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Research and Development of $ZnBO_4$ (B = W, Mo) Crystal Scintillators for Dark Matter and Double Beta Decay Searching

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Oxide crystal scintillators play a considerable role in fundamental and applied researches. However, working out of new generation of high-sensitivity equipment and new methods of research puts higher requirements. The $ZnBO_4$ (B = W, Mo) crystals were grown from charge in platinum crucibles with high frequency heating, using the Czochralski method. The raw powder with optimum composition was prepared by solid phase high temperature synthesis using ZnO and BO_3 (B = W, Mo) with 4–5N purity. Single crystals with sizes up to $\oslash 50 \times 100$ mm were grown and scintillation elements of various sizes and shapes (cylinders, rectangular and hexahedron prisms) were produced. High spectrometric characteristics were obtained for $ZnWO_4$: R = 8–10% under excitation by ^{137}Cs (E_γ = 662 keV), low radiation background (less than 0.2 mBq/kg) and low afterglow (0.002%, 20 ms after excitation). The obtained results demonstrate good prospects for $ZnWO_4$ and $ZnMoO_4$ crystal scintillators for application in low-count rate experiments, searching for double beta decay processes, interaction with dark matter particles, and also studies of rare decay processes. The material has also a good potential for application in modern tomography, scintillation bolometers and for other major researches using scintillators.

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1. Introduction

Oxide crystal scintillators, in particular, tungstates and molybdates, are widely used in high energy physics, outer space research, medical diagnostics, etc. [1, 2]. Their application is based on such unique properties as high density, high scintillation efficiency, thermal and radiation stability, non-hygroscopicity, etc.

Recently, growing interest has emerged in experiments on search for rare events, such as double beta decay or interaction with dark matter particles, where these materials also seem very promising. In this relationship, search for new crystals based on tungstates and molybdates is under way. As noted in [3–5], single crystals on the basis of zinc tungstate and molybdate ($ZnWO_4$ and $ZnMoO_4$) are promising for these applications. However, the use of these crystals in the search for rare events imposes additional requirements to their characteristics: high light output in the mK temperature range and extremely low intrinsic radiation background. Also, the scintillator size should be not smaller than $\oslash 40 \times 40$ mm^3. $ZnWO_4$ single crystals of such size had been grown, but they appeared to be colored [2]. Until recently, there were no literature data on preparation of $ZnMoO_4$ single crystals of such size. Only in 2007 first reports appeared on preparation of large-sized high quality $ZnWO_4$ [6] and $ZnMoO_4$ crystals [7, 8].

The main objective of this work was preparation of large $ZnWO_4$ crystals with improved characteristics and new $ZnMoO_4$ crystals, as well as studies of their properties from the viewpoint of application in cryogenic detectors used in search for rare events.

2. Preparation and characterization of $ZnWO_4$

$ZnWO_4$ crystals are of monoclinic structure. They have cleavage plane (010) and two gliding planes (100) and (010). No phase transitions have been found for the compound $ZnWO_4$ in the range from room temperature up to the melting point [9].

For synthesis of zinc tungstate charge for growth, we used the solid-phase method. Mixtures of the initial components in the form of oxides, taken both in stoichiometric ratios and with controlled deviations from stoichiometry, were ground and annealed in air. Synthesis of $ZnWO_4$ charge was carried out at 900–950 °C during not least 20 h; qualification of the initial oxides was 99.995 mass%. The obtained products were checked for distribution homogeneity of the main components, and their phase composition was determined. The product thus prepared consisted of the phase of symmetry and

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Fig. 1. $ZnWO_4$ single crystal of $\oslash 50 \times 100$ mm size grown by the Czochralski method.

parameters corresponding to $ZnWO_4$ single crystal. The last synthesis stage was carried out at $T = 950(\pm 10)$ °C for 5 h in oxygen atmosphere to ensure the highest oxidation level of tungsten (+6).

Crystal ingots were grown by using seed crystals oriented along crystallographic directions [100], [010], [110]. Rate of pulling and speed of rotation were $v = 1.5$–3 mm/h and $\omega = 20$–35 rpm, respectively. Optimum conditions were chosen for growth of $ZnWO_4$ single crystals. Single crystals with sizes up to $\oslash 50 \times 100$ mm were obtained (Fig. 1) in the Institute for Scintillation Materials [10].

The crystals obtained were used for fabrication of scintillation elements of different shapes and sizes for further studies.

TABLE I

Scintillation characteristics of $ZnWO_4$ crystals. The light output of $ZnWO_4$ samples was determined at room temperature relatively to a $CdWO_4$ reference sample with dimensions $10 \times 10 \times 10$ mm^3.

