Progress in growth mixed $(Zn_{1-x}Cd_x)(W_{1-x}Mo_x)O_4$ crystals for γ-Ray Detection.

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Crystals Growing SIA, Riga, Latvia

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Abstract

Large size (65 mm × 50 x 90 mm (2.3 kg)) of mixed $(Zn_{1-x}Cd_x)(W_{1-x}Mo_x)O_4$ crystals with excellent quality were grown by the low temperature gradient Czochralski method (LTG Czochralski). We measured radioluminescence spectra, optical transmittance, light yield and energy resolution of the crystalline elements with a typical shape of computed tomography detectors. When substituting x=0.1, the energy resolution was a record 8.3%, with absolute light output 9300 photons/MeV. The study showed that the mixed $(Zn_{0.9}Cd_{0.1})(W_{0.9}Mo_{0.1})O_4$ crystals is the promising candidate for the γ-Ray detection equipment.

Introduction

Zinc tungstate $ZnWO_4$ is a widely known scintillator with high density and large effective number. This crystal is widely used in high-energy calorimetry, cryogenic detectors and other scientific applications [1]. Low-cost large-sized pure crystals can be obtained by the low-gradient Czochralski method [2]. Doping ZnWO4 crystals with various elements can significantly improve their scintillation characteristics, expanding their application in industry, for example, for use in CT γ-Ray detectors [3]. However, there is no mention in the literature of the production of large volume mixed crystals based on zinc tungstate.

In this article, we have focused on crystal growth mixed $(Zn_{1-x}Cd_x)(W_{1-x}Mo_x)O_4$ crystals and characterization of detector elements for computed tomography.

Experimental

High quality large volume mixed $(Zn_{1-x}Cd_x)(W_{1-x}Mo_x)O_4$ crystal scintillators have been developed in Crystal Growing Sia (Latvia) with the help of the low-thermal gradient Czochralski technique (LTG Cz) . The samples studied in the present work were produced in air atmosphere in a platinum crucible 70 mm in diameter and 100 mm height, installed into three zone resistance heater.

The ratio between ZnO and WO_3 in the initial powder for the crystal growth was chosen according to the phase diagram of the ZnO-CdO-WO_3-MoO_3 system. The powder was synthesized by using reaction WO_3 + ZnO →$ZnWO_4$. High purity grade zinc oxide (99.995%) produced by Umicore (Belgium) and high purity grade tungsten oxide (99.995%) manufactured by Nippon Tungsten Co., Ltd. (Japan) was used. Doping oxides MoO_3 and CdO were added in the ratio of 3, 5 and 10 atomic %, at the stage of solid-phase synthesis. Three formulations were used: Z1 = $(Zn_{0.97}Cd_{0,03})(W_{0.97}Mo_{0.03})O_4$, Z2 = $(Zn_{0.95}Cd_{0.05})(W_{0.95}Mo_{0.05})O_4$, Z3 = $(Zn_{0.9}Cd_{0.1})(W_{0.9}Mo_{0.1})O_4$.

The rotation speed during the crystal growth was in the range from 3 rpm to 6 rpm, the crystallization rate was 2 mm/h, and all crystals were grown in the [010] direction by using oriented crystal seeds. After the crystal growth process, the crystal boules were annealed in air atmosphere over 24 h. As a result, faceted crystals of high optical quality weighing up to 2.3 kg were obtained. The crystalline boule of mixed $(Zn_{0.9}Cd_{0.1})(W_{0.9}Mo_{0.1})O_4$ crystal are shown in Fig. 1.

Fig. 1 The crystalline boule mixed (Zn0.9 Cd0.1)(W0.9 Mo0.1)O4 crystal

Samples with sizes 30 x 14 x 8 mm^3 (typical shape for elements of scanning detector of computed tomography) with frosted and polished faces were cut from the boules of appropriate composition for characterization. A cadmium tungstate crystal (production by Crystal Growing SIA) was used as a reference standard.

Methods & Results

Evaluation of absolute light yield and energy resolution was done through acquisition of a Cs-137 pulse height spectrum. Crystals were coupled to the PMT with mineral oil and covered with Teflon to reflect light. The signal from the PMT was processed with a Canberra 2005 preamplifier, an Ortec 672 amplifier set to a 10 us shaping time, and a Tukan 8K multi-channel analyzer.

