Optical and Scintillation Properties of $Bi_4(Ge_xS_{1-x})_3O_{12}$ Single Crystal

X.-F. Xiao[a,b,c], J.-Y. Xu[b,*], B.-L. Lu[b], W. Cai[a], Y. Zhang[b], H. Shen[b], B.-B. Yang[b] and W.-D. Xiang[a]

[a]School of Materials Science and Engineering, Tongji University, Shanghai 201804, P.R. China
[b]School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai 201418, P.R. China
[c]Department of Fundamental Science, Beifang University of Nationalities, Yinchuan 750021, P.R. China

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The solid solution crystals, $Bi_4(Ge_xSi_{1-x})_3O_{12}$ (BGSO) with $x = 0$, 0.05, and 0.15, have been grown by the modified vertical Bridgman method. The as-grown crystals show 80% of transmittance with an absorption edge of 285 nm. The relative light yields of BGSO crystals are found to be 7.2%, 6.3%, and 4.2% of CsI(Tl) crystal for $x = 0$, 0.05, and 0.15, respectively. The energy resolutions of these crystals are 18.9%, 21.3%, and 24.7%, respectively, with PMT for 662 keV gamma rays at room temperature when exposed to ^{137}Cs γ-ray. The scintillation performance of BGSO crystals clearly deteriorates with the increase of Ge content. However, the appropriate number of germanium ions doped to BSO crystal can improve its crystallization behavior and effectively restrain component segregation. It is expected that large size crystals of BGSO will be grown and applied to the dual readout calorimeter in the nearest future.

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1. Introduction

Inorganic scintillators play an important role in radiation detection in many sectors of fundamental and applied research [1–3]. The eulytite crystals $Bi_4M_3O_{12}$ (M = Si, Ge) have attracted much attention because of their excellent characteristics such as luminescent decay constant, light output and energy resolution. These features make both $Bi_4Ge_3O_{12}$ (BGO) and $Bi_4Si_3O_{12}$ (BSO) materials useful for applications in nuclear physics, high energy physics, nuclear medical imaging and many industrial measuring systems [4, 5].

BGO crystal is one of the most important scintillators that has been used in CERN calorimeter in 1980's and PET medical devices in GE company in the past decades because of its excellent characteristics, such as high density (7.13 g/cm^3), short radiation length ($X = 1.12$ cm) and light output as large as 10% of NaI:Tl [6–10]. However, it has some drawbacks such as the slow decay time ($\tau = 300$ ns) and high cost of GeO_2 raw materials. Anyway, it is still regarded as a very good reference material and the values of light output of studied scintillators are often expressed in "BGO units" [11]. On the contrary, BSO crystal has a fast decay time of 100 ns but lower light yield (2% of NaI:Tl) [12, 13]. It is difficult to grow large size BSO crystal due to its serious segregation. Considering the same structure and similar scintillation properties, it is reasonable that the solid solution of BGO and BSO should be a novel scintillator. Recently, the dual-readout calorimeter is a hot research topic in high energy physics and BSO crystal is regarded as the most attractive candidate for the experimental programs in USA and Europe [5]. However, BSO crystal still cannot be grown large enough up to now due to its compositional segregation. If doping small amount of BGO into BSO, it may modify the crystallization behavior and be helpful to grow high quality crystals. $Bi_4(Ge_{0.5}Si_{0.5})_3O_{12}$ crystals were grown via the Czochralski method by Vaithianathan in 2005 [14, 15] and Jiang in 2011 [16], respectively. But the BGSO crystals with $x = 0.5$ showed unsatisfactory quality and scintillation properties [15]. Recently, we have reported the Bridgman growth of $Bi_4(Ge_xSi_{1-x})_3O_{12}$ crystals and obtained high quality crystal [17]. Thus, $Bi_4(Ge_xSi_{1-x})_3O_{12}$, the solid solution crystal of BGO and BSO, is expected to be an alternative material for the dual-readout calorimeter. In the present study, the optical properties, including the transmittance, refractive index and extinction coefficient, were measured. The scintillation properties of BGSO crystals with different content of Ge were investigated and compared with that of BGO and BSO crystals.

