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GADOLINIUM-BASED HYBRID ULTRA-LOW-BACKGROUND MATERIAL FOR PROTECTING THE DARKSIDE20K DARK MATTER DETECTOR FROM BACKGROUND NEUTRONS

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A laboratory technique was developed for obtaining an ultra-low-background hybrid material based on organic glass — polymethyl methacrylate (PMMA). ^{157}Gd nuclei are used as an efficient absorber of thermal neutrons in the hybrid material. A uniform distribution of gadolinium in the PMMA matrix is achieved by introducing the gadolinium in the form of a coordination compound — gadolinium acetylacetonate — into the hybrid material. A uniform gadolinium distribution was achieved in a 5 cm thick matrix of hybrid material with gadolinium mass content from 1.0 to 1.5%. It is shown that at 298 K the mechanical characteristics of the hybrid material samples coincide with nominally pure PMMA, but at 77 K the hybrid material is inferior to pure PMMA within admissible requirements.

Key words: gadolinium, uranium, thorium, polymethyl methacrylate, hybrid material, mass spectrometry with inductively coupled plasma.

The present study is a continuation of the work on the development of technology for ultra-low-background agents based on gadolinium for the manufacture of the functional elements of detectors used in studies of rare physical processes [1]. One of the elements of this design is the VETO screen, which serves to protect the working volume of the detector from background thermal neutrons [2 – 7].

The technological creature of the ultra-low-background hybrid material for VETO based on an organic polymer impregnated with ^{157}Gd nuclei resides in the fact that the DarkSide20k detector project requires at least 12 tons of material that must contain at least 250 kg of gadolinium. The practice of selecting a limited batch meeting the conditions for ultralow background of radioactive elements such as U and Th from large batches of commercial samples emerged in similar projects on the study of rare processes, such as the study of nonradiative double-beta decay — NEMO, XENON, LUX [6].

However, this practice can be successfully implemented when large batches of cheap products are available on the market from which a selection can be made. It is a question of a ratio of the order of 10,000 : 1 between a batch of commercial products and batches of ultra-low-background material. In this approach a significant number of expensive analyses are performed in the selection process in order to determine ultra-low amounts of U and Th as well as other long-lived radioactive elements in the materials under study. The result of such a selection process is that the amount of obtained ultra-low-background material is limited. If the amount of ultra-low-background material needs to be increased, the entire selection procedure is repeated anew. Such an approach entails significant risks in terms of the time required to reach a positive result and cost uncertainty of expensive analyses.

In the case of gadolinium agents two factors complicate the implementation of the described approach.

1. Gadolinium-based agents are not cheap, so that they cannot be selected from large commercial consignments.

2. An analysis of Gd-containing agents available on the market showed [1] that their content of U and Th is largely determined by the origin of the feedstock. But the main suppliers from the People's Republic of China do not guarantee that the raw-material source will be duplicated in deliveries of different batches of Gd-containing agents.

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TABLE 1. Thorium and Uranium Concentrations Determined in Samples of Commercial Polymeric Materials

No.	Substance	Manufacturer	Element concentration, ng/g	
			Th	U
1	Polyurethane EP SKU PT-74, grade 5	Elastoplast Production LLC (Russia)	< 0.1	1.60 ± 0.03
2	Polystyrene	Institute of Physicotechnical Problems JSC (Russia)	< 0.1	< 0.1
3	Polyvinyl alcohol	JAPAN VAM&POVAL CO., LTD (Japan)	0.41 ± 0.06	< 0.1
4	Polymethylmethacrylate	Donchamp Acrylic Co., Ltd. (China)	0.060 ± 0.018	0.021 ± 0.010
5	Polymethylmethacrylate	Mat Group database (Germany)	0.001^{*}	0.0029^{*}
6	Polymethylmethacrylate	Research Institute of Polymers (Dzerzhinsk, Russia)	0.050 ± 0.015	0.018 ± 0.006

* Manufacturer's data.

In this connection we reckoned that it would be expedient to develop in parallel a technology for an ultra-low-background, hybrid, Gd-containing material and a technology for the purification of the gadolinium agent from radioactive impurities. This approach is the one implemented in the course of this study.

PROCEDURE

The method for analyzing the impurity content in Gd-containing compounds by means of mass spectrometry with inductively coupled plasma is described in detail in [1].