Measurement of energy resolution was done with a Hamamatsu R6231 PMT operated at 1 kV. The 662 keV Cs-137 photopeak was fit with a Gaussian function to determine the peak centroid and full width at half maximum (FWHM). Percent energy resolution was calculated by dividing the FWHM by the peak centroid. A second Gaussian function was fit to the tungsten escape peak. A Hamamatsu R2059 PMT operated at 1.5 kV was used for measurement of light yield. Absolute light yield was calculated by accounting for the position of the single photoelectron (SPE) centroid and the quantum efficiency of the PMT, as described in [**Error! Reference source not found.**].

Pulse height spectra and fits used to determine energy resolution are show in Fig. 2. Table 1 summarizes energy resolution and absolute light yield for all samples.

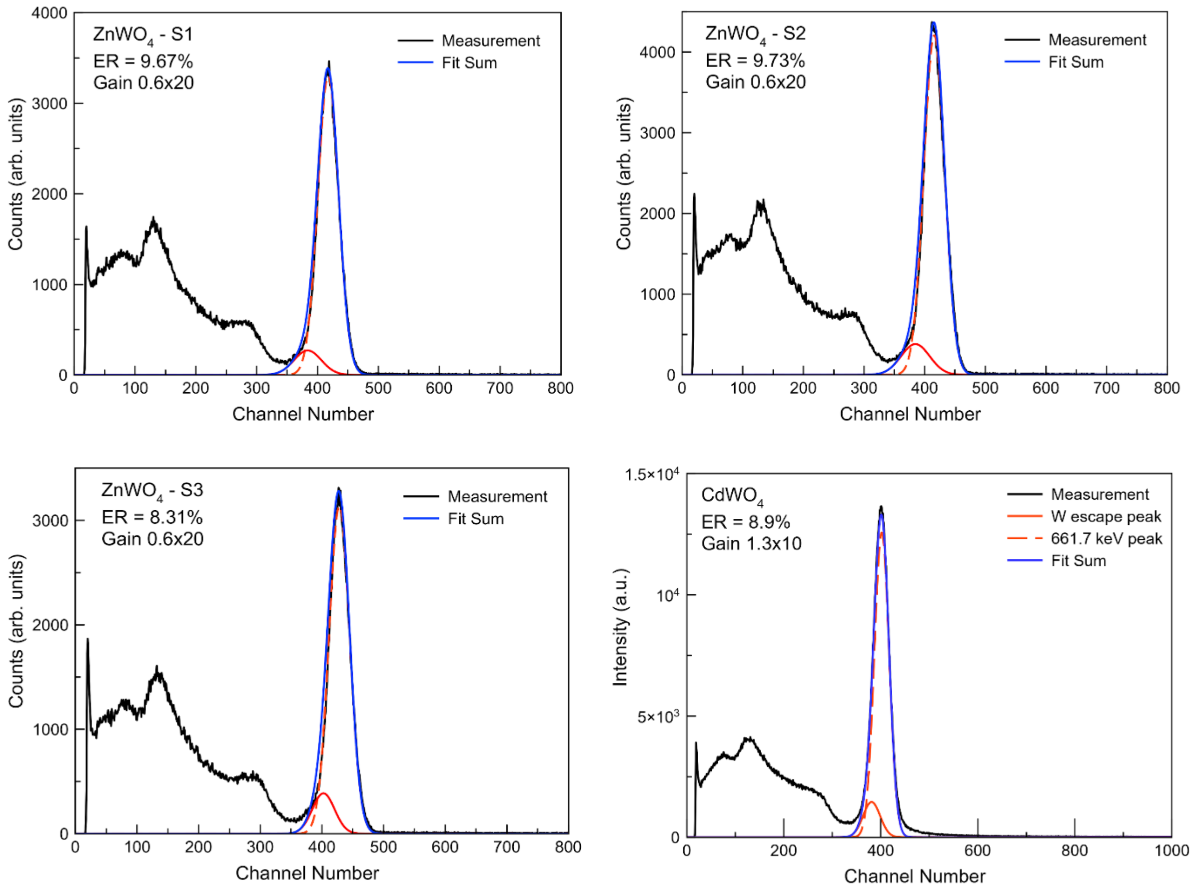

Fig. 2 Cs-137 pulse height spectra acquired for mixed zinc tungstate samples and the cadmium tungstate reference crystal

