THE SINGLE CRYSTALLINE SCINTILLATORS OF *p*-TERPHENYL GROWN BY THE MODIFIED SELF-SEEDING VERTICAL BRIDGMAN METHOD

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The single crystals of *p*-terphenyl with high scintillation and optical properties were grown using the modified self-seeding vertical Bridgman method. Unlike the classical self-seeding vertical Bridgman (SSVB) method, where crystal growth occurs from a single point in the ampoule, the modified method involves the spontaneous nucleation of the single crystal on the crystallization front plane. This method does not require the use of complex growth ampoules, significantly reduces the risk of raw material contamination, and is promising for the production of organic single crystals with a π-conjugated crystalline structure.

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INTRODUCTION

Due to the high hydrogen content in organic substances, 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 single crystals of *p*-terphenyl possess a monoclinic symmetry with the space group P21/a, with lattice parameters a = 8.12 Å, b = 5.62 Å, and c = 13.62 Å. The only indirect angle, β = 92.4°, is formed between the (a, b) plane and the c axis [1]. The single crystal of *p*-terpheny**l** has a π-complex crystal structure, which largely determines its properties.

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].

Earlier [6], the new approach for the fabrication of polycrystalline scintillators based on *p*-terphenyl was proposed, which ensures a significant improvement in their scintillation and optical properties compared to existing analogs. Building on this experience and implementing a series of technological enhancements, a single crystal of *p*-terphenyl with high scintillation and optical characteristics was obtained. The method used to grow the experimental single crystal is one of the simplest among known modifications of the Bridgman-Stokbarger method [7], although no information on the growth of organic crystals using this method could be found. The approach employed in this work differs from widespread and well-known methods, such as the self-seeding vertical Bridgman (SSVB) method [8, 9]. In this method, the single crystal grows from a single point due to the sharp conical bottom of the ampoule, or the single crystal growth begins from an oriented seed. In the method we use, spontaneous nucleation of the single crystal occurs on the crystallization front plane.

SAMPLE PREPARATION

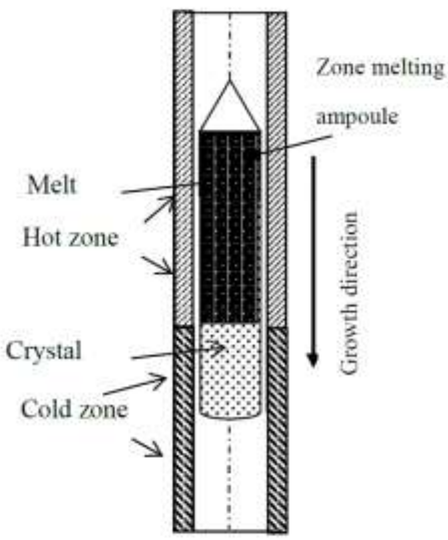

Fig. 1. Cross section of the Bridgman furnace for growing of crystals

In this study, *p*-terphenyl from the company "Acros" was used, which was initially purified using the zone melting method in a Pyrex glass ampoule. For this, *p*-terphenyl was placed into a washed and dried ampoule. The air was evacuated from the ampoule, and then argon was introduced to a pressure of 0.5 atm. The ampoule was sealed, and it underwent eight purification zones in the zone melting setup at a speed of 10 mm/hour. Next, in a two-zone Bridgman crystal growth furnace (Fig. 1), a single crystalline ingot was obtained (Fig. 2). The temperature of the upper zone was 220°C, and the lower zone was 115°C. The growth was conducted by lowering the ampoule at a speed of 1.25 mm/h.

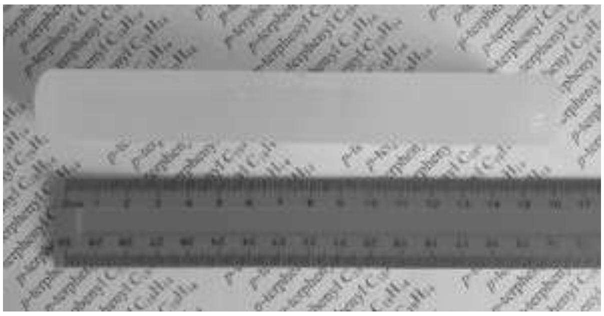

Fig. 2. The p-terphenyl single crystal which was grown using the modified self-seeding vertical Bridgman method

After annealing, the ampoule is broken, and the single crystalline ingot is carefully extracted. To process the side surface of the ingot, it is turned on a lathe. Then, the ingot is cut into cylinders of various thicknesses (Fig. 3), and the bases of the cylinders are ground and polished.

