

Progress in Growth of Mixed (Zn_{1-x}Cd_x)(W_{1-x}Mo_x)O₄ Crystals for γ -Ray Detection

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Abstract

Large-size (65 mm × 50 mm × 90 mm, 2.3 kg) mixed (Zn_{1-x}Cd_x)(W_{1-x}Mo_x)O₄ crystals of excellent quality were grown by the low-temperature-gradient Czochralski method (LTG Czochralski). Radioluminescence spectra, optical transmittance, light yield and energy resolution were measured on crystalline elements with a shape typical for computed-tomography detectors. At the substitution level $x = 0.1$ the energy resolution reached a record value of **8.3%**, with an absolute light output of **9300 photons/MeV**. The study shows that the mixed (Zn_{0.9}Cd_{0.1})(W_{0.9}Mo_{0.1})O₄ crystal is a promising candidate for γ -ray detection equipment.

1 Introduction

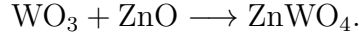
Zinc tungstate ZnWO₄ is a widely known scintillator with high density and a large effective atomic number. This crystal is widely used in high-energy calorimetry, cryogenic detectors and other scientific applications [1]. Low-cost, large-sized pure crystals can be obtained by the low-gradient Czochralski 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 focus on crystal growth and detector-element characterisation for computed tomography of mixed (Zn_{1-x}Cd_x)(W_{1-x}Mo_x)O₄ crystals.

2 Experimental

High-quality large-volume mixed $(\text{Zn}_{1-x}\text{Cd}_x)(\text{W}_{1-x}\text{Mo}_x)\text{O}_4$ crystal scintillators were developed at Crystal Growing SIA (Latvia) using the low-thermal-gradient Czochralski technique (LTG Cz). The samples studied were produced in air atmosphere in a platinum crucible (70 mm diameter, 100 mm height) installed in a three-zone resistance heater.

The ratio between ZnO and WO_3 in the initial powder was chosen according to the phase diagram of the ZnO–CdO– WO_3 – MoO_3 system. The powder was synthesised via the reaction



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) were used. Doping oxides MoO_3 and CdO were added at 3, 5 and 10 atomic % during the solid-phase synthesis stage. Three formulations were studied:

- Z1 = $(\text{Zn}_{0.97}\text{Cd}_{0.03})(\text{W}_{0.97}\text{Mo}_{0.03})\text{O}_4$
- Z2 = $(\text{Zn}_{0.95}\text{Cd}_{0.05})(\text{W}_{0.95}\text{Mo}_{0.05})\text{O}_4$
- Z3 = $(\text{Zn}_{0.9}\text{Cd}_{0.1})(\text{W}_{0.9}\text{Mo}_{0.1})\text{O}_4$

The rotation speed during crystal growth ranged from 3 to 6 rpm; the crystallisation rate was 2 mm/h; all crystals were grown in the [010] direction using oriented crystal seeds. After growth, the crystal boules were annealed in air for 24 h. Faceted crystals of high optical quality weighing up to 2.3 kg were obtained. The crystalline boule of mixed $(\text{Zn}_{0.9}\text{Cd}_{0.1})(\text{W}_{0.9}\text{Mo}_{0.1})\text{O}_4$ is shown in Fig. 1.



Figure 1: The crystalline boule of mixed $(\text{Zn}_{0.9}\text{Cd}_{0.1})(\text{W}_{0.9}\text{Mo}_{0.1})\text{O}_4$ crystal.

Samples with dimensions $30 \times 14 \times 8 \text{ mm}^3$ (typical shape for elements of a scanning detector in computed tomography), with frosted and polished faces, were cut from the

boules. A cadmium tungstate crystal (production: Crystal Growing SIA) was used as the reference standard.

