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Synthesis, Growth and Scintillation Properties of Large Size $Bi_4Si_3O_{12}$ Crystals

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Abstract: Using stoichiometric $Si(OC_2H_5)_4$ and $Bi(NO_3)_3{\cdot}5H_2O$ as precursors and citric acid as solvent, polycrystalline $Bi_4Si_3O_{12}$ (BSO) powders were synthesized by Sol-Gel method and sintered at high temperature. Batch production of 250 g powders was realized. Using as-synthesized BSO powders and <001>-oriented BSO seeds, BSO crystals were grown in the vertical Bridgman furnace. The crystallization behavior was discussed and high quality BSO crystal up to 30 mm × 30 mm × 210 mm was obtained. The scintillation characteristics of BSO single crystals were investigated. The energy resolution of the BSO crystal was 18.9% and the relative light yield of the crystal was 7.2% compared with CsI(Tl) at the same conditions.

Key words: Sol-Gel method; $Bi_4Si_3O_{12}$ crystal; vertical Bridgman method; crystal growth; scintillation property

Bismuth silicate ($Bi_4Si_3O_{12}$, hereafter abbreviated as BSO) crystal has potential applications in high-energy physics, nuclear medical imaging, and geophysical exploration in the future[1-3]. Compared with widely used $Bi_4Ge_3O_{12}$ (BGO) crystal, BSO has some better scintillation properties such as a faster decay time, a greater radiation hardness and a lower raw material cost, so it is considered to be the substitute for an alternative to BGO crystals[4-5]. Recently, BSO crystal is regarded as the most attractive candidate for the large experimental programs of the dual-readout method (DREAM) projects in USA and Europe[6-7]. In addition, BSO crystal has shown to be a good host to incorporate trivalent rare earth ions along with their good electro-optical properties which make the RE^{3+} doped BSO crystals promising materials for optical amplifiers[8-9], or multifunctional optical laser devices[10].

BGO and BSO have the same structure and similar melting point, but different crystallization behavior[11]. BSO showed sever phase segregation during the crystal growth because Bi_2O_3 and SiO_2 have considerable differences in density and melting pointing[12]. In order to grow high quality BSO crystals, it is necessary to prepare stoichiometric raw materials with pure $Bi_4Si_3O_{12}$ phase. The solid state reaction is a common method. However, it has some disadvantages, including high reaction temperature, high volatility of Bi_2O_3 and difficulty of grinding the sintered sample. In fact, multiple-step sintering process was used to obtain pure BSO phase during Bridgman growth of BSO crystals[5]. Alternatively, the Sol-Gel method allows the synthesis of a material with a high homogeneity since the alkoxides are mixed at the molecular level in the solution[13]. In the present work, pure BSO powders were prepared by Sol-Gel method using stoichiometric $Si(OC_2H_5)_4$ and $Bi(NO_3)_3{\cdot}5H_2O$ as precursors and acetic acid as solvent. The as-synthesized powders were characterized by X-ray diffraction (XRD) and SEM. Large size and high quality BSO crystals were grown using as-synthesized powders. The scintillation characteristics of BSO single crystal, such as light yield and energy resolution, were investigated.

1 Experimental procedure

AR-grade reagents $Si(C_2H_5O)_4$, $Bi(NO_3)_3{\cdot}5H_2O$, $C_6H_8O_7{\cdot}H_2O$, C_2H_5OH and 68% HNO_3 were used in the experiment. The tetraethyl orthosilicate (TEOS) was pre-hydrolyzed in a closed system to prevent its volatility. 30 g citric acid, 250 mL water, 250 mL absolute ethyl alcohol, and 500 mL TEOS were put into a round flask with a plug at room temperature and mixed to a transparent solution under the magnetic stirring. $Bi(NO_3)_3$ solution was prepared by adding 1450 g $Bi(NO_3)_3{\cdot}5H_2O$ into 1000 mL 1.5 mol/L HNO_3 solution under the magnetic stirring for 1 h. Then the solution was slowly dropped to the pre-hydrolyzed TEOS solution with stirring. After 12 h gelling at room temperature, the transparent solution changed into a nearly trans-

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parent gel. The gel was dried in an air-blast oven step by step at 80℃/24 h, 110℃/24 h, 160℃/12 h and 230℃/12 h. The dried gel was grinded into fine powders and then heated slowly to 850℃ and hold for 12 h. The obtained powders were characterized by SEM and XRD.

