum of 662keV γ-rays from a 137Cs source with a high voltage of 600V ,850V and 1500Vwas obtained respectively in comparison with a standard CsI(Tl) sample of 10 mm × 10 mm × 8 mm was also measured under the same experimental conditions. The decay time was measured using a R9779 PMT with a multialkali photo cathode and a quartz window. For the details of measurement process and parameters, it can be referenced [17,19].

3. Results and discussions

3.1. X-ray powder diffraction

The XRD patterns of the pure BSO and BSO:Tm crystals are presented in Fig. 4 and the lattice parameters were calculated according to the XRD patterns, as shown in Table 2. The results show that the lattice constants of BSO crystals decrease with the increase of doped Tm^{3+} content. The Tm^{3+} is considered to replace Bi^{3+} in the crystal field of BSO; however, the lattice constants decrease because the ionic radius of Tm^{3+} (0.088 nm) is less than that of Bi^{3+} (0.096 nm).

Table 1. The starting materials of BSO:Tm crystals growth

Oxide	Quantity (g)	Tm^{3+} (mol%)	Bi_2O_3 (g)(5N)	SiO_2 (g) (4N)
	0.5096g	0.5	252.3787	47.6213
Tm_2O_3(4N)	1.0191g	1.0	252.3787	47.6213
	2.0383g	2.0	252.3787	47.6213

Fig. 1. The $(Bi_{0.99}Tm_{0.01})_4Si_3O_{12}$ crystal grown by the modified vertical Bridgman method
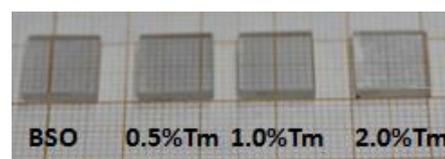
Fig. 2. The cut and polished BSO:Tm crystals for optical properties testing
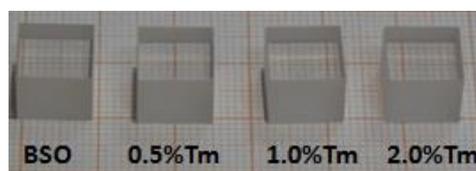
Fig. 3. The cut and polished BSO:Tm crystals for scintillation properties testing
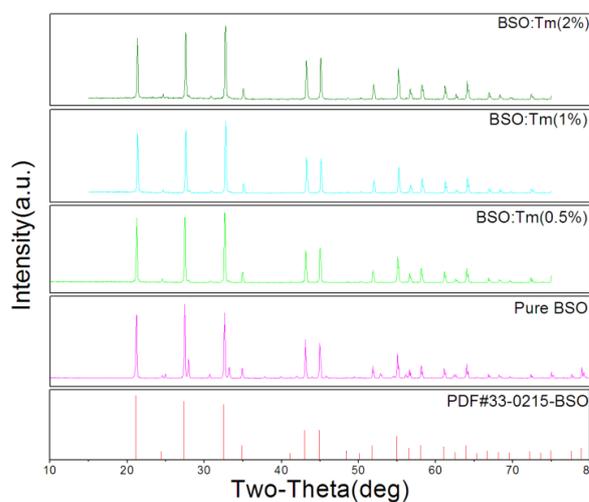
Fig. 4. XRD patterns of the pure BSO and BSO:Tm transparent crystal (color online)

Table 2. The lattice constant of pure BSO and BSO:Tm crystals

Lattice Constants	PDF#33-0215-Bi$_4$Si$_3$O$_{12}$	BSO	BSO:Tm (0.5mol%)	BSO:Tm (1.0mol%)	BSO:Tm (2.0mol%)
a=b=c (nm)	1.0291	1.028699	1.028145	1.026606	1.025978
esd	0	0.000475	0.000945	0.001813	0.002162
Vol(nm^3)	1.08987	1.08859	1.08683	1.08196	1.07998

