

## <sup>arch</sup>PbWO<sub>4</sub> WITH IMPROVED OPTICAL PARAMETERS FROM ARCHAEOLOGICAL LEAD

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Technological principles of manufacturing a lead tungstate crystal from archaeological lead for use in low-background experiments to search for rare events are presented. The influence of the conditions for obtaining single crystals of <sup>arch</sup>PbWO<sub>4</sub> on the photochromic effect in single crystals is investigated. By minimizing deviations from the stoichiometric composition, it was possible to improve the optical parameters of the lead tungstate single crystal. Single crystals with improved optical parameters have been obtained using double crystallization and the introduction of an excess of <sup>arch</sup>PbO, which makes it possible to consistently influence various defects in crystals of <sup>arch</sup>PbWO<sub>4</sub>.

### INTRODUCTION

The search for rare events such as interactions with non-baryonic “dark matter”, double (without the participation of neutrinos) beta-decay of nuclei or radioactive decay of isotopes with a long lifetime is a very actual problem in modern elementary particle physics. It is expected that these events will prove the existence of new fundamental particles, as well as expand the understanding of the structure of the Universe [1–4]. Further progress in research in these areas requires new detectable technologies that are able to distinguish between weak and rare interaction signals against the background of significant radioactivity caused by extraneous factors, namely geological, cosmogenic or anthropogenic [5–7].

Low-background experiments using the spectrometric method are carried out in deep underground laboratories. Radioactive contaminants with natural, cosmogenic or anthropogenic origin are present in all of the parts of the experimental apparatus. The detectors, their components, the nearby environment and the shields can be source of possible background, a limiting factor for the achievable sensitivity of the experiments [1, 5].

The sensitivity of an experiment dedicated to a rare event search is roughly inversely proportional to the square root of the background rate. A wide set of requirements have to be satisfied to achieve the highest sensitivity in ultralow level detection: primarily, the choice of a suitable underground laboratory that allows a reduction of the cosmic rays induced background by several orders of magnitude, also protecting the equipment of underground laboratories from the radioactive environment, mainly from gamma radiation and gaseous radon, for this purpose, passive or active screens are used [5].

Scintillation single crystals are the main material used in detectors. The sensitivity of the experiment depends on their properties.

The uniqueness of the properties of the lead tungstate crystal makes it possible to use it not only as an element in a cryogenic scintillation-bolometric

detector for searching for dark matter, rare events, studying coherent neutrino scattering on the nuclei of heavy elements, but also in spectrometric experiments as an active protection of photomultiplier tube (PMT) radioactivity [1, 5]. But lead tungstate crystals have a fairly high intrinsic radiation background due to the presence of <sup>210</sup>Po and <sup>210</sup>Pb isotopes, which are always present in modern lead. The idea of using archaeological lead with a low content of these isotopes was realized in the work.

Recently, the RES-NOVA project aimed to search neutrinos from core-collapse supernovae (SN) via coherent elastic neutrino-nucleus scattering (CEvNS) using an array of archaeological lead (Pb) based massive cryogenic detectors. This project proposes the development and application of new neutrino telescopes based on lead tungstate and lead molybdate crystals [8].

In this work, we have developed a technique for obtaining raw materials, as well as the technological methods for growing low-background optically high-quality crystals of <sup>arch</sup>PbWO<sub>4</sub> with improved functional parameters.

### 1. EXPERIMENTAL

We used Teflon glassware (this material does not contain its own radioactive isotopes) and reagents: ammonia solution (32%) Extra pure from Merck, nitric acid (65%) Extra pure from Merck for <sup>arch</sup>PbO·nH<sub>2</sub>O synthesis from <sup>arch</sup>Pb.

The synthesis of the charge <sup>arch</sup>PbWO<sub>4</sub> was carried out in a chamber furnace of the SNOL-40/1300 type with intermediate stirring.

The growing of single crystals was carried out by Czochralski method in “Donets-1” and “Kristall-607A” type modified induction installations from a platinum crucible. Heat treatment of each crystal was carried out in SNOL 7.2/1300 type muffle furnace with heating speed and temperature automatic control.

X-ray phase analysis (XRD) of the mixture and single crystals was carried out on a Siemens D 500 powder diffractometer (Cu K $\alpha$ , nickel filter, Bragg-Brentano geometry). The identification of powder X-ray

diffraction patterns was carried out on the basis of the card index of the International Center for Diffraction Data (JCPDS-IC).

