

Engineering of mixed $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$ scintillation crystals

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A full range of BGSO crystals from BGO to BSO was grown by the Czochralksi method. A set of procedures such as changing of stoichiometry, recrystallization and thermal treatment was applied to improve optical and scintillation parameters of the crystals. The relationships between scintillation yield, energy resolution, decay constants and $\text{Si}^{4+}/\text{Ge}^{4+}$ ratio in the crystals are discussed with regard to ongoing experiments on high energy physics. Crystal composition with better energy resolution 16.2 % at 662 keV irradiation was obtained.

Keywords: scintillators, BGSO, oxides, crystal growth.

Методом Чохральського вирощено кристали повного ряду твердих розчинів $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$ (BGSO) від BSO до BGO. Для удосконалення оптичного і сцинтиляційного якості кристалів використано такі технологічні процедури, як зміщення стехіометрії, перекристалізація і післяростовий відпал. Обсуджується вплив співвідношення іонів $\text{Si}^{4+}/\text{Ge}^{4+}$ на світловий вихід, енергетичне розрешення і час затухання сцинтиляцій. Отримано кристалічну композицію BGSO з найкращим енергетичним розрешенням 16.2 % при облученні гамма-квантами 662 кеВ.

Інженерія змішаних сцинтиляційних кристалів $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$. *Є.Галенін, М.Біатов, Я.Герасимов, Б.Гриньов, О.Сідлецький, В.Баранов, Ю.Будагов, Ю.Давидов, В.Глаголев.*

Методом Чохральського вирощено низку кристалів твердих розчинів $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$ (BGSO) від BSO до BGO. З метою вдосконалення оптичних та сцинтиляційних характеристик кристалів застосовано такі технологічні процедури, як зміщення стехіометрії, перекристалізація та післяростовий відпал. Проведено дослідження впливу співвідношення іонів $\text{Si}^{4+}/\text{Ge}^{4+}$ на світловий вихід, енергетичне розділення та час загасання сцинтиляцій. Отримано кристалічну композицію BGSO з найкращим енергетичним розділенням 16.2 % при збудженні гама-квантами 662 кеВ.

1. Introduction

There is a demand for novel dense and cheap scintillation crystals with high efficient atomic number for utilization in high energy physics, in particular, in new projects on elementary particle physics including the projects aimed at the search for

electron-muon conversion. For example, in Mu2e project in Fermilab, scintillators with the size of $3 \times 3 \times 20 \text{ cm}^3$ should possess the spatial resolution $\sigma_{r,z} = 1 \text{ cm}$, the time resolution $\approx 0.5 \text{ ns}$, and the decay time $< 100 \text{ ns}$ [1, 2]. Lead tungstate (PbWO_4) light output is too small to achieve the needed energy resolution.

$\text{Lu}_{2x}\text{Y}_{2-2x}\text{SiO}_5\text{:Ce}$ (LYSO:Ce) crystals, which were planned to be used in the Mu2e project [3], meet these requirements. However, LYSO:Ce contains up to 90 wt.% of Lu_2O_3 which is very expensive raw material.

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) crystals with the high density of 7.13 g/cm^3 , the high atomic number (74), and the radiation hardness of $10^5\text{--}10^6$ rad performed well in L3 detector of Large Electron-Positron Collider (LEP) in CERN [4]. However, 300 ns scintillation decay time in BGO does not meet the requirements of Mu2e and similar projects. The dramatic increase of germanium oxide raw material price in recent years results in increase of BGO production cost by 2–3 times. Meanwhile, the latter does not relate to bismuth silicate $\text{Bi}_4\text{Si}_3\text{O}_{12}$ (BSO), which is the BGO analog with the same eulitine crystalline structure. Despite of lower light yield in BSO (2000 ph/MeV vs. 8000 ph/MeV in BGO) and worse energy resolution at 662 keV (20–25 % vs. 9–12 % in BGO), the BSO decay time is significantly faster (100 ns vs. 300 ns in BGO). The BSO density (6.8 g/cm^3) is similar to BGO. The main drawback of BSO is the difficulty to obtain large crystals owing to incongruent melting of this composition.

