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NEW METHOD OF OBTAINING ORGANIC POLYCRYSTALLINE SCINTILLATORS

Ya.I. Polupan*, N.L. Karavaeva, A.V. Krech, I.V. Lazarev, S.V. Makhota, E.V. Martynenko, S.S. Minenko, O.A. Tarasenko
Institute for Scintillation Materials, National Academy of Sciences of Ukraine, Kharkiv, Ukraine
****E-mail: polupan.yaroslava@gmail.com***

One of the disadvantages of polycrystalline scintillators is a significant degradation of their scintillation and optical characteristics with an increase in thickness of a scintillator. This work proposes a new approach to obtaining the initial material for polycrystals based on *p*-terphenyl, in which zone melting and an additional stage of reverse movement allows producing material for pressing in the form of an ingot. This method of producing polycrystals provides a significant improvement in their scintillation and optical characteristics in relation to existing analogues.

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INTRODUCTION

The priority scientific direction is the creation of the novel scintillation materials and detectors on their base for solving a wide range of modern problems of scintillation materials science and instrument engineering. First of all this is the development of detectors for experiments in high-energy physics and solving the problems of environmental radioecology.

Currently, we have developed the methods for obtaining organic polycrystalline scintillators by cold [1–3] or hot pressing [3–7] of crystalline grains or plates. Grains are obtained by grinding either a pre-grown single crystal or a crystalline ingot, which is formed during the purification of the source material by the zone melting method. Plates are grown by recrystallization of a raw material from an organic solvent. The hot pressing method makes it possible to obtain polycrystals with significantly better characteristics compared to the cold pressing method [8]. The use of a crystal ingot instead of a single crystal made it possible to reduce significantly the cost of polycrystals, since in this case the most expensive stage of growing a single crystal is excluded from the technical process [8, 9].

However, there are still problematic points in the existing method of obtaining scintillation polycrystals. The main ones include the following: i) the stages of multiple grinding of the crystal ingot, sieving of the obtained grains and growing of plates from an organic solvent are quite long; ii) the use of an organic solvent and liquid nitrogen leads to contamination of the scintillation material, which make worse its quality; iii) selection of only a separate fraction of grains for further pressing reduces the efficiency of material use.

In addition, a significant lack of organic polycrystalline scintillators, which are obtained from crystalline grains or plates, is a significant deterioration of its optical and scintillation characteristics with an increase in its thickness [10]. Therefore, the problem of increasing the transparency and light output of the polycrystalline scintillator, which will ensure more reliable operation of the detector, remains relevant. This is extremely important in the tasks of detecting radiation with low energy, when the amplitude of the signal becomes comparable to the amplitude of the noise pulses of the measuring equipment.

The authors noticed that the introduction of an additional stage of reverse motion to the standard process of zone melting leads to the formation of a transparent and solid crystalline ingot. Therefore, we explored the possibility to obtain an organic polycrystal of *p*-terphenyl directly from a quasi-crystal of *p*-terphenyl after its cutting. This method excludes not only the expensive technological process of growing a perfect single crystal, but also the aforementioned problematic points.

1. EXPERIMENTAL

1.1. OBTAINING OF POLYCRYSTALLINE SAMPLES

The method of obtaining polycrystalline scintillators of *p*-terphenyl includes obtaining the material by zone melting at a speed of 10 mm per hour. After two stages of zone melting, the reverse movement of the ampoule is additionally carried out at a speed of 1.5 mm per hour and obtain the material in the form of a quasi-crystalline ingot. A quasi-crystalline ingot of *p*-terphenyl is formed because of the self-orientation of the majority of *p*-terphenyl molecules at the crystallization front in an energetically favorable direction, perpendicular to the *ab* plane of the crystallographic lattice, during the reverse movement of the ampoule. An increase in the transparency of the ingot occurs due to a decrease in the number of block boundaries and micropores (Fig. 1).

The quasi-crystalline ingot is cut into parts, after that each part is hot-pressed. Hot pressing of parts of the *p*-terphenyl ingot was carried out on a hydraulic press by uniaxial compression at an increase in pressure from 20 to 200 MPa in the temperature range from 150 to 180 °C and the exposure time from 0.5 to 2 h, followed by a decrease in pressure to atmospheric during 5…15 min and slow cooling to the room temperature.