The content of the main impurity elements in PbO and WO<sub>3</sub> oxides was determined by inductively coupled plasma atomic mass spectrometry (ICP MS).

Transmission spectra were measured by Shimadzu UV mini-1240 single-beam spectrophotometer with an operating range of 190...1100 nm. UV irradiation of the samples was carried out with two LUFCH-6 lamps (365 nm, power 2 × 6 W).

## 2. RESULTS AND DISCUSSION

### 2.1. PURIFICATION OF RAW MATERIALS

Ordinary lead contains the radioactive isotope <sup>210</sup>Pb, the activity of which can be tens or even thousands of Bq/kg, which is unacceptable for the creation of low-background scintillation devices. The half-life of <sup>210</sup>Pb is 22.3 years. In archaeological lead (Fig. 1), made after tens of half-lives, <sup>210</sup>Pb is almost completely absent (Table 1) [9–11]. Lead tungstate, obtained from ordinary lead, contained much more radionuclides, especially <sup>210</sup>Pb (Table 2).



Fig. 1. <sup>arch</sup>Pb samples [11]

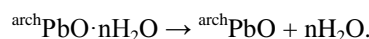
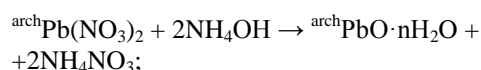
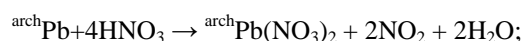
Table 1  
Radioactive impurities in <sup>arch</sup>Pb samples [11]

Chain	Nuclide	Activity, mBq/kg
<sup>232</sup> Th	<sup>40</sup> K	< 7
	<sup>60</sup> Co	< 0.2
	<sup>137</sup> Cs	< 0.5
	<sup>226</sup> Ra	< 0.4
	<sup>228</sup> Th	< 1.2
<sup>238</sup> U	<sup>234m</sup> Pa	< 21
	<sup>226</sup> Ra	< 10
	<sup>210</sup> Pb	< 30
	<sup>210</sup> Po (α)	< 0.3

Table 2  
Radioactive impurities in PbWO<sub>4</sub> from ordinary lead (data obtained using γ-spectroscopy at LNGS [12])

Chain	Nuclide	Activity, mBq/kg
<sup>232</sup> Th	<sup>226</sup> Ra	≤ 13
<sup>238</sup> U	<sup>226</sup> Ra	≤ 10
	<sup>210</sup> Pb	(53...79)·10 <sup>3</sup>

It is clear that for the production of high-quality scintillation crystals of <sup>arch</sup>PbWO<sub>4</sub>, the initial lead and the lead oxide obtained from it must have not only a high degree of radioactive purity, but also a high degree of purity for other chemical impurities. In this work, we used archaeological lead, a complex method of refining which by distillation in a vacuum was developed and implemented at the National Science Center “Kharkov Institute of Physics and Technology” [13]. Purified archaeological lead oxide (<sup>arch</sup>PbO) was obtained by a series of chemical transformations:



Initially, the lead samples were dissolved in nitric acid solution (3.54 M) of at 250 °C. Thereafter, the lead nitrate solution was treated with ammonia vapor. Lead oxide hydrate PbO·nH<sub>2</sub>O precipitated at a pH of the mother liquor of 9...11 units. The precipitate was washed with distilled water several times, centrifuged and dried at 150 °C for 3 h. Thereafter, PbO·nH<sub>2</sub>O was annealed at 600 °C for 12 h to obtain stoichiometric lead oxide PbO. The resulting sample had an inhomogeneous color from yellow to orange, which indicates the presence of several multi-colored phases.

It is known that the PbO system includes six compounds [14]. There are two stable modifications of PbO: the tetragonal form α-PbO (red litharge) and the rhombic form β-PbO (yellow massicot). Their compositions may deviate from stoichiometric ones [14, 15].

The β → α polymorphic transition proceeds more slowly than α → β; therefore, β-PbO can exist at room temperature in metastable states, but upon rubbing it transforms into α-PbO. The main properties of lead oxides are presented in Table 3 [14].