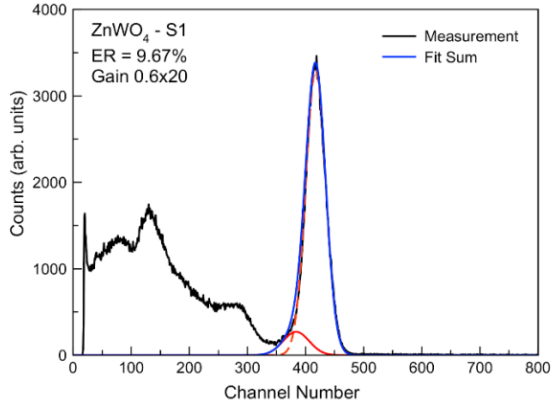
3 Methods & Results

3.1 Energy Resolution and Light Yield

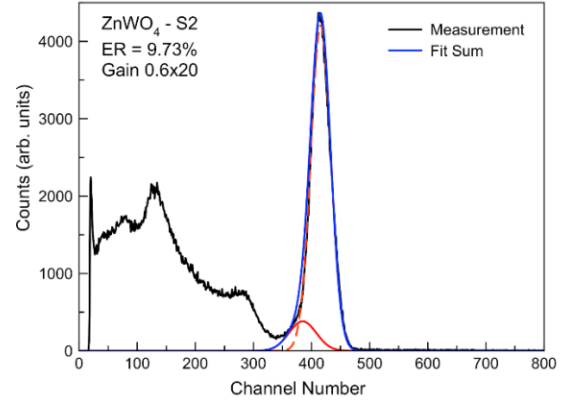
Absolute light yield and energy resolution were evaluated from Cs-137 pulse-height spectra. Crystals were optically coupled to the PMT with mineral oil and wrapped in Teflon to improve light collection. The PMT signal was processed with a Canberra 2005 preamplifier, an Ortec 672 amplifier set to a $10\ \mu\text{s}$ shaping time, and a Tukan 8K multi-channel analyser.

Energy resolution was measured with a Hamamatsu R6231 PMT operated at 1 kV. The 662 keV Cs-137 photopeak was fitted with a Gaussian function to determine the peak centroid and full-width at half-maximum (FWHM). Percent energy resolution was calculated as $\text{FWHM}/\text{centroid}$. A second Gaussian was fitted to the tungsten escape peak. A Hamamatsu R2059 PMT operated at 1.5 kV was used for absolute light-yield measurements, which account for the single photoelectron (SPE) centroid position and PMT quantum efficiency.

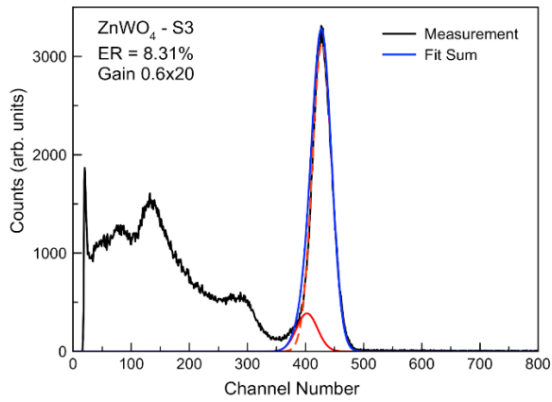
Pulse-height spectra and fits are shown in Fig. 2. Table 1 summarises energy resolution and absolute light yield for all samples.



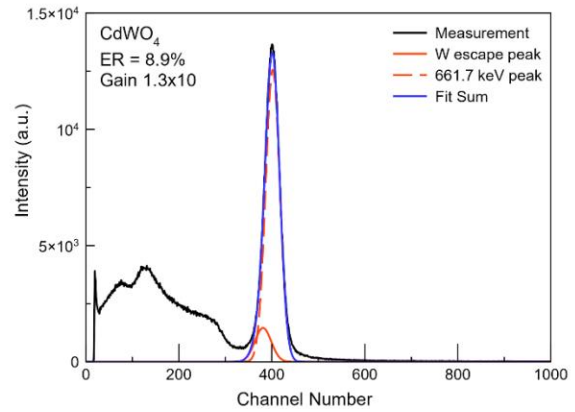
(a) ZnWO_4 -S1 (ER = 9.67 %)



(b) ZnWO_4 -S2 (ER = 9.73 %)



(c) ZnWO_4 -S3 (ER = 8.31 %)



(d) CdWO_4 reference (ER = 8.9 %)