2. Experiments

2.1. Crystal growth

The 4N pure Bi_2O_3, GeO_2 and SiO_2 powders were used as starting materials. Polycrystalline BGSO powders should be synthesized by the solid state reaction to meet the request of crystal growth. For $x = 0.05$, the reaction is as following:

$$2\,Bi_2O_3 + 2.85\,SiO_2 + 0.15\,GeO_2 \longrightarrow Bi_4(Ge_{0.05}Si_{0.95})_3O_{12}.$$

The raw materials were weighed according to its stoichiometric composition after drying at 500 °C for 3 h. Then, these chemicals were mixed uniformly and sintered at 850 °C for 3 h. The sintered powders were then ground

*corresponding author; e-mail: xujiayue@sit.edu.cn

into fine particles. In order to obtain pure BGSO single phase, the process was repeated several times. Finally, the synthesized powders were loaded into a cylindrical platinum (Pt) crucible. The Pt crucible was designed with a seed well and the crucible size depended on the desired size of BGSO crystal. The size of the BSO crystal seed used first was 50 mm of length and 10 mm in diameter. The crucible with the charge was moved into the furnace and positioned the top of the seed. The furnace temperature was set to 50 °C higher than the melting point of BSO (1025 °C) and controlled by a DWT-702 automatic temperature controller with an accuracy of ±2 °C. The charge was kept at high temperature for several hours to ensure the seed was completely melted and to provide a stable temperature distribution. Then the crucible system was cooled at a rate of 0.2–0.5 °C/h to room temperature, and the crystal was taken out by tearing the crucible. The growth cycle was estimated according to the charge and the crucible size. The as-grown and polished BGSO ($x = 0.05$) crystals are shown in Fig. 1.

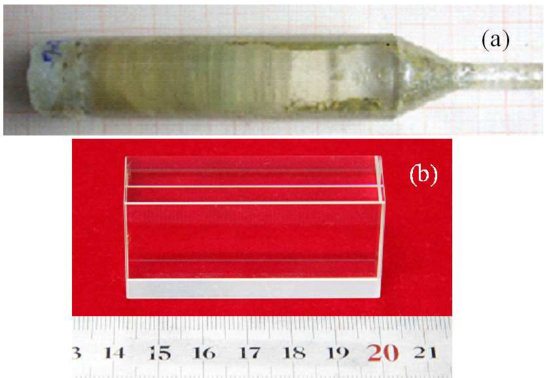

Fig. 1. (a) The as-grown and (b) polished $Bi_4(Ge_{0.05}Si_{0.95})_3O_{12}$ ingot.

2.2. *Optical properties measurements*

A sample with the dimensions of 10 × 10 × 2 mm^3 was cut and polished from the ingot for the study of optical properties. In order to verify the phase purity of BGSO 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 2θ range from 10° to 80° by using the Philips XPERT-MED X-ray diffractometer with a conventional Cu K_α radiation. The refractive index (n) and extinction coefficient (k) were measured from 260 to 800 nm by spectroscopic ellipsometer (GES5E). The transmittance spectrum of BGSO crystal was measured by UV-visible spectrophotometer (UV765PC) from 200 to 800 nm at room temperature.

2.3. *Scintillation properties measurement*

The samples having the dimensions of $10 \times 10 \times 8$ mm^3 was cut and polished from the ingot for the study of scintillation properties. The polished sample of BGSO crystal was wrapped with teflon sheet, as shown in Fig. 2. The light output of BGSO sample irradiated with a ^{137}Cs γ-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 (PHA) operated in the peak voltage mode. To compare the light output of BGSO with that of CsI(Tl), a standard CsI(Tl) sample 10 × 10 × 8 mm^3 in size (the left one in Fig. 2) was also measured under the same experimental conditions. The energy resolution of BGSO crystal was determined by using the same equipment excited with 662 keV γ-rays from a ^{137}Cs source.