Table 3  
Lead oxides properties [14]

Characteristic	α-PbO	β-PbO	α-Pb <sub>3</sub> O <sub>4</sub>	β-Pb <sub>3</sub> O <sub>4</sub>	α-PbO <sub>2</sub>	β-PbO <sub>2</sub>
Color	Red	Yellow	–	Red	Brown	Black
Syngonia	Tetragonal	Rhombic	Rhombic	Tetragonal	Tetragonal	Rhombic
Phase transformation temperature	550...590 <sup>a</sup>	887 <sup>b</sup>	-90 <sup>a</sup>	–	–	–

<sup>a</sup>polymorphic transformation α → β temperature;

<sup>b</sup>melting point.

$\beta$ -PbO (mascot) is used for the synthesis of the  $\text{PbWO}_4$  charge.  $\beta$ -PbO (JCPDS No. 38-1477) was obtained by annealing PbO according to the following scheme:  $\beta$ -PbO (yellow powder I)  $\rightarrow$   $\alpha$ -PbO (red powder II)  $\rightarrow$   $\text{Pb}_3\text{O}_4$  (orange powder III)  $\rightarrow$   $\beta$ -PbO (yellow powder IV).

The phase composition of PbO was determined by X-ray diffraction. Data of stepwise transformations of PbO showing in Table 4. Yellow  $\beta$ -PbO powder was

obtained after stepwise calcinations of the original sample with intermediate mechanical homogenization.

High-purity tungsten oxide  $\text{WO}_3$  was manufactured at the Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the RAS (Novosibirsk). The content of basic impurity elements in oxides (Table 5), measured by atomic mass spectrometry with induction-coupled plasma, meets the requirements for the purity of the source components for the production of scintillators.

Table 4

PbO stepwise transformations data

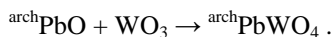
No	Source substance: color and X-ray data	Processing temperature and duration	Final product: color and X-ray data
1	Yellow powder I: 23-1159 $\text{Pb}(\text{NO}_3)_2 \cdot 5 \text{PbO}$ 28-0536 $\text{Pb}_5\text{O}_3(\text{OH})_4$ 28-0537 $3\text{Pb}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ 22-0661 $\text{Pb}(\text{NO}_3)_2 \cdot 3 \text{Pb}(\text{OH})_2$	350 °C 5 h	Red powder II: 23-1159 $\text{Pb}(\text{NO}_3)_2 \cdot 5 \text{PbO}$ 36-1462 $\text{Pb}(\text{NO}_3)_2$ 27-1201 $\text{PbO}_{1,37}$
2	Red powder II	420 °C 5 h	Orange powder III: 38-1477 $\beta$ -PbO Massicot 5-0561 $\alpha$ -PbO Litharge 8-0019 $\text{Pb}_3\text{O}_4$
3	Orange powder III	600 °C 12 h	Yellow powder IV: 38-1477 $\beta$ -PbO Massicot

Table 5

The basic impurity elements content in the initial oxides

Element	ppm		Element	ppm	
	$\text{apxPbO}$	$\text{WO}_3$		$\text{apxPbO}$	$\text{WO}_3$
Mg	< 5	15	Co	< 0.02	< 0.05
Al	< 1	1	Ni	< 0.1	< 0.05
K	< 10	2	Cu	< 0.2	< 0.05
Ca	< 5	0.5	Zn	< 0.3	–
Ti	< 0.5	–	Ag	< 0.2	< 0.05
V	< 0.01	–	Cd	< 0.05	–
Cr	< 0,1	< 0.1	Ba	–	< 0.1
Mn	0.1	< 0.5	Th	< 1	< 0.2
Fe	< 10	1	U	< 1	< 0.2

The charge for growing crystals of  $\text{archPbWO}_4$  was obtained by high-temperature solid-phase synthesis method with  $\text{archPbO}$  and  $\text{WO}_3$  by the reaction:



The synthesis of the charge  $\text{archPbWO}_4$  was carried out by stepwise heating and holding the mixture of starting oxides in air at temperature range 250...800 °C with mixture grinding in a ball mill (rotation speed 70...80 rpm) for 20...30 min.

## 2.2. GROWING A SINGLE CRYSTAL BY THE CZOCHRALSKI METHOD

Since single crystals of lead tungstate melt congruently, the Czochralski method with induction heating of a crucible was applied to grow them, which made it possible to dynamically control thermal conditions.