The use of a quasi-crystalline ingot as a material for hot pressing allows to eliminate the effect of anisotropy of thermal expansion of the scintillation material and to avoid contamination of the polycrystal, in contrast to the

case of using grains or plates, when adsorption of components of the air environment, liquid nitrogen and organic solvent takes place. As an example, Fig. 2 shows samples of *p*-terphenyl polycrystals. Sample (a) was obtained by pressing crystalline grains, while a more transparent sample (b) was obtained by pressing a fragment of a quasi-crystalline ingot.

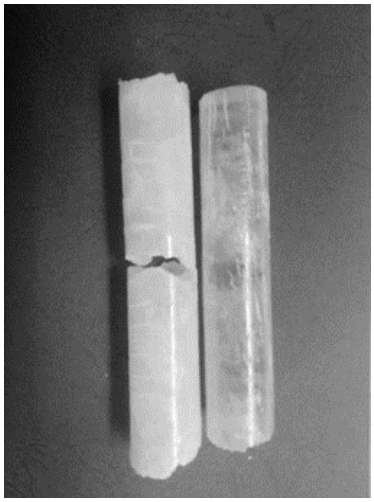

Fig. 1. Samples of p-terphenyl ingots obtained after zone melting. To the left is the sample obtained by the standard method, to the right is the quasi-crystalline ingot obtained after an additional stage of reverse movement of an ampoule

Fig. 2. The photograph of p-terphenyl polycrystals with a diameter of D = 20 mm and a thickness of h = 5 mm obtained by hot pressing of: a – crystalline grains; b – a fragment of a quasi-crystalline ingot

1.2. EXPERIMENTAL METHODS

The relative light output of polycrystalline scintillators was determined by the standard method using scintillation amplitude spectra. The photomultiplier 9208A was used as a photodetector [11]. The amplitude distribution of scintillation pulses was obtained using an amplitude-to-digital converter. The value of the relative light output L was calculated according to (1)

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

where J is the value of the amplitude that corresponds to the center of gravity of the peak in the spectrum of the scintillator under investigation; J_{ref} is the value of the amplitude that corresponds to the center of gravity of the peak in the spectrum of the reference scintillator. The single crystal of *p*-terphenyl was used as a reference detector. We used the following types of ionizing radiations: alpha particles from ^{239}Pu with energy E_α = 5.15 MeV, conversion electrons from ^{137}Cs with energy E_β = 0.622 MeV.

The optical transmittance of the samples was determined using a Shimadzu UV 2450 spectrophotometer [12]. We calculated the value of optical transmittance T as follows:

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

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

To develop the technology of obtaining polycrystals in a new way (from fragments of quasi-crystals), we investigated the influence of pressing parameters on the scintillation and optical characteristics of the obtained polycrystals. To carry out these studies we have obtained a series of fragments of quasi-crystalline ingots of a cylindrical shape with a diameter of D = 20 mm and a height of h = 5 mm. We have measured the values of the relative light output L, energy resolution R, and optical transmittance coefficient T of fragments of quasi-single crystals before pressing and corresponding polycrystals. We varied the following technological parameters: pressure P, temperature C, and sample exposure time t during the pressing process.

Measurements of the amplitude scintillation spectra of organic scintillators upon excitation by alpha-particles and conversion electrons, calculations of the energy resolution R of the corresponding peaks (the ratio of the position of the peak maximum to the value of the width of the peak at half height, expressed in percentages), as well as measurements of the optical transmittance T of the samples is a standard procedure. Typical results of such studies one can find, for example, in [1, 5]. Therefore, in this work, only the final results, based on the analysis of the original experimental data, are presented.

2.1. THE MEASUREMENTS OF QUASI-CRYSTALLINE SAMPLES

Fig. 3 shows the values of the relative light output L (1), which were determined for quasi-crystals before the process of their pressing. We have measured 24 quasi-crystals with a diameter of D = 20 mm and a height of h = 5 mm. As can be seen from the results, the samples of quasi-crystals show a rather strong spread of L values, namely, in the range from 133 to 169% for the case of excitation by alpha particles and from 138 to 164% when excited by conversion electrons. A large spread was also obtained for the values of the energy resolution R and the optical transmittance T. The value of R varied from 8.7 to 14.6% when excited by alpha particles and from 8.2 to 9.7% when excited by conversion electrons. T-values varied from 27 to 50% for a wavelength of 390 nm (a maximum of luminescence) and from 40 to 70% for 700 nm (the range of optical transparency).

