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The influence of temperature gradient on energy resolution of $Bi_4Ge_3O_{12}$ (BGO) crystal

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Abstract

In this work, we grew $Bi_4Ge_3O_{12}$ (BGO) crystals of two types by Bridgmen–Stockbarger technology in different temperature gradients and compared their optical transmissions and energy resolutions before and after ultraviolet irradiation. It was found that the optical transmissions and energy resolutions of the two types of BGO crystals are similar before UV-irradiation. After UV-irradiation, the optical transmissions at 480 nm of the first type of BGO crystals which were grown in higher temperature gradient cut down about 20% and their energy resolutions obviously deteriorated from about 12–18%. But the optical transmissions and energy resolutions of the second type of BGO crystals which were grown in lower temperature gradient keep unchanged on the whole. After 250 °C/4 h annealing, the optical transmissions and energy resolutions of the second type of BGO crystals can be completely recovered, whereas the optical transmissions and energy resolutions of the first type of BGO crystals cannot be completely recovered until through 600 °C/8 h annealing. The reason for the difference between the first and second type of BGO crystals is discussed.

Keywords: $Bi_4Ge_3O_{12}$ crystal; Energy resolution; Radiation damage

1. Introduction

Bismuth germanate $Bi_4Ge_3O_{12}$ is commonly abbreviated as BGO. When exposed to radiation of high energy particles or other sources such as gamma-rays, X-rays, BGO crystal will emit a green fluorescent light with a peak wavelength of 480 nm. With its high stopping power, high scintillation efficiency and non-hygroscopic, BGO crystal is a good scintillation material and has found a wide range of applications in high energy physics, nuclear physics, space physics, geological prospecting and other industries. At present, BGO has been also used in nuclear medicine diagnostic systems, particularly in Positron Emission Tomography (PET) as a scintillation material to detect pairs of 511 keV photons produced when a positron emitted from the positron emitter (^{11}C, ^{13}N, ^{15}O etc.) annihilates with an atomic electron. So good energy resolution and radiation hardness of BGO crystal is necessary for PET. Previous studies indicated that the presence of impurities such as Fe, Pb is the cause of radiation damage of BGO crystal [1–3]. Not long before, Gusev [4], reported the influence of temperature gradient on radiation damage of BGO crystal grown by Czochralski technique. In this paper, we will discuss the influence of temperature gradient on energy resolution and radiation damage of BGO crystal grown by Bridgman–Stockbarger technique.

2. Experiment

2.1. Crystal growth and preparation of samples

Raw powder materials with purity of 99.99% were mixed according to stoichiometry of Bi_2O_3:GeO_2 = 2:3(mol%). A Pt crucible with this mixture was placed in a self-made Bridgman–Stockbarger furnace and lowered down at a specific speed in the course of crystal growth. The growth conditions are described in Table 1. Crystals of first type I, samples 1–5, were grown in temperature gradients higher than 44 °C/cm, and crystals of second type II, samples 6–8, were grown in temperature gradients lower than 25 °C/cm.

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Table 1
Information of samples used in this experiment

	Sample numbers							
	1	2	3	4	5	6	7	8
Temperature grade near solid–liquid interface (°C cm^{-1})	60	62	56	45	44	20	25	23
Maximum temperature of melt (°C)	1333	1300	1370	1332	1318	1230	1250	1245

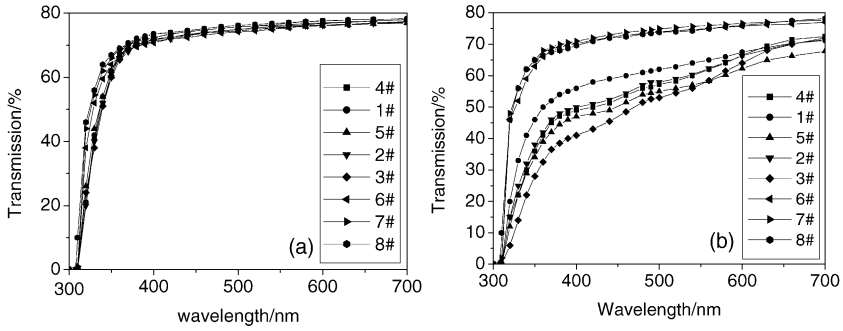

Fig. 1. Transmission spectra of BGO samples before (a) and after UV-irradiation (b).