As-synthesized BSO powders were pressed into dense disc and loaded into Pt crucible. <001>-oriented BSO seed with a size of Φ10 mm × 50 mm was inserted into the seed well in advance. The crucible with the charge was simple sealed and moved into the Bridgman furnace. The furnace temperature was set up to about 1080℃. The position of the crucible in the furnace was modified to ensure the top of the seed complete melting. Then the crucible was lowered down at a rate of ~ 0.5 mm/h. The crystal growth was performed at a temperature gradient of 40℃/cm and the growth cycle was about 15–20 d. When the growth was completed, the crucible was cooled to room temperature. As-grown crystal was checked and oriented by X-ray. Then it was cut into a block of 10 mm × 10 mm × 8 mm and then polished for measurement. The polished sample was wrapped with Teflon sheet. ^{137}Cs γ-ray source was used to excite the crystal at energy of 662 keV. Pulse height spectra were measured with the gamma emitting radioisotopes ^{137}Cs (662 keV). BSO scintillator is attached to a two inches bialkali photomultiplier tubes (PMT) to measure the pulse height spectra. Signals from PMT is fed to a low noise preamplifier and then shaping amplifier. The output signals are then fed into a 25 MHz flash analog-to-digital converter (FADC). A software threshold setting is applied to trigger an event using a self-trigger algorithm on the field programmable gate array (FPGA) chip of the FADC board. The FADC output is recorded and analyzed with a C++ data analysis program.

2 Results and discussion

2.1 Powders synthesis

The melting point of Bi_2O_3 is 850℃ and that of SiO_2 is about 1750℃, which means the sintering temperature for solid state reaction should be controlled under 850℃. It was found that some SiO_2 particles were wrapped by Bi_2O_3 in sintered raw materials and a white layer occurred on the top of the crystal boule during the Bridgman growth[5]. Sol-Gel method allows the synthesis of BSO pure phase by chemical reaction, but high volatility of TEOS is a problem. In order to keep the stoichiometric ratio of SiO_2: Bi_2O_3 (3:2), the excess TEOS even times of the ratio was used to compensate the volatility of TEOS[14]. Recently, Xie, *et al*[13] reported the Sol-Gel synthesis of BSO micro-crystals using the stoichiometric starting materials. The volatilization of TEOS was avoided by pre-hydrolysis of TEOS in a closed system and citric acid as the catalyst. However, only small amount of BSO powders were obtained and it is not suitable for crystal growth. In our experiment, we dedicated to batch production of pure phase BSO powders to meet the need of crystal growth. Based on the process, we optimized the synthesis parameters and realized 250 g batch production.

Fig. 1 shows the transparent gel and batch powders. The gel was dried in an oven at several temperatures step by step. Then they were grinded into fine powders and calcined at an optimum temperature of 850℃ for 12 h. XRD patterns of sintered BSO powders were shown in Fig. 2 and it revealed that a pure BSO phase has been obtained. Fig. 3 shows the morphology of dried gel powders and the sintered BSO polycrystalline. The clear crystal facets show that the BSO powders synthesized by the Sol-Gel method have a good crystallinity.

2.2 Crystal growth

According to the phase diagram of SiO_2-Bi_2O_3 system[10], BSO is a congruent compound with a melting point of 1025℃. It can be grown by the traditional methods, such as Czochralski[15] and Bridgman[5,16] method. The volatilization of Bi_2O_3 is the main problem during Czochralski growth while the segregation often occurred in the Bridgman growth. To prevent the segregation, the temperature should be controlled in a narrow range

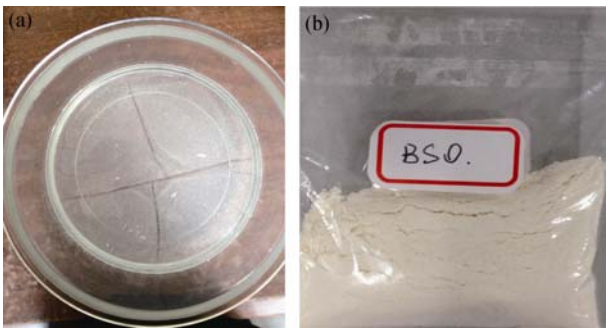

Fig. 1 The transparent gel (a) and 250 g batch BSO powders (b)

