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Research and development of alkali earth tungstate and molybdate crystal scintillators for search for rare events

L.L.Nagornaya, A.M.Dubovik, B.V.Grinyov,
K.A.Katrunov, I.A.Tupitsyna, Yu.Ya.Vostretsov

Institute for Scintillation Materials, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

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Large volume $ZnWO_4$ scintillator with improved performance characteristics have been obtained. Due to its favorable light yield values at low temperatures and extremely low intrinsic radioactivity, zinc tungstate is a material of very good prospects for cryogenic double beta-decay and dark matter experiments. The $ZnMoO_4$ single crystals were produced for the first time using Czochralski technique. The suitability of this material for cryogenic rare event search experiments has been studied and identified the ways to improve the scintillation properties of the crystal have been outlined. The manufacturing methods of $MgWO_4$ crystals have been investigated and the manufacturing possibility by pulling from the solution-melt on a seed has been established. The experimental $MgWO_4$ single crystals of ca. 1 cm^3 volume have been prepared for the first time and the luminescence and scintillation characteristics thereof have been measured.

Получены сцинтилляторы $ZnWO_4$ большого объема с улучшенными характеристиками. Хорошие параметры светового выхода в области низких температур и исключительно низкая собственная радиоактивность делают вольфрамат цинка одним из самых перспективных материалов для криогенных экспериментов по поиску двойного бета-распада и темной материи. Впервые получены монокристаллы $ZnMoO_4$ методом Чохральского. Исследована возможность использования этого материала для криогенных экспериментов по поиску редких событий и намечены пути улучшения сцинтилляционных характеристик. Исследованы методы получения кристаллов $MgWO_4$, естановлена принципиальная возможность выращивания объемных кристаллов методом вытягивания из раствора в расплаве на затравку. Впервые получены экспериментальные образцы монокристаллов $MgWO_4$ объемом ~1 см^3 и измерены их люминесцентные и сцинтилляционные характеристики.

The advances in 2β-decay studies would not be possible without progress in experimental techniques. The success of experiments depends upon many factors, including as the most important ones a good choice of the nuclide to be studied and development of an adequate detector with required characteristics (maximum content of the nuclei under study in the detector volume, high efficiency and selectivity of the effect detection, extra low background level, possibility of prolonged measurements, etc.). At present, studies of neutrino-less 2β-decay using oxide scintillators containing isotopes of cadmium, tungsten, zinc, molybdenum etc. have been shown to be promising. Prospects of these compounds are also supported by a possibility to prepare scintillators of sufficiently large size, high resolution, and required radiation purity. Among oxide scintillators, of great interest are crystals of alkaline-earth tungstates and molybdates ($CdWO_4$, $ZnWO_4$, $ZnMoO_4$, $PbWO_4$, $PbMoO_4$, $CaMoO_4$, $MgWO_4$).

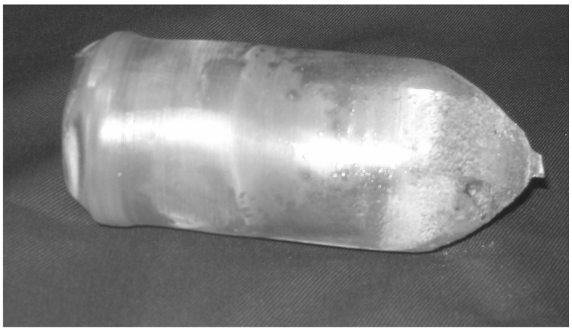

Fig. 1. $CdWO_4$ single crystal (3 kg).