It was necessary to minimize the temperature fluctuation of the melt in the longitudinal and cross-sections of crystals in the growth process and cooling taking into account the specific properties of the compounds (complex disordered low-symmetry structure, violation of stoichiometry, increased viscosity and low thermal conductivity of melts) for growing single crystals suitable for the manufacture of large-sized samples with specified parameters. For this purpose, well-known measures were tested and improved: placement of additional heaters over the crucible in the form of a platinum cylindrical screen and symmetric blowing of a crystal with a gas flow near the crystallization front.

The most technologically advanced was the method of placing a platinum cylindrical and ceramic screens over the crucible (Fig. 2). Improvement made it possible to regulate the axial temperature gradient in the growth zone in the range of 30...100 deg/cm and create

relatively autonomous thermal conditions with a monotonic temperature distribution in the cooling chamber in the same crystallization unit. The dimensions of the screens and rings in the crystallization unit were correlated in a certain proportion to the diameter of the crucible. However, in the absence of melt feeding while growing large-sized single crystals by an automated method a programmed change in the rotation and displacement speeds of the single crystal was used in a Kristall-607A installation to ensure the stability of crystallization conditions.

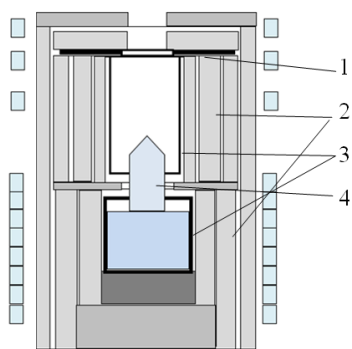


Fig. 2. Crystallization unit for  $^{arch}PbWO_4$  crystals growing: 1 – additional platinum diaphragm; 2 – fire-resistant ceramics; 3 – platinum screen with a crucible; 4 – crystal

An analysis of the experimental results showed that monophasic and optically uniform lengthwise crystals of  $^{arch}PbWO_4$  can be obtained only in the case of a monotonic and smooth change in the heating capacity required to maintain a constant radius of the growing crystal within a certain region. This type of capacity change corresponds to a monotonic change in thermal conditions during the extraction of the crystal and guarantees high quality of the crystal. In this case, the crystal growth occurs from the melt, the thermochemical stability of which is not violated.

In our case, experiments have shown that the most preferable conditions for growing colorless single crystals of  $^{arch}PbWO_4$  with a diameter of about 45 mm and a mass of 1300 g (Fig. 3) were:

- gaseous medium – argon;
- gradient in the crystallization zone  $Tz \leq 20$  deg/cm;
- gradient in the cooling zone  $Tz \leq 40 \dots 45$  deg/cm;
- extraction speed  $v = 2.0$  mm/h;
- mass increment  $dm/dt = 40$  g/h;
- rotation speed  $\omega = 10 \rightarrow 20$  rpm;
- the ratio of the crystal diameter  $dk$  to the crucible diameter  $dt = dk/dt = 0.50$ .

Obtaining scintillators consists of two main stages: growing crystals (in our case, the traditional Czochralski method) and thermal treatment of crystals before and during their mechanical treatment. Moreover, the second stage was the most difficult and important, because such tasks as maintaining the integrity of the crystals during mechanical processing were solved, and the spectral-luminescent properties of the  $^{arch}PbWO_4$  scintillators were corrected. To improve the optical characteristics and reduce impurities, including radioactive ones, double crystallization was applied.

From the crystals of the first crystallization, cylindrical parts were cut out, which were used as raw materials for the melt. Were grown two single crystals were double crystallization, from which samples of sizes  $\varnothing 40 \dots 83$  mm were made. The samples of  $^{arch}PbWO_4$  of the second crystallization were transparent, had no visible gas inclusions and other phases creating scattering centers (Fig. 4).