Transfer to mixed crystals with eulitine structure by partial substitution of Ge by Si in the host [5, 6] is one of the possible ways to overcome this complication. There is a continuous range of solid solutions in $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$ (BGSO) system. Characteristics of the BGSO crystals obtained by the Stockbarger and Czochralski methods [7, 8] are similar rather to BSO than to BGO crystal. The obtained energy resolution in BGSO at 662 keV was not better than 19 % [8]. Authors claim this effect to large quantity of bubbles and foreign phase inclusions. Since future high energy physics experiments require large amount of the high quality crystals with similar characteristics [9], the methods of their obtaining must be optimized.

In this work we describe in detail the obtaining of improved BGSO crystals by the Czochralski method. The Si/Ge ratio, melt stoichiometry, recrystallization and post-growth annealing conditions are optimized.

2. Experimental

Bismuth with purity of 99.999 %, germanium and silicon oxides both with the purity of 99.99 % were taken as raw materials. Crystals were grown from stoichiometric mixtures with the common

formulae $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$, where $x = 0, 0.1, 0.4, 0.7, 0.9, 1$. After mixing and homogenization of the oxides the obtained mixtures were calcined at 850°C during 10 h to obtain the eulitine phase by solid state reaction. The upper and more transparent parts of ingots previously grown from the stoichiometric mixtures of the oxides were used as the raw materials at recrystallization.

The crystals with 20 mm diameter were grown by the Czochralski method using Pt crucibles with RF heating. Pulling rates were in the range of 0.5–2 mm/h, crystal rotation rates were 10–30 rot/min. {100} growth orientation was set with BGO seed. To reduce the amount of growth runs the effect of melt stoichiometry, as well as effect of recrystallization were studied only with the crystals at $x = 0$ (BSO composition).

Samples of the crystals with the sizes of $4\times 4\times 6 \text{ mm}^3$ were fabricated for scintillation measurements and $10\times 10\times 2 \text{ mm}^3$ were fabricated for optical and X-ray luminescence measurements, all faces are polished. Post-growth annealing of the samples was carried out in air at 850°C during 10 h.

Optical transmission spectra were measured by Specord40 spectrophotometer in 200–800 nm wavelengths range. X-ray luminescence spectra of the BGSO samples were obtained using KSVU-23 spectrometric complex and REIS X-ray apparatus at voltage of 40 kV at X-ray tube and current of 30 mA. Signal passes through the sample were recorded with FEU-100 photomultiplier (PMT) with the spectral sensitivity region of 160–850 nm.

The scintillation characteristics of the samples were studied at 662 keV irradiation by γ -sources ^{137}Cs . The samples were coupled to a PMT photocathode with optical grease, the rest of faces were covered with PTFE tape. Light output and energy resolution measurements were made by using Canberra setup consisting of the PMT Hamamatsu R1307, 2007B scintillation pre-amplifier, 2022 spectroscopy amplifier, 3002D HV power supply, Multiport II multichannel analyzer and 2100 NIM Bin/power supply.

Decay time were studied at test stand using EMI9813B PMT. Signals from the PMT without additional amplification were sent to ADC 2249W (LeCroy) and used for triggering of data acquisition as well. For this purpose, electronic modules of NIM and CAMAC standards were utilized. The scintillation decay constants were evaluated