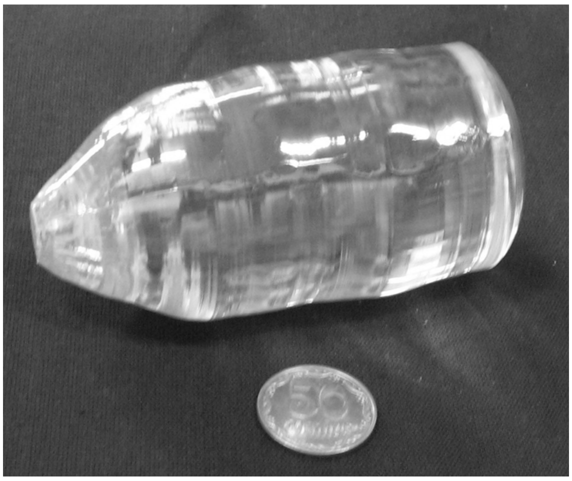

Fig. 2. $ZnWO_4$ single crystal.

At the Institute for Scintillation Materials (Kharkiv, Ukraine), works on preparation of such crystals are in progress. The crystals are grown mainly using the Czochralski technique from the melt on seed in furnaces with induction heating in platinum or iridium crucibles. The raw charge used is obtained mostly by high-temperature solid phase synthesis from metal oxides or by coprecipitation method.

$CdWO_4$ and $ZnWO_4$. From this group of crystals, the most extensive studies were carried out on the developed before large $^{113}CdWO_4$ and $^{116}CdWO_4$ crystals distinguished by high spectrometric quality and high radioactive purity (Fig. 1). Large $ZnWO_4$ crystals with nuclides ^{64}Zn, ^{70}Zn, ^{180}W, ^{186}W with improved scintillation characteristics and radiopurity are of a considerable interest in detection of rare events [1, 2]. In this connection, we have started works on development and studies of this crystal. Our first results were published in [3]. Along with optimization of the large $ZnWO_4$ crystal preparation process, studies were carried out on the effects of stoichiometric and admixture defects and univalent dopants.

In Table 1, data are presented on the effects of these factors upon scintillation characteristics, including afterglow. It can be seen that some of the univalent dopants are able to improve these characteristics substantially.

As a result of our studies, we have developed a preparation method for colorless and highly transparent $ZnWO_4$ single crystals of up to 50 mm diameter and 80 mm height (Fig. 2). The thermally stimulated luminescence data displayed in Fig. 3 demonstrate that there is a correlation between the afterglow and the intensity of peaks at $T > 233$ K. It is assumed that the traps associated with these TSL peaks are responsible for the ac-

Table 1. $ZnWO_4$ scintillation properties

#	Dopant	Size of samples, mm	LY, % CWO	Energy resolution for Cs-137 (E = 662 keV), %	Afterglow, % (20 ms)
1	–	10×10×10	11	23	0.79
2	MeF	10×10×10	32	11	0.104
3	ZnF_2 Me_2O	10×10×10	47	10.2	0.005
4	Me_2O	30×30×14	39	11	
		10×10×10	47.5	9.3	
5	Me_2O ZnF_2	10×10×10	50	8.5	0.002
6	Me_2O	∅40×40	27	10.7	
7	Me_2O	∅44×55	15	13.7	

The light output of $ZnWO_4$ samples was determined relative to that of a $CdWO_4$ sample with dimensions 10×10×10 mm^3.

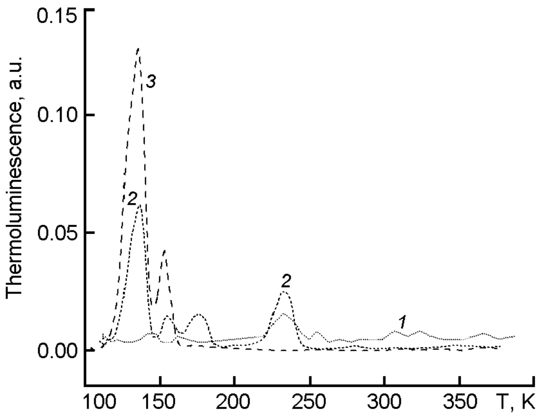

Fig. 3. TSL of $ZnWO_4$ crystal. The numbers at the graphs correspond to the number of the sample in Table 1.

cumulation of charge carriers at room temperature, and this accounts for the observed slow decay process. The doping provides shallow trapping centers with activation energy so low that storing carriers at room temperature is impossible. This causes a noticeable improvement in the afterglow characteristics of the crystals: it reduces drastically from 0.79 % in the undoped crystal #1 to 0.005 % in the co-doped sample #3. The results of these studies made it possible to optimize the crystal growth process. The largevolume $ZnWO_4$ crystals with improved scintillation properties [4] were obtained this way.

