

# Growing of $^{106}\text{CdWO}_4$ , $\text{ZnWO}_4$ , and $\text{ZnMoO}_4$ scintillation crystals for rare events search by low thermal gradient Czochralski technique

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$\text{ZnWO}_4$  and  $\text{CdWO}_4$  crystals of 1000 mL volume have been grown using the Czochralski technique at low temperature gradients.  $\text{ZnMoO}_4$  and  $^{106}\text{CdWO}_4$  crystals of high optical quality have been obtained. The developed  $\text{MoO}_3$  purification technique provides the  $\text{ZnMoO}_4$  crystals free of absorption bands typical of the crystals grown using the commercial available oxide.

Методом Чохральского в условиях низких градиентов температуры выращены кристаллы  $\text{ZnWO}_4$  и  $\text{CdWO}_4$  объемом 1000 мл. Получены кристаллы  $\text{ZnMoO}_4$  и  $^{106}\text{CdWO}_4$  высокого оптического качества. Показано, что разработанная методика очистки  $\text{MoO}_3$  обеспечивает получение кристаллов  $\text{ZnMoO}_4$ , не имеющих полос поглощения, характерных для кристаллов, выращенных из коммерчески доступного оксида.

## 1. Introduction

The crystals of divalent cation molybdates and tungstates, in particular  $\text{CdWO}_4$ ,  $\text{ZnWO}_4$  and  $\text{ZnMoO}_4$ , have attracted a special attention during the recent years due to their promising use in the experiments aimed at the search for rare events (neutrino-less 2-beta decay) when the scintillation crystal contains the isotopes under investigation —  $^{106}\text{Cd}$ ,  $^{116}\text{Cd}$ ,  $^{70}\text{Zn}$ , or  $^{100}\text{Mo}$ , as well as in the cryogenic bolometers for the search for the dark matter [1, 2]. High-quality large-sized crystals with the low radioactive background are required for such experiments [3, 4]. In addition, in the case of isotope-enriched crystal growth, it is necessary to provide a high charge utilization factor due to the extremely high cost of initial materials. The growing process of the crystals having general formula  $\text{Me}^{2+}[(\text{W},\text{Mo})\text{O}_4]^{2-}$  is

accompanied with essential difficulties. Among the factors that bring complications into the growth and are typical of this compound class, an increased trend to cracking under the appearing thermoelastic stresses connected with the existence of a cleavage plane in their structure is to be mentioned first of all. A common feature for the compounds under consideration is also isomorphous inclusion of the iron-group metals into the cation lattice; that is why the repeated crystallization is an ineffective way to improved crystal quality [5]. Finally, the volatility of melt components can cause a distortion of the initial  $\text{Me}/(\text{W},\text{Mo})$  ratio during the growth process. Furthermore, molybdates and tungstates split out oxygen easily at high temperatures (similar to higher tungsten and molybdenum oxides), thus causing point defects and other distortions of the crystal structure. The crystals

of  $\text{CdWO}_4$ ,  $\text{ZnMo}_4$ , and  $\text{ZnWO}_4$  as well as other molybdates and tungstates are grown as a rule using Czochralski technique with RF heating. The goal of the present work was to demonstrate the advantages of the low temperature gradient Czochralski technique (LTG Cz) [6] in growing molybdates and tungstates of divalent cations. The effect of complicating factors is weakened substantially by using this procedure.

## 2. Experimental procedure

In view of a small amount of isotope-enriched charge and the specific features of the low-gradient procedure with the preferred conditions requiring such an arrangement that the diameter of the growing crystal should be only slightly smaller than the crucible diameter, we have developed a special setup for the growing of the crystals, Fig. 1. A platinum crucible is covered with a conic lid supplied with pipe socket through which a sapphire rod of the seed-holder passes into the crucible; the crucible is placed into a three-zone furnace with a good bottom and top thermal insulation. The growing crystal remains inside the crucible during the entire growth process. There are orifices in thermal protection plates: the upper one has a hole for the seed-holder rod, the bottom thermal insulation plate has a hole for the load rod at the end of which the crucible is mounted. The lower end of the load rod is fixed at the scale pan. The scale is mounted in a tightly closed case connected with the furnace housing through a joint assembly. Above the furnace, there is an auxiliary chamber with a window for the setup loading and unloading; the seeding is carried out by the operator according to the weighing sensor readout. The setup operates in the air; the sealing serves only to eliminate convection.