The polymeric materials were dissolved using Ultrapur (Merck) 96% high-purity sulfuric acid with microwave decomposition of the sample and a SPEEDWAVE system (Berghof, Germany) equipped with DAP-100 polytetrafluoroethylene autoclaves (Berghof, Germany). The dissolution product was transferred into polypropylene (PP) tubes, aliquots were taken, and subsequent dilution and analysis were performed. Analytical measurements were performed on a NexION 300D inductively coupled plasma mass spectrometer (ICP-MS) (Perkin Elmer, USA). The impurity purity of the preparations for 65 chemical elements was assessed using the TotalQuant method [8]. In the present work, quantitative analysis of the content of uranium and thorium in polymer preparations was performed by constructing calibration dependences taking into account the concentration of the main (matrix) elements in the analyzed solution.

On the basis of the results it was found that the content of uranium and thorium in commercial polymers is relatively low (Table 1). Polymethyl methacrylate (PMMA) possesses the best metrics.

It was found that the integral chemical purity of the homegrown compound PMMA 99.998% (by weight) was slightly higher than the chemical purity of the purest compound from the Chinese company Donchamp Acrylic Co., Ltd. (99.996 wt.%) (see Fig. 2c and d).

Taking the mechanical characteristics into consideration, polymethyl methacrylate, having the highest room-temperature strength among the materials studied, was chosen as the material for the organic matrix of the hybrid material [9 – 13].

The hybrid material (HM) for VETO must meet a number of requirements, specifically, uniform distribution of gadolinium nuclei over HM with thickness 5 cm and mechanical strength comparable to that of undoped PMMA at room temperature and at 77 K. The latter requirement is due to the fact that all of the HM in the detector will be situated in liquid argon. The requirement of 5 cm thickness can be met only if the PMMA thermal polymerization technology is implemented [13]. Attempts to incorporate the nano-sized powder compound Gd_2O_3 (20 – 80 nm) did not lead to the required results. Despite the nanoscale character of the grains, considering the large density difference in densities ($\rho_{Gd_2O_3}$ = 7.407 g/cm^3 [18], ρ_{PMMA} = 1.18 g/cm^3 [9]) and long thermal polymerization process (12 h to 20 days, depending on the size of the product) the nanosized Gd_2O_3 particles agglomerated and sedimented during the process of polymerization. In these experiments the difference in the gadolinium concentration over the HM thickness of 5 cm exceeded one order of magnitude.

In connection with this circumstance, the following scheme for obtaining HM with a Gd-containing component was adopted and implemented in this work:

1) purification of $GdCl_3$;

2) synthesis of acetylacetonate $Gd(C_5H_7O_3)$;

3) dissolution of $Gd(C_5H_7O_2)_3$ in methyl methacrylate and preparation of the pre-polymer;

4) thermal polymerization of the hybrid material.

The basic idea was that a uniform distribution of Gd can be obtained only if a true solution, and not a suspension, is polymerized.

Analysis of possible Gd-containing agents that could dissolve in the starting methyl methacrylate (MMA) with the commercial component taken into account showed that most promising is gadolinium acetylacetonate — $Gd(C_5H_7O_2)_3$ $(Gd(acac)_3)$ [14]. To obtain $Gd(acac)_3$ it is necessary to have ultra-low-background starting materials: ammonia, acetylacetonate, and gadolinium chloride. Analysis of commercial preparations NH_4OH (25% by volume) (ultrapure, 23-5,

TABLE 2. Physical Properties of Thorium and Uranium Chlorides [16, 17]

Compound	ΔH_0^{298}, kJ/mol	T_{melt}, °C	T_{boil}, °C
$ThCl_4$	−1189	770	920
UCl_3	−891.2	835	1657
UCl_4	−1051	590	789
UCl_5	−1094	Unstable, disproportionates	–
UCl_6	−1133	177.5	550

Fig. 1. Laboratory setup for chlorination of powder preparations: *1*) resistance heating furnace; *2*) quartz reactor; *3*) flanges; *4*) glassy carbon containers; *5*) thermostat; *6*) a cylinder with hydrogen chloride; *7*) Drexel vessel.

GOST 24147–80), bidistilled water (GOST 6709–72), and acetylacetone $C_5H_8O_2$ (analytical grade, GOST 10259–78) showed that the content of U and Th in these preparations was less than 0.1 ng/g.

