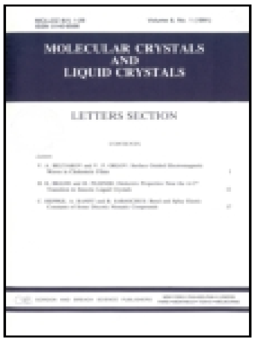

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Distribution Coefficient of 1,4-diphenyl-1,3-butadiene in *p*-terphenyl Single Crystal and Its Influence on Scintillation Crystal Light Output

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The method of gas chromatography-mass spectrometry (GC-MS) was used to determine the amount of 1,4-diphenyl-1,3-butadiene(DFB) in p-*terphenyl (PTP) crystal. We studied five* p-*terphenyl single-crystal boules with different initial DFB concentrations. Values of DFB concentration determined in different part of such the boule are presented. These data are used to estimate the values of distribution coefficient. The value of distribution coefficient which calculated experimentally was compared with theoretical calculated value. The effect of 1,4-diphenyl-1,3-butadiene concentration on light output was studied. The dependence of a number of useable fragments of the boule from initial amount of DPB was analyzed.*

Keywords Distribution coefficient; gas chromatography-mass spectrometry; light output; organic crystal; *p*-terphenyl; 1,4-diphenyl-1,3-butadiene

Introduction

The *p*-terphenyl (PTP) has good rugged clear crystals and can be readily grown by Bridgman technique. They have the sufficiently high radiation resistance among organic crystals [1]. Due to the processes of delayed radioluminescence occurring in them, they are suitable for pulse shape discrimination, have a short decay time of fast component and fairly high light output values. Therefore these scintillation crystals are used to obtain the energy spectra of fast neutrons, alpha and beta particles, in the presence of background photons of gamma-radiation [2–6]. Doping of single crystal of PTP by 1,4-diphenyl-1,3-butadiene (DPB) result in the growth of light output values, or to increasing the number of photons produced by this type of excitation [7–9]. Increasing of light output values for doped single crystals as compared with undoped single crystals, can be explained by effective transfer of electronic excitation energy from the guest molecules (PTP) to the molecules of dopant (DPB). At the same time, the light output values tend to decrease when samples have extra DPB

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concentration, due to concentration quenching processes. Indeed, if DPB concentrations for the samples of different boule parts differ from each other, then not all parts of this boule may be optimal from the viewpoint of scintillation properties. It is highly probable that for some initial concentration C_0 in the melt it is possible to use only some of the boule fragments.

Usually, the concentration of DPB is assumed as an initial amount of the activator added to the melt, but it is not the real concentration of DPB in a crystal. Therefore, the study of addition agents in doped single crystals of PTP is an important problem. The distribution coefficient k may be calculated as the ratio of the solute concentration in the freezing solid to that in the main body of the liquid. The value of k will be greater or less than unity, depending on whether the solute raises or lowers, respectively, the melting point of the solvent. The investigations relative to this matter have been carried out in [10], but only for initial concentration $C_0 = 0.1\%$.

The problem under discussion is interesting not only for single crystals production, but also for polycrystalline [7–9] and composite [11] scintillators. Both polycrystalline and composite scintillators are obtained from the similar granules. The granules were obtained by grinding a single crystal at a low temperature under a layer of liquid nitrogen with subsequent steps of separation through sieves. Polycrystals are obtained from the granules by single-axial pressing at pre-melting temperatures. In the case of composite scintillators, the granules are introduced into dielectric gel.

Theory

The equilibrium distribution coefficient k_0 can be determined on the basis of the thermodynamic laws for the dilute solution. There is simple method of determining the equilibrium distribution coefficient, proposed by van Laar [12]. On the other hand the real solutions are not ideal and accurate calculation of the value of k_0 becomes impossible. These calculations only give a rough estimate of the value k_0. The equation has the following form if to assume that the solid and liquid phases are ideal solutions:

$$\ln k = \frac{\Delta H_2}{R \cdot T_2} \frac{T - T_2}{T} \tag{1}$$

where T is the melting point of the host component, T_2 is the melting point of the guest component, ΔH is the molar enthalpy of reaction for the guest component, kJ/mol.

The melting point of PTP is 214°C. The melting point of DPB is 152°C. So as follows from Eq. (2), $k < 1$ because the melting point of addition agent is less than the melting temperature of the basic substance. Therefore, the addition agent is rejected by the freezing solid and is accumulated in the liquid.