The furnace heating capacity is less than 500 W, the cooling being natural. The beam type crucible load cell with electromagnetic compensation was specially developed for this setup. The weighing unit provides a resolution  $\pm 3$  mg in the range 0–1 kg. Thermocouple Input Modules (I-7011D, ICP DAS) were used to control temperature in three independent circuits. The control system is based on programmable logic controller PLC100 produced by OWEN. The HMI/SCADA software was used. Due to the independent temperature control in three heater zones, temperature gradients in the melt are maintained at a level not exceeding  $\sim 1$  K/cm. Such a gradient almost completely

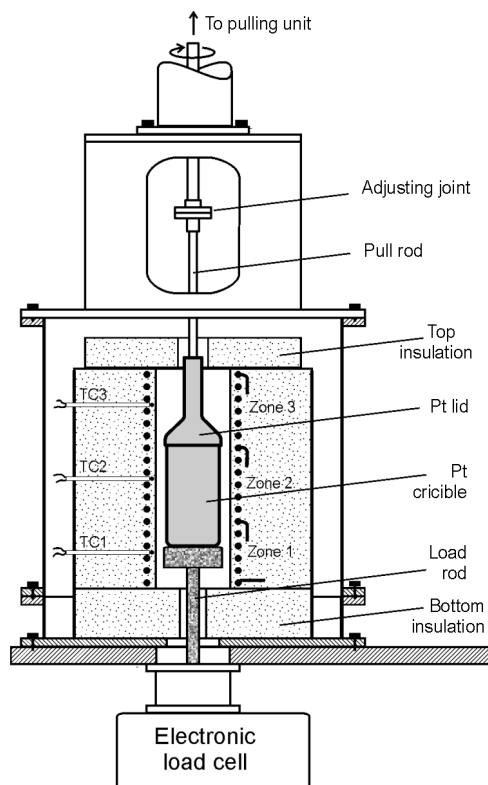


Fig. 1. Schematic representation of puller for growing of oxide crystals by the LTG Cz technique with melt volume about 40 cc.

excludes essentially thermoelastic stresses. In addition, crystal withdrawing from the melt after the process does not cause any thermal shock.

Two commercially available reagents were used in the study,  $\text{CdO}$  99.99 manufactured by Toho Zinc (Japan) and  $\text{ZnO}$  99.995 manufactured by Umicore (Belgium). High-purity  $\text{WO}_3$  was synthesized according to the original technology [7]. According to the chemical spectral analysis results of the resulting product, the concentration of the major admixture Si was 50 ppm, while the concentrations of other analyzable admixtures (16 elements including transition metals) was below the detection limits (less than 5 ppm). In this work, the above-mentioned technology was modified to synthesize  $\text{MoO}_3$  with the major impurity content (Zn) less than 0.1 wt. %; the other 10 analyzable impurities are below the detection limits for these elements (less than 5 ppm).

The charge of cadmium tungstate enriched in the  $^{106}\text{Cd}$  isotope was synthesized at the NeoChem Joint Stock Company, (Moscow, RF).

### 3. Results and discussion

A high degree of morphological similarity was discovered between the crystals of  $\text{CdWO}_4$ ,  $\text{ZnWO}_4$ , and  $\text{ZnMoO}_4$  depending on growth conditions. An important growth feature of these crystals under the low temperature gradient conditions is the combination of faceted and rounded shapes at the growth front, that is, both the layer-by-layer and the normal mechanism of crystal growth are realized; development of faceted shapes and a decrease in the area occupied by rounded areas occur with an increase in crystallization rate [8, 9]. However, as the crystallization rate exceeds a certain limit, the stability of crystal faces is lost, which results in a polycrystal growth. The coexistence of the two growth mechanisms is undesirable due to the capture of inclusions at the boundaries between the faceted and rounded growth shapes. By varying the crystallization rate, either completely rounded or completely faceted growth front can be obtained. Under the low temperature gradient, the rounded front is formed only at extremely low growth rates, so the conditions under which the front is completely faceted are of practical interest for obtaining perfect crystals.

