Growth of $ZnWO_4$ Crystal Scintillators for High Sensitivity 2β Experiments

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***Abstract*—Large volume zinc tungstate crystal scintillators (up to 50 mm in diameter and 100 mm length) with improved energy resolution were developed as result of advances in crystal growth. The energy resolution of one-centimeter cube $ZnWO_4$ crystals showed energy resolution in the range 8–10% for 662 keV γ line of ^{137}Cs. A value of 13.7% has been obtained with a large sample $\varnothing 44 \times 55$ mm. The radioactive contamination of a $ZnWO_4$ $26 \times 24 \times 24$ mm detector was tested in the Solotvina Underground Laboratory. The obtained results demonstrate ability to use $ZnWO_4$ in order to search for 2β-decay of Zinc and Tungsten.**

***Index Terms*—Double beta decay, scintillation detectors, tungsten compounds, zinc compounds.**

I. Introduction

As it has been already demonstrated by several experiments, the scintillation method is promising to investigate the double beta decay processes [1]–[4], search for dark matter [5]–[7], study of rare α and β decays. Scintillation detectors possess a range of important characteristics for a high sensitivity low background experiment: high registration efficiency for the processes, reasonable energy resolution, pulse-shape discrimination ability to reduce radioactive background, operation stability, low cost.

Zinc tungstate ($ZnWO_4$) single crystals is a well-known scintillation material for γ- and X-ray detectors. A small $ZnWO_4$ crystal scintillator 4.5 g of mass has been already used to search for double beta decay of ^{64}Zn, ^{70}Zn, ^{180}W, and ^{186}W [8]. $ZnWO_4$ was also considered as target crystal in cryogenic experiments to search for weakly interacting massive particles [8]–[10]. In [8] $ZnWO_4$ detector was also proposed to investigate very rare α decay of natural tungsten. The experiments call for extremely low level of background of a detector and therefore for very low level of radioactive contamination of crystal scintillators less than a few mBq/kg.

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Studies of optico-luminescent characteristics of $ZnWO_4$ and conditions for its preparation were reported in a number of papers [11]–[18]. However, preparation of large-sized $ZnWO_4$ single crystals of high spectrometric quality has remained an important problem.

The purpose of our work was development of radiopure $ZnWO_4$ crystal scintillators of large volume with high scintillation characteristics for the low-counting experiments.

II. Experimental

Relative light output of $ZnWO_4$ samples was determined by γ-ray spectroscopy using γ line 662 keV of a ^{137}Cs source [19].

Optical transmission was measured with the help of a spectrophotometric complex KSVU-23.

Measurements of afterglow were carried out using a measuring-calculating complex for studies of kinetic characteristics. Samples were irradiated by X-ray pulses with duration 2 s emitted by a RAPAN-200 X-ray source ($U = 120$ kV, $I = 3$ μA).

Radioactive contaminations of one $ZnWO_4$ crystal ($26\times24\times24$ mm of sizes, 119 g of mass) was measured in the Solotvina Underground Laboratory built in a salt mine 430 m underground ($\approx$1000 m w. e., cosmic muon flux 1.7×10^{-6} cm^{-2} s^{-1}, neutron flux $< 2.7 \times 10^{-6}$ cm^{-2} s^{-1}, radon concentration in air < 30 Bq m^{-3}).

III. Results and Discussion

Zinc tungstate single crystals have tungstite structure, monoclinic syngony and spatial group P 2/c. Marked cleavage plane is (010), while planes (100) and (010) show weak cleavage.

The $ZnWO_4$ crystals were grown by the Czochralski method in platinum crucibles with high frequency heating. The raw powder was prepared by solid phase high temperature synthesis. A stoichiometric $ZnWO_4$ composition or controlled admixtures of zinc and tungsten oxides were used as starting materials.

Crystal ingots were grown by using seed crystals oriented along crystallographic directions [100], [010], [110]. Rate of pulling and speed of rotation were $\nu = 1.5$–3 mm/hour and $\omega =$ 20–35 rpm, respectively. Optimum conditions were chosen for growth of $ZnWO_4$ single crystals. The process was performed in atmospheres of different compositions, including the normal atmospheric composition. Single crystals with sizes up to $\varnothing 50\times 100$ mm were obtained (Fig. 1).