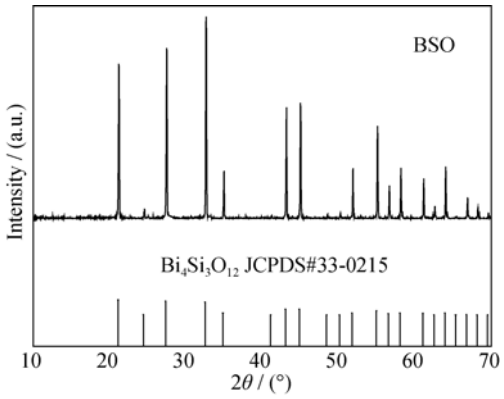

Fig. 2 XRD patterns of the sintered BSO

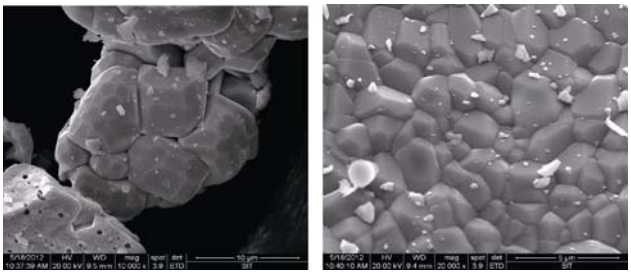

Fig. 3　SEM images of the dried gel powders (a) and the sintered BSO polycrystalline (b)

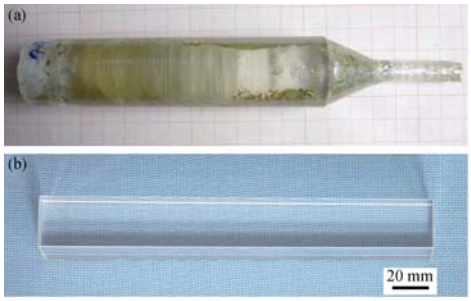

Fig. 4　Photos of as-grown *Φ*28 mm crystal (a) and polished crystal up to 30 mm × 30 mm × 210 mm (b)

(20–50℃) and the feed materials of pure phase BSO were necessary. Generally, polycrystalline BSO was prepared by solid state reaction of SiO_2 and Bi_2O_3 mixture at high temperature. The existence of impurity phases, such as SiO_2 particles, may result in a layer of white residual on the top of the crystal because SiO_2 has a higher melting point of 1720℃ and it is lighter than the melt of $Bi_4Si_3O_{12}$. In the experiment, crystalline $Bi_4Si_3O_{12}$ powders with a pure phase have been synthesized, as mentioned above.

Fig. 4(a) gives the Bridgman growth results using as-synthesized BSO powders. The as-grown crystal has a smooth surface, which means that the synthesized raw materials restrained phase segregation partly. However, there are still some white residuals on the top of the crystal. This may be caused by the incongruent characteristics of $Bi_4Si_3O_{12}$ compound[16-17]. When we grow *Φ*2″ BSO crystals, the segregation is so serious that the crystal growth usually failed in the last stage even using pure phase raw materials. By optimizing growth parameters, we have successfully grown long crystals. Fig. 4(b) shows a polished BSO crystal up to 30 mm × 30 mm × 210 mm. The crystal has good transmittance without visible macro-defects which shows that as-synthesized raw materials are suitable for BSO crystal growth.

2.3　Scintillation properties

The BSO crystal is optically coupled with PMT (CR105) and irradiated with 662 keV γ-rays from a ^{137}Cs source. The pulse height spectrum of 662 keV γ-rays from a ^{137}Cs source with 817 high voltage is shown in Fig. 5(a). The obtained photo peak is fitted to a Gaussian to evaluate the peak position and full-width at half maximum (FWHM) to obtain the energy resolution. The energy resolution measured at 662 keV is about 18.9% (FWHM). This energy resolution is similar to the former results[18], and a little lower than that of the literature[1, 15]. The same experimental setup is used to determine the light yield of BSO crystal as mentioned before for the pulse height measurement. The light output of BSO crystal is measured by comparing its response and the response of a calibrated CsI(Tl) crystal to 662 keV γ-rays from a ^{137}Cs source using windowed DV4096. The pulse height spectrum of 662 keV γ-rays from a ^{137}Cs source with 610 high voltage is shown in Fig. 5(b). The light output at room temperature is 7.2% of CsI(Tl) crystal. It is known that the relative light yields of the CsI(Tl) and BGO crystal are 45% and 13% of NaI(Tl)[19]. So the relative light yield of the BSO is about 25% of BGO crystal. Table 1 summarized the relative light yield and energy resolution compared with other literatures.