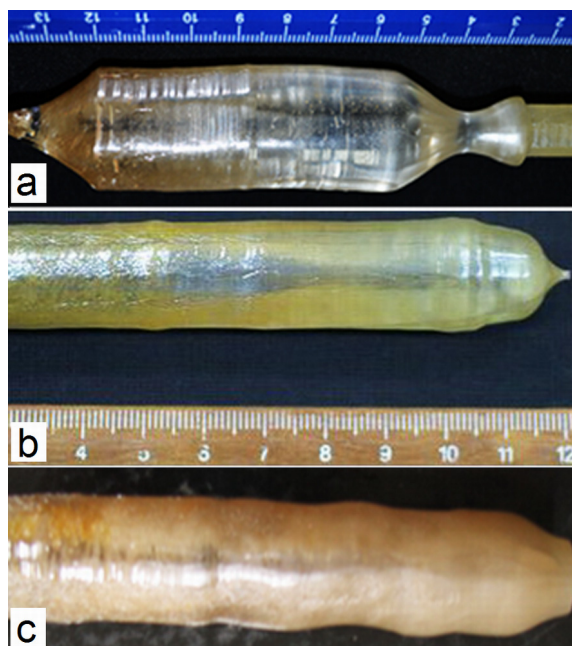


Fig. 1. BSO crystals grown with different Bi_2O_3 excess in melt: a — 0.5 mol.%; b — 2 mol.%; c — 3 mol.%.

from the positions of the full absorption peaks versus the ADC time gate under the 662 keV γ -quanta irradiation from ^{137}Cs source.

3. Results and discussion

3.1. Effect of melt non-stoichiometry

Control of melt stoichiometry is of special importance at growth of crystals with the eulitine structure [10, 11] due to bismuth oxide evaporation from the melts. This leads to deviation of melt stoichiometry and formation of foreign phase inclusions in the crystals. To overcome this complication 3 mol.% excess of Bi_2O_3 was introduced into the melt at BSGO growth [6]. However, excess of SiO_2 in the melt, if the evaporation rate is smaller than expected, might also deteriorate the crystal parameters. The optimal value of bismuth oxide excess introduced into the melt should be determined.

In this paper the impact of melt composition deviation from the stoichiometry to crystal quality was studied at $x = 0$ (BSO) with the Bi_2O_3 excess of 0.5 mol.%, 2 mol.% and 3 mol.% relatively to the stoichiometric composition. Photos of the crystals grown with the different Bi_2O_3 excesses are presented in Fig. 1. At 0.5 mol.% excess the most of the crystal volume looks transparent with almost no coloration. No distinct absorption bands are

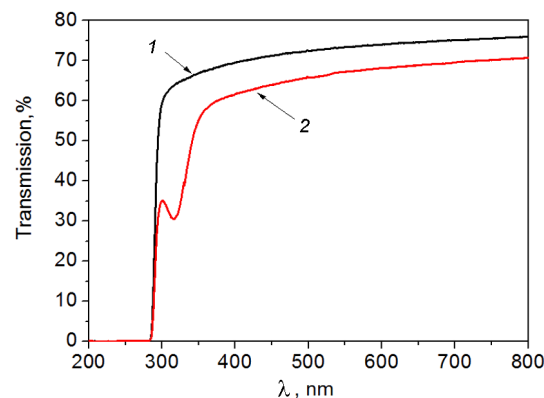


Fig. 2. Transmission spectra of BSO crystals grown from melt with different stoichiometry: 1 — Bi_2O_3 excess 0.5 mol.%, 2 — Bi_2O_3 excess 3 mol.%.

observed at wavelength of >300 nm (Fig. 2). Increasing the Bi_2O_3 excess up to 2 mol.% leads to greenish coloration and worsening of the transparency. At 3 mol.% of Bi_2O_3 excess the crystal surface is opaque and the boule has beige coloration. Appearance of the new absorption peak near 320 nm in the spectrum of this crystal (Fig. 2) and the coloration can be attributed to presence of the foreign phases with another stoichiometry. The coloration arises, because the foreign phases, for example, silenite phase [12], have smaller bandgaps and, as the issue, longer wavelength of the fundamental absorption peak than that in the eulitine phase. The crystals grown from melt with the stoichiometric ratio of oxides contain a lot inclusions and colored precipitates of other phases. More probably, the optimal bismuth oxide excess also depends on the Si/Ge ratio and thermal conditions of the growth.