Table 1. Energy resolution and absolute light yield for mixed zinc tungstate samples and the cadmium tungstate reference crystal

Sample and Dimensions	Energy Resolution (% at 662 keV)	Absolute Light Yield (Photons/MeV)
$ZnWO_4$ - "S1" (29.7x13.8x8.2 mm)	9.7%	10,400
$ZnWO_4$ - "S2" (29.8x13.9x8.3 mm)	9.7%	9,100
$ZnWO_4$ - "S3" (29.8x13.5x8.3 mm)	8.3%	9,300
$CdWO_4$ (80.4x18.2 mm)	8.9%	* 8,800

Radioluminescence (RL) emission spectra were measured by excitation with a Cu target X-ray tube operated at 35 kV and 0.1 mA with a transmission geometry (i.e. X-rays pass through the sample to the monochromator). The spectra were acquired over a range of 200 - 800 nm, using an integration time of 50 milliseconds.

The radioluminescence emission spectra of all samples consisted of a single emission peak, centered at a wavelength of approximately 486 nm for all three zinc tungstate samples, and at a wavelength of approximately 500 nm for $CdWO_4$.. The radioluminescence emission spectra of each sample is shown in Fig. 3.

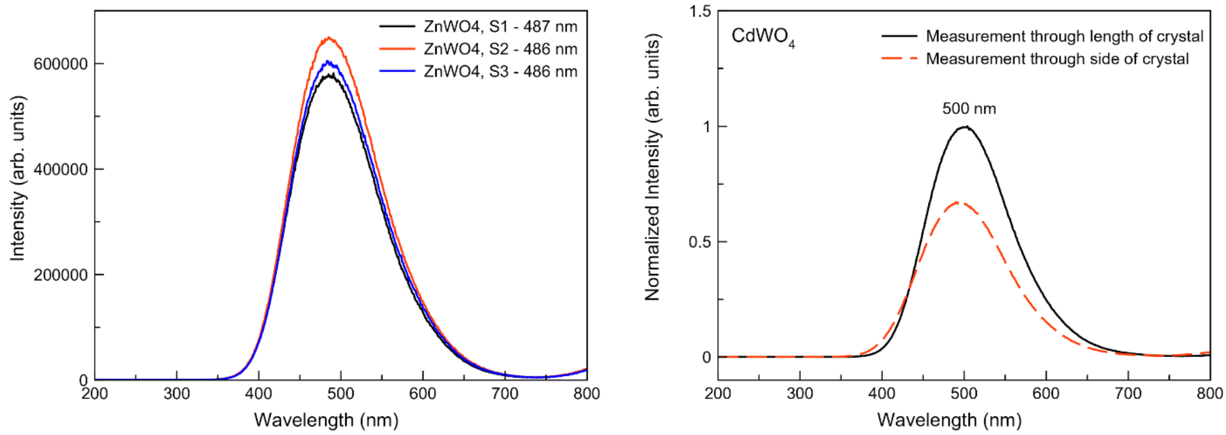

Fig. 3 Radioluminescence spectra for mixed zinc tungstate samples and cadmium tungstate reference

Optical transmittance measurements of the zinc tungstate samples were performed using a Varian Cary 500 UV-VIS-NIR Spectrophotometer. Two sample orientations were evaluated. In orientation 1, the largest faces of the sample (~30 mm x 14 mm), both of which were opaque ("frosted" appearance), were facing the source and detector. This is illustrated in Fig. 4(a). In orientation 2, the side of the samples (~30 mm x 8 mm), were facing the source and detector. One of these faces was opaque, and the other was polished; the polished surface was facing the detector. Orientation 2 is illustrated in Fig. 4(b). Optical transmittance is shown in Fig. *5*.