Fig. 3. Single crystal  $^{arch}PbWO_4$  of the first crystallization



Fig. 4. The samples of  $^{arch}PbWO_4$  of the second crystallization

## 2.3. OPTICAL CHARACTERISTICS OF $^{arch}PbWO_4$ CRYSTALS

### 2.3.1. Photochromic effect investigation

It is known that high-quality pure  $PbWO_4$  crystals are transparent to light with a wavelength of more than 330 nm [16]. Structural defects and most impurities lead to a narrowing of the transparency band due to the shift of the absorption edge to longer wavelengths. It would seem that the best purity of the raw material for crystal growth is the key to obtaining crystals with the best optical parameters. However, crystals with low impurity content exhibit very high sensitivity to ionizing radiation, which leads to the appearance of induced absorption (IA). A cylindrical element made from a crystalline boule of  $^{arch}PbWO_4$  of the first crystallization acquired a noticeable green color, which was later found to be caused by irradiation with ultraviolet light during mechanical processing under the light of mercury discharge lamps.

In [17–19], a significant effect of stoichiometric defects was found for very transparent crystals with a low content of impurities in the charge under conditions of radiation coloration. It has been established that the spectrum of IA, caused by light, is equivalent to the spectrum of IA after ionizing irradiation. Thus, the use of UV irradiation gives qualitatively the same effect as gamma irradiation [17].

Under the influence of visible or ultraviolet radiation, the color of the crystal and, accordingly, its transparency, undergo significant changes. The induced color is sometimes restored after some time in the dark, either under the influence of radiation of a different frequency, or when heated. Studies have shown that under the action of visible light, crystals of  $^{arch}PbWO_4$  restore transparency [20].

Detailed studies of the spectral properties of  $^{arch}PbWO_4$  of the first crystallization under different conditions were carried out on a crystal sample  $10 \times 10 \times 7$  mm in size. Studies of the effect of UV irradiation have confirmed our assumption that the color of the crystal during mechanical processing is due to

UV irradiation. UV irradiation for 1 h led to a significant color (Fig. 5, curve 2), which was reflected in the intensity of the absorption bands.

The colored crystal sample was annealed in air at 900 °C for 12 h, after which it lost its color (see Fig. 5, curve 3).

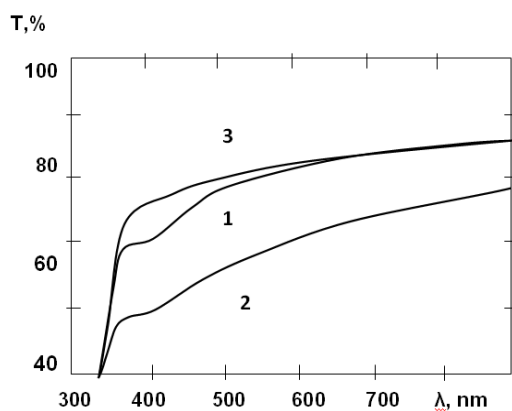


Fig. 5. Optical transmission spectrum of a 7 mm thick  $^{arch}PbWO_4$  crystal sample: 1 – before treatment; 2 – after UV irradiation; 3 – after heat treatment (750 °C for 24 h)

During UV irradiation, defects capture charge carriers, and color centers (CC) are formed, which can represent not only point defects, but also associates of CC or clusters such as those arising under radiation exposure and give a broad absorption band. Annealing leads to the release of charge carriers from the traps, but does not destroy them, because after annealing in any atmosphere and subsequent UV irradiation, the color reappears. As indicated in [21], heat treatment and irradiation in any atmosphere do not significantly affect the regular crystal lattice. We see the same thing with our crystals.

After growing, many  $PbWO_4$  crystals exhibit broad absorption bands with maxima at 330...370, 420, or 550...600 nm. The 420 nm band imparts a characteristic yellow color to the  $PbWO_4$  crystals and negatively affects the light yield, since the spectrum of this band overlaps the spectrum of the scintillation pulse [22].

There were different opinions on the nature of the optical absorption bands in  $PbWO_4$ . In [23], the absorption band at 420 nm was assigned to 3-valent impurity ions in place of Pb. The 350 nm band was associated with cation vacancies, since it disappears upon doping of niobium samples [24].

IA in the 620 nm region and the absorption band at 350 nm were associated in [24] with a tungsten ion with an uncompensated charge associated with a 3-valence ion at the Pb site (420 nm) or with a hole  $O^-$ -center in the lead vacancy region (35 nm). It was believed that the absorption band at 420 nm is due to hole centers, the ion  $O^-$ , while the 350...370 nm band is due to the ion  $Pb^{3+}$  [25].