$^{106}\text{CdWO}_4$ . The unique growing character of these crystals was connected with the limited amount of the initial raw material enriched in  $^{106}\text{Cd}$  isotope, from which the crystal was to be grown with the maximal yield. The growing of  $\text{CdWO}_4$  crystals using the LTG Cz procedure was reported for the first time in [6]. The growth along the [100] direction was considered as a preferable way to defect-free crystals. Along this direction, the crystals up to 200 mm long and up to 100 mm in the cross size were grown. Later on, the possibility to grow defect-free crystals along the [010] direction with the flat crystallization front was demonstrated in [8]. The [010] direction is perpendicular to the cleavage plane, and the growth along this direction has an advantage in that the optical treatment of the side surface of the cylindrical elements is simplified substantially. In this connection, we have chosen this direction to grow cadmium tungstate crystals from the isotope enriched raw material.

The isotope-enriched  $^{106}\text{CdWO}_4$  crystals were grown using the setup shown in Fig. 1, from a 100 mm high crucible of 40 mm in diameter at the rotation frequency of 6 r.p.m., crystallization rate 0.9 mm/h. As a result, we obtained the 60 mm long crystals of about 27 mm in di-



Fig. 2. Large-size  $\text{ZnWO}_4$  crystal.

ameter; the mass being 230.5 g. The charge use factor was 87 %. Losses due to melt evaporation did not exceed 0.8 g. The optical and scintillation characteristics of  $^{106}\text{CdWO}_4$  were measured at the Institute for Nuclear Research, National Academy of Sciences of Ukraine using the 50 mm high element of about 27 mm in diameter, with the (010) butt plane, obtained by cleaving the initial ingot. In spite of the irregular shape, the energy resolution of PHR was 10.5 % at 662 keV [10].

$\text{ZnWO}_4$ . The growth of  $\text{ZnWO}_4$  crystals by conventional Cz is described in [11]. The LTG Cz technique to grow  $\text{ZnWO}_4$  crystals of up to 2 kg mass was used for the first time by us in [9]. In this work, we tried to obtain the larger crystals. We used a 250 mm high crucible of 120 mm in diameter. It has been found that the growth conditions [9] allow successful scaling. The best results were obtained when growing  $\text{ZnWO}_4$  along the [010] direction with the flat front formed by the [010] face. We have obtained inclusion-free crystals with a diameter up to 90 mm, up to 240 mm long, having the mass up to 8 kg (Fig. 2). The crystals show a pink tint that disappears almost completely during annealing in oxygen. The optical and scintillation characteristics of the crystals were examined using the cylindrical elements of 40 mm in diameter and 40 mm high. The PHR energy resolution for 662 keV gamma quanta was ~15 % prior to and ~10 % after the annealing. Typical optical transmission spectra of  $\text{ZnWO}_4$  elements of this size prior to and after annealing are shown in Fig. 3.

$\text{ZnMoO}_4$ . A new cryogenic scintillator  $\text{ZnMoO}_4$  combines the low radioactivity background (there are no natural radioactive isotopes of zinc) and high light yield at low temperatures. However, as is stressed in review [1], optimization of this crystal "is only at the very beginning." To date, there are only a few papers describing the

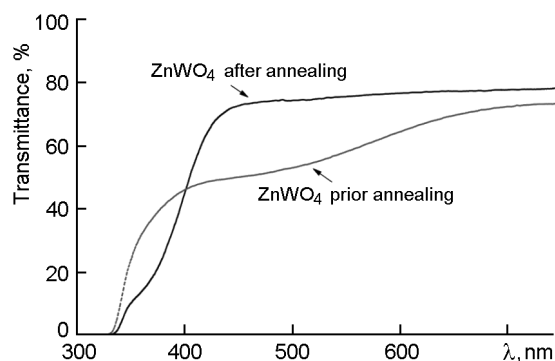


Fig. 3. The optical transmittance of a 40 mm  $\text{ZnWO}_4$  crystal prior to and after annealing.

growing of crystals more than 1 cc in volume. The growing of crystals having the diameter and height up to 30 mm was described in [12]. The crystals had "an intensive orange color" of unknown origin. The authors of [13] reported the growing of the  $\text{ZnMoO}_4$  crystals using Czochralski and Kyropoulos procedures. To reduce the effect caused by  $\text{MoO}_3$  evaporation, excess  $\text{MoO}_3$  in the range from 1.0 to 7.0 wt. % above stoichiometry was introduced into the melt. With the excess of 6.5 %,  $\text{ZnMoO}_4$  crystals characterized by the absence of bubbles, cracks, and inclusions of foreign phases were successfully obtained. Nevertheless, the crystals had yellow color or even red-brown coloration supposed to be due to iron impurity [14].