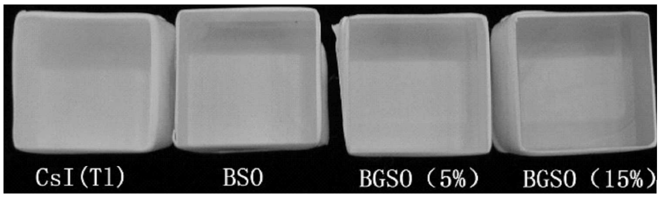

Fig. 2. The CsI(Tl) and BGSO crystal wrapped with teflon sheet.

3. Results and discussion

3.1. *Crystal growth and characterization*

BGO crystal is a congruent melting compound and can be grown by the Czochralski method or the vertical Bridgman method. BSO crystal, however, is an eutectic compound and the compositional deviation often occurs during crystal growth [5, 12, 13]. It was reported that the evaporation of Bi_2O_3 component made it difficult to grow large size and high quality crystal by the Czochralski method. BSO crystal was grown by the modified vertical Bridgman method with a local sealed crucible and a lower temperature gradient, but the as-grown crystal was covered by a layer of separated phase, exactly Bi-rich phase [5]. The phase segregation degraded the crystal quality, even caused the failure of crystal growth. Figure 1 shows the as-grown BGSO crystal with $x = 0.05$. Obviously, the as-grown crystal looks transparent although it still has a small amount of Bi-rich phase. Thus, it is expected that BSO crystal doped with small amount of BGO may restrain component segregation and improve its crystallization behavior.

The X-ray diffraction patterns of $Bi_4(Ge_xSi_{1-x})_3O_{12}$ (x = 0, 0.05, 0.15) crystals are presented in Fig. 3. The diffraction peaks of these samples can be well assigned to the eulytite structure (I-43d space system) with the characteristics of $Bi_4Si_3O_{12}$ phase. No new peak was found in Fig. 3 and it was inferred that BGO and BSO formed a solid solution crystal. The lattice parameters were calculated according to the XRD patterns. For

BGSO crystals with x = 0, 0.05 and 0.15, the lattice parameters are 1.028696, 1.030195 and 1.032636 nm, respectively. The results showed a linearly increase with the increase of Ge content, as we reported previously [17].

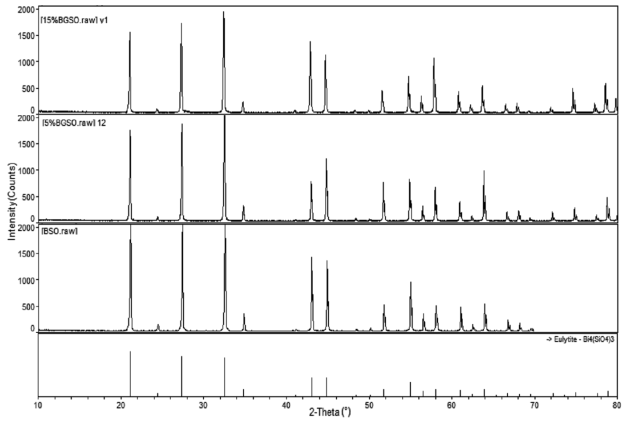

Fig. 3. XRD patterns of the BGSO transparent crystal.

3.2. Refractive index and transmittance

The refractive index (n) and extinction coefficient (k) were measured from 260 to 800 nm by spectroscopic ellipsometer (GES5E), as shown in Fig. 4. The refractive index of BGSO ($x = 0.05$) is 1.98 at 480 nm, very close to pure BSO crystal (2.06) [4]. The extinction coefficient decrease slightly from 0.4 to 0.2. Figure 5 shows the transmittance spectrum of $Bi_4(Ge_{0.05}Si_{0.95})_3O_{12}$ crystal by UV-visible spectrophotometer (UV765PC). It has about 80% of transmittance in the range of 350 to 800 nm with an absorption edge at 285 nm. The Fresnel reflectivity R and the ideal transmittance T were calculated from the following equations [18]:

$$R = \frac{(n-1)^2}{(n+1)^2}, \tag{1}$$

$$T = \frac{1-R}{1+R}, \tag{2}$$

where n is refractive index of the crystal. The ideal transmittance was also shown in Fig. 5. The results show that the BGSO ($x = 0.05$) crystal has good transmittance and the measured transmittance is very close to the ideal transmittance.