3.2. Effect of recrystallization

It is known that BGO crystal quality can be improved by recrystallization of the grown crystals, i.e. upper parts of the crystals grown from the mixture of powders are loaded into the crucible and the growth process is repeated [13]. This provided an improvement of the crystal transparency and decrease of the quantity of gaseous admixtures and the foreign phase inclusions. By the analogy, the effect of recrystallization on optical transmittance was verified with the BSO grown from melt with the stoichiometric ratio of the oxides. The absorption peaked at 320 nm on the BSO transmission spectrum (Fig. 3) disappears after the recrystallization (Fig. 3). This ab-

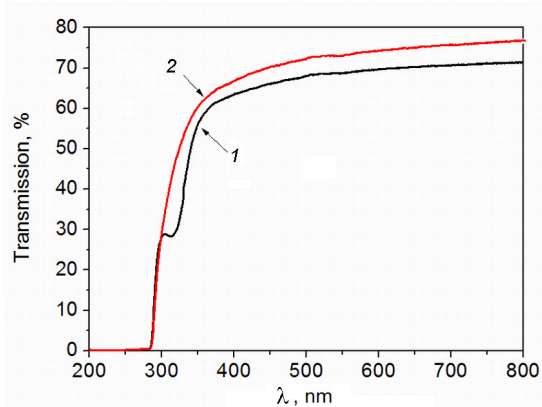


Fig. 3. Optical transmission spectra of BSO crystals: 1 — grown from stoichiometric ratio of oxides, 2 — recrystallized.

sorption peak is similar to that observed in the crystals grown from the raw material with 3 mol.% of Bi_2O_3 excess (see Fig. 2). Evidently, likewise in the case of stoichiometry shift, it is caused by the foreign phases presence in the crystals.

3.3. Effect of post-growth annealing

The method for improvement of energy resolution of the BGO crystals by high-temperature annealing in oxidizing atmosphere [14, 15] can be implemented for BSO and BGSO crystals having the same structure and similar optical characteristics. The transmission of two BGSO crystals with different Si/Ge ratios is improved in all the measured wavelength range after annealing during 10 h at 850°C (Fig. 4). In particular, it increases by 5 % and 7 % for $x = 0.1$ and $x = 0.9$ in the maximum of luminescence band at 480 nm. The shape of difference transmission spectra (inset in Fig. 4) indicate that the effect of improving the transparency of the crystals after annealing is probably associated with the decrease of number of scattering centers.

3.4. Effect of Si/Ge ratio

All grown BGSO crystals are transparent in the region of 300–800 nm (Fig. 5). Shift of the fundamental absorption edge on the optical transmission spectra of the crystals from 300 to 285 nm with increasing Si concentration corresponds to the wider bandgap in BSO theoretically predicted in [16]. The highest transmittance at the maximum of luminescence (480 nm) is registered in the sample with $x = 0.4$, as well as in BSO and BGO.

The X-ray luminescence spectra of BGSO with the varied Ge content (Fig. 6) are rep-

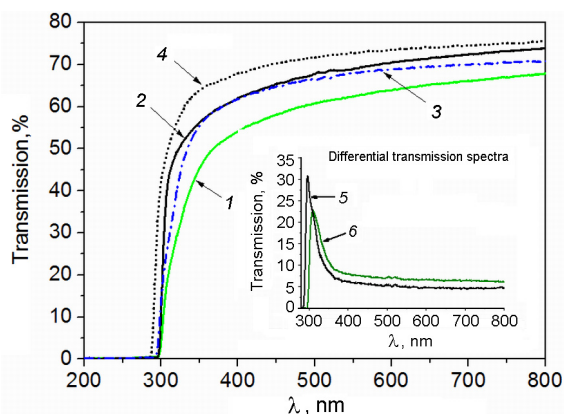


Fig. 4. Optical transmission spectra of as grown and annealed $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$ crystals with different x values: 1 — $x = 0.9$ as grown, 2 — $x = 0.9$ treated, 3 — $x = 0.1$ as grown, 4 — $x = 0.1$ treated, 5 — $x = 0.1$ differential spectra, 6 — $x = 0.9$ differential spectra.