Equation of the impurity distribution during the normal crystallization was first derived by Gulliver [13] and a bit later by Scheil [14]:

$$C = k_0 C_0 (1 - g)^{k_{0-1}}, \tag{2}$$

where C is the concentration of addition agent in the crystal at the point, where a fraction g of the original liquid has frozen, C_0 is the initial concentration; k_0 is the equilibrium distribution coefficient. This equation was derived for the casting of metals in metallurgy. At a later data this formula was applied by Pfann to study the distribution of impurities when purification of semiconductors [15], and by Herington [16] to use it for organic substances.

It is assumed that k_0 is a constant during the growth. There is no diffusion in the solid phase and concentration in the liquid is homogeneous. Eq. (2) is approximate, since it is not observed for all the range of g variation. In any real system, the value of k_0 must be changed according to the impurity concentration, and cannot be constant over the entire range of g.

There is a method for the experimental determination of the effective distribution coefficient k. For this, it is necessary to solidify a cylinder of the materials by normal freezing; determine solute concentration C, as a function solidified, g, by some analytical method; plot concentration against fraction solidified. A logarithmic plot of the normal freezing equation is useful for this purpose because it is a straight line. Both sides of Eq. (2) have been divided by C_0 and after taking the logarithm of both sides of this expression we obtain the equation of the line (3):

$$\lg\left(C/C_0\right) = \lg k + (k-1)\lg(1-g) = a + b\lg(1-g). \tag{3}$$

From Eq. (3) follows that a value of k can be obtained as slope and as well as the intercept at $g = 0$.

The effective distribution coefficient k is equal to the equilibrium distribution coefficient k_0 if to assume that rate of the growth is very low. The increasing of the growth rate leads to a decrease of separation efficiency and to increase in the difference between k_0 and k values according to the equation of Barton-Prim-Schlichter (4) [17]:

$$k = k_0 = \frac{1}{k_0 + (1-k_0)\exp(-fd/D)}, \tag{4}$$

where k_0 is the equilibrium distribution coefficient, f is a travel velocity of the crystallization front, D is a diffusion velocity of the impurity in the liquid, and d is a characteristic boundary layer width.

There are two reasons to assume that equation between k_0 and k values is right. The growth of organic molecular crystal must be carried out at very low speeds, that making possible formation of a crystal lattice. Besides, organic compounds crystallize more slowly than metals, because of lower thermal conductivity.

It is quite important that the guest molecule and the host molecule are of the similar size. In this case, guest molecules form a substitutional solid solution with host molecules. The host molecules are replaced by the guest molecules in units of the crystal lattice [18]. Fig. 1 that was constructed by use of Hyper Chem. program [19] demonstrates their similarity.

Experimental

Sample Preparation

Six single crystal boules of *p*-terphenyl 15 mm in diameter were grown to study the distribution of DPB molecules along the growth direction. For this purpose, five weighed portions of *p*-terphenyl (20.0 g) purified by zone melting were mixed with 10.0, 20.0, 60.0, 100.0, 140.0 mg of DPB. It result in values C_0 equal to 0.05, 0.1, 0.3, 0.5 and 0.7 mass%, respectively. These mixtures and the weighed portion of PTP (20.0 g) without DPB were filled into glass ampoules. An ampoule contains the mixture was vacuumed, was filled with dry argon, was sealed, and was placed in the vertical tube furnace with two heaters. The growth of single crystals was carried out consecutively in the same furnace at a speed of 1.0 mm/hr by the Bridgman–Stockbarger method at the temperature 230°C. At the end

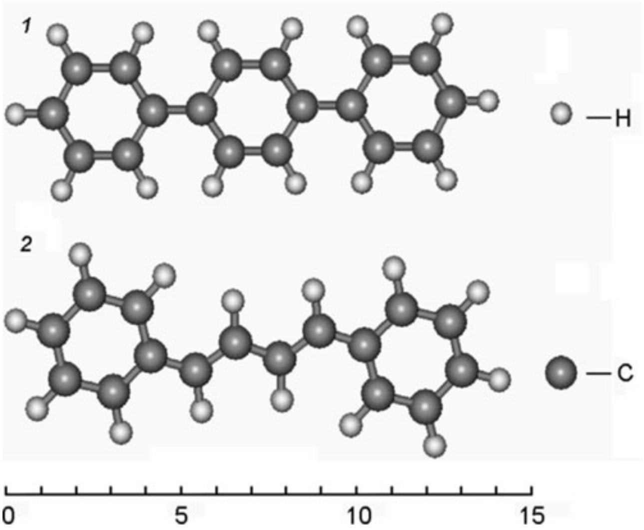

Figure 1. Schematic representation of *p*-terphenyl (1) and 1,4-diphenyl-1,3-butadiene (2) molecules.

of the growth process, the temperature in the furnace was smoothly lowered at a rate of 1 C/hour to a room temperature. Each boule was carefully removed from an ampoule and was sawed on seven segments by use of thread saw. The scheme of sawing is shown in Fig. 2.