3　Conclusions

Polycrystalline BSO powders were synthesized by the Sol-Gel method from the starting materials of $Si(OC_2H_5)_4$ and $Bi(NO_3)_3{\cdot}5H_2O$ in stoichiometric ratio. A batch production of 250 g BSO powders was realized and the

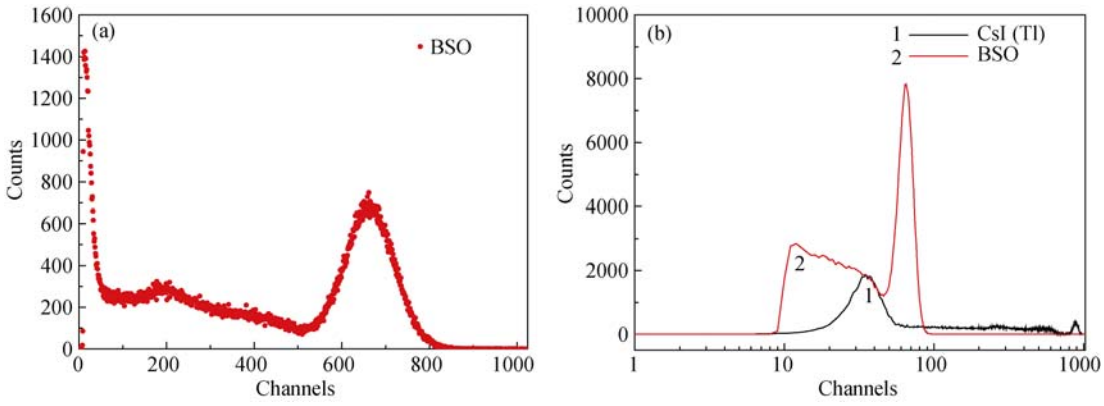

Fig. 5　Pulse height spectrum of the BSO crystal excited with 662 keV γ-rays from a ^{137}Cs source
(a) Energy resolution; (b) Relative light yield

Table 1 Scintillation properties of BSO crystals

Sample	Growth technique	Relative light yield	Energy resolution at 662 keV γ-rays/%	Reference
BSO	Bridgman	25	18.9	This work
BSO	Bridgman	20	31	[1]
BSO	Bridgman	25	22	[18]
BSO	Bridgman	23	18	[16]
BSO	Micro-pulling-down	21	33	[20]
BSO	Czochralski	26	22	[15]
BGO[a]	Czochralski	100	16	[1]

[a]BGO crystal is used as a reference for BSO crystal

as-synthesized raw materials were used in the growth of BSO crystals. Large size BSO crystal up to 30 mm × 30 mm × 210 mm has been obtained by the vertical Bridgman method. The energy resolution of BSO single crystal at 662 keV was measured as 18.9% (FWHM) and the relative light yield was obtained as 7.2% of CsI(Tl) crystal or 25% of BGO crystal. The results showed that Sol-Gel method is a potential approach to supply pure phase BSO feed materials for crystal growth.

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大尺寸硅酸铋晶体的原料合成、晶体生长及闪烁性能研究

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摘 要: 以 $Si(OC_2H_5)_4$ 和 $Bi(NO_3)_3{\cdot}5H_2O$ 作为前驱体、柠檬酸作为溶剂, 按化学计量比配料, 采用溶胶–凝胶法合成并经高温烧结制备了纯相 $Bi_4Si_3O_{12}$ 多晶粉末, 每批次可合成 250 g。以此为原料、<001 >取向 BSO 为籽晶, 在坩埚下降炉内生长了 BSO 晶体, 讨论了晶体的析晶行为, 获得了 30 mm × 30 mm × 210 mm 的高质量 BSO 晶体。闪烁性能测试表明, 该晶体能量分辨率为 18.9%, 光输出为同等条件下 CSI(T1)晶体的 7.2%。

关 键 词: 溶胶–凝胶法; 硅酸铋晶体; 坩埚下降法; 晶体生长; 闪烁性能

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