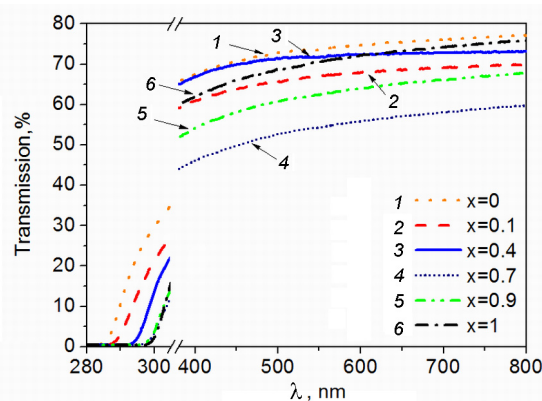


Fig. 5. Optical transmission spectra of $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$ crystals with different x value.

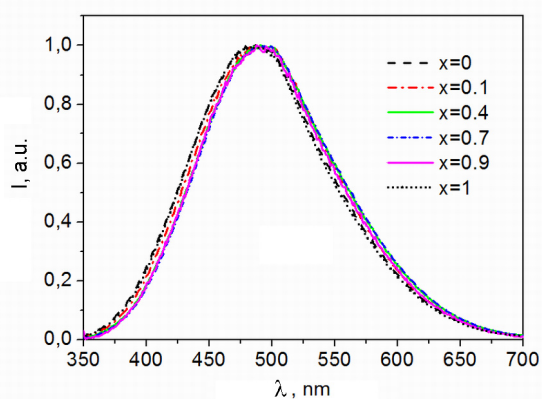


Fig. 6. X-ray luminescence spectra of $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$ crystals with different x value. The spectra are normalized by their maxima.

Table. Scintillation properties of $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$ crystals at 662 keV gamma-irradiation

x	0	0.1	0.4	0.7	0.9	1
Relative LY, %	24	18	29	46	48	100
Energy resolution (FWHM), %	21.7	39.1	19.5	16.2	18.2	10.0
Decay time τ , ns	100.6	109.5	132.9	152.3	220.3	292.4
Constant P_0	72.25	16.57	18.86	18.72	16.3	5.83
Constant P_1	-13.47	56.4	72.38	138.4	164.8	496.6

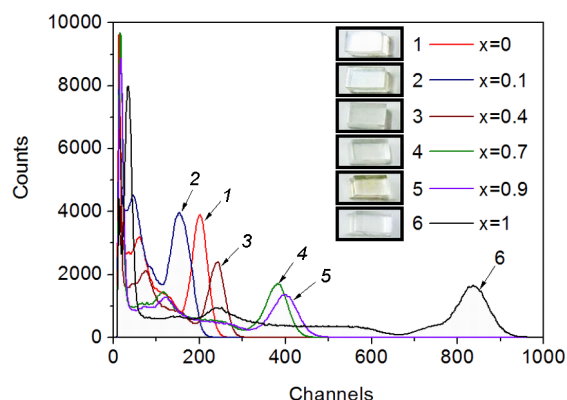


Fig. 7. Pulse height spectra of $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$ crystals with different x value at irradiation by γ -quanta with the energy of 662 keV from ^{137}Cs source.

represented by the single wide band in 350–700 nm range with the maxima near 480 nm. These coincide with the previously obtained data [17].

The pulse height spectra of BGSO at irradiation by 662 keV γ -quanta from ^{137}Cs source are presented in Fig. 7. The light yield tends to increase with increasing of x value (Fig. 8, Table). Contrary to most of studied mixed scintillation crystals [18, 19] this trend is not linear, with negative deviation from the additivity rule. Such a trend is similar to the dependences for BGSO obtained in [8] with the crystals grown by the Stockbarger and Czochralski methods. Thus, it is not dependent on the crystal growth method. The negative deviation from the additivity rule in BGSO contrary to many other scintillators based on mixed crystals can be attributed to the lower transparency of BGSO (excluding $x = 0.4$) compared to its constituents — BGO and BSO (see Fig. 5) and/or due to spatial inhomogeneity of distribution of competing Si^{4+} and Ge^{4+} ions [20]. The presence of the inclusions, evidently, is an issue of the very large difference between the ionic radii of substitution cations of Si^{4+} and Ge^{4+} . It is 32.5 %,