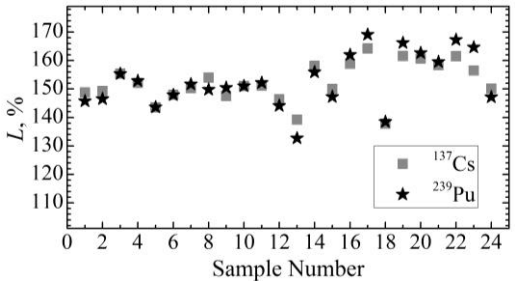

Fig. 3. The values of the relative light output L of p-terphenyl quasi-crystals excited by alpha particles (^{239}Pu) or conversion electrons (^{137}Cs)

Therefore, in order to estimate correctly the influence of the pressing conditions on the characteristics of the obtained polycrystals we used the following approach. Firstly, the groups of such quasi-crystals were selected for further pressing, the value of L for which differed no more then on 5% within the group. Secondly, for each a sample the change in the values of ΔL, ΔR, and ΔT were calculated, which was observed after the pressing process of this sample relative to the value of the same value before the pressing process. Namely:

$$\Delta A = \frac{A_{before} - A_{after}}{A_{before}} \times 100\ \%, \qquad (3)$$

where A may be the value of L, R or T; ΔA is the change of the corresponding values; A_{before} is the value of L, R or T before pressing the samples; while A_{after} is the value of these parameters after the pressing process. The values of ΔL, ΔR, and ΔT are normalized to the original values of L, R, and T for each individual sample. This makes it possible to eliminate the influence of the spread of the initial values of scintillation and optical characteristics and to analyze only the influence of the pressing parameters, namely, the values of pressure P, temperature C, and exposure time t.

2.2. INFLUENCE OF PRESSURE *P* ON CHARACTERISTICS OF POLYCRYSTALLINE SAMPLES

A series of polycrystals was produced for the following values of pressure P: 20, 50, 100, 150, and 200 MPa. For all samples, the pressing temperature was 165 ºC, and the exposure time was 2 h. The values of the light output ΔL, energy resolution ΔR and optical transmittance coefficient ΔT were obtained as the function of pressure P. The corresponding results are presented in Figs. 4–6.

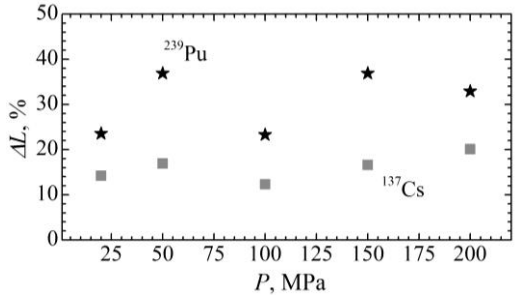

Fig. 4. The dependence of the ΔL-value on pressure P. The symbols are the same as in Fig. 3

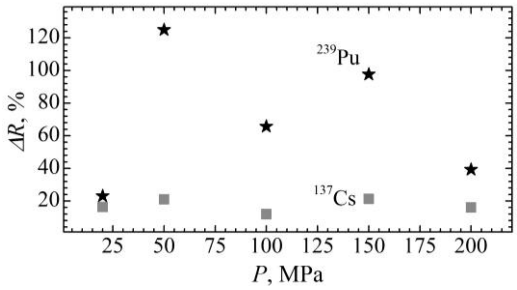

Fig. 5. The dependence of the ΔR-value on pressure P. The symbols are the same as in Fig. 3

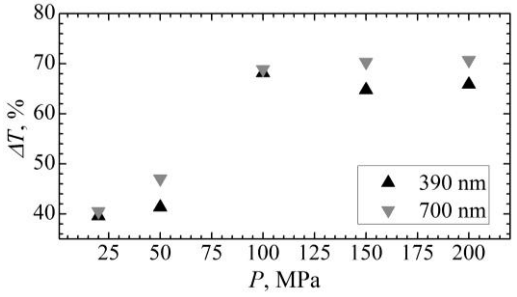

Fig. 6. The dependence of the ΔT-value on pressure P for the wavelengths of 390 and 700 nm