The crystals then were annealed in oxygen atmosphere ($T = 800 - 1000$°C). After the thermal treatment $ZnWO_4$ crystals changed their color from brownish to slightly pink-violet.

Fig. 1. $ZnWO_4$ single crystal.

Mechanical characteristics of pure $ZnWO_4$ and crystals doped with univalent metals on plane (010) were different. The undoped crystals were rather brittle, they have substantial stresses with considerable anisotropy in (100) direction. The stresses were slightly reduced by thermal treatment, though brittleness remained high. Anisotropy also remained after annealing. The activated crystals were of better plasticity, destructions were much less significant. However, the activated samples have substantial anisotropy, apparently due to differences in bond energies over different crystallographic planes and directions.

The samples $10 \times 10 \times 10$ mm were prepared from the crystal boules for optical transmission and relative light output investigation. Afterglow was measured with $10 \times 10 \times 2$ mm samples. Results of the measurements are presented in Table I.

The crystals of stoichiometric composition (#2–9 in Table I) were obtained using raw charge with extra WO_3 content. Samples of these crystals shown somewhat better scintillation characteristics than that the crystal grown from raw material with initial stoichiometric composition (#1 in Table I).

Effects of activation by metals of the first and second groups, as well as by elements with high electric negativity were studied. Doping with bivalent metals do not affect the color of single crystals, and do not improve scintillation properties. Doping of univalent metals results in discoloration of crystals and improves their scintillation parameters (see Fig. 2, curves 3, 4, 5, and Table I #3–8). Doping of univalent metals in combination with doping of zinc fluoride allow to improve transparency (Fig. 2, curve 5), and scintillation properties of $ZnWO_4$. The best light output (50% relatively to $CdWO_4$ scintillator) and energy resolution 8.5% were obtained with the sample cut from crystal #8 (see Table I and Fig. 3). To our knowledge such an energy resolution was never reported for $ZnWO_4$ crystal scintillators (energy resolution 11% was obtained in [8] with $ZnWO_4$ crystal $\varnothing 14 \times 7$ mm).

It is worth to stress that optimization of the growing process allows to reduce noticeably (more than two order of magnitude, see Table I) the afterglow in $ZnWO_4$ crystal scintillators.

Radioactive contamination of a $ZnWO_4$ crystal scintillator $26 \times 24 \times 24$ mm was investigated in the Solotvina Underground Laboratory. The scintillator was viewed by a special

TABLE I
$ZnWO_4$ 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	
		10× 10× 2			0.79
2	WO_3	10× 10× 10	30	15	
		10× 10× 2			0.031
3	MeF	10× 10× 10	32	11	
		10× 10× 2			0.104
4	MeF	Ø20×20	39	12.8	
	WO_3	10× 10× 10	41	9.6	
		10× 10× 2			0.004
5	ZnF_2	10× 10× 10	47	10.2	
	Me_2O	10× 10× 2			0.005
	WO_3				
6	Me_2O	30×30×14	39	11	
	WO_3	10×10×10	47.5	9.3	
		10×10×5	59	9.5	
7	Me_2O	23×23×23	30	10.9	
	WO_3	23×23×23	21	12.8	
		10×10×10	37	9.5	
8	Me_2O	10× 10× 10	50	8.5	
	ZnF_2	10× 10× 2			0.002
	WO_3				
9	MeO	10× 10× 10	24	13.6	
		10× 10× 2			0.026
10	Me_2O	26×24×24	25	12.0	
	WO_3				
11	Me_2O	$\varnothing 44 \times 55$	15	13.7	
	WO_3				

The light output of $ZnWO_4$ samples was determined relative $CdWO_4$ sample with dimensions $10 \times 10 \times 10$ mm.