First, the measurements of light output values for the samples 1–6 were carried out. After that, these samples were analyzed by gas chromatography-mass spectrometry method (GC-MS). The measurement of the cone (sample number 0) by use of the GC-MS method was carried out without the light output measurement.

The Method of Gas Chromatography Mass Spectrometry (GC-MS)

The concentration of 1,4-diphenyl-1,3-butadiene in the sample of single crystals of *p*-terphenyl was determined in the following way [10]. Analysis was performed on a Varian 1200 L GC-MS instrument in GC-MS mode with EI at 70 eV equipped with Optima-5 capillary column with 5% polyphenylsiloxane and 95% polydimethylsiloxane as a stationary phase. Heating was fulfilled as following: 1 min holding at 100°C then heating to 300°C with 20°/min heating rate. Anthracene was used as an internal standard; the injection probe volume was 1 μL at the temperature 300°C. Average of three independent determinations was used for quantitative analysis.

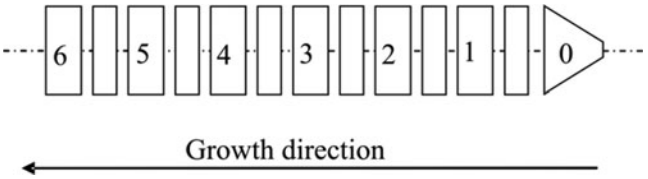

Figure 2. Sawing scheme of boule with samples numbers accepted in further.

Measuring the Light Output

Measurements of light output values for the single-crystal samples were carried out by scintillation amplitude spectra upon irradiation by photons of gamma radiations (^{137}Cs) with the energy $E_e = 0.662$ MeV, conversion electrons (^{137}Cs) with the energy $E_e = 0.622$ MeV, and alpha particles (^{239}Pu) with the energy $E_e = 5.15$ MeV. Spectrum of scintillation amplitude was obtained by accumulating signals of elementary acts measurements in the memory of the multichannel amplitude analyzer AMA-03F. Analyzer scale was calibrated by energy lines, which correspond to the edge of Compton spectra with using ^{22}Na, ^{60}Co, and ^{137}Cs radionuclide sources. Values for scintillators were calculated by the comparison method [20] with using the reference undoped single crystal of *p*-terphenyl. It light yield is 16,890 photons for excitation by photons of gamma radiations, 18,730 photons for excitation by conversion electrons and 1,475 photons for excitation by alpha particles. Relative light output of this single crystal was taken as one.

Results

DFB Content Values for Samples Under Investigation

Results of determination of DPB content by use of the GC-MS method are shown in Table 1.

The Distribution Coefficient Calculated by Thermodynamic Method

As mentioned above, there is simple method of calculating the distribution coefficient using values of melting heat and values of melting points of these components. To do this, it is necessary to substitute values of ΔH, T, and T_2 in Eq. (2). Value of T is equal 214°C and value of T_2 is 152°C respectively. The ΔH value is equal -8475 kJ/mol [21]. The value of distribution coefficient calculated by this way is equal 0.137.

The Distribution Coefficient Calculated by Graphic Methods

Based on obtained data (Table 1), the values of lg C/C_0 were plotted against lg $(1-g)$. The values of the sample weight and the boule weight were used to calculate the value of g. Accordingly to the Eq. (3), the values of distribution coefficient k can be estimated for each of the samples (see Fig. 2) using the concentration DBD molecules in it. These values were obtained by the GC-MS method and are demonstrated by Table 1. Least squares method was used to obtain approximation solution (3). The values of the distribution coefficient k, was found both from slope of such line ($k = \exp(a)$), and as the value of the intercept of ordinate axis ($k = b + 1$). The results obtained for all the concentrations are presented in Table 2.