3.3. Scintillation properties

The pulse height spectrum of 662 keV γ-rays from a ^{137}Cs source is shown in Fig. 6. The light outputs of $Bi_4(Ge_xSi_{1-x})_3O_{12}$ crystals at room temperature are found to be 7.2%, 6.3%, and 4.2% of CsI(Tl) crystal for $x = 0, 0.05, 0.15$, respectively. The relative light yields of BGSO crystals decrease obviously with the increase of Ge content. It is reported that the light yields of CsI(Tl) and BGO crystal are 45%, 13% of NaI(Tl), respectively [19]. So the relative light yield of the BGSO crystals with

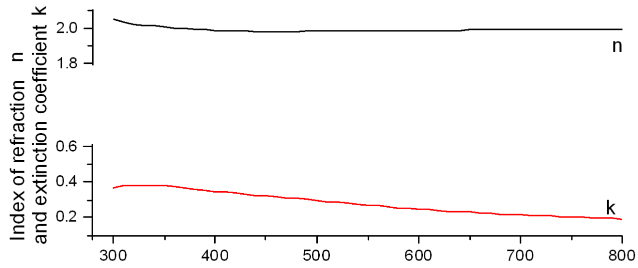

Fig. 4. Refractive index and extinction coefficient of the $Bi_4(Ge_{0.05}Si_{0.95})_3O_{12}$ crystal.

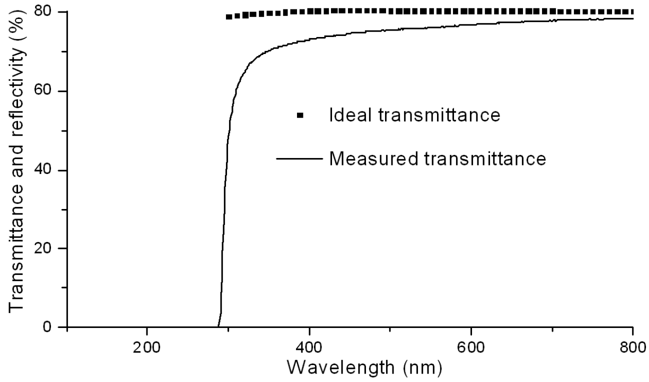

Fig. 5. Transmittance spectrum of $Bi_4(Ge_{0.05}Si_{0.95})_3O_{12}$ crystal.

$x = 0$, 0.05 and 0.1 are about 24.9%, 21.8%, and 14.5%, respectively, of BGO crystal. Table presents the scintillation properties of BGSO, BSO, and BGO crystals.

TABLE

Scintillation properties of BGSO, BSO and BGO crystals.

Sample	Relative light yield	Energy resolution at 662 keV γ-rays [%]	Ref.
BGO	100	16	[4]
BSO ($x = 0$)	24.9	18.9	this work
BGSO ($x = 0.05$)	21.8	21.3	this work
BGSO ($x = 0.10$)	15	29	[20]
BGSO ($x = 0.15$)	14.5	24.7	this work

The energy resolution of BGSO crystal was determined by using the same equipment excited with 662 keV γ-rays from a ^{137}Cs source at room temperature, as shown in Fig. 7. The energy resolution is the ratio of the full width at half maximum (FWHM) of a given energy peak to the peak position, usually expressed in %. The obtained peak is fitted to a Gaussian curve and the energy resolution is given by

$$\eta = \frac{\Delta E}{E} = \frac{\Delta \mathrm{CH}}{\mathrm{CH}} = \frac{\mathrm{FWHM}}{\mathrm{CH}} \times 100\%, \tag{3}$$

where CH is the channel number of peak position. The energy resolutions of the BGSO crystals compared

