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Growing of $ZnWO_4$ single crystals from melt by the low thermal gradient Czochralski technique

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The shape formation regularities of $ZnWO_4$ scintillation crystals grown along the [001] and [010] directions by the low-temperature-gradient Czochralski technique have been studied. It has been established that increasing crystallization speed is accompanied by the development of faceted shapes at the crystallization front. The inclusion-free crystals can be grown with both completely rounded or completely faceted solid-liquid interface, while the coexistence of faceted and rounded surfaces may result in capturing inclusions at their boundaries. The inclusion-free $ZnWO_4$ crystals of 45 mm diameter and the length up to 150 mm have been grown. Absorption spectra of the crystals prior to and after annealing have been measured. For the samples of ∅40 and l=40 mm size, the energy resolution of 11 % for gamma radiation with the energy of 662 keV has been obtained.

Изучены закономерности формообразования сцинтилляционных кристаллов $ZnWO_4$ при их росте низкоградиентным методом Чохральского по направлениям [001] и [010]. Установлено, что повышение скорости кристаллизации сопровождается развитием на фронте кристаллизации гранных форм. Кристаллы, свободные от включений, образуются как при полностью округлом, так и при полностью гранном фронте кристаллизации, тогда как сосуществование гранных и округлых форм может сопровождаться захватом включений на их границах. Выращены свободные от включений кристаллы $ZnWO_4$ диаметром 45 и длиной до 150 мм. Измерены спектры поглощения кристаллов до и после их отжига. Для образцов размером ∅40 и длиной 40 мм получено энергетическое разрешение 11 % для гамма-излучения с энергией 662 keV.

The interest in zinc tungstate $ZnWO_4$ (ZWO) crystals is increased recently due to the potential of this scintillator as a target material in cryogenic bolometers for rare event search [1, 2]. Moreover, zinc tungstate is expected to be an alternative to highly toxic $CdWO_4$ which has only slightly better light yield. At the same time, high-quality crystals of zinc tungstate are still commercially unavailable, though the features of their growth had been under investigation long ago [3, 4]. The growth of ZWO crystals is complicated due to the volatility of the melt, moreover, the trend to cracking along the cleavage plane (010) forms a barrier to an increase in crystal size. There are still only few works reporting the growth of high-quality crystals [5].

The goal of the present work was to study the potentials of the low temperature gradient Czochralski technique (LTG Cz) for growing of high-quality large-sized $ZnWO_4$ crystals. In this method developed at the A.Nikolaev Institute of Inorganic Chemistry (NIIC), the gradients in the melt were decreased to a level of about 1 K/cm [6, 7].

Evaporation of the melt components causing usually the stoichiometry distortions is suppressed by keeping the crystal during the whole process in a crucible closed with a lid furnished with a pipe socket through which a rod of the seed holder is introduced into crystallization space. In addition, the melt never gets overheated because the melt temperature almost coincides with the melting point. It should be noted that the LTG Cz technique has been successfully used before in NIIC to grow $CdWO_4$ crystals similar in the growth behavior to $ZnWO_4$ [8].

The $ZnWO_4$ crystals were grown in an upgraded HX620 puller with weighing monitoring and computerized process control. A three-zone resistance furnace with three independent temperature control circuits was used as a heater. The crystals were grown in air using platinum crucibles of 70 mm diameter and 150 and 200 mm height. Loss for melt evaporation during the growth process did not exceed 0.2 wt. %.

Initial materials. Isomorphous entering of such impurities as Fe, Co, Mn, and other transition metal ions in $ZnWO_4$ lattice makes re-crystallization ineffective as a way to improve the crystal quality, so the initial materials must be of high purity. In this work, we used as initial reagents special purity grade WO_3 synthesized at NIIC [9] and HP grade ZnO (99.995 %) produced by Umicore (Belgium). The major impurity in WO_3 was silicon, its content reaching 50 ppm. The concentrations of transition metals (Cr, Co, Mn, Ni) in tungsten oxide did not exceed 0.1 ppm. According to the certificate of the manufacturer, the content of the major component in zinc oxide was 99.995 %; the concentrations of impurities $Pb < 10$ ppm, $Cd < 5$ ppm, other metals maximum 1 ppm. According to the our analysis results, the actual content of impurity metals in zinc oxide was considerably lower, except for Ca (1 ppm). The solid-phase synthesis was carried out directly within the crystal growth system. The charge use factor reached 90 %.