The results of the calculations show, that the values of ΔL and ΔR for all values of P in the case of excitation by alpha particles are greater than in the case of excitation by conversion electrons. The obtained data do not make it possible to conclude that there is any dependence of the ΔL and ΔR values on the value of pressure P (see Figs. 4 and 5). At the same time, there is a noticeable increase in the value of ΔT (see Fig. 6) with an increase in P both for the wavelength of 390 nm and for 700 nm. That is, the T-value decreases with increasing pressure P. The ΔT-value is slightly higher for a wavelength of 700 nm. This can be explained by the fact that pressing leads to a stronger increase in the influence of the light scattering process than its absorption. This result is in good agreement with the fact that the values of ΔL and ΔR in the case of excitation by alpha particles are higher than in the case of excitation by conversion electrons. For an alpha particle, the path length in p-terphenyl is about 30 μm, so light photons of are arisen, in fact, on the surface of the scintillator and must pass through the entire thickness of the sample before they are detected. Therefore, light scattering processes in the case of excitation by alpha particles have a stronger effect on L- and R-values than in the case of excitation by conversion electrons, which have a greater penetration depth (~ 2 mm). Therefore, the reduction of the transparency of the samples because of pressing will have a greater effect on the values of L and R in the case of excitation by alpha particles of ^{239}Pu than by conversion electrons of ^{137}Cs.

The massive of the above-mentioned results indicates that when obtaining polycrystals of p-terphenyl from fragments of quasi-crystals, the optimal value for P is 20 MPa. This agrees with the optimal value of P when obtaining polycrystals from crystalline grains according to the previously developed technology.

2.3. INFLUENCE OF TEMPERATURE *C* ON CHARACTERISTICS OF POLYCRYSTALLINE SAMPLES

The next step of the research was to determine the optimal pressing temperature *C*. A series of polycrystals was obtained at the following values of *C*: 150, 165, and 180 ºC. All samples of this series were obtained at the optimal pressure value *P* of 20 MPa. The exposure time was 2 h. For this series of samples, the values of Δ*L*, Δ*R*, and Δ*T* were also obtained. These values are presented, correspondingly, as the function of the pressing temperature *C* in Figs. 7–9.

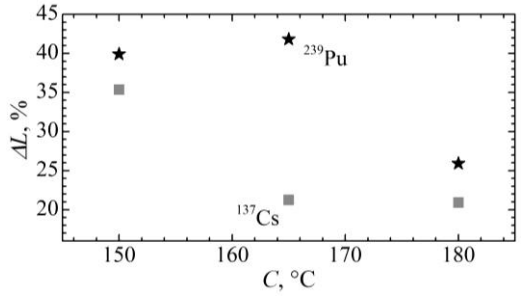

Fig. 7. The dependence of the ΔL-value on temperature C. The symbols are the same as in Fig. 3

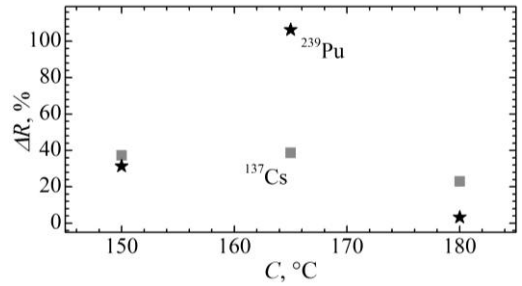

Fig. 8. The dependence of the ΔR-value on temperature C. The symbols are the same as in Fig. 3

The obtained results demonstrate a tendency to decrease the Δ*L*- and Δ*R*-values with increasing pressing temperature *C*. On the other hand, the value of Δ*T* increases with increasing temperature *C*. This result one can explain by the influence of the light collection processes, when the light signal for a more opaque scintillator can be higher than for a scintillator with a high transparency at its small thicknesses.

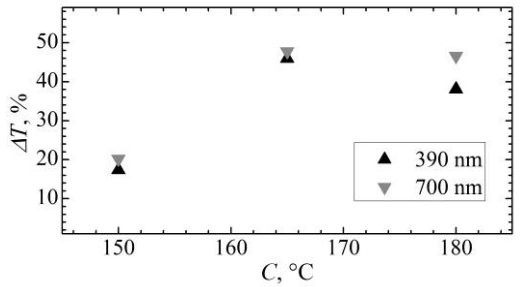

Fig. 9. The dependence of the ΔT-value on temperature C for the wavelengths of 390 and 700 nm

The experimental results show that when obtaining polycrystals from quasi-crystal fragments, the optimal pressing temperature *C* is 180 °C. An increase in temperature above 180 °C is unacceptable due to the sublimation of *p*-terphenyl. It should be noted that when obtaining polycrystals from crystalline grains according to the previously developed technology, the optimal temperature is 165 °C. Such a difference most likely is due to the fact, that in our case we used for pressing not single crystal grains, but a quasi-crystalline ingot.