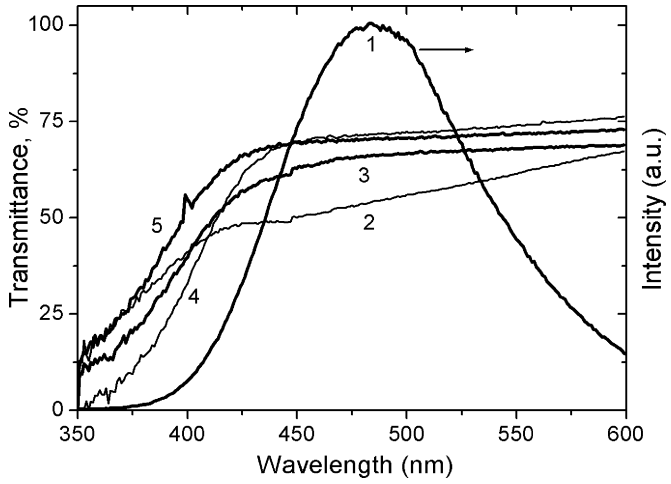

Fig. 2. X-ray luminescence spectra at RT of $ZnWO_4$ crystal (1). Transmission spectra of the $ZnWO_4$ samples #1 (2), #3 (3), #4 (4), and #8 (5).

low radioactive 5″ PMT (EMI D724KFLB) through a high pure quartz light-guide 10 cm in diameter and 33 cm long. The detector was surrounded by a passive shield made of teflon (3–5 cm), plexiglass (6–13 cm), high purity copper (3–6 cm) and lead (15 cm). For each event in the detector the amplitude of a signal and its arrival time were recorded. In addition, scintillation pulses of the $ZnWO_4$ scintillator were digitized with a 20 MHz sampling frequency. The energy spectrum measured with

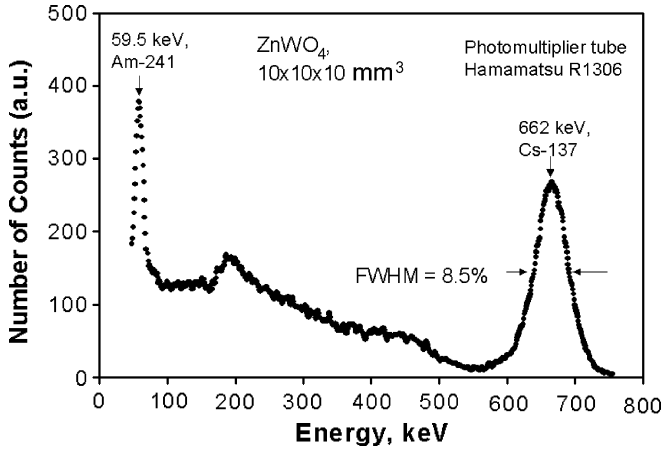

Fig. 3. Pulse amplitude spectra of $ZnWO_4$ scintillation crystal (sample #8, Table I) when irradiated with 662 keV γ-rays (^{137}Cs).

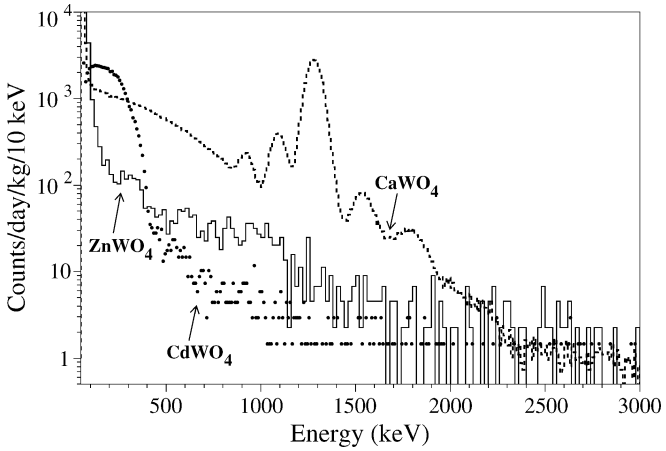

Fig. 4. Energy spectra of $ZnWO_4$ (119 g, 44.7 h), $CaWO_4$ (189 g, 1734 h), and $CdWO_4$ (448 g, 37 h) scintillation crystals measured in the low background set-up. The $CaWO_4$ crystal is considerably polluted by radionuclides from U/Th chains. Beta decay of ^{113}Cd dominates in the low energy part of the $CdWO_4$ spectrum. The background of the $ZnWO_4$ detector is caused mainly by external γ-rays.

the $ZnWO_4$ crystal scintillator during 44.7 h in the low background set-up is presented in Fig. 4.