Fig. 4 shows scintillation characteristics of a detecting element prepared from $ZnWO_4$ crystal. The energy resolution of scintillation elements made from $ZnWO_4$ crystals was 10.7 % with a large hexagonal scintillation element of ∅40×40 mm^3 for 662 keV γ line of ^{137}Cs.

The crystal anisotropy effects upon light output have been studied. The light output of the crystal demonstrates the directional dependence of about 7 %. This gives a possibility to improve light output of $ZnWO_4$ scintillation detector by using the crystals with certain orientation of a scintillation element relatively to the crystal axes.

The relative intensity and scintillation decay kinetics were studied over the temperature range 7–300 K. The light yield of $ZnWO_4$ demonstrates about two-fold increases and decay time becomes about three times longer at temperature decrease from 300 K to 7 K [4].

A special attention was paid to radiopurity of $ZnWO_4$ single crystals [3]. The measurements were carried out at Solotvina Underground Laboratory (Ukraine) (see Table 2).

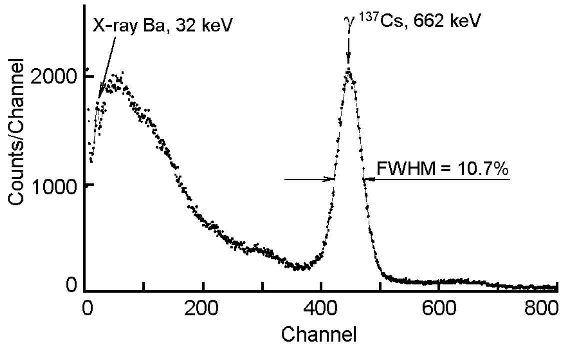

Fig. 4. Pulse amplitude spectra of $ZnWO_4$ scintillation element irradiated with 662 keV γ-quanta (^{137}Cs).

$ZnWO_4$ is among the best candidates as a detector for cryogenic 2β-decay and Dark Matter experiments.

$PbWO_4$ and $PbMoO_4$. Crystal $PbWO_4$ had been developed before at the Institute for Scintillation Materials as scintillation detector for high energy physics [5]. Thanks to these studies, we have developed the production technology of this material and currently we can grow large, high-quality crystals. Furthermore, there are ample possibilities for the modification of the material properties that makes this crystal an excellent choice for testing and implementing new ideas on material development. To a lesser extent, this is also applicable to $PbMoO_4$, which has been use widely for decades as an optoelectronic material.

The suitability of lead tungstate and molybdate in rare event searches has been first pointed out in [6] and [7]. It has been shown that $PbMoO_4$ is an interesting material to search for the double beta-decay of ^{100}Mo [6, 8], while $PbWO_4$ can be used as a screen against the PMT radioactivity [7].

Table 2. Radioactive contamination of $ZnWO_4$ crystals (mBq/kg)

Chain	Source	$ZnWO_4$	$ZnWO_4$ Ref. [1]
^{232}Th	^{228}Th	≤0.1	≤3.3
^{238}U	^{226}Ra	<0.16	≤0.4
Total α		2.4(3)	≤20
	^{40}K	≤14	≤12
	^{90}Sr–^{90}Y	≤15	≤1.2
	^{137}Cs	≤2.5	≤20
	^{147}Sm	≤5	≤1.8

