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SCINTILLATION AND OPTICAL STABILITY OF THE *P*-TERPHENYL SINGLE CRYSTALS GROWN BY THE MODIFIED SELF-SEEDING VERTICAL BRIDGMAN METHOD

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Growth of organic crystals from melt is an expensive and time-consuming process, but it is one of the short list of methods to obtain them. Melt-growth techniques are limited to the Bridgman method, which requires either perfect seed crystal or specially constructed single-use sophisticated ampoule. Recently we managed to significantly improve the melt-growth technique of *p*-terphenyl, a famous π-stacked organic scintillator, by eliminating the process of transferring the zone-melting purified material to the special growth ampoule, proceeding the growth in the same ampoule. This work is dedicated to study of the scintillation and optical characteristics of the obtained crystals, namely their stability throughout the boule. It is shown that there are short zones of low crystallinity and excessive amount of light impurities in the studied boule.

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INTRODUCTION

Organic scintillation single crystals are of great interest because of their unique set of properties. They are fast (decay time usually lies in tens of nanoseconds), non-hygroscopic, non-flammable and have relatively high light yield (tens of thousands of photons per MeV). Organic scintillation materials are effective for detecting short-range radiation and for the selective detection of fast neutrons in the presence of gamma radiation. *p*-Terphenyl is one of the most commonly used organic scintillation materials.

The potential application of a compact detector based on a *p*-terphenyl single crystal in equipment for space research with signal registration by a silicon photomultiplier is highlighted in [1]. A small prototype of a high-resolution TOF detector based on a silicon photomultiplier and a *p*-terphenyl crystal was described in [2]. The development of a medical device for radiosurgery using a detector based on a single crystal of *p*-terphenyl as a *β*-particle counter is presented in [3]. The high efficiency of neutron detection and neutron/gamma discrimination by single crystals of *p*-terphenyl was noted in the results of research presented in [4]. Single crystals of *p*-terphenyl have become widely used in the field of molecular electronics [5].

On the other hand, obtaining of such crystals is long and expensive process. There are few techniques, most popular of which are solution-growth (when the scintillation material is dissolved in the respective solvent and its slow evaporation leads to the growth of the crystal) and melt-growth (when melted scintillation material is slowly cooled under special conditions, forming the crystal lattice). The first method is not capable of producing high-grade scintillators due to incorporation of the solvent molecules into resulting crystal in such amount that significantly lowers its light yield. At the same time, the second method requires high purity of the initial material and special conditions to start the single-crystal phase that is capable to fill the maximum reachable volume of the growth ampoule. Most of the time the Bridgman method is used for this purpose [6–8]. It is time-consuming, and usually requires intricate ampoule to obtain decent single-crystal.

Recently we were able to significantly improve the Bridgman technique to obtain *p*-terphenyl single crystals using modified "self-seeding" vertical Bridgman (SSVB) method [9]. It was shown that the growth of this scintillator is possible without the transferring of the material that purified by the zone-melting to the special growth ampoule, growing the crystal in the zone-melting ampoule instead. We attribute this to its π-stacked structure, which allows the molecules to arrange in the energetically favorable orientation during the growth process.

At the same time, it is important to access the information on the stability of the key parameters of the scintillator throughout the obtained boule. This is the key study of this paper.

1. EXPERIMENTAL

1.1. OBTAINING OF SINGLE-CRYSTAL SAMPLES

The *p*-terphenyl single-crystal samples were obtained from *p*-terphenyl powder purchased from ACROS ORGANICS BVBA. We purified the material by recrystallization and zone melting [10], then grew the boule in a zone-melting ampoule using the modified SSVB method [9] (Fig. 1); we cut the boule into samples h = 5 mm thick, and polished the sides by the same method to avoid surface conditions influencing the experimental results. We obtained a total of 28 samples from one boule (Fig. 2). The samples were numbered starting from the bottom of the boule (10 mm from the start of crystallization).