The main problem was getting ultra-low-background $Gd(acac)_3$. For its synthesis within the framework of the adopted strategy it was necessary to develop a method for obtaining a powder preparation with a reduced content of uranium and thorium. We used $GdCl_3$ as the initial Gd-containing preparation.

PURIFICATION OF GADOLINIUM CHLORIDE

According to published data, in most compounds thorium acts as a tetravalent element. Thorium tetrachloride $ThCl_4$ exhibits noticeable volatility: its vapor pressure at 650°C is equal to 10 mm Hg. This fact can be used to separate and sublimate $ThCl_4$ from gadolinium chloride. The temperature dependence of the vapor pressure of solid $ThCl_4$ is described by the following equation [15]:

$$\log P \text{ (mm Hg)} = -\frac{7987}{T} + 9.57. \qquad (1)$$

The sublimation enthalpy $\Delta H_{subl} = 218$ kJ/mol; the evaporation enthalpy $\Delta H_{evap} = 173$ kJ/mol.

Uranium exhibits the oxidation states +2, +3, +4, +5, and +6 [15] and, correspondingly, forms a number of chlorides (Table 2).

The vapor pressure of UCl_4 is described by Eqs. (2) and (3) for various temperature ranges [18] and is about 70 mm Hg at 650°C:
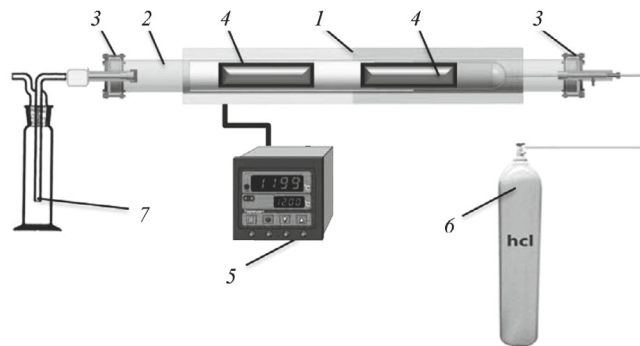
$$\log P \text{ (mm Hg)} = -\frac{10,427}{T} + 13.2995.$$
$$T \in (350; 505°C); \qquad (2)$$

$$\log P \text{ (mm Hg)} = -\frac{7205}{T} + 9.65.$$
$$T \in (590; 790°C). \qquad (3)$$

Thus, taking as a basis the possibility of reducing the concentrations of uranium and thorium in gadolinium chloride by their being transferred in the chlorination process to compounds that are more volatile than $GdCl_3$ we implemented the following stages of purification of gadolinium chloride:

1) chlorination of the initial gadolinium chloride with UCl_4 and $ThCl_4$ being formed;

2) vacuum thermal annealing with the volatile products UCl_4 and $ThCl_4$ being removed.

The chlorination process was conducted using standard laboratory equipment, which included a laboratory quartz reactor, a resistive heating furnace, a thermostat (Termodat-13K6), glassy carbon containers, and a Drexel vessel (Fig. 1).

The initial $GdCl_3$ was loaded into a glassy carbon container and placed in a reactor. Chlorination was conducted using high-purity hydrogen chloride gas (99.999% by volume). The gas flow rate corresponded to 1 L/h. The outgoing vapors were neutralized in a 10% NaOH solution with phenolphthalein added as an indicator.

At the completion of the chlorination process the container with the preparation was transferred to a laboratory unit for high-temperature annealing in a dynamic vacuum. The conditions for conducting experiments to reduce the concentrations of U and Th in the gadolinium chloride preparations are given in Table 3.

The best results were obtained with annealing at 500°C and passing through high-purity hydrogen chloride followed by vacuum-heat treatment for 20 h at 630°C. The gadolinium chloride samples KhG-05 and KhG-06 reached Th and U concentration less than 0.1 ng/g (10^{-8}% by weight) and their general chemical purity was no worse than 99.999% by weight (Fig. 2*a* and *b*).

The synthesis of $Gd(acac)_3$ was performed according to the following procedure. In a Teflon beaker (PTFE), 12 mmol of gadolinium (III) chloride was dissolved in 15 ml of bidistilled water, continuously stirring with a magnetic stirrer. Then, 5 ml of CH_3OH methanol (chemically pure grade, TU 20.14.22-018-29483781–2018) was added. Using a drop funnel, 38 mmol of acetylacetone $C_5H_8O_2$ was added.