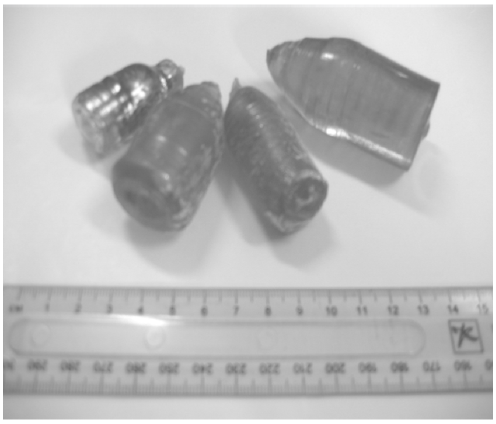

Fig. 5. $ZnMoO_4$ single crystals.

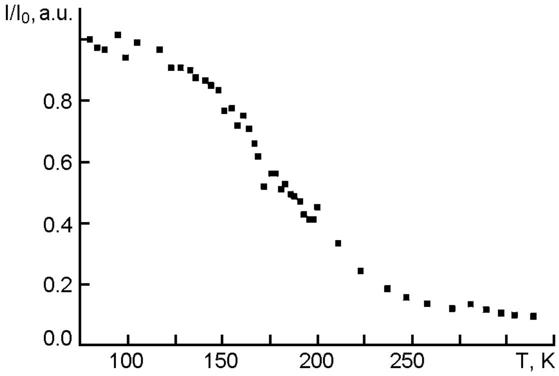

Fig. 6. Temperature dependence of X-ray luminescence intensity of $ZnMoO_4$.

Nonetheless, the high intrinsic radioactivity (~100 Bq/kg) due to ^{210}Pb is the main obstacle limiting the use of these materials in low-background experiments. To address this issue, we have started a work on the purification of archaeological lead for growing lead tungstate and molybdate crystals with low radioactive background. It has been shown that due to natural decay of radioactive ^{210}Pb in archaeological lead, its contribution to the intrinsic radioactivity of a sample can be as low as a few mBq/kg [9]. The use of ancient lead (discovered in Ukraine [10]) for crystal growth should permit producing lead tungstate and molybdate with substantially reduced intrinsic radioactivity. This can pave the way for their application in rare event search experiments.

$ZnMoO_4$. Works have been started on development of the Chochralski growing of zinc molybdate ($ZnMoO_4$) crystals. A method has been developed for preparation of charge by solid state synthesis. Physico-chemical conditions of the crystal growth and annealing have been studied, as well as effects of stoichiometric composition upon the crystal quality. The grown crystals were of up to 30 mm in diameter and height (Fig. 5). The crystals show an intense orange color. Our first studies suggest that the coloring was due to uncontrolled impurities. However, further studies in this direction are necessary. For the samples obtained, optical luminescence and scintillation characteristics were measured, as well as temperature dependence of X-ray luminescence intensity in the range from liquid nitrogen to room temperatures. The luminescence intensity increased by an order and more at lowering temperatures (Fig. 6).

$MgWO_4$. Recent studies of $MgWO_4$ powder samples demonstrated that this compound is an attractive scintillation material for cryogenic applications because of its high scintillation light output which is comparable to $ZnWO_4$ [11]. Due to its high-temperature phase transition, $MgWO_4$ cannot be grown using the conventional Czochralski method. Therefore, we have developed the growth technology from the solution-melt and prepared a $MgWO_4$ single crystal. The crystal shows an intense luminescence under X-ray excitation (see Fig. 7). The broad emission band exhibits a maximum at 475 nm. This agrees well with the room temperature data obtained for a powder sample [11]. For the first time, the $MgWO_4$ single crystal was characterized as a scintillation detector. Fig. 8 shows the pulse amplitude spectrum of $MgWO_4$ excited by γ-quanta and X-ray of ^{241}Am. The energy resolution of the sample for the 56.5 keV γ line is found to be 37 %, being very close to the value of 35 % observed for a large $ZnWO_4$ scintillator. The energy resolution 15 % is obtained for the 662 keV γ line of ^{137}Cs. These results confirm the excellent prospects of magnesium tungstate for scintillation applications. Therefore, furthering the production technology of large $MgWO_4$ scintillators is currently in progress.