Fig. 3. Single crystals of p-terphenyl of various heights after cutting and polishing

EXPERIMENTAL TECHNIQUE

THE METHOD OF INVESTIGATING RELATIVE LIGHT OUTPUT

The relative light output of polycrystalline scintillators was determined by the standard method using scintillation pulse spectra. We used photomultiplier tube 9208A. The output circuit of photomultiplier had the integration time $\tau_{RC} = 2\ \mu$s.

The scintillation pulse spectra were obtained using 10-bit nuclear-physical spectrometric multi-channel amplitude analyzer. The relative light yield was calculated using Eq. (1):

$$L = \left({}^{J}\!/_{J_{\text{ref}}} \right) \cdot 100\ \% , \qquad (1)$$

where J is value of the amplitude corresponding to the peak maximum in the spectrum of the test sample, J_{ref} is the value of the amplitude corresponding to the peak maximum in the spectrum of the reference detector. The error in determining the relative light output was equal to 5%.

The source of alpha-particles ^{239}Pu was used (the energy E_α = 5.15 MeV, specific energy losses $dE/dx \sim 10^3$ MeV/cm, activity $\sim 10^3$ Bq) with a multihole collimator to eliminate the effect of lateral radiation. We also used the isotope ^{137}Cs as a source of conversion electrons (the energy E_e = 0.622 MeV, specific energy losses $dE/dx \sim 10^0$ MeV/cm, activity $\sim 10^4$ Bq).

THE METHOD OF MEASURING OPTICAL TRANSMISSION USING AN INTEGRATING SPHERE

The optical transmission of the samples was measured using a Shimadzu UV2450 spectrophotometer with an integrating sphere. The measurements were performed in the wavelength range from 200 to 800 nm. At the beginning of the experiment, the instrument was calibrated, establishing the 100% transmission line. Then, a sample was placed in the path of one of the beams. The sample was tightly applied to the outer surface of the sphere, as the accuracy of the measurements depends on this. The comparison channel of the spectrophotometer remained empty, and the light flux in this channel was the same as the light flux falling on the sample in the measurement channel. The measurement error was ±0.5%.

The value of transmittance T was calculated as follows:

$$T = \left({}^{L}\!/_{L_0} \right) \cdot 100\ \% , \qquad (2)$$

where L_0 is the light flux incident on the sample, L is the light flux that passes through the sample.

At the beginning of each measurement, the light flux in the comparison channel and the empty measurement channel was adjusted to ensure they were equal. In practice, the value of T (2) represents the relative light transmission, where T = 100% corresponds to the light transmission of air at room temperature under fixed laboratory conditions.

EXPERIMENTAL RESULTS

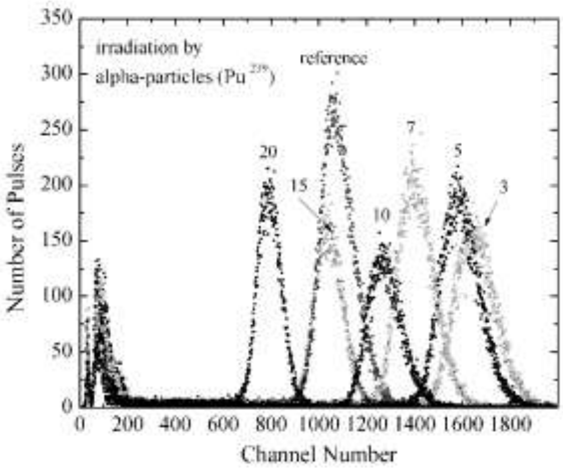

Fig. 4. The amplitude scintillation spectra of the investigated p-terphenyl single crystals and the reference p-terphenyl single crystal with h of 5 mm upon alpha-particles irradiation. The numbers indicated in the figure show the thickness of the sample for which the corresponding spectrum was obtained

Fig. 4 shows the amplitude scintillation spectra for the investigated *p*-terphenyl single crystals with thicknesses *h* ranging from 3 to 20 mm, as well as for the reference *p*-terphenyl single crystal with a thickness of 5 mm upon alpha-particles irradiation. The *h*-values for the investigated single crystals are 3, 5, 7, 10, 15, and 20 mm.

The amplitude scintillation spectra of the investigated samples, obtained upon irradiation with electron conversion (^{137}Cs), are shown in Fig. 5.