The need for local compensation of excess charge allows the localization of charge carriers at defective lattice sites. Evaporation of lead at different growth phases of a long crystal is compensated by anionic vacancies ( $V_o$ ) and F-centers, either by trapping a hole on a single oxygen (type  $O^-$  defect), or by molecular

oxygen with two antiparallel electron spins  $(O-V_o-O)^{2-}$ . The last two defects can be easily recharged by trapping free charge carriers during irradiation, which is the main source of the CC in  $PbWO_4$  crystals.

When developing a lead tungstate crystal for collider experiments, a lot of research was carried out aimed at obtaining radiation-resistant crystals. Pure  $PbWO_4$  crystals, even of very high quality, are not used in experiments in high-energy physics, they do not meet the requirements of the CMS project on radiation resistance, since the effect of radiation coloration turns out to be more significant for crystals with a low content of impurities in the batch (1 ppm or less) [17–19]. For this reason, crystals doped with rare earth elements were used. The production of undoped radiation-resistant  $PbWO_4$  crystals is currently an unresolved problem.

The effects of radiation damage are caused by pre-radiation defects and defects formed under the influence of ionizing radiation. Under UV irradiation, the crystal is exposed only to primary pre-radiation defects, capturing free charge carriers. Under ionizing irradiation, additional IA appears in a wide wavelength band in  $PbWO_4$  crystals, which reduces the light yield due to reabsorption.

In accordance with this, the effect of radiation bleaching is possible only in crystals with a large initial absorption in the region of 420 nm. This conclusion is confirmed in [27], where radiation bleaching was observed only in the region of 420 nm in crystals doped with Gd and La. In the latter case, the crystal was grown in a gas atmosphere with the presence of oxygen. The bleaching of yttrium-doped  $PbWO_4$  samples is described in [28]. In [26, 27], the effect of radiation clearing of  $PbWO_4$  after  $\gamma$ -irradiation was observed, which the authors associate with the radiation transformation of the charge state of 3-valent lead present in such crystals, that is, with the  $Pb^{3+} \rightarrow Pb^{2+}$  transition. It was found that the radiation dose of  $PbWO_4$ , corresponding to the saturation IA, is very small (units of krad). Further irradiation up to doses of  $10^7$  rad leads to a slight increase in IA, possibly associated with the formation of structural defects [29]. This means that IA in  $PbWO_4$  is associated with the recharge of impurity or intrinsic defects, and similar processes are observed under UV irradiation. It is noticed that crystals with high radiation resistance have a higher initial transparency in the region of 350...370 nm. The authors of [30] found that the radiation sensitivity and the shape of the optical transmission spectrum in the 360 nm region have a clear relationship. Crystals with high radiation resistance have a sharp drop in transmission in the short-wavelength region (350 nm). Crystals with low radiation resistance have an absorption band in the region of 350...370 nm, which overlaps the short-wavelength absorption edge. The light yield of the best samples is reduced by 70% after a dose of 2 krad, then by another 50...60% after a dose of 1 Mrad. All characteristics of the samples were self-healing at room temperature.

The IA reduction rate differs significantly for different samples and has no significant relationship

with the initial optical absorption spectra. The restoration of optical transmission occurs very quickly (in 10 min by 30...40%) if the samples are exposed to sunlight. When held in the dark, self-healing is insignificant in the first 10...60 min. This is due to the photochromic effect in  $\text{PbWO}_4$  crystals [30].

At present, two ways have been proposed for discoloration of a lead tungstate crystal, in which a photochromic effect is observed. This is annealing at a temperature of more than 500 °C in any of the atmospheres: in argon or oxygen, or in air. In this case, thermal emptying of charge carrier traps occurs. Or the required activation energy to empty the traps is achieved by irradiating the crystal with visible light with a wavelength of more than 450 nm.

After annealing the  $^{\text{arch}}\text{PbWO}_4$  crystal for 24 h in air at a temperature of 750 °C, its color decreased significantly (Fig. 6, curves 2), which improved the crystal transmission. The inset to Fig. 6 shows the difference ( $T_2-T_1$ ) of the absorption bands for curves 2 and 1. This difference spectrum is an intense broad band with a maximum at about 420 nm, which is typical for  $\text{PbWO}_4$ , as described above. A sufficiently large half-width of the strip and a complex shape indicate that it is not elementary.