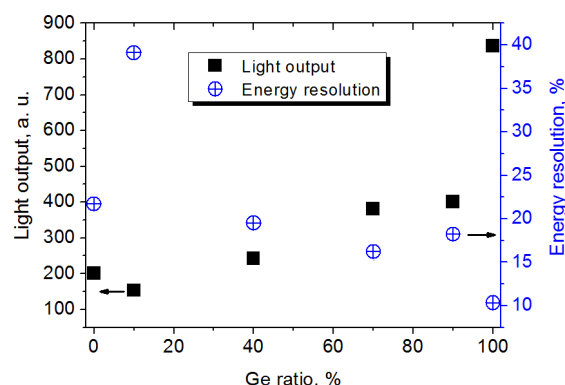


Fig. 8. Dependencies of light output and energy resolution on x value in $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$.

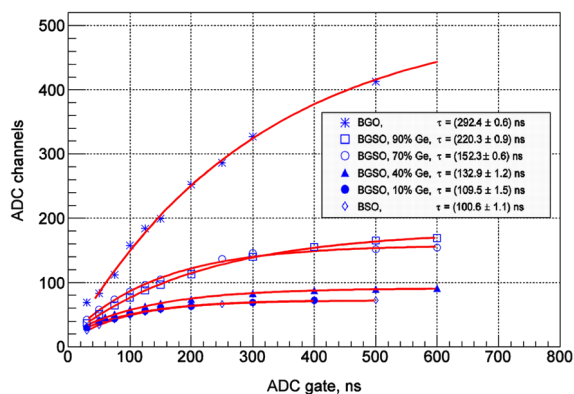


Fig. 9. Position of 662 keV ^{137}Cs peak in dependence on time gate value.

which is far beyond the 15 % limit of the Holdsmid's solubility range.

Nevertheless, the achieved energy resolution in BGSO (Fig. 8, Table 1) is better than in any previous reported data. There is a trend to improvement of energy resolution from BSO to BGO corresponding to the light yield increase. For all crystals within the $0.4 < x < 0.9$ range the energy resolution is better than 20 %. The best energy resolution of 16.2 % (FWHM) is achieved with the $x = 0.7$ sample.

BGSO scintillation decay time has been defined by measuring full absorption peak

position versus ADC gate width, i.e. light output versus the integration time [9]. The scintillation decay in BGSO can be fit by 1, 2, or even 3 exponents [8]. Skipping discussion on the features of BGSO decay fitting, here we evaluate the scintillation decay (Fig. 9) by single-exponential fit: $P = P_0 + P_1(1 - \exp(-t/\tau))$, where τ — decay time, P_0 , P_1 — constants, t — time (Table). The main scintillation decay constant of $\text{Bi}_4(\text{Ge}_x\text{Si}_{1-x})_3\text{O}_{12}$ increases with Ge content. However, this increase is not linear, and at $x < 0.7$ the decay constant is below 150 ns (Table). Therefore, in the most of x range the scintillation decay in BGSO crystals is by 2–3 times faster than that in BGO.

4. Conclusions

The presented set of data shows the potential for improvement of $\text{Bi}_4(\text{Ge}_x\text{S}_{1-x})_3\text{O}_{12}$ optical and scintillation characteristics by optimization of crystal obtaining methods. In particular, the best ever energy resolution of 16.2 % at 662 keV irradiation is reached in BGSO at $x = 0.7$. The crystal optical transmission can be improved by optimization of Bi_2O_3 excess, recrystallization, as well as by the post-growth annealing. Since large amount of detectors is needed for future high-energy physics experiments, the focus of the further work is to show a feasibility to produce the big crystals with stable characteristics.

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