Fig. 1. Photo: the melting ampoule after the crystal grew using the modified SSVB method (left); the crystal bulk section used to cut samples (center); a zoomed-in view of the crystal of the start zone of crystallization (right)



Fig. 2. Photo of the samples obtained before polishing

1.2. EXPERIMENTAL METHODS

The relative light output of the studied samples was determined by the standard method using scintillation amplitude spectra.

The photomultiplier 9208A was used as a photodetector with the high voltage set well within its operation limits. The amplitude distribution of scintillation pulses was obtained using an amplitude-to-digital converter connected to the personal computer. The value of the relative light output L can be calculated according to (1)

$$L = \left(J \middle/ J_{ref} \right) \times 100\ \%, \qquad (1)$$

where J is the value of the amplitude that corresponds to the center of gravity of the special point in the spectrum of the studied sample and J_{ref} is the value of the amplitude that corresponds to the same special point in the spectrum of the reference scintillator. We used the conversion electrons from ^{137}Cs with energy E_β = 0.622 MeV to investigate the inner processes in the crystals under study, as they can be affected by the possible impurities and crystal lattice defects.

The optical transmittance of the samples was determined using a Shimadzu UV 2450 spectrophotometer. We calculated the value of optical transmittance T as follows:

$$T = \left(L \middle/ L_0 \right) \times 100\ \%, \qquad (2)$$

where L_0 is the flux of light falling on the sample, L is the flux of light that propagates through the sample. The T-value (2) is the relative light transmittance, where T = 100% is the light transmittance of air at the room temperature.

2. RESULTS OF STUDIES AND THEIR ANALYSIS

The light output was measured according to the method described in 1.2. Using the ^{137}Cs source, the peaks corresponding to its conversion electrons were obtained and evaluated for all 28 samples. The results are shown on Fig. 1.

As can be seen from the Fig. 3, there is a general trend of a slight decrease in light output (with a coefficient of -11.06 at Δh = 5 mm and a constant value of 3488.8) as the distance from the bottom of the growth ampoule increases. This trend is qualitatively described by a linear function with a quadratic deviation of 0.62. At the same time, edge processes occurring near the initial single-crystal nucleation site at the phase boundary account for improved single-crystallinity across two samples (totaling 10 mm) – confirmed by a relatively sharp rise in light output. The edge processes near the upper samples drive the segregation of impurities toward the top of the boule [11] and affect two-three samples in total. The obtained results fall within a 5% margin of error.

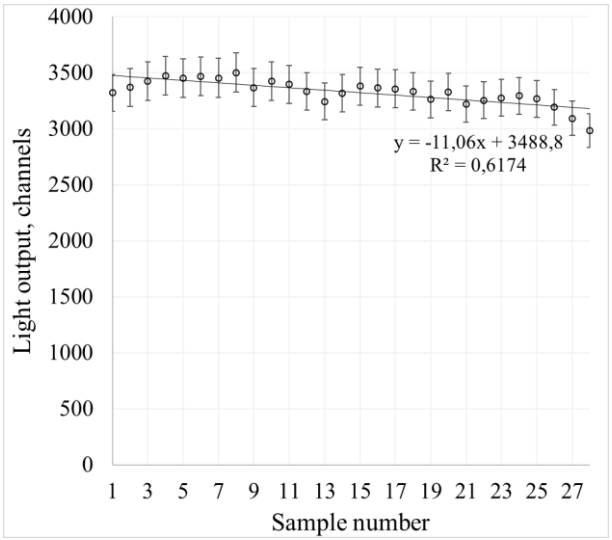


Fig. 3. Light output of the p-terphenyl single crystals under ^{137}Cs irradiation

The obtained results clearly show that there is major part of the boule that is stable enough to be used in practical applications. Using the obtained results, they can be interpolated on the future boules with different linear dimensions to avoid the visually usable zones that are either not crystalline enough or contain impurities.