Morphological features. The effect of growth conditions on the morphology and quality of $ZnWO_4$ crystals was investigated at their pulling in the [010], [100], [001] directions within the crystallization speed range of 0.5 to 3 mm/h and rotation speeds of 5 to 20 rpm. The variation in rotation frequency within the indicated range, as well as the application of reverse rotation, has been established to have no essential effect on the growth process. Using the temperature redistribution between the heater sections, it is possible to vary the growth front sag within a broad range, the its shape similarity being retained. A specific feature of the zinc tungstate crystal morphology at low temperature gradient in the case of convex growth front is the coexistence of rounded and developed faceted shapes. For $ZnWO_4$ growth along the [001] direction, the faces of pinacoid {100}, {010} and prism {110} are observed at the crystallization front. For growth along the [010] direction, the faces of the prism {110} and pinacoid {010} are observed.

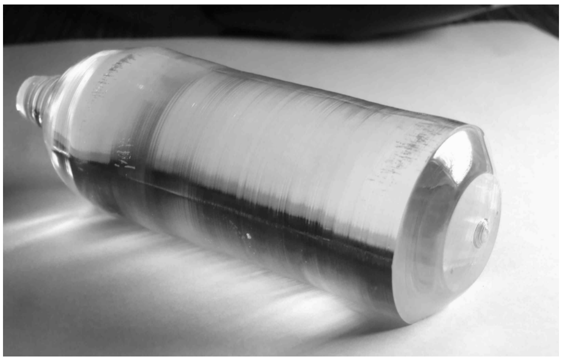

Fig. 1. $ZnWO_4$ crystal with the (010) facet in the center of crystallization front rounded at the periphery.

It was found that the crystallization speed under constant temperature gradient conditions has a determinative effect on the relation between the faceted and rounded shapes. For instance, for growth along [010], an increase in crystallization speed is accompanied by the appearance of of pinacoid {010} and prism {110} facets on the initially rounded growth front. As the crystallization speed increases, the {010} facet may occupy almost the whole front. In this situation, the crystal may become to be flattened due to the development of the lateral pinacoid {100} facets. A further increase in crystallization speed is accompanied by the formation of macro-steps on the front causing a polycrystalline growth. A photographic image of the crystal with rounded periphery at the front and the (010) facet in the center is shown in Fig. 1. A typical evolution of the crystallization front shape is shown schematically in Fig. 2.

For growth along the [100] and [001] directions, the trend to increase the area of faceted shapes at the growth front is conserved at increasing crystallization speed; however, it is impossible to avoid completely the rounded shapes preceding the appearance of macro-steps. At the boundaries between

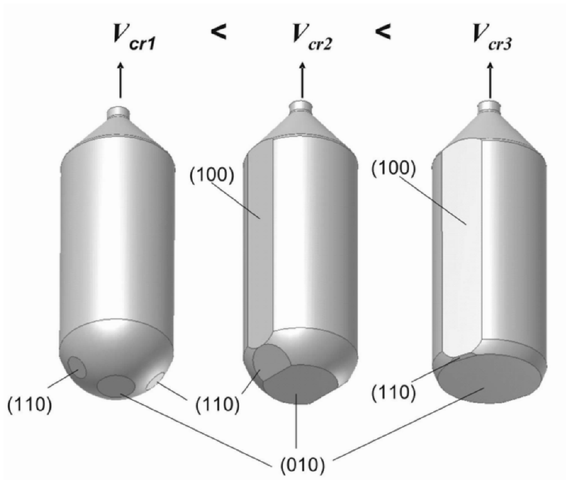

Fig. 2. Schematic image of the relations between the faceted and rounded shapes at the growth front depending on crystallization speed V_{cr}. Growing direction: [010].

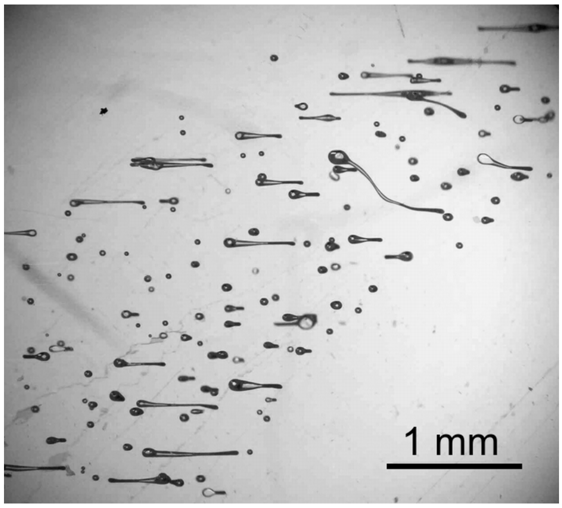

Fig. 3. The zone of macro-inclusions at the boundary between faceted and round growth shapes. Plane (010).

the faceted growth shapes with the rounded ones at the crystallization front, capture of macro-inclusions extended along the direction [001] may occur (Fig. 3).