TABLE 3. Conditions for Experiments to Reduce the Concentration of Thorium and Uranium in Gadolinium Chloride Preparations

Sample No.	Stage, conditions	Temperature, °C	Time, h	Atmosphere	Obtained concentration, ng/g	
					Th	U
KhG-05	1) chlorination	500	6	HCl	0.08 ± 0.01	0.09 ± 0.01
	2) vacuum thermal annealing	630	12	Vacuum 10^{-4} mm Hg		
KhG-06	1) chlorination	500	9	HCl	0.07 ± 0.01	0.06 ± 0.01
	2) vacuum thermal annealing	650	20	Vacuum 10^{-4} mm Hg		

The resulting mixture was heated to 65°C and a solution of ammonia NH_4OH (25% by volume) was slowly introduced up to neutral pH = 7.0 – 7.3. A white precipitate formed within 120 min. The Teflon beaker with the sediment was placed in an ice bath. The formed precipitate was filtered off on a Buchner funnel under vacuum.

The compound $Gd(acac)_3$ obtained in this manner contained a significant amount of water, which adversely af-

fected the polymerization process and the final mechanical characteristics of the hybrid material. To remove the water the synthesized compound $Gd(acac)_3$ was subjected to additional annealing in a dynamic vacuum with stepped heating and holding at different temperatures (Table 4).

The residual water content in the $Gd(acac)_3$ preparations was estimated using IR spectroscopy (FTIR Tensor 27, Bruker, Germany). According to the analysis of the IR ab-
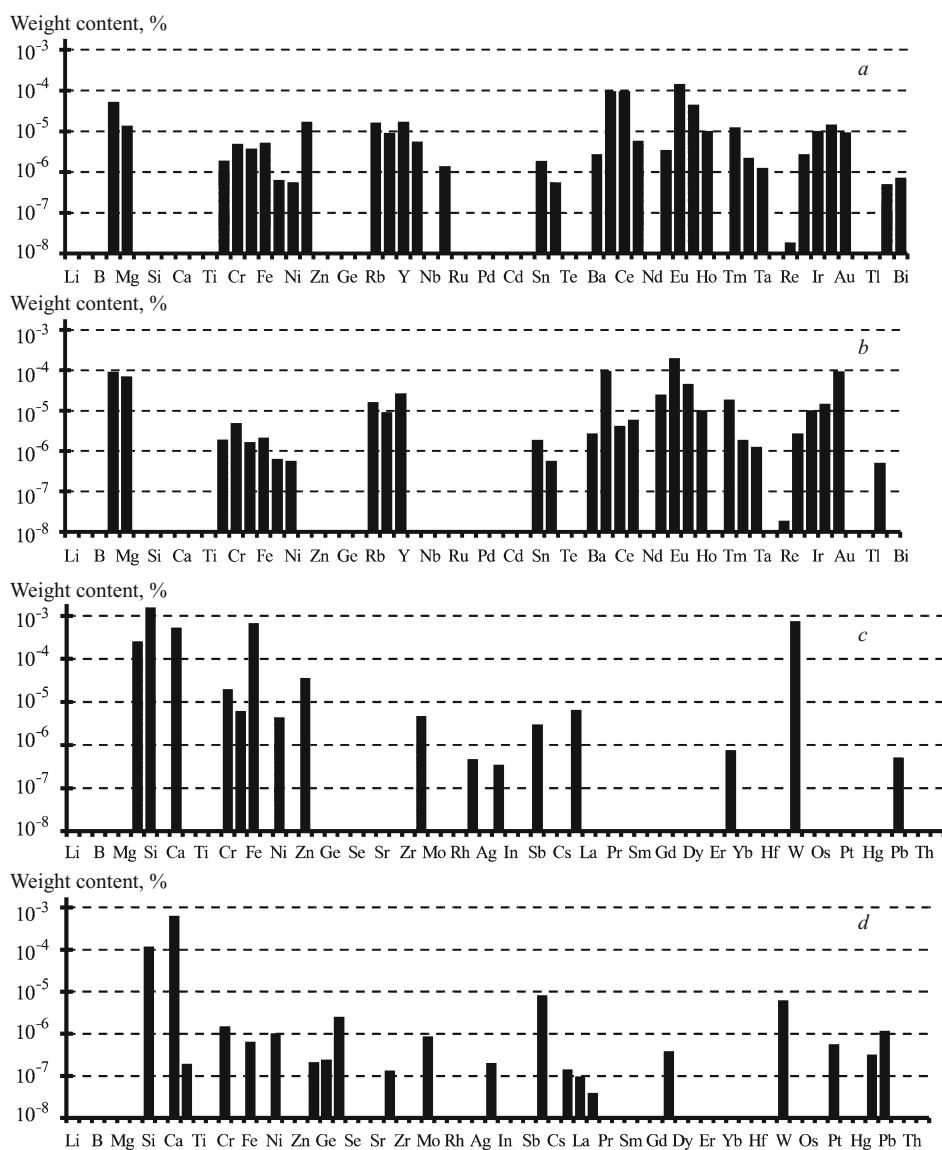
Fig. 2. Content of impurities in preparations of gadolinium chloride (CG) and PMMA from various manufacturers according to the results of analysis by ICP-MS: *a*) KhG-05; *b*) KhG-06, PMMA; *c*) Donchamp Acrylic Co., Ltd. (China); *d*) Research Institute of Polymers (Dzerzhinsk).