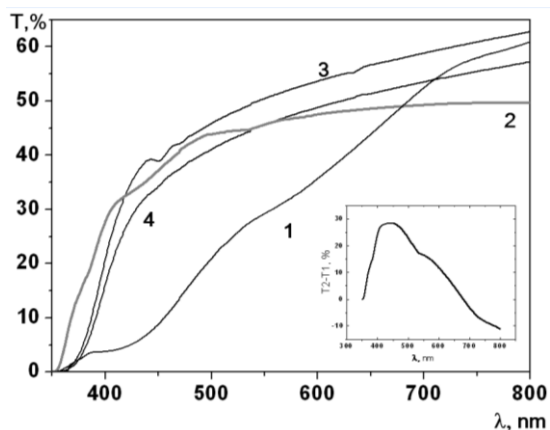


Fig. 6. Transmission spectra of  $^{\text{arch}}\text{PbWO}_4$  crystals ( $\varnothing 40 \times 83$  mm): 1 – colored crystal of the first crystallization before heat treatment; 2 crystals of the first crystallization after heat treatment; 3 and 4 – crystals obtained by the method of double crystallization. Insert: difference of absorption bands for samples 2 and 1

As shown by the study [31, 32], cluster defects are formed in lead tungstate crystals, which include reduced tungsten. The same defects are formed when exposed to high-energy radiation. In the IA spectra, broad bands are observed [21]. When grown in a crystal, similar inclusions can also form, which is associated with redox processes. Their number can be changed by irradiation (see increase, Fig. 5, curve 2) or heat treatment (see decrease, Fig. 5, curve 3; Fig. 6, curve 2), which we observe in our samples.

In [1], the energy spectra of  $^{137}\text{Cs}$  and  $^{207}\text{Bi}$   $\gamma$ -quanta were investigated, measured with a  $\text{CdWO}_4$  scintillation crystal ( $\varnothing 20 \times 20$  mm) mounted directly on the PMT and mounted on a fiber made of an  $^{\text{arch}}\text{PbWO}_4$  crystal ( $\varnothing 40 \times 83$  mm) after its bleaching. The relative pulse

amplitude of the detector with the fiber was 65% with respect to the crystal mounted directly on the PMT. The quality of this fiber met the requirements of a low-background experiment to study the double neutrinoless beta decay of  $^{106}\text{Cd}$ , measured using a  $^{106}\text{CdWO}_4$  scintillation crystal. Under the conditions of this low-background experiment, the parameters of the crystals did not change [33].

### 2.3.2. Methods for improving the optical characteristics of $^{\text{arch}}\text{PbWO}_4$

For collider experiments, the optical quality and radiation resistance were improved by alloying with rare earth elements. For low-background nuclear spectrometry, this method is unacceptable, since rare-earth elements contaminate the crystal with radiation isotopes. To improve the optical characteristics of the crystal and reduce the number of stoichiometric defects, we added an excess of  $^{\text{arch}}\text{PbO}$  to the stoichiometric mixture of the starting oxides in an amount of 0.05 wt.%. During crystal growth,  $^{\text{arch}}\text{PbO}$  evaporates more intensively than tungsten oxide, which leads to the appearance of a deposit of this substance inside the growth chamber. This process leads to a violation of the stoichiometry of the melt and the appearance of a photochromic effect in the crystal, as shown by experiments. The introduction of an excess of  $^{\text{arch}}\text{PbO}$  prevents the formation of intrinsic defects associated with deviations from stoichiometry, namely,  $\text{Pb}^{2+}$  and  $\text{O}^{2-}$  vacancies, as well as hole centers of O-centers. In Fig. 7 shows the transmission spectrum of a crystal sample of  $^{\text{arch}}\text{PbWO}_4$  from a charge with an excess of  $^{\text{arch}}\text{PbO}$  of 0.05 wt.%. A crystal grown from a charge with an excess of  $^{\text{arch}}\text{PbO}$  0.05 wt.% did not exhibit a photochromic effect (see Fig. 7).