3.2. Transmission spectra

The transmittance spectra of pure BSO and BSO:Tm crystal samples were measured in the range of 200–900 nm, as shown in Fig. 5. Obvious absorption peaks were observed, which were attributed to the transitions of 4f electrons of Tm^{3+}. The transmission spectra showed weak absorption peak at 360 nm and 480 nm and strong absorption peaks at 680 nm and 796 nm, respectively corresponding to transitions from the ground state $^3H_6$ to the excited states $^1D_2$, $^1G_4$, $^3F_2$, and $^3H_4$. As the concentration of Tm^{3+} increased, the absorptions became stronger. However, in the range of 350–900 nm the samples of BSO and BSO:Tm had nearly 80% transmittance. It was concluded that a small amount of Tm^{3+} doping did not change the transmittance of BSO crystals.
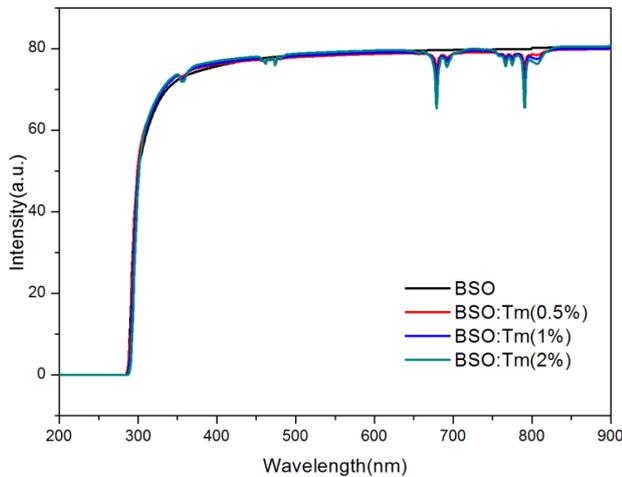
Fig. 5. Transmittance spectra of pure and BSO:Tm crystal samples (color online)

3.3. Relative light yield

Fig. 6 is the pulse height spectrum when excited by 662 keV γ-rays from a 137Cs source with a high voltage of 600V. The spectrum peak position and corresponding to channel numbers of 2.0 mol% Tm^{3+} doped BSO crystal is less than that of the pure BSO crystal. The relative light yields of BSO crystals decrease obviously with increasing of Tm^{3+} content. However, compared to pure BSO, the spectrum peak position and corresponding to channels of

0.5 mol% and 1.0 mol% Tm^{3+} doped BSO crystals are slightly higher than the pure BSO crystal. The results show that the relative light yield increases by doping the crystal with a small amount of Tm^{3+}; BSO:Tm crystals with 0.5 mol%, 1.0 mol%, and 2.0 mol% Tm^{3+} are found to have respective light yields of 5.0%, 5.2%, 5.2%, and 4.0% relative to CsI(Tl) crystals. Table 3 presents the scintillation properties of pure BSO and BSO:Tm crystals.
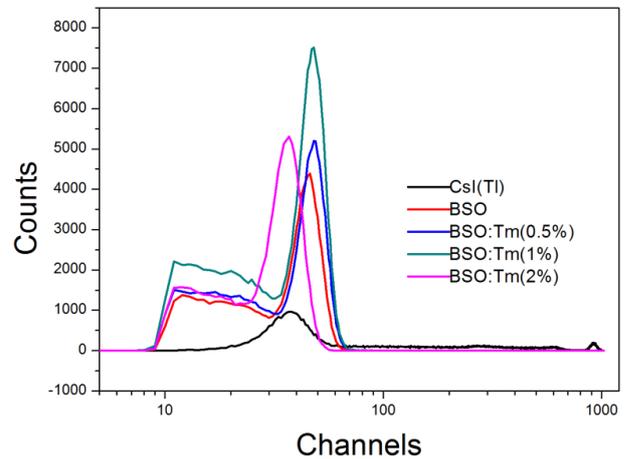
Fig. 6. Pulse height spectra of BSO:Tm crystal samples excited with 662 keV γ-rays from 137 Cs source (relative light yield) (color online)

Table 3. Presents the scintillation properties of pure BSO and BSO:Tm crystals

Crystals	Doping concentration	Relative light yield	Energy resolution
CsI(Tl)		100.0%	
BSO		5.0%	23.9%
	0.5%	5.2%	23.1%
BSO:Tm	1.0%	5.2%	19.4%
	2.0%	4.0%	24.0%

3.4. Energy resolution

Fig. 7 is the energy resolution of pure BSO and BSO:Tm crystals were determined by exciting with 662keV γ-rays from a 137Cs source with a high voltage of 850V. The energy resolution is given by

$$\eta = \frac{\Delta E}{E} = \frac{\Delta CH}{CH} = \frac{FWHM}{CH} \times 100\%$$