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

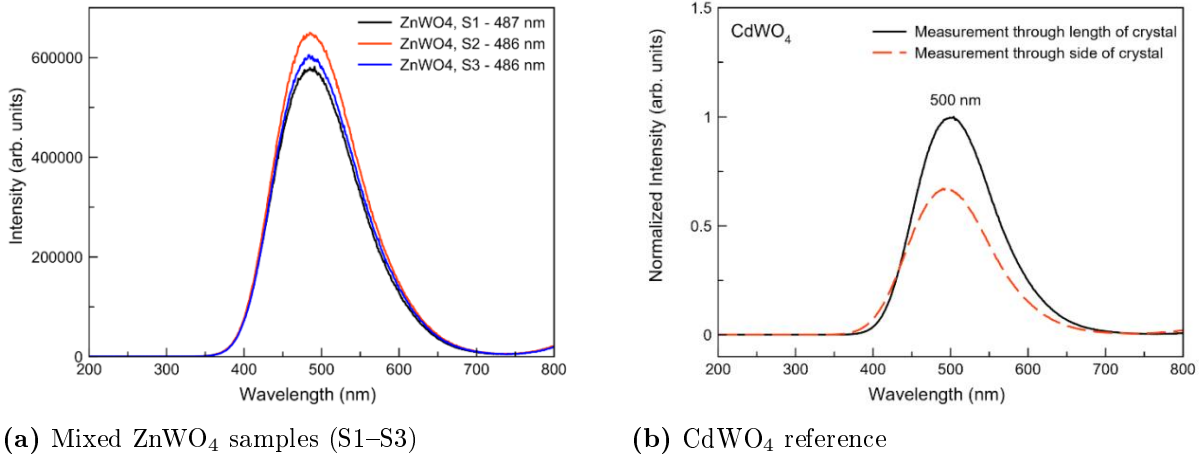
Table 1: Energy resolution and absolute light yield for mixed zinc tungstate samples and the cadmium tungstate reference crystal.

Sample and Dimensions	Energy Resolution (% at 662 keV)	Absolute Light Yield (Photons/MeV)
ZnWO_4 - "S1" (29.7 × 13.8 × 8.2 mm)	9.7 %	10 400
ZnWO_4 - "S2" (29.8 × 13.9 × 8.3 mm)	9.7 %	9 100
ZnWO_4 - "S3" (29.8 × 13.5 × 8.3 mm)	8.3 %	9 300
CdWO_4 (80.4 × 18.2 mm)	8.9 %	*8 800

3.2 Radioluminescence Spectra

Radioluminescence (RL) emission spectra were measured by excitation with a Cu-target X-ray tube operated at 35 kV and 0.1 mA in transmission geometry (X-rays pass through the sample to the monochromator). Spectra were acquired over 200–800 nm with a 50 ms integration time.

The RL spectra of all samples consisted of a single emission peak, centred at approximately 486 nm for all three zinc tungstate samples and at approximately 500 nm for CdWO_4 . The RL emission spectra are shown in Fig. 3.



(a) Mixed ZnWO_4 samples (S1–S3)

(b) CdWO_4 reference

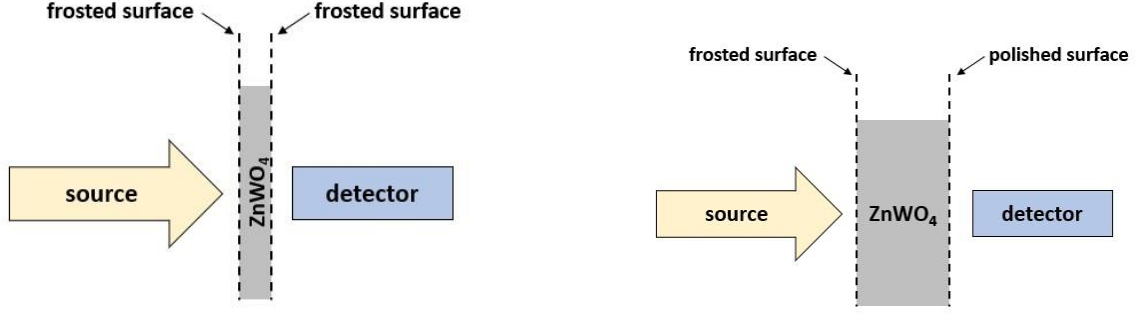
Figure 3: Radioluminescence spectra for mixed zinc tungstate samples and the cadmium tungstate reference.