Table 2
Energy resolution (%) of BGO samples before and after UV-irradiation

	Sample numbers							
	1	2	3	4	5	6	7	8
Before UV-irradiation	11.4	12.4	12.6	12.0	12.4	12.1	12.5	12.2
After UV-irradiation	16.5	18.2	19.6	18.2	18.3	13.0	12.9	12.7

Table 3
Energy resolution (%) of irradiated BGO samples after 250 °C/4 h annealing

	Sample numbers							
	1	2	3	4	5	6	7	8
Energy resolution (%)	13.5	14.1	13.6	14.2	14.7	12.2	12.3	12.3

All crystals of two types were colorless and transparent without any scattering under a laser beam of 650 nm. The samples with dimensions of 15 mm × 15 mm × 50 mm were cut from middle part of crystal boules and all faces polished for transmission measurement.

2.2. Scintillation property measurements

First, all samples were annealed at 250 °C/4 h and then irradiated with 80 W mercury vapor lamp for 60 min. The transmissions of BGO crystals before and after UV-irradiation were measured using a UV-265 spectrophotometer made by SHIMADZU. The light path of samples was 50 mm. The energy resolutions of BGO crystals were measured by using a multi-channel analyzer with ^{137}Cs radiation source. The content of major elements in BGO crystal were quantitatively determined by X-ray fluorescence spectral (XFS) analysis. The trace elements were measured by glow discharge mass spectrometry(GDMS). Both the samples for XFS and GDMS were also cut from the middle part of boules.

3. Results and discussion

Measurement results indicate that before UV-irradiation the optical transmission spectra of the two types of crystals are similar and their energy resolutions are in the same range of 11.4–12.6% that means the two types of crystal have close discriminative ability for gamma–ray of ^{137}Cs (see Fig. 1a and Table 2).

Compared with crystals before UV-irradiation, the absolute degradations of transmitance of crystal type I were obviously found to be lower than 20% and they were tinted faint gray after UV-irradiation, their energy resolutions change dramatically from about 12–18%, whereas the transmissions

Table 4
Energy resolution of irradiated BGO samples after 600 °C annealing

	Sample numbers		
	2	5	6
Energy resolution (%)	11.6	12.5	12.3

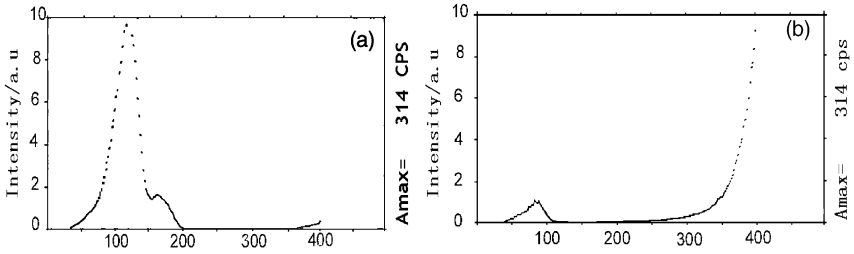

Fig. 2. Thermoluminescence curves of BGO crystals. (a) Grown with higher temperature gradient and (b) with lower temperature gradient.

Table 5
Content of trace elements in BGO crystals (ppm)

Sample number	Mg	Al	Ca	Ti	Cr	Fe	Mn	Ni	Co	Pb
1	0.59	1.01	1.13	0.18	0.41	0.23	0.76	1.61	0.25	0.08
6	0.11	1.36	0.47	0.06	0.26	0.30	0.79	1.07	0.12	0.08

and energy resolutions of crystal type II keep unchanged on the whole (see Fig. 1b and Table 2).