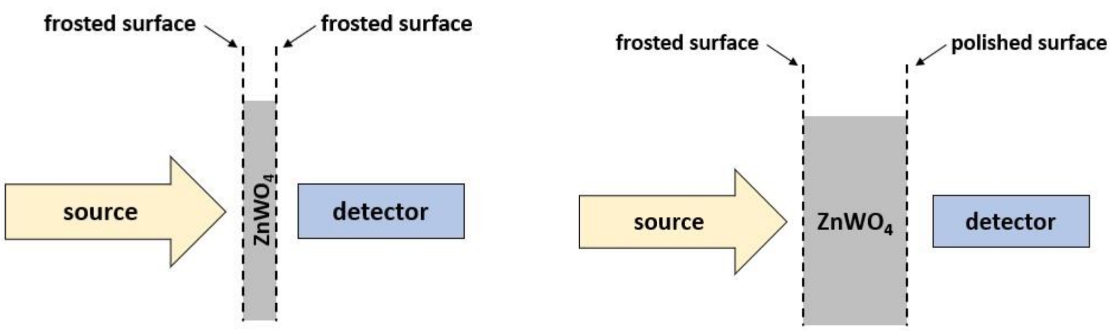

Fig. 4 In orientation 1 (a), frosted surfaces were facing both the source and detector. In orientation 2 (b), a frosted surface was facing the source and a polished surface was facing the detector.

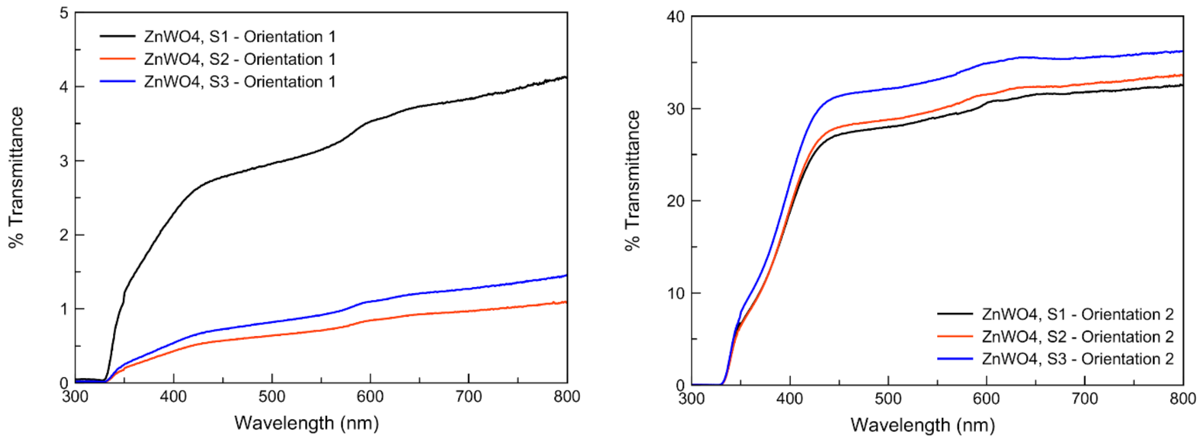

Fig. 5 Optical transmittance of zinc tungstate samples in (a) orientation 1 and b) orientation (2)

Conclusions

High quality large volume mixed $(Zn_{1-x}Cd_x)(W_{1-x}Mo_x)O_4$ crystal scintillators weighing up to 2.3 kg have been grown. Detector elements, with a shape typical for scanning detectors of computed tomography, were fabricated and their radioluminescence, optical and scintillation characteristics were measured. The best results were shown by elements of the composition $(Zn_{0.9}Cd_{0.1})(W_{0.9}Mo_{0.1})O_4$ with energy resolution 8.3% (at 662 KeV) and absolute light output 9,300 photons/MeV. In terms of their characteristics, these crystals are superior to cadmium tungstate crystals with energy resolution 8.9% (at 662 KeV) and absolute light output 8,800 photons/MeV. It shows that the mixed $(Zn_{0.9}Cd_{0.1})(W_{0.9}Mo_{0.1})O_4$ crystals is the promising candidate for the γ-Ray detection equipment.