3.3 Optical Transmittance

Optical transmittance measurements were performed with a Varian Cary 500 UV-VIS-NIR Spectrophotometer. Two sample orientations were evaluated:

Orientation 1 The largest faces ($\sim 30 \text{ mm} \times 14 \text{ mm}$), both opaque (frosted), faced the source and detector [Fig. 4(a)].

Orientation 2 The side faces ($\sim 30 \text{ mm} \times 8 \text{ mm}$) faced the source and detector; one face was frosted (facing source) and the other polished (facing detector) [Fig. 4(b)].

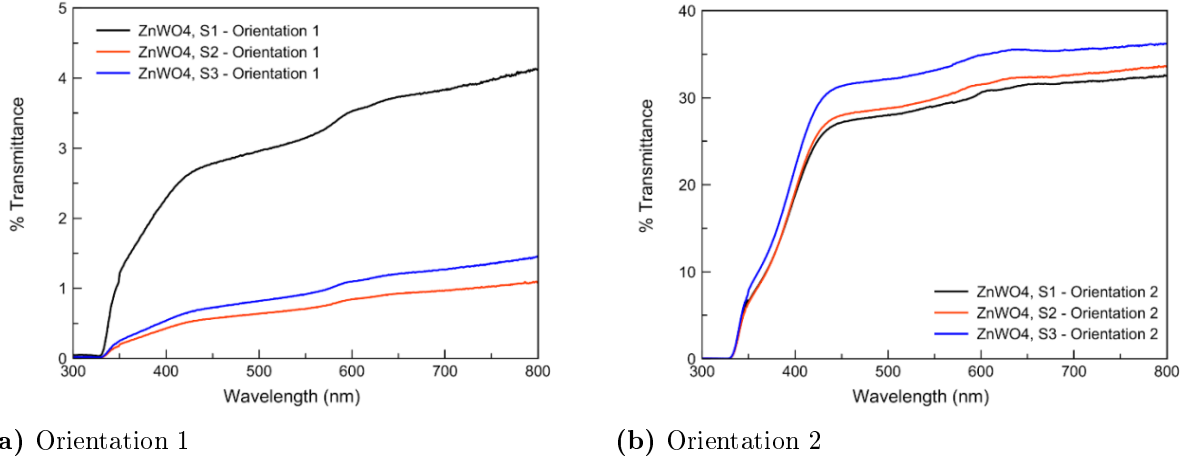


(a) Orientation 1: frosted surfaces facing both source and detector.

(b) Orientation 2: frosted surface facing source; polished surface facing detector.

Figure 4: Schematic of the two sample orientations used for optical transmittance measurements.

Optical transmittance results are shown in Fig. 5.



(a) Orientation 1

(b) Orientation 2

Figure 5: Optical transmittance of zinc tungstate samples in (a) Orientation 1 and (b) Orientation 2.

4 Conclusions

High-quality large-volume mixed $(\text{Zn}_{1-x}\text{Cd}_x)(\text{W}_{1-x}\text{Mo}_x)\text{O}_4$ crystal scintillators weighing up to 2.3 kg have been successfully grown. Detector elements with a shape typical for scanning detectors of computed tomography were fabricated and characterised for radio-luminescence, optical, and scintillation properties.

The best results were achieved for the composition $(\text{Zn}_{0.9}\text{Cd}_{0.1})(\text{W}_{0.9}\text{Mo}_{0.1})\text{O}_4$, with:

- Energy resolution: **8.3 %** at 662 keV
- Absolute light output: **9300 photons/MeV**

These values are superior to the cadmium tungstate reference crystal, which showed an energy resolution of 8.9 % at 662 keV and an absolute light output of 8800 photons/MeV.

These results confirm that the mixed $(\text{Zn}_{0.9}\text{Cd}_{0.1})(\text{W}_{0.9}\text{Mo}_{0.1})\text{O}_4$ crystal is a promising candidate for γ -ray detection equipment.

References

- [1] [Reference 1 – high-energy calorimetry / cryogenic detectors]
- [2] [Reference 2 – low-gradient Czochralski method]
- [3] [Reference 3 – CT γ -ray detectors application]