No.	Dopant	Sample size [mm]	Light output [%CWO]	Energy resolution for Cs-137 (E = 662 keV) [%]	Afterglow [%] (20 ms)
1	–	$10 \times 10 \times 10$ $10 \times 10 \times 2$	11	23	 0.79
2	WO_3	$10 \times 10 \times 10$ $10 \times 10 \times 2$	30	15	 0.031
3	MeF	$10 \times 10 \times 10$ $10 \times 10 \times 2$	32	11	 0.104
4	MeF WO_3	$\oslash 20 \times 20$ $10 \times 10 \times 10$ $10 \times 10 \times 2$	39 41	12.8 9.6	 0.004
5	ZnF_2 Me_2O WO_3	$10 \times 10 \times 10$ $10 \times 10 \times 2$	47	 10.2	 0.005
6	Me_2O WO_3	$30 \times 30 \times 14$ $10 \times 10 \times 10$ $10 \times 10 \times 5$	39 47 59	11 9.3 9.5	
7	Me_2O WO_3	$23 \times 23 \times 23$ $23 \times 23 \times 23$ $10 \times 10 \times 10$	30 21 37	10.9 12.8 9.5	
8	Me_2O ZnF_2 WO_3	$10 \times 10 \times 10$ $10 \times 10 \times 2$	50	8.5	 0.002
9	MeO	$10 \times 10 \times 10$ $10 \times 10 \times 2$	24	13.6	 0.026
10	Me_2O WO_3	$\oslash 44 \times 55$	15	13.7	
11	Me_2O WO_3	$\hexagon 40 \times 40$	27	10.7	

Effects of the initial charge stoichiometry, dopants, various fluorides, bivalent and univalent metals upon optical, scintillation and luminescent properties of these crystals were studied [10].

The excess WO_3 in the initial charge improved scintillation characteristics as compared with crystals grown from the charge of stoichiometric composition (Table I, Nos. 1, 2).

Doping with bivalent metals does not affect the color of single crystals, and does not improve scintillation properties. Doping by univalent metals in combination with zinc fluoride improves transparence (Fig. 2, curve 5) and scintillation properties of $ZnWO_4$. The best light output (50% with respect to $CdWO_4$) and energy resolution of 8.5% were obtained for samples made of crystal No. 8 (Table I). Such energy resolution is substantially smaller than reported earlier by Danevich et al. (11% for a crystal of diameter 14 mm and height 7 mm) [11].

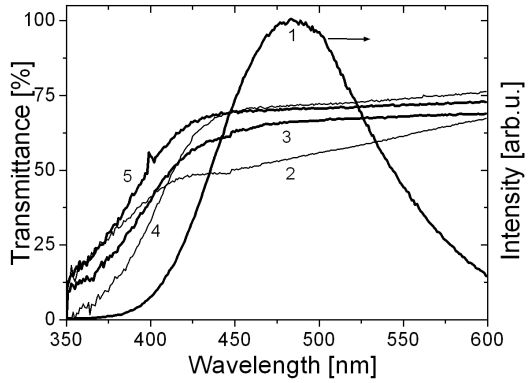

Fig. 2. Normalized X-ray luminescence spectra for all $ZnWO_4$ samples (1) and optical transmission spectra of $ZnWO_4$ samples No. 1 (2), No. 3 (3), No. 4 (4) and No. 8 (5). The sample numbers correspond to the crystals of Table I.

Figure 3 shows the pulse amplitude spectrum of a scintillation element in shape of hexagonal prism of ⌀ 40 × 40 mm size under gamma radiation of 662 keV (^{137}Cs). The energy resolution was 10.7%. The afterglow intensity for the best samples (Table I, No. 8) was 0.002% in 20 ms after irradiation.

Studies of scintillation characteristics of $ZnWO_4$ crystals carried out in a broad temperature range in Oxford University [8] showed that their relative scintillation yield with respect to $CaWO_4$ crystal was 77% at T = 7 K. Figure 4 shows the light output of $ZnWO_4$ crystal scintillator as function of temperature in the 7–300 K range. The total internal α activity of our best sample studied is smaller than 0.2 mBq/kg [12].

The data obtained show that scintillators based on zinc tungstate single crystals with improved characteristics can be widely used in cryogenic detectors for detection of rare processes in experiments on search for dark matter and 2β decay.