Values of the optical transmittance of the p-terphenyl single crystals at their maximum of luminescence (360 nm)

Sample №	1	2	3	4	5	6	7	8	9	10	11
T, %	71.341	67.85	68.625	66.57	67.824	66.258	68.047	59.941	63.931	61.835	64.522
Sample №	12	13	14	15	16	17	18	19	20	21	22
T, %	62.753	72.473	70.001	61.807	62.271	63.315	63.281	69.553	68.045	67.491	70.674
Sample №	23	24	25	26	27	28					
T, %	66.278	69.962	64.322	65.125	64.906	68.326					

The optical transmittance of the samples was measured according to the method described in 1.2. The results are shown on Fig. 4.

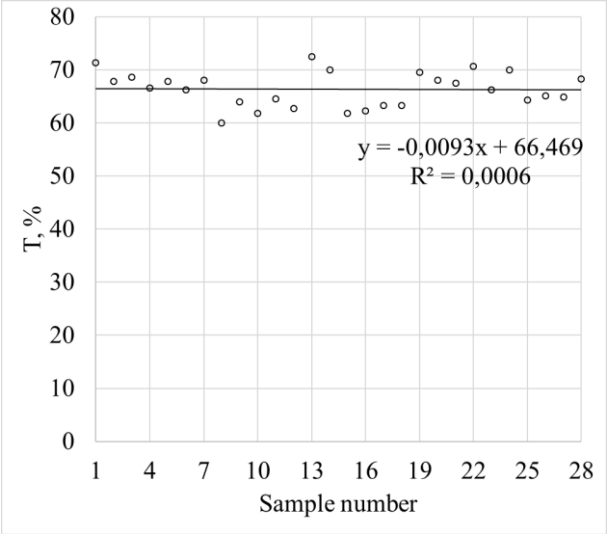


Fig. 4. Optical transmittance of the p-terphenyl single crystals at their maximum of luminescence (360 nm)

As can be seen from the Fig. 2, there is almost horizontal line that approximates the optical transmittance (slope equals -0.0093) at the 66.47% constant, with the quadratic deviation only 0.0006. It can be interpreted as a high optical transmittance stability throughout the boule, and the effect that has been observed on the stage of light output studies is depends purely on the peculiarities of the energy exchange in such media. The exact values of the optical transmittance are listed in Table.

As shown in Figs. 3, 4, and Table, the crystal structure affects light output more than light transmittance. This information on crystal-structure stability also helps us select the appropriate region of the crystal bulk to ensure sufficient purity, high LO, and transmittance.

CONCLUSIONS

Use of the modified "self-seeding" vertical Bridgman (SSVB) method is capable of producing scintillators with close to constant light output and optical transmittance throughout the boule volume.

The lower part of the visually perfect section of the boule contains the low-crystallinity area that not exceed 10 mm. Nevertheless, this part still falls within the 5% measurement margin of error.

The upper part of that boule contains the sufficient amount of light impurities that dragging down the light output, and this area also does not exceed 10…15 mm and falls within the 5% measurement margin of error.

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СЦИНТИЛЯЦІЙНА ТА ОПТИЧНА СТАБІЛЬНОСТІ МОНОКРИСТАЛІВ *П*-ТЕРФЕНІЛУ, ВИРОЩЕНИХ МОДИФІКОВАНИМ МЕТОДОМ САМОЗАТРАВНОГО ВЕРТИКАЛЬНОГО БРІДЖМЕНА

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Вирощування органічних кристалів із розплаву – це дорогий і тривалий процес, проте він належить до небагатьох наявних методів їх отримання. Серед технологій вирощування з розплаву переважає метод Бріджмена, який потребує або ідеального затравкового кристала, або спеціально сконструйованої складної одноразової ампули. Нещодавно нам вдалося суттєво вдосконалити методику вирощування з розплаву *n*-терфенілу – відомого органічного сцинтилятора з ялинковою структурою. Це було досягнуто завдяки відмові від перенесення матеріалу, очищеного методом зонної плавки, до спеціальної ампули для вирощування та проведення самого процесу вирощування в тій самій ампулі. Ця робота присвячена дослідженню сцинтиляційних та оптичних характеристик отриманих кристалів, зокрема їхньої однорідності по всій довжині вирощеної булі. Показано, що в досліджуваній булі наявні короткі зони з низьким ступенем кристалічності та підвищеним вмістом легких домішок.