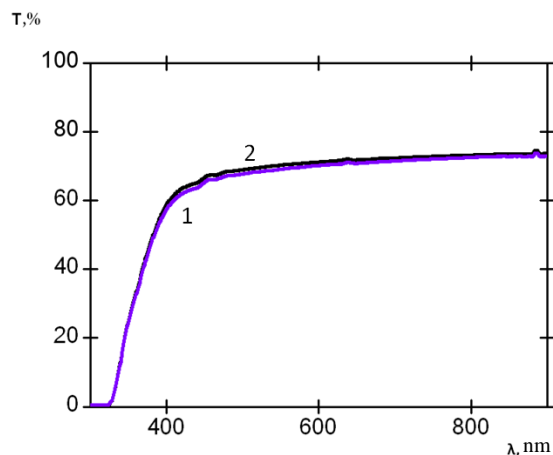


Fig. 7. Transmission spectrum of a crystal sample of  $^{\text{arch}}\text{PbWO}_4$  ( $d = 1$  cm) with an excess of  $^{\text{arch}}\text{PbO}$  0.05 wt.%. 1 – before UV irradiation; 2 – after UV irradiation

We applied the double crystallization method in order to further improve the optical characteristics of lead tungstate single crystals. The positive effect of double crystallization (recrystallization) on the level of radioactive contamination of crystalline scintillators was demonstrated by the example of  $\text{CaWO}_4$ : the level of radio purity of the crystal increased by an order of magnitude (for example,  $^{238}\text{U}$  was rejected by the crystal

with a segregation coefficient of  $\approx 0.3$ ), which made it possible to improve the energy resolution of the scintillators [34].

The transmission of crystals obtained using the double crystallization method (see Fig. 6, curves 3, 4) in the visible region is better than the transmission of the single crystal of the first crystallization (see Fig. 7, curve 2). The difference between the transmission levels of the studied single crystals is insignificant. In our work we used high quality raw materials with a low level of uncontrolled impurities. Therefore, the parameters of single crystals after two crystallizations improved compared to the annealed crystal of the first crystallization.

## CONCLUSIONS

Technological principles of growing scintillation crystals  $^{\text{arch}}\text{PbWO}_4$  have been developed, observance of the principles of which allows to control the stoichiometric composition of the charge during the growth of crystals. Methods for improving the optical parameters of lead tungstate crystal from archaeological lead have been developed. It is shown that the photochromic effect in  $^{\text{arch}}\text{PbWO}_4$  crystals at extremely low impurity content is associated with deviations from the stoichiometric composition of the crystal. The introduction of excess lead oxide into the charge during crystal growth and the use of double crystallization allows to consistently affect various defects in  $^{\text{arch}}\text{PbWO}_4$  crystals and significantly improve the optical and scintillation parameters of these single crystals and scintillators based on them.

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Article received 06.12.2021

### **$^{арх}\text{PbWO}_4$ С УЛУЧШЕННЫМИ ОПТИЧЕСКИМИ ПАРАМЕТРАМИ ИЗ АРХЕОЛОГИЧЕСКОГО СВИНЦА**

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Приведены технологические основы изготовления кристалла вольфрамата свинца из археологического свинца для применения в низкофоновых экспериментах по поиску редких событий. Исследовано влияние условий получения монокристаллов  $^{арх}\text{PbWO}_4$  на фотохромный эффект в монокристаллах. Путем минимизации отклонений от стехиометрического состава удалось улучшить оптические параметры монокристалла вольфрамата свинца. Полученные монокристаллы с применением двойной кристаллизации и введением избытка  $^{арх}\text{PbO}$  позволяют последовательно влиять на различные дефекты в кристаллах  $^{арх}\text{PbWO}_4$  с улучшенными характеристиками

### **$^{арх}\text{PbWO}_4$ З ПОКРАЩЕНИМИ ОПТИЧНИМИ ПАРАМЕТРАМИ З АРХЕОЛОГІЧНОГО СВИНЦЮ**

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Наведено технологічні основи виготовлення кристала вольфрамату свинцю з археологічного свинцю для застосування в низькофонових експериментах із пошуку рідкісних подій. Досліджено вплив умов одержання монокристалів  $^{арх}\text{PbWO}_4$  на фотохромний ефект у монокристалах. Шляхом мінімізації відхилень від стехіометричного складу вдалося поліпшити оптичні параметри монокристала вольфрамату свинцю. Одержані монокристали із застосуванням подвійної кристалізації та введенням надлишку  $^{арх}\text{PbO}$  дозволяють послідовно впливати на різні дефекти в кристалах  $^{арх}\text{PbWO}_4$  з покращеними характеристиками.