2.4. INFLUENCE OF THE EXPOSURE TIME *T* ON CHARACTERISTICS OF POLYCRYSTALLINE SAMPLES

At the last stage of determining the optimal conditions for obtaining *p*-terphenyl polycrystals we varied the exposure time *t* of the samples at the optimal values of pressure *P* (20 MPa) and temperature *C* (180 °C) of pressing. The exposure time *t* of the samples under these conditions was 0.5, 1, and 2 h. Dependencies of Δ*L*-, Δ*R*-, and Δ*T*-values on the exposure time *t* demonstrate Figs. 10, 11 and Fig. 12, respectively.

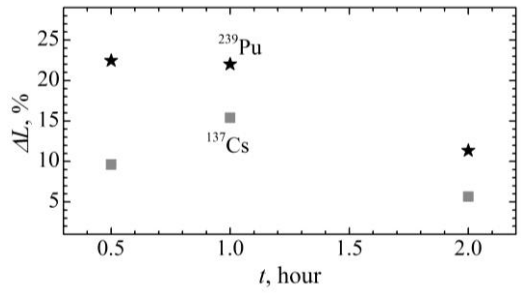

Fig. 10. The dependence of the ΔL-value on the exposure time t. The symbols are the same as in Fig. 3

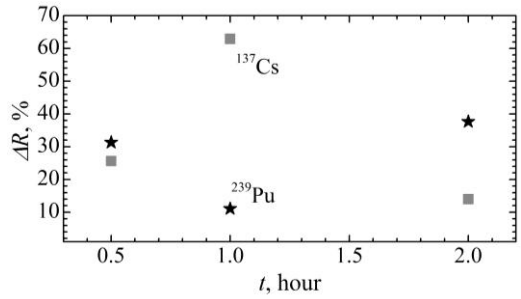

Fig. 11. The dependence of the ΔR-value on the exposure time t. The symbols are the same as in Fig. 3

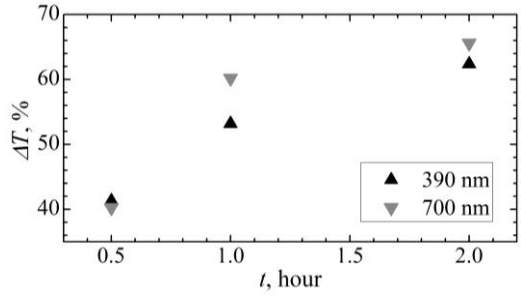

Fig. 12. The dependence of the ΔT-value on the exposure time t for the wavelengths of 390 and 700 nm

We can see a tendency for the value of Δ*L* to decrease with increasing the exposure time *t*. At the same time, the value of Δ*T* increases with increasing *t*. These results correlate with similar results for a series of samples that were obtained for different pressing temperatures *C*, and can be explained by the similar considerations.

At the same time, for the values of P = 20 MPa, C = 180 °C, and t more than 0.5 h, a melting of a polycrystal surface during pressing is observed. The longer the pressing process takes place under such conditions (temperature and pressure), the larger the near-surface volume of the polycrystalline scintillator is affected. In turn, this leads to clouding of a scintillator surface and, as a consequence, to a decrease in the transmittance of light. That is confirmed by the results of the measurements (see Fig. 11), namely, when the exposure time t increases, the optical transmittance of light T decreases (or ΔT-value increases).

Taking into account the obtained results, it is advisable to determine the optimal exposure time t not by a single value, namely by the range from 0.5 to 2 h, since changing the parameter t allows to vary the optical and scintillation characteristics of the polycrystal according to a specific task. Therefore, in the case when the value of the relative light output L is a priority, the exposure time t should be longer (2 h). When the transparency of the sample is more important, the value of t should be minimal (0.5 h).

2.5. COMPARISON OF CHARACTERISTIC OF POLYCRYSTALLINE SAMPLES OBTAINED BY DIFFERENT METHODS

The above results of the study showed that the optimal technological conditions for obtaining *p*-terphenyl polycrystals from fragments of quasi-crystals are the following parameters: pressure P = 20 MPa, pressing temperature C = 180 °C and the exposure time t in the range from 0.5 to 2 h.

To compare the proposed method of obtaining polycrystals with the traditional one, we produced a *p*-terphenyl polycrystal from crystalline grains according to the previously developed technology (P = 20 MPa, C = 165 °C, t = 1 h, grain sizes in the range from 1.7 to 2.5 mm). For this sample, we also studied the values of the relative light output L, energy resolution R, and optical transmittance coefficients T. The values of L, R, and T for three polycrystals obtained under optimal conditions from fragments of a quasi-crystal and for the polycrystal obtained from crystalline grains are presented in Table.