TABLE 4. Conditions for Conducting Experiments on Stepwise Annealing of Gd(acac)$_3$ Compounds in Dynamic Vacuum

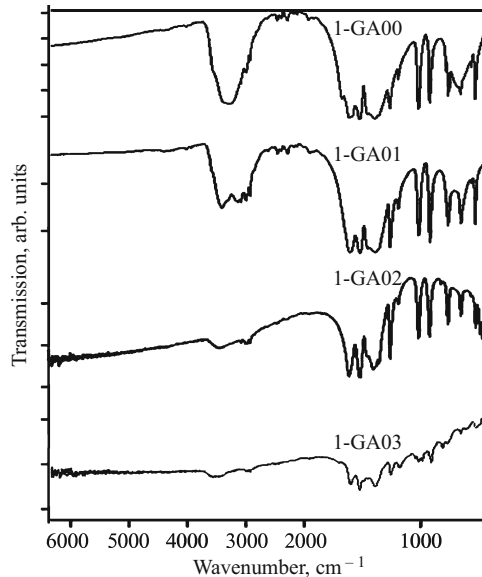| Sample No.	Temperature, °C	Annealing time, h	Annealing conditions
1-GA00	80	10	In air
1-GA01	80	5	Vacuum 10^{-5} mm Hg
1-GA02	$80 \to 150$	$1 \to 3$	Vacuum 10^{-5} mm Hg
1-GA03	$80 \to 150 \to 240$	$1 \to 3 \to 3$	Vacuum 10^{-5} mm Hg

Fig. 3. IR spectra of Gd(acac)$_3$ preparations after annealing (see Table 3 for a description of the samples).

sorption spectra at wave numbers $3600 - 3200$ cm^{-1}, where the characteristic absorption bands of hydroxyl groups are located [19], a significant decrease in the concentration of hydroxyl groups occurred on annealing in dynamic vacuum 10^{-5} mm Hg at temperature 150°C with an exposure time of at least 3 h (Fig. 3). An increase in temperature to 240°C resulted in a reduction in the absorption intensity of OH groups and yellowing of the Gd(acac)$_3$ sample, which indicated its partial decomposition.

PREPARATION AND INVESTIGATION OF THE CHARACTERISTICS OF THE HYBRID MATERIAL

The hybrid material based on PMMA and Gd(acac)$_3$ was prepared in two stages. At the first stage a prepolymer was prepared. For this, benzoyl peroxide was added as an initiator into the monomer MMA, after which a powder preparation of dehydrated Gd(acac)$_3$ and PMMA polymer chips were added with constant stirring at temperature 45°C. Thus, two HM samples were made with nominal weight content in terms of gadolinium 1.0 and 1.5%.

In the second step, the prepolymer was placed in a mold, air was removed, and the assembly hermetically sealed. Polymerization was conducted by heating in steps. The sample was kept for 10 h at each temperature step. After the polymerization process, the HM was additionally annealed at 120°C for 10 h.