If assumptions made to derive Eq. (2) is still right then k values obtained by these two approaches should be identical. One of these assumptions is the invariability of the distribution coefficient k_0 during the growth process i.e. for different samples in Fig. 2. The k-values obtained from line slope and from the intercept of the axis of ordinates are different (see Table 2). Therefore the approximation (2) is not correct for the case under discussion. The k value is not the same for different samples in boule (see Fig. 2), and this difference is not too large to be neglected.

Let us take into account the C data for the first n samples (see Fig. 2) and plot the approximations (3) for different values of n. Figure 3 demonstrates that k value increases with n for the case of $C_0 = 0.05$ mass%. The C values are taken from experiment (see

Table 1. Content of DPB in the samples

	Sample number (see Fig.2)						
	0	1	2	3	4	5	6
C_0	Content of DPB in the sample, mass%.						
0.05	0.0083 ± 0.0010	0.0094 ± 0.0005	0.0087 ± 0.0006	0,0107 ± 0.0011	0.0161 ± 0.0003	0.0219 ± 0.0017	0.0764 ± 0.0054
0.1	0.0168 ± 0.0015	0.0169 ± 0.0017	0.0184 ± 0.0015	0.0178 ± 0.0007	0.0332 ± 0.0041	0.0517 ± 0.0047	0.2320 ± 0.0065
0.3	0.0478 ± 0.0007	0.0544 ± 0.0005	0.0685 ± 0.0022	0.0859 ± 0.0053	0.1581 ± 0.0143	0.2608 ± 0.0132	0.7979 ± 0.0105
0.5	0.1115 ± 0.0109	0.1204 ± 0.0062	0.1250 ± 0.0017	0.1791 ± 0.0174	0.2399 ± 0.0125	0.3877 ± 0.0253	1.8418 ± 0.0596
0.7	0.1563 ± 0.0030	0.1832 ± 0.0083	0.2091 ± 0.0082	0.2352 ± 0.0188	0.3165 ± 0.0210	0.5768 ± 0.0439	2.7281 ± 0.1522

Table 2. Distribution coefficient k values for different DPB concentration calculated from Eq.(3)

C_0,%	0.05	0.1	0.3	0.5	0.7
$k = \exp(a)$	0.146	0.132	0.164	0.193	0.198
$k = b + 1$	0.289	0.156	0.093	0.102	0.099

Table 1). The slope of the line $b_n = k_n - 1$ grows with the n increase. The same tendency is observed for higher concentration C_0. Therefore we can affirm that the value of k_n increases constantly with n-value. Let us assume that the growths of concentration result in of the surface roughness. It causes the raise of the probability of a dopant molecule capture during the crystal growth process. Of course to prove assumption the separate study is necessary.

Determining Light Output Values

Measurements of light output for the samples were run to find the optimal initial concentration C_0 that allows us to use each of the boule fragments (Fig. 2) effectively. Light output values were measured for the following excitation. It was photons of gamma radiation (Fig. 4), conversion electrons (Fig. 5), and alpha particles (Fig. 6). The sample number was taken according to Fig. 2.

These results show that all the samples have high light output values for C_0 not exceed 0.1 mass %. The samples with $C_0 \geq 0.3$ mass% have high light output values only for the 2/3 part of the boule. The rest of the boule is of low quality. Future increase of DPB concentration results in an appreciable influence of concentration quenching on radioluminescence of crystal. That is why, it is important to determine the optimal concentration of DPB in the crystal lattice of PTP which corresponds to the maximum light output values. Figures 7 and 8 will help us to answer this question.

Figure 7 show the light output versus DPB concentration values in the case of excitation by conversion electron. The samples with DPB concentration in crystal $C < 0.3\%$ have

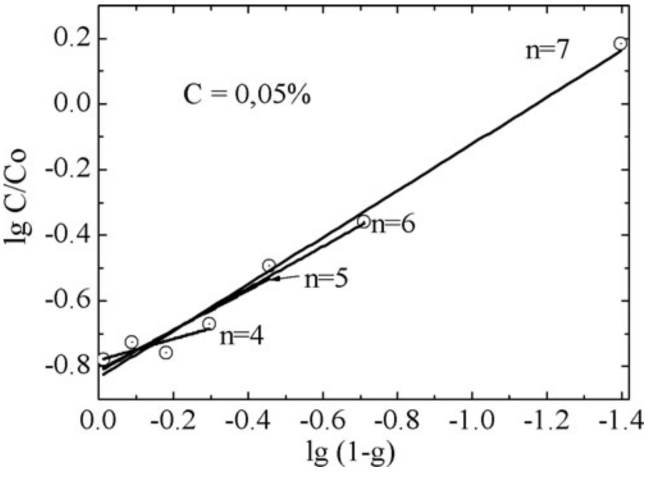

Figure 3. The lg(C/C_0) plotted against lg (1-g) for different n.