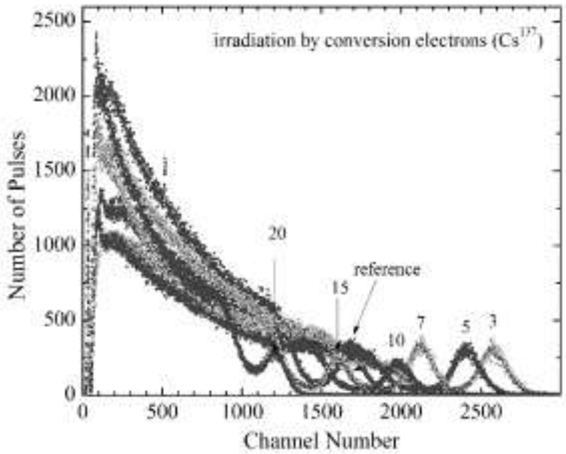

Fig. 5. The amplitude scintillation spectra of the investigated p-terphenyl single crystals and the reference p-terphenyl single crystal with h of 5 mm upon conversion electrons irradiation. The symbols are the same as in Fig. 4

Fig. 6 presents the results of optical transmission measurements for three selected *p*-terphenyl single crystal samples with thicknesses h =3, 5, and 7 mm.

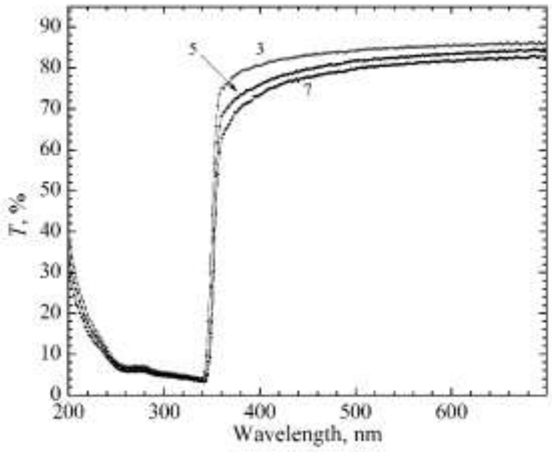

Fig. 6. The values of optical transmittance T for p-terphenyl single crystals with h of 3, 5, and 7 mm

Table presents the results of calculations for the relative light output L (1) and energy resolution R for the investigated *p*-terphenyl single crystal samples with different thicknesses h. The calculations are based on the analysis of the centroid positions of the peaks and the full width at half maximum (FWHM) values of each peak in the scintillation spectra, both for the case of sample excitation by alpha-particles (see Fig. 4) and for the case of excitation by conversion electrons (see Fig. 5). For the reference single crystal, the value of L was taken as unity separately for alpha excitation and conversion electron excitation.

The values of the relative light output L (1) and energy resolution R for the *p*-terphenyl single crystal samples with different thicknesses h are presented for the cases of excitation by alpha particles from ^{239}Pu and conversion electrons from Cs^{137}

h, mm	L, %		R, %	
	Type of irradiation		Type of irradiation	
	^{239}Pu	^{137}Cs	Pu^{239}	Cs^{137}
5 (reference)	100	100	11.6	8.4
3	151	151	8.63	4.97
5	147	140	9.38	6.74
7	132	125	9.57	6.02
10	116	115	8.89	7.85
15	97	95	11.1	8.43
20	73	70	13.8	12.7

The analysis of the results presented in Figs. 4,5, and in Table 1 allows the following conclusions. A comparison of the relative light output values L for the reference sample with a thickness of h =5 mm and the experimental sample of the same thickness h = 5 mm shows that the L-value of the experimental *p*-terphenyl single crystal exceeds that of the reference crystal by more than 40% when detecting both alpha particles and conversion electrons, while the energy resolution R decreases by 20…25 %.

The analysis of the results presented in Fig. 3 and Fig. 6 leads to the following conclusions. The optical transmission of the experimental single crystals does not significantly decrease with increasing thickness h. Along with the visual analysis of Fig. 3 this indicates their high optical characteristics.

CONCLUSIONS

The paper proposes the modified vertical Bridgman method with spontaneous crystal nucleation at the crystallization front plane for growing organic scintillators. Using this method, *p*-terphenyl single crystals with high scintillation and optical properties were grown. Although the melting temperatures of organic materials are relatively low, the growth of organic single crystals is a complex and time-consuming process due to the low thermal conductivity and molecular structure of organic single crystals. The proposed method significantly simplifies the growth of organic single crystals, as it does not require the fabrication of a complex growth ampoule, greatly reduces the risk of contamination of the raw materials, and so on. Therefore, this method is promising for obtaining *p*-terphenyl single crystals, and possibly other organic single crystals as well.

The crystals grown using this method have over 40% higher light output compared to the single crystal grown using the classical Bridgman-Stokbarger method, while the energy resolution decreases by approximately 20%.

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