After 250 °C/4 h (Table 3) annealing, the energy resolutions of crystal type II recover to same level as before UV-irradiation, but for crystal type I, they could recover completely only through annealing at 600 °C/8 h (see Table 4).

Irradiated by ultraviolet light, the stimulated carriers could be captured by traps caused by defects in crystal. When the UV-irradiated crystals were heated from room temperature the captured carriers could be released out and complex with capture centre giving signals of thermoluminescence. The thermoluminescence curves of the two types of UV-irradiated crystal with heating speed of 2 °C/min are displayed in Fig. 2. There is significant difference between the two thermoluminescence curves. The thermoluminescence curve for crystal type II has only a weak peak at 85 °C (see Fig. 2b), whereas, besides at 85 °C, two strong peaks at 130 and 170 °C appear on the thermoluminescence curve for crystal type I (see Fig. 2a).

The position of thermoluminescence peak depends on the depth of the trap. The higher the temperature corresponds to thermoluminescence peak, the deeper the trap exists in crystal. So we may infer that the traps corresponded to defects in crystal are deeper and the defects are more dence in crystal type I.

According to the viewpoint of Yin [2], the radiation damage of BGO crystal is caused by the existence of oxygen ion vacancies created by unequal valence exchange of Ge^{4+} with impurity ions, such as Fe^{3+}, Pb^{2+} and Cr^{3+}. But the result of GDMS analysis indicated that the contents of these impurity ions, such as Fe^{3+}, Pb^{2+} and Cr^{3+}, are all less than 1 ppm (see Table 5). It means that the difference of energy resolutions between two types of BGO crystals after UV-irradiation is not caused by existence of impurity ions, such as Fe^{3+}, Pb^{2+} and Cr^{3+}.

From Table 1, it can be seen that crystal type I, such as samples of 1–5, were grown in higher temperature gradients and the temperatures of melting zone in furnace are higher than those for crystal type II thus leading to the easier volatilization of Bi_2O_3 in BGO melt. The results of XFS analysis show that the content of Bi_2O_3 in BGO crystal is less than the content of Bi_2O_3 in stoichiometry, Bi_2O_3:GeO_2 = 74.81%:25.19% (wt.%) (See Table 6). The content of Bi_2O_3 in crystal sample 4 of crystal type I is less than that in crystal sample 6 of crystal type II.

Table 6
Content of major elements in BGO crystals

	Sample number	
	4	6
Concentration of GeO_2 (wt.%)	25.30	25.27
Concentration of Bi_2O_3 (wt.%)	74.70	74.73

The volatilization of Bi_2O_3 in the melt makes appearance of vacancies of Bi^{3+} and O^{2-}. In fact, there are many vacancies remained in crystal at high temperature during growing. The equilibrium amount of vacancies in crystal depends on the temperature of crystal:

$$N \sim \exp\left(-\frac{E_v}{KT}\right)$$

Here, N is the equilibrium amount of vacancies in crystal, E_v is the energy needed for creating these vacancies, K is Boltzman constant, and T is the absolute temperature. When crystal was draw down at higher temperature, for example for crystal type I, It was cooled quickly, the vacancies in crystal did not move to the surface of crystal in time so being in over saturation condition and more vacancies remained. The vacancies of O^{2-} are acting as electron traps that make damage under UV-ray irradiation.

4. Conclusion

1. The measurement results of transmission and energy resolution for the two types of crystals were similar before UV-irradiation.

2. The trasmittance and energy resolutions for crystal type I change dramatically, whereas they would keep fixed on the whole for crystal type II after UV-irradiation.
3. The trasmittance and energy resolutions for the type II of UV-irradiated crystals could be completely recovered through 250 °C/4 h annealing, but the trasmittance and energy resolutions for the type I of UV-irradiated crystals could not be recovered until through 600 °C/8 h annealing.
4. The radiation damage of crystal type I might be caused by the existence of the deeper and denser traps of defects in crystals.

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