Our experiments on the growth of  $\text{ZnMoO}_4$  crystals were carried out starting from the stoichiometric melt using the platinum crucibles of 40 mm in diameter along the  $\{001\}$  direction. The rate of crystallization was varied within the range 0.5–1 mm/h. According to [15], zinc molybdate melts under decomposition at about  $1000^\circ\text{C}$ . In a later work [16], the  $\text{ZnMoO}_4$  melting is characterized as a congruent one. In our experiments, when the melt was heated above  $\sim 1015^\circ\text{C}$ , we observed the formation of needle-like crystals, most likely  $\text{Zn}_3\text{Mo}_2\text{O}_9$ , in addition to  $\text{ZnMoO}_4$ . At a lower melt overheating, only  $\text{ZnMoO}_4$  is crystallized, and the growth process took place without complications. The inclusion-free and colorless  $\text{ZnMoO}_4$  crystals of a length up to 70 mm, up to 30 mm in diameter and the mass up to 120 g (Fig. 4) were grown at the crystallization rate of 0.8–1 mm/h with the growth front formed by the  $\{001\}$  face. The transmission spectra of the crystals grown from different raw materials are presented in Fig. 5. It is seen in Fig. 5



Fig. 4. Colorless  $\text{ZnMoO}_4$  crystals.

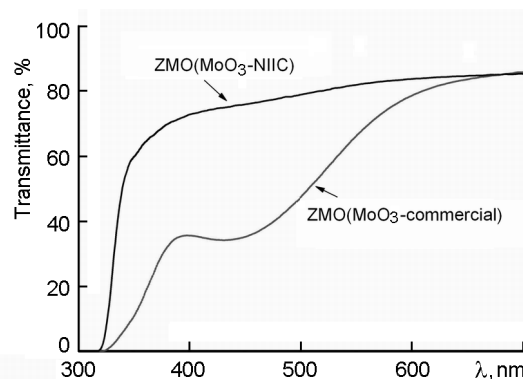


Fig. 5. The optical transmittance of the 28 mm  $\text{ZnMoO}_4$  crystals grown from commercial  $\text{MoO}_3$  and  $\text{MoO}_3$  synthesized in NIIC.

that a broad absorption band in the visible spectral area reported in [14] is absent here. This confirms the supposition [13] that the coloring of  $\text{ZnMoO}_4$  crystals is due to the presence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations. However, we assume that, in addition to iron impurities, the coloration may be caused by deviations from the stoichiometry caused by intense evaporation from the melt surface, which is typical for the conventional Czochralski technique. For example, in [12], where the conventional Czochralski technique was used, temperature differences in the melt reached 50 K.

#### 4. Conclusion

The results presented herein allow us to conclude that the LTG Cz procedure provides a way to the mass production of molybdate and tungstate crystals of required size and quality for physical experiments aimed at the search for rare events.

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## **Вирощування сцинтиляційних кристалів $^{106}\text{CdWO}_4$ , $\text{ZnWO}_4$ та $\text{ZnMo}_4$ для пошуку рідкісних процесів низькоградієнтним методом Чохральського**

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Методом Чохральського в умовах низьких градієнтів температури вирощено кристали  $\text{ZnWO}_4$  та  $\text{CdWO}_4$  об'ємом 1000 мл. Одержано кристали  $\text{ZnMo}_4$  та  $^{106}\text{CdWO}_4$  високої оптичної якості. Показано, що розроблена методика очищення  $\text{MoO}_3$  забезпечує одержання кристалів  $\text{ZnMo}_4$ , які не мають смуг поглинання, характерних для кристалів, вирощених із наявного на ринку оксиду.