The spectra of widely used calcium ($CaWO_4$) and cadmium tungtates ($CdWO_4$) scintillators measured in similar conditions are given for comparison (the spectra are normalized by their measurement times and by the detector masses). The background of the $ZnWO_4$ detector is substantially lower than that of the $CaWO_4$ and is comparable with that of the $CdWO_4$ above $\approx$0.5 MeV. Note, that below 0.5 MeV the counting rate of the $ZnWO_4$ detector is one order magnitude lower than that of $CdWO_4$. Obviously, it is due to presence in the $CdWO_4$ crystals of the β active ^{113}Cd isotope (natural abundance of 12%, $Q_\beta = 320$ keV; $T_{1/2} = 7.7 \times 10^{15}$ years).

There are no peculiarities in the spectrum which can be interpreted as certain radioactivity. Therefore, only limits on contaminations of the crystal by nuclides from U/Th families as well as by ^{10}K, $^{90}Sr - ^{90}Y$, ^{137}Cs, and ^{147}Sm were set on the basis of the experimental data. With this aim the spectrum was fitted in different energy intervals by simple model composed of an exponential function (to describe external γ rays) and background components searched for (simulated with the GEANT4 package). Different parts of the families (^{208}Tl, ^{210}Bi, ^{214}Bi, ^{234m}Pa) were considered separately because equilibrium of U/Th families in crystals is expected to be broken. The pulse-shape discrimination between γ/β events and α particles [3], [8] was used to estimate total α activity of U/Th, while the fast chains $^{214}Bi \rightarrow ^{214}Po \rightarrow ^{210}Pb$ (it gives activity of ^{226}Ra from ^{238}U family) and $^{220}Rn \rightarrow ^{216}Po \rightarrow ^{212}Pb$ (^{228}Th from ^{232}Th) were selected with the help of the time-amplitude analysis [2], [3].

TABLE II
RADIOACTIVE CONTAMINATION OF $ZnWO_4$ CRYSTALS (mBq/kg)

Chain	Source	$ZnWO_4$ present study	$ZnWO_4$ [8]
^{232}Th	^{228}Th	≤ 0.1	≤ 3.3
^{238}U	^{226}Ra	< 0.16	≤ 0.4
Total α activity		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

The summary of the measured radioactive contamination of the $ZnWO_4$ scintillator (or limits on their activities) is given in Table II in comparison with the results presented in [8].

The limits on activities of ^{40}K and ^{147}Sm obtained in the present study are worse than the limits from [8]. It is due to slightly higher background of the $26 \times 24 \times 24$ mm detector near the energy 0.3 MeV (where alpha peak of ^{147}Sm is expected), and in the energy region 0.5–0.9 MeV where is the maximum of ^{40}K beta spectrum.

Recently new improved half-life limits on different modes of double electron capture and electron capture with positron emission in ^{64}Zn were obtained in a pilot experiment carried out at the Gran Sasso National Laboratories with the help of a $ZnWO_4$ crystal scintillator $19 \times 20 \times 40$ mm [20].

IV. CONCLUSIONS

$ZnWO_4$ crystal scintillators of large volume (up to $\varnothing 50 \times 100$ mm) with advanced scintillation properties and reasonable mechanical characteristics were developed. It was achieved thanks to optimization of growth conditions and initial composition by doping $ZnWO_4$ charge with metals of the first and second groups, as well as by elements with high electric negativity.

Optical and scintillation properties of $ZnWO_4$ crystals were studied. The best one-centimeter samples shown energy resolution at the level of 8–10% for 662 keV γ line of ^{137}Cs. A value of 13.7% has been measured with a large sample $\varnothing 44 \times 55$ mm.

Low level of afterglow (0.002%, 20 ms after excitation) was obtained with one of $ZnWO_4$ scintillators, while typical value do not exceeds 0.1%.

The radioactive contamination of a $ZnWO_4$ $26 \times 24 \times 24$ mm detector was tested in the Solotvina Underground Laboratory. Alpha activity at the level of 2.4 mBq/kg (daughters of U/Th)

was detected in the scintillator, $^{228}\mathrm{Th}$ contamination is less than 0.1 mBq/kg, activity of $^{226}\mathrm{Ra}$ do not exceeds 0.16 mBq/kg.

Requirements to the level of radioactivity of $\mathrm{ZnWO_4}$ detectors, as well as ways to improve their radiopurity have to be an object of further studies. Some experimental research and simulations are already in progress.

The obtained results demonstrate possibility to apply $\mathrm{ZnWO_4}$ crystal scintillators to search for 2β processes in Zinc and Tungsten.

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