To conclude, the development results of oxide scintillators for rare event search experiments are reviewed. Large volume $ZnWO_4$ scintillator with improved performance characteristics have been obtained. Due to its favorable scintillation properties at low temperatures and extremely low intrinsic radioactivity, zinc tungstate is a material of very good prospects for cryogenic double beta decay and dark matter experiments. The $ZnMoO_4$ single crystals were produced for the first time using Czochralski technique. The suitability of this material for cryogenic rare event search experi-

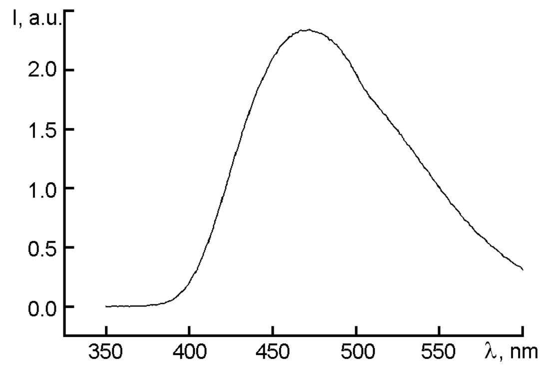

Fig. 7. X-ray luminescence of $MgWO_4$ crystal.

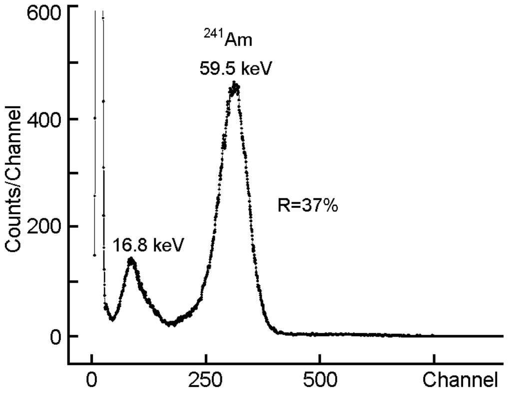

Fig. 8. Pulse amplitude spectra of $MgWO_4$ scintillation element irradiated with 59.5 keV (^{241}Am).

ments has been studied. The manufacturing methods of $MgWO_4$ crystals have been investigated and the manufacturing possibility by pulling from the solution-melt on a seed has been established. The experimental $MgWO_4$ single crystals of ca. 1 cm^3 volume have been prepared for the first time and the luminescence and scintillation characteristics thereof have been measured.

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Розробка і дослідження сцинтиляторів на основі кристалів лужноземельних вольфраматів і молібдатів для пошуку рідкісних подій

Л.Л.Нагорна, О.М.Дубовик, Б.В.Гриньов, К.О.Катрунов, І.А.Тупіцина, Ю.Я.Вострецов

Отримано сцинтилятори $ZnWO_4$ великого об’єму з поліпшеними характеристиками. Хороші параметри світлового виходу в області низьких температур і виключно низька власна радіоактивність роблять вольфрамат цинку одним з найперспективніших матеріалів для кріогенних експериментів з пошуку подвійного бета-розпаду і темної матерії. Вперше отримано монокристали $ZnMoO_4$ методом Чохральського. Досліджено можливість використання цього матеріала для кріогенних експериментів з пошуку рідкісних подій та намічено шляхи поліпшення сцинтиляційних характеристик. Досліджено методи отримання кристалів $MgWO_4$, встановлено принципову можливість вирощування об’ємних кристалів методом витягування з розчину у розплаві на затравку. Вперше отримано експериментальні зразки монокристалів $MgWO_4$ об’ємом ~1 см^3 і виміряно їх люмінесцентні та сцинтиляційні характеристики.