The distribution of gadolinium over the thickness of the sample was analyzed by making a 1 mm thick vertical section along the thickness of the sample. Then the sample was polished and placed in a scanning electron microscope (VEGALMU, Tescan). The gadolinium content was determined by x-ray fluorescence analysis (INCA ENERGY 3-MAX, Oxford Instruments) (Fig. 4). The analysis showed that in both samples the spread of the gadolinium concentration from the average value did not exceed 20%. This spread meets the requirements of the VETO design.

Mechanical tensile tests of the samples were performed on an Instron 5882 testing machine. The tests were performed at 22 ± 1°C (298 K) and the temperature of liquid nitrogen (77 K) in accordance with GOST 11262–2017 and GOST 9550–81. Before testing, the samples were kept in liquid nitrogen for at least 10 min.

According to the mechanical tests performed, the characteristics of the HM and PMMA samples at temperature 298 K were practically identical. At temperature 77 K HM is

Fig. 4. Photograph of a sample of hybrid material (*a*) and distribution of Gd over its thickness according to x-ray fluorescence analysis data (*b*).
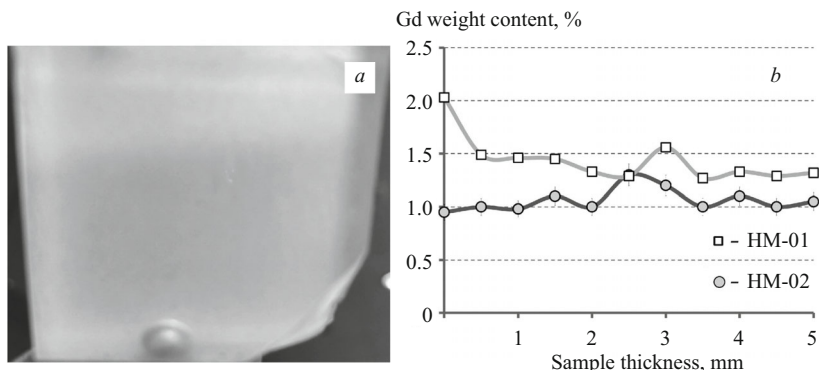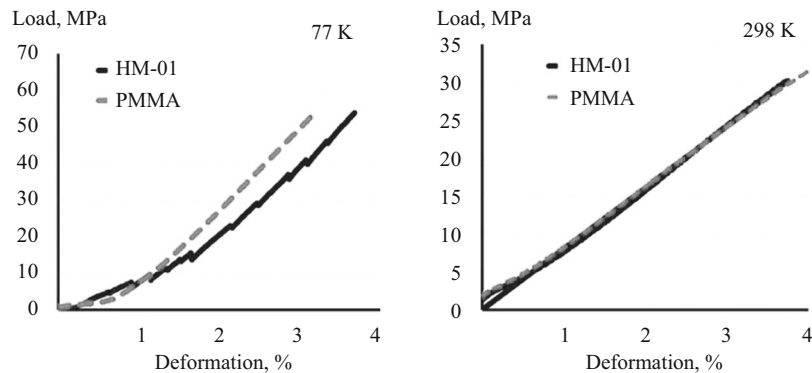
Fig. 5. Results of mechanical tests performed on samples of nominally pure PMMA and HM-01 under tension at liquid nitrogen temperature 77 K and room temperature 298 K.

inferior to pure PMMA within the permissible requirements of 20 rel.% (Fig. 5).

Chemical analysis of the HM samples showed that the obtained hybrid materials meet the requirements of the VETO design in terms of the content of uranium and thorium (U < 0.01 ng/g, Th < 0.01 ng/g).

In summary, it can be concluded that the laboratory technology developed for producing a hybrid material based on a polymer matrix of organic glass polymethyl methacrylate makes it possible to obtain samples up to 5 cm thick and uniformly doped with gadolinium in concentrations up to 1.5% (by weight) over the entire volume. Taking into account the fact that the matrix is doped with an ultra-low-background dehydrated preparation of gadolinium acetylacetonate with residual U and Th concentrations 0.09 and 0.08 ng/g, respectively, and the initial PMMA from the Research Institute of Polymers (see Fig. 2*d*) is characterized by residual concentrations of U and Th < 0.018 and .05 ng/g, respectively, the resulting hybrid material has integral residual concentrations of U and Th at the level of 0.04 and 0.08 ng/g, respectively. This concentration level suggests that the developed hybrid material is promising for the manufacture of VETO components.