, where CH is the channel number of the peak position, and FWHM is the full width at half maximum of a given energy peak to the peak position. The pure BSO and BSO:Tm crystals have very similar FWHM of peaks, but the peak position and corresponding to channel numbers are different. The channel numbers of the BSO crystal doped with 2.0 mol% Tm^{3+} show an obvious decrease. The energy resolution is closely associated with the relative light yield; a smaller value of energy resolution correlates to better scintillation properties. Table 3 indicates a decrease in energy resolution with decreasing of Tm^{3+} content. Thus, the ability to distinguish between particles will be improved for BSO crystals with a small amount of Tm^{3+} dopant.
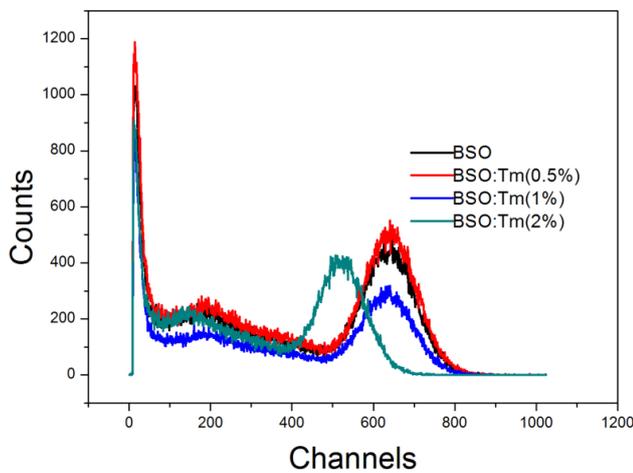
Fig. 7. Pulse height spectra of the BSO:Tm crystals excited with 662 keV γ-rays from a 137Cs source (energy resolution) (color online)

3.5. Decay time

Fig. 8 is the decay time spectrum for the 0.5 mol% Tm^{3+} doped BSO crystal, the Fast and Slow components are 14.40ns and 39.20ns, respectively. Table 4 shows the decay times for the pure BSO and BSO:Tm crystals. The results show that the fast components are almost unaffected by doping, and the slow components are reduced in BSO crystal doped with Tm^{3+}. It was concluded that the decay time of BSO crystals will reduce because of the introduction of Tm^{3+}. The cause of this is that the sensitization effect of the Tm^{3+} dopant enables the reduction of intrinsic defects, thus accelerating the optical transmission of Bi^{3+} luminescence; consequently, the decay time of BSO crystal is reduced with a small amount of Tm^{3+} dopant [19].

Fig. 8. The decay time spectrum of 0.5mol% Tm^{3+} doped BSO crystal, a) Fast component; b) Slow component (color online)

Table 4 . The results of the decay time for pure BSO and BSO:Tm crystals

Crystals	Doping concentration	Fast component (ns)	Slow component (ns)
BSO		14.00	65.00
	0.5%	14.40	39.20
BSO:Tm	1.0%	15.60	50.40
	2.0%	14.00	35.60

3.6. Luminescent mechanism

The relative light yield is improved and the energy resolution is reduced in BSO crystals doped with a small amount of Tm^{3+}. With the increasing of Tm^{3+} molar concentration, BSO crystals will show the trend of decrease in scintillation properties. This is because the BSO crystal is an intrinsic luminescent scintillator and the luminescence mechanism depends on the Bi^{3+}[16]. Bi^{3+} ions are in the distortion of the octahedron, with six ligand oxygen ions in the BSO crystal. The scintillation properties of the BSO crystal are weakened because of its intrinsic defects [21,22]. The sensitization effect of a small amount of Tm^{3+} dopant enables the reduction of intrinsic defects, and thus improves the light yield. A larger amount of Tm^{3+} dopant can cause the crystal field to distort further, consequently affecting the intrinsic luminescence of Bi^{3+}.

4. Conclusions

The initial raw materials of BSO:Tm crystals were prepared. After drying, weighing, mixing and sintering, the prepared Pt crucible was loaded into the crucible for the growth of BSO:Tm crystals by the modified vertical Bridgman method. Under γ-ray irradiation, the light yield of BSO doped with small doses of Tm^{3+} increased slightly, and the energy resolution improved mildly compared to pure BSO. The reason for this is that a small amount of Tm^{3+} doping sensitizes the Bi^{3+} ions. The sensitization

effect of a small amount of Tm^{3+} doping enables the reduction of intrinsic defects, and thus improves the light yield. A large amount of Tm^{3+} doping can cause the crystal field to distort further, consequently affecting the intrinsic luminescence of Bi^{3+}. The sensitization effect also accelerates the optical transmission of Bi^{3+} luminescence in BSO crystals, which reduces the decay time. The improved light yield and energy resolution in BSO:Tm crystals with small doses Tm^{3+} are considered an impressive achievement in the optimization of this scintillator, which is already suitable for applications such as dual-readout calorimeters and homogeneous hadron calorimeters.

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