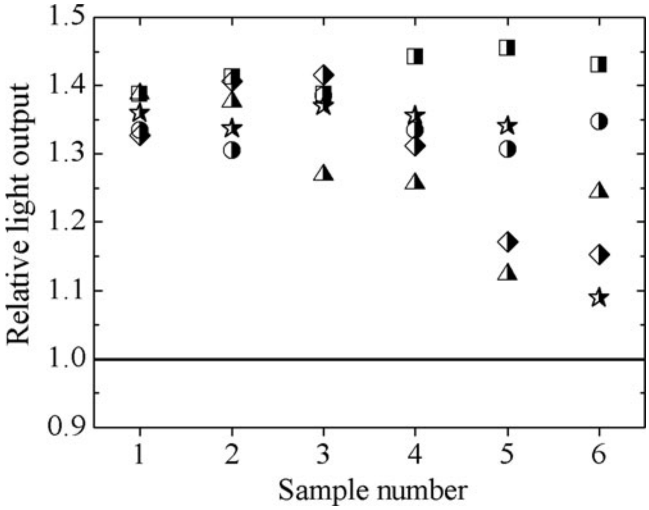

Figure 4. Relative light output as a function of sample number for excitation by photons of gamma radiation. Squares, circles, triangles, rhombs, and stars correspond to the samples with C_0 equal to 0.05, 0.1, 0.3, 0.5, and 0.7%, respectively. Line marks the value of the undoped single crystal.

high light output values; the samples with DPB concentration in the crystal $C \geq 0.3\%$ have low values of light output. Figure 8 demonstrates that for $C = 0.1$–0.3% in the case of excitation by alpha-particles the values of light output is maximally.

Previously, the effect of DPB concentration on relative light output of polycrystalline scintillators obtained from the granules by hot-pressing we studied in [9]. Accordingly to this work, technology the melt contains the concentration C_i solidified quickly. After that, the obtained materials was grinding to prepare the granules. Accordingly to that technology

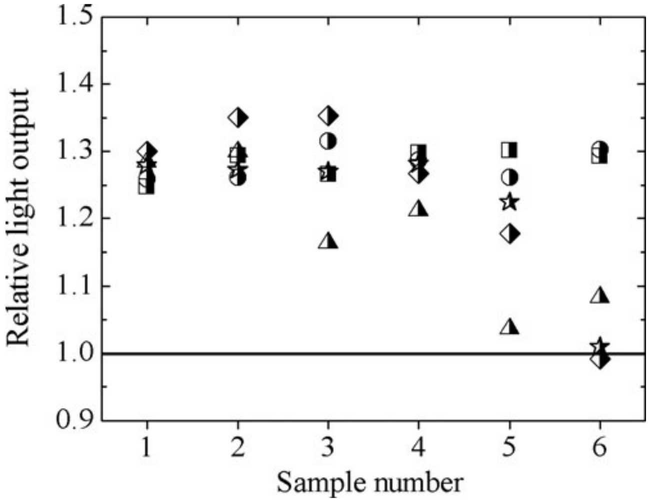

Figure 5. Relative light output as a function of sample number for excitation by conversion electrons. The symbols are the same as in Fig. 4.

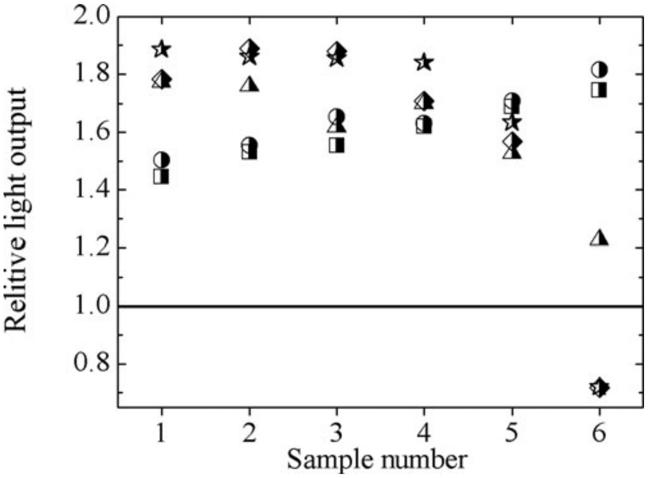

Figure 6. Relative light output as a function of sample number at α-excitation. The symbols are the same as in Fig. 4.