REFERENCES

1. M. P. Zykova, I. V. Stepanova, A. S. Chepurnov, and I. Kh. Avetisov, "Technology of ultra-low-background gadolinium-based preparations. Part 1. Impurity composition investigations of gadolinium-containing preparations for the determination of promising raw materials," *Tsvetn. Met.,* No. 11, 35 – 41 (2020).
2. P. Agnes, L. Agostino, I. F. M. Albuquerque, et al., "The VETO system of the DarkSide-50 experiment," *J. Instrumentation*, **11**, 03016 (2016).
3. I. K. Kikoin (ed.), *Tables of Physical Quantities: Reference* [in Russian], Atomizdat, Moscow (1976).
4. D. M. Poehlmann, D. Barker, H. Chagani, et al., "Characterization of gadolinium-loaded plastic scintillator for use as a neutron veto," arXiv:1812.11267v1[physics.ins-det] [Electronic resource] (2018). URL: https://arxiv.org/abs/1812.11267v1
5. J. Dumazert, R. Coulon, Q. Lecomte, et al., "Gadolinium for neutron detection in current nuclear instrumentation research: A review," *Nuclear Inst. Methods Phys. Res. A*, **882**, 53 – 68 (2018).
6. K. Hagiwara, T. Yano, T. Tanaka, et al., "Gamma-ray spectrum from thermal neutron capture on gadolinium-157," *Progr. Theor. Exp. Phys.*, No. 2, 023D01 (2019).
7. D. S. Akerib, C. W. Akerlof, S. K. Alsum, et al., "Projected WIMP sensitivity of the LUX-ZEPLIN (LZ) dark matter experiment [Electronic resource], in: *Astrophysics. Instrumentation and Methods for Astrophysics*, Cornell University (2019). URL: https://arxiv.org/abs/1802.06039v2
8. E. Pruszkowski and P. E. Life, *Total Quant Analysis of Teas and Wines by ICP-MS*, Perkin Elmer Life and Analytical Sciences, Field Application Report, ICP Mass Spectrometry, USA (2004).
9. D. J. Carbaugh, J. T. Wright, R. Parthib, and F. Rahman, "Photolithography with polymethyl methacrylate (PMMA)," *Semicond. Sci. Technol.*, **31**(2), 025010 (2016).
10. D. W. Krevelen and K. Nijenhuis, *Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*, Elsevier (2009).
11. G. Holden, "Elastomers, thermoplastic," in: *Encyclopedia of Polymer Science and Technology*, Wiley & Sons (2004), Vol. 12, pp. 63 – 88.
12. *Polymethylmethacrylate (PMMA, Acrylic)*. URL: https://www.makeitfrom.com/material-properties/Polymethylmethacrylate-PMMA-Acrylic (Date of access: 08.07.2020).
13. E. A. Bratsykhin and E. S. Shulgina, *Technology of Plastic Masses* [in Russian], Khimiya, Leningrad (1982).
14. K. Binnemans, "Rare-earth beta-diketonates," *Handbook on the Physics and Chemistry of Rare Earths*, **35**(5), 107 – 272 (2005).
15. V. I. Boiko, V. A. Vlasov, and I. I. Zherin, et al., *Thorium in the Nuclear Fuel Cycle* [in Russian], Izd. Dom Ruda i Metally, Moscow (2006).
16. I. I. Zherin and G. N. Amelina, *Chemistry of Thorium, Uranium, Plutonium* [in Russian], Izd. TPU, Tomsk (2010).
17. V. A. Rabinovich and Z. Ya. Khavin, *Brief Chemical Handbook* [in Russian], Khimiya, Leningrad (1991).
18. J. Katz, G. Seaborg, and L. Lorss (eds.), *Chemistry of Actinides* [Russian translation], Mir, Moscow (1999), Vol. 3.
19. E. Pretsch, F. Bühlmann, and K. Affolter, *Spectral Data Tables: Structure Determination of Organic Compounds* [Russian translation], Binom. Knowledge Laboratory, Mir, Moscow (2006), pp. 251 – 318.