The crystals free of inclusions can be successfully obtained in the case of growth either with completely rounded front or with completely faceted one. The best results were obtained for the $ZnWO_4$ growth along the [010] direction with a flat front formed by the {010} plane. Under these conditions, inclusion-free $ZnWO_4$ crystals of 45 mm diameter and up to 150 mm long were grown by means of LTG Cz. It should be noted that these dimensions are limited by the technical characteristics of the equipment used. We did not encounter any essential difficulties in further increase of crystals size.

Scintillation and optical characteristics. The crystals for the investigations were obtained by a single crystallization. The as-grown crystals were slightly rose-tinted; the tint disappeared almost completely after the post-growth annealing. The annealing was carried out in oxygen atmosphere for 10 hours at 800°C.

The spectra of complete internal optical losses in zinc tungstate were measured using a Shimadzu UV-3100 spectrophotometer and a 45 mm high sample of 42 mm in diameter. The absorption was measured in the sample central part and at its periphery prior to and after annealing. It is seen in Fig. 4 representing the results of measurements that after annealing, the absorption in the band with a maximum at 500 nm

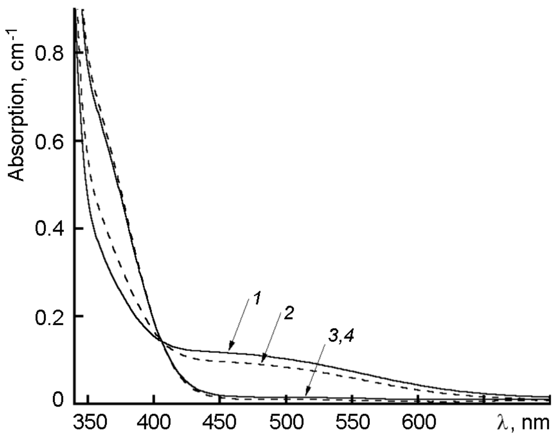

Fig. 4. Spectral dependences of complete optical losses in $ZnWO_4$ prior to (*1*, *2*) and after annealing (*3*, *4*) recorded in the center (solid line) and at the periphery (dotted line) of the crystal.

(that is, around of the scintillation emission spectrum maximum) is decreased by more than one decimal order and amounts ~0.015 cm^{-1} and ~0.01 cm^{-1} for the central and peripheral parts of the sample, respectively. However, quite contrary, absorption in the band adjacent to the fundamental absorption edge, which as a rule characterizes the structural perfection and ordering of the material, is increased. It should be noted that in this spectral region, the absorption at the periphery of non-annealed sample is considerably higher than in its center. After annealing, the difference in absorption spectra of the crystal central and peripheral parts becomes negligibly small.

The light yield and energy resolution were measured after annealing using a 40 mm high cylinder of 40 mm in diameter. The contact surface of the sample was polished and coupled with photomultiplier Hamamatsu R6322-01; other surfaces were ground and covered with a reflecting screen made of the 3M VM2000 film. The shaping time was 13 μs. At room temperature, energy resolution of 11 % was obtained for 662 keV gamma quanta.

Cylindrical elements of $ZnWO_4$ ∅(25–40)×40 mm^2 were transferred for further characterization to the Institute for Nuclear Research, National Academy of Sciences of Ukraine (Kiev) and to the Max Planck Institute (Munich).

Thus, it is possible to grow high-quality $ZnWO_4$ crystals with a good yield using LTG Cz growth technique. This method can be also used in large scale production. In the future, it is planned to study in more detail the processes occurring during annealing and to study the effect of non-stoichiometry with respect to oxygen on the crystal properties.

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Вирощування монокристалів $ZnWO_4$ з розплаву низькоградієнтним методом Чохральського

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Досліджено закономірності формоутворення сцинтиляційних кристалів $ZnWO_4$ при їх рості низькоградієнтним методом Чохральського у напрямах [001] та [010]. Встановлено, що збільшення швидкості кристалізації супроводжується розвитком на фронті кристалізації огранованих форм. Кристали, вільні від включень, утворюються як при повністю округлому, так і при повністю ограненому фронті кристалізації, в той час як співіснування огранених та округлих форм може супроводжуватися захопленням включень на їхніх межах. Вирощено вільні від включень кристали $ZnWO_4$ діаметром 45 та довжиною до 150 мм. Виміряно спектри поглинання кристалів до та після їх відпалу. Для зразків ∅40 та l=40 мм одержано енергетичне розрішення 11 % для гамма-випромінювання з енергією 662 кеВ.