[9], the maximum values of light output was obtained for $C = 0.1$–0.3% as well as in our paper.

The doped single crystals of PTP have higher light output than the undoped ones. If we take as 100% the relative light output of undoped crystal then accordingly to result obtained in the work we have the following: the increase of 135% for conversion electrons, 141% for photons of gamma-ray and 189% for alpha-particles was obtained. For excitation by alpha-particles scintillation generated directly on the detector surface and pass through the entire thickness of single crystal. Therefore the high optical transmittance for intrinsic emission may explain the maximum of light output for excitation by alpha-particles.

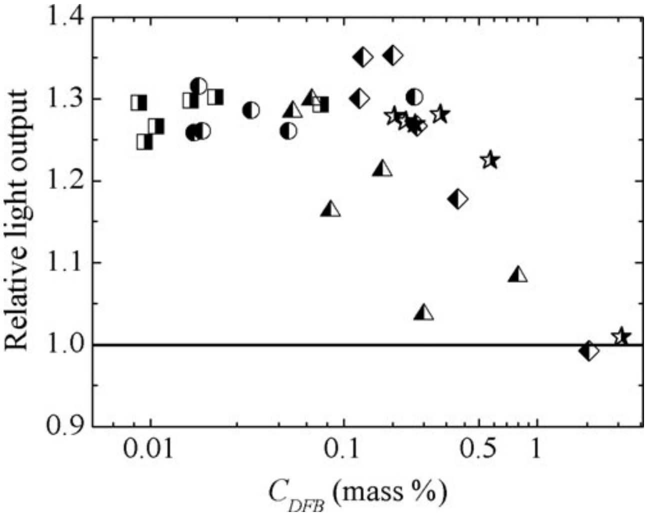

Figure 7. Relative light output as a function of DFB concentration for excitation by conversion electrons. The symbols are the same as in Fig. 4.

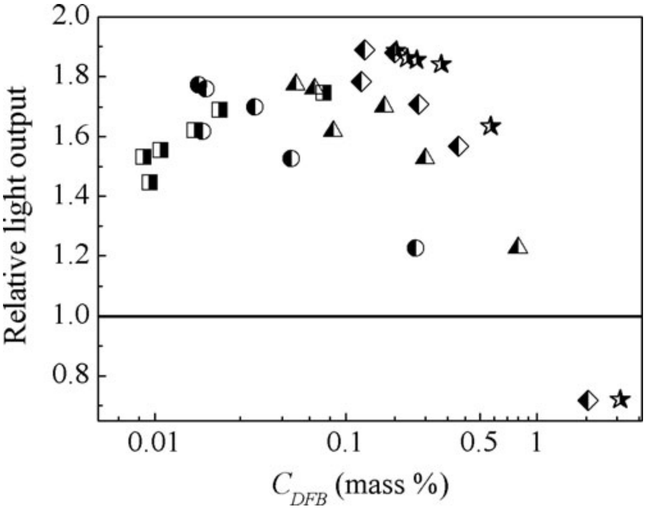

Figure 8. Relative light output against DFB concentration at excitation by α-particles. The symbols are the same as in Fig. 4.

Conclusion

The method of gas chromatography mass spectrometry (GC-MS) was used to find the values of DPB concentration for different part of doped single crystal boule of *p*-terphenyl. The value of effective distribution coefficient *k* calculated using this data about the same as the value of distribution coefficient estimated by thermodynamic method. The increase C_0 from 0.1% to 0.7% results in to increase *k* from 0.14 to 0.21. The value of *k* is not constant and tends to increase during the crystal growth process. All boule fragments with $C_0 = 0.1\%$ have high light output values. Fragments with $C_0 \geq 0.3\%$ have high light output only for 2/3 of the boule. The rest of the boule has low scintillation parameters. The concentration quenching of the radioluminescence in the samples $C_0 \geq 0.3\%$ causes the low light output. The maximum values of light output correspond to the range of DPB concentration in the crystal 0.1–0.3%.

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