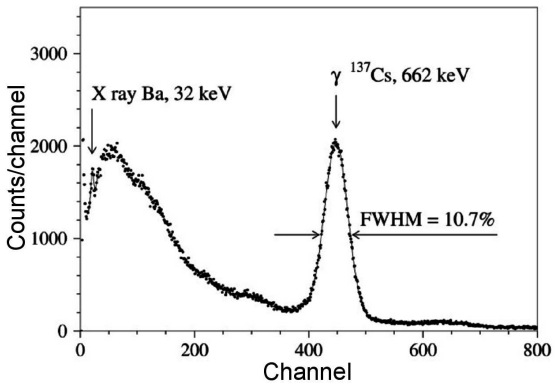

Fig. 3. Amplitude spectrum of $ZnWO_4$ crystal of ⌀ 40 × 40 mm size irradiated by ^{137}Cs (energy 662 keV).

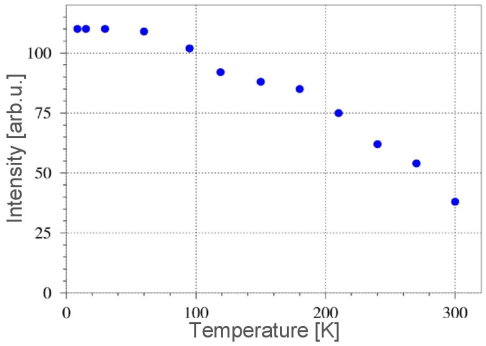

Fig. 4. Light output of $ZnWO_4$ single crystal as function of temperature under α-excitation (^{241}Am).

3. Preparation and characterization of $ZnMoO_4$

As shown in [13, 14], the structure of $ZnMoO_4$ depends upon synthesis conditions. Heating of the oxide mixture in a vacuum-sealed quartz ampoule at 1000 °C for 1–2 days leads to formation of α-$ZnMoO_4$. In hydrothermal conditions at 700 °C and 3 kbar pressure, $ZnMoO_4$ of the structure unknown before was obtained. Using high-pressure equipment, at 900 °C and 60–65 kbar zinc molybdate was synthesized, which was isostructural to the corresponding tungstate [14–16].

The conditions of $ZnMoO_4$ synthesis were determined using the results of derivatographic analysis up to T = 900 °C (Fig. 5). The measurements were carried out using a Q-1500 D derivatograph with heating rate 10 K/min; aluminum oxide was used as reference. The optimum synthesis regime was worked out by studying the conversion degree of the initial components and the structure of products obtained in stepwise temperature–time annealing at T = 325–750 °C using X-ray phase analysis (Table II).

In Ref. [7] $ZnMoO_4$ synthesis at T = 700 °C (according to DTA data) was carried out. The differences in derivatograms are probably related to different purity of the initial oxides. As shown in Fig. 5, when a mixture of $ZnMoO_4$ initial components is heated up to T = 900 °C,

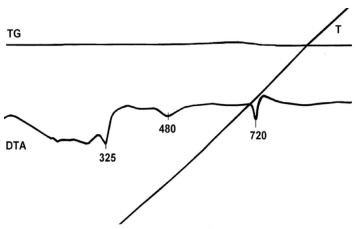

Fig. 5. Thermogram of solid-phase reaction of initial oxides in synthesis of $ZnMoO_4$.

TABLE II

Content of $ZnMoO_4$ phase in charge samples of different composition according to X-ray fluorescence analysis data.

No.	Preparation conditions	Phase content [%]		
		$ZnMoO_4$	ZnO	MoO_3
1	heating $V_T \leq 2.5$ K/min, keeping for $\Delta t = 6$ h at 350 °C	16.9(6)	51.9(7)	31.2(6)
2	as No. 1 $\Delta t = 6$ h at 520 °C	83.7(7)	6.2(2)	10.2(3)
3	as No. 1 $\Delta t = 6$ h at 740 °C	100	–	–
4	as No. 1 $\Delta t = 30$ h at 550 °C, + annealing in oxygen $\Delta t = 4$ h	100	–	–
5	ground single crystal	100	–	–

three endothermic effects are observed. The heat absorption process at 325 °C is probably due to the loss of moisture accumulated from atmosphere, and the other process near 480 °C — to formation of an intermediate phase. The endothermic peak at higher temperatures is related to the residual process of synthesis of $ZnMoO_4$ phase (720±5) °C. Since MoO_3 sublimates at $T = 600$ °C, synthesis of zinc molybdate should be carried out at $T \leq 600$ °C.

The validity of such interpretation has been confirmed by X-ray fluorescence analysis (Table II) of samples obtained by thermal treatment of mixtures of initial components at temperatures corresponding to the effects considered.

The developed synthesis methods ensured preparation of high quality monophase charge of zinc molybdate.