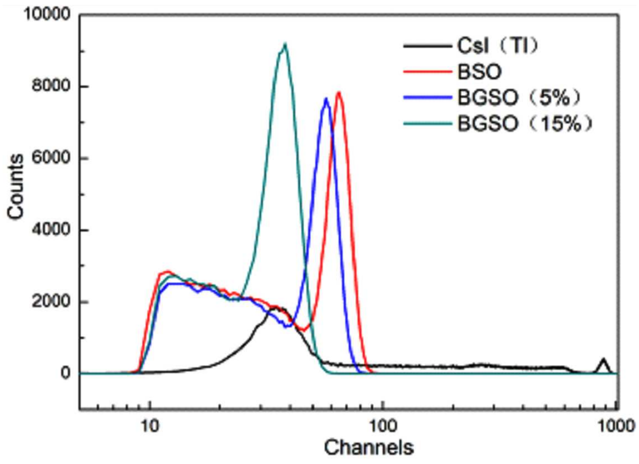

Fig. 6. Pulse height spectra of the BGSO crystals excited with 662 keV γ-rays from a ^{137}Cs source (relative light yield).

with BGO and BSO crystals are listed in Table. Due to lack of BGSO crystal with $x = 0.10$, we used the result from the literature [20]. The energy resolution is closely associated with light yield. The small value of the energy resolution means better scintillation property. Table indicates an increase of the energy resolution with the increase of Ge content. Although BGSO ($x = 0.10$) has a larger value than that of BGSO ($x = 0.15$), we note that this particular sample comes from a different growth series and a direct comparison makes little sense. The deterioration in energy resolution of the BGSO ($x = 0.10$) can be just related to the presence of imperfections, such as voids, bubble inclusions and other defects.

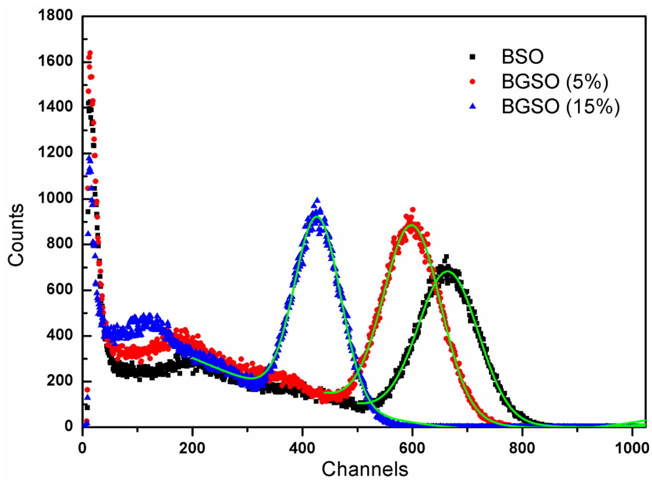

Fig. 7. Pulse height spectra of the BGSO crystals excited with 662 keV γ-rays from a ^{137}Cs source (points — experiment, solid lines — Gaussian fits).

Although BGO and BSO can form a solid solution crystal, the introduction of germanium ions to BSO crystal may affect the scintillation properties. As mentioned above, the relative light yield and the energy resolution of BGSO crystals decrease with the increase of Ge content. We mention here that BGO and BSO crystals are regarded as self-activated scintillators. Bi^{3+} is the luminescent center but the emission peaks of BGO and BSO are located at different wave numbers. It is found that BGSO crystal displays two luminescent peaks [21]. This competition degrades the scintillation properties. This is the reason why the BGSO ($x = 0.5$) crystal reported in literature [15] showed poor scintillation properties.

4. Conclusions

The $Bi_4(Ge_xSi_{1-x})_3O_{12}$ ($x = 0$, 0.05, 0.15) single crystals have been successfully grown by the modified vertical Bridgman method. The transparent BGSO single crystals have very good transmittance in the region of 350–800 nm with an absorption edge of 285 nm. The relative light yields of BGSO crystals are found to be 7.2%, 6.3%, and 4.2% of CsI(Tl) crystal and the energy resolutions of BGSO crystals are 18.9%, 21.3%, and 24.7% for $x = 0$, 0.05, and 0.15, respectively. Compared with pure BSO crystal, the mixed crystal BGSO has somewhat weaker scintillation properties due to the competition of two luminescent peaks. However, the crystallization behavior has been modified by doping a small amount of BGO in the BSO crystal and transparent BGSO crystals can be easily grown by the vertical Bridgman method. We can deduce it as an alternative for the application in the dual readout calorimeter.

Acknowledgments

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