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CRYSTAL GROWTH

Growth and Properties of $ZnMoO_4$ Single Crystals

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Abstract—The conditions for obtaining zinc molybdate single crystals by Czochralski and Kyropoulos crystallization from a flux have been studied. The growth parameters of large single crystals of optical quality are determined. The physicochemical and spectral-luminescent characteristics of the single crystals are studied.

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INTRODUCTION

Molybdenum-containing single crystals attract attention as a material for cryogenic scintillating bolometers, where the ^{100}Mo isotope is a promising element for the experimental search for double neutrinoless β-decay [1, 2]. Effective molybdenum-containing materials can implement the source of an event and record it in the same substance without energy loss, which is typical of event recording in high energy physics. The scintillation materials based on divalent metal molybdates that are currently known, including $CaMoO_4$ and $PbMoO_4$, have one essential drawback: the unavoidable background caused by the presence of radioactive isotopes of the main cations. Zinc molybdate is considered a promising material for scintillation detectors of double neutrinoless β-decay, because zinc has no radioactive isotopes and, hence, does not produce any noise during signal recording. A high light yield is also one of the most important factors in the search for effective scintillators. The lithium and magnesium molybdates that have been studied to date are characterized by low luminescence intensity even at low temperatures [3, 4]. The luminescent properties of zinc molybdate have not been investigated to date, because very small crystals (1–2 mm^3) grown by spontaneous crystallization were used in the experiments [4]. The purpose of this study is to investigate the possibility of growing relatively large crystals (1 cm^3 and more in size) of optical quality from flux and to evaluate their suitability for use as scintillation detectors and optical elements.

CRYSTAL GROWTH

The starting charge for the crystal growth from flux was prepared by solid-phase synthesis from zinc and molybdenum oxides of special purity grade taken in the stoichiometric ratio. The differential thermal analysis of the stoichiometric mixture of ZnO and MoO_3 allowed us to determine the interaction temperature of these oxides (704 ± 5°C), the melting temperature of $ZnMoO_4$ (1003 ± 5°C), and the flux crystallization temperature (975 ± 5°C) (Fig. 1). The analysis was performed on a Q1500D derivatograph, the heating and cooling rates were 10 °C/min, and the weight was 365 g. Sodium chloride was used as a reference. The synthesis at 700°C during 6 h led to the formation of a single-phase charge, which was confirmed by X-ray phase analysis.

Crystals were grown in a commercial Crystal 3M system. The charge was placed in a platinum crucible and growth was performed in air. Strong evaporation of the most volatile component—MoO_3—from flux was observed in the experiments, which was confirmed by X-ray phase analysis. The same phenomenon was observed previously in the growth of other crystals of divalent metal molybdates [2]. According to the X-ray phase data, the growth from a flux of stoichiometric composition led to the formation of polycrystals with two phases ($ZnMoO_4$ and $Zn_3Mo_2O_9$), which is a result of molybdenum oxide evaporation and a fact indicating a significant deviation from the flux stoichiometry. To decrease the MoO_3 loss, which occurs during the long-term growth of $ZnMoO_4$ single crystals, excess MoO_3 in the range from 1.0 to 7.0 wt % above stoichiometry was introduced into the flux. The choice of the MoO_3 concentration range was based on the growth parameters (the temperature gradients in the crystallization zone, the area of free flux surface, and growth time). If the MoO_3 concentration in the flux is 1.0 wt % below or 7 wt % above stoichiometry, polycrystal growth occurs. According to the experimental data obtained, the rate of MoO_3 evaporation is 0.025 g/(h cm^2) at a growth tem-

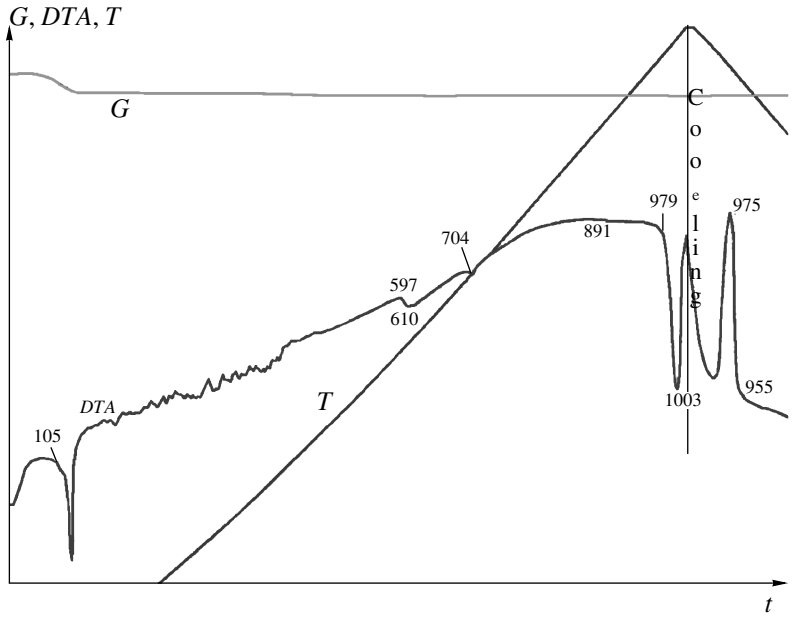

Fig. 1 Derivatogram of the $ZnMoO_4$ charge. Changes in the weight (*G*), differential thermal analysis (*DTA*) data, and temperature (*T*) with time (*t*).