For growth of $ZnMoO_4$ single crystals in optimum conditions, platinum crucibles of cylindrical shape were used with 40–100 mm diameter and 40–100 mm height, with wall thickness 1 mm or 2 mm.

High sensitivity of $ZnMoO_4$ single crystals to non-uniformity of thermal effects due to anisotropy of their structure required creation of clearly stated thermal conditions both in growth and cooling zones. Zinc molybdate single crystals are very sensitive to melt overheating, leading to formation of zinc paramolybdate ($Zn_3Mo_2O_9$), which results in formation of polycrystals. The temperature gradient in the crystallization zone ΔT_z should not exceed 50 K/cm.

The melt-crystal boundary was kept planar or slightly convex towards the melt. The crystal pulling and rotation rates were maintained within $v = 1.2$–1.9 mm/h and $\omega = 20$–35 rpm, respectively; the axial temperature gradient in the growth zone grad T_z was smaller than 35 K/cm. As a result of experimental testing, thermal conditions were determined allowing growth of single crystals of ⌀ 44 × 100 mm size (Fig. 6).

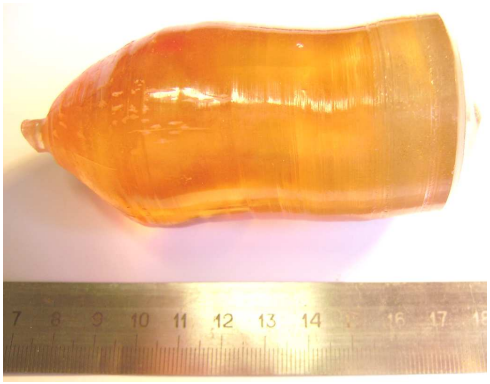

Fig. 6. $ZnMoO_4$ single crystal of ⌀ 44 × 100 mm size grown by Czochralski method.

The grown single crystals and scintillation elements showed orange color. The transmission spectrum has absorption band with maximum at 450 nm (Fig. 7).

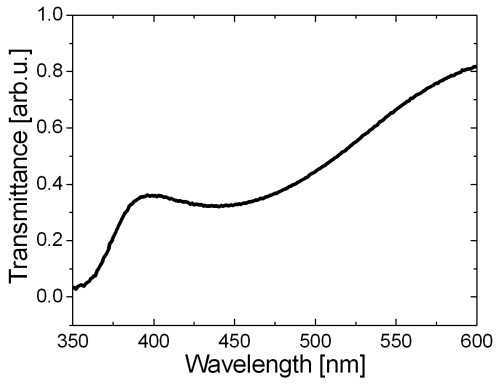

Fig. 7. Transmission spectrum of $ZnMoO_4$ crystal at room temperature.

The results of the luminescence intensity at nitrogen temperature (Fig. 8) show that zinc molybdate is a promising material for cryogenic scintillation bolometers and for detection of neutrino-less double β decay [6], but certain improvement of its optical and scintillation characteristics is still necessary.

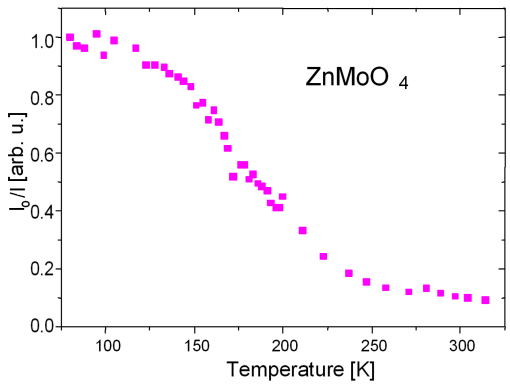

Fig. 8. Temperature dependence of X-ray luminescence intensity of $ZnMoO_4$.

4. Conclusions

Complex studies have been carried out and conditions optimized for synthesis of $ZnWO_4$ and $ZnMoO_4$ charge and growth of large-sized single crystals.

Crystals of $ZnWO_4$ and $ZnMoO_4$ of dimensions $\oslash 40 \div 50 \times 100$ mm and high optical quality have been obtained.

Studies of the scintillation elements made from these crystals have shown that $ZnWO_4$ and $ZnMoO_4$ are suitable for their use in experiments on detection of rare processes: neutrino-less double β decay, interaction with dark matter particles, as well as in other important studies in astrophysics using scintillators. Moreover, the $ZnWO_4$ crystals were characterized by higher scintillation parameters in comparison with the $ZnMoO_4$ single crystals. R and D for improvement of optical and scintillation characteristics of zinc molybdate is necessary.

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