Comparison of the relative light output L, energy resolution R and optical transmittance coefficients T for *p*-terphenyl polycrystals obtained from both quasi-crystal fragments and crystalline grains

Sample	L, %		R, %		T, %	
	^{137}Cs	^{239}Pu	^{137}Cs	^{239}Pu	λ =390 nm	λ = 700 nm
p-terphenyl single crystal (reference)	100.0	100.0	10.9	14.3	56.0	74.1
Polycrystals of *p*-terphenyl obtained from fragments of quasi-crystals						
p-terphenyl polycrystal # 1	146.0	129.0	10.3	13.5	23.5	33.8
p-terphenyl polycrystal # 2	136.0	127.0	14.0	13.3	17.7	24.6
p-terphenyl polycrystal # 3	152.0	148.0	9.9	12.0	17.3	22.1
p-terphenyl polycrystals obtained from crystalline grains						
p-terphenyl polycrystal (our production)	95.0	69.0	no resolution	21.8	9.4	13.1
p-terphenyl polycrystal (2.0…2.2 mm) [13]	72.0	64.0	no data	no data	13.0	19.0
p-terphenyl polycrystal (2.2…2.5 mm) [13]	81.0	76.0	no data	no data	14.2	19.7
p-terphenyl polycrystal (2.5…3.0 mm) [13]	81.0	81.0	no data	no data	16.6	21.8

Table also shows the values of L and T for *p*-terphenyl polycrystals obtained from crystalline grains (P = 30 MPa, C = 165 °C, t = 1 h, the ranges of grain size 2.0…2.2, 2.2…2.5, and 2.5…3.0 mm), which were studied by the authors in [13]. The presented results clearly demonstrate that polycrystals of *p*-terphenyl, which were obtained from fragments of quasi-crystals under the optimal pressing conditions, have better scintillation and optical characteristics than polycrystals that were made from crystalline grains. According to Table, for *p*-terphenyl polycrystals obtained by the new approach the values of L, relative to the reference single crystal, are 125…150 and 135…150% upon excitation by alpha particles and conversion electrons, respectively.

The proposed pressing method makes it possible to obtain scintillators with lower fragility (compared to a single crystal), which makes them more functional and facilitates their mechanical processing.

CONCLUSIONS

1. The new method of obtaining polycrystalline scintillators by direct pressing fragments of a quasi-crystalline ingot is proposed. The scintillation and optical characteristics of the obtained samples of quasi-crystals and polycrystals were studied; a comparison of these characteristics with similar characteristics of the samples obtained by the standard method was carried out.

2. The effect of pressure, temperature, and the exposure time of *p*-terphenyl polycrystals during pressing on their optical and scintillation properties was studied. We obtained that the optimal parameters of pressing are the following: pressure P = 20 MPa,

temperature C = 180 °C, the exposure time t in the range from 0.5 to 2 h. Polycrystals with the exposure time t of 0.5 h had greater transparency, and polycrystals with the exposure time t of 2 h demonstrated a higher light output.

3. It is shown that for *p*-terphenyl polycrystals obtained by the new method, the values of the light output relative to the standard *p*-terphenyl single crystal are 125…150 and 135…150% when excited by alpha particles and conversion electrons, respectively.

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НОВИЙ ПІДХІД ЩОДО СТВОРЕННЯ ОРГАНІЧНИХ ПОЛІКРИСТАЛІЧНИХ СЦИНТИЛЯТОРІВ

Я.І. Полупан, Н.Л. Караваєва, А.В. Креч, І.В. Лазарєв, С.В. Махота, Є.В. Мартиненко, С.С. Міненко, О.А. Тарасенко

Одним із недоліків полікристалічних сцинтиляторів є значне погіршення їх сцинтиляційних і оптичних характеристик із збільшенням товщини сцинтилятора. Запропоновано новий підхід щодо отримання вихідного матеріалу для полікристалів на основі *n*-терфенілу, при якому зонною плавкою і додатковою стадією реверсного руху одержують матеріал для пресування у вигляді злитка. Такий спосіб отримання полікристалів забезпечує суттєве поліпшення їх сцинтиляційних та оптичних характеристик по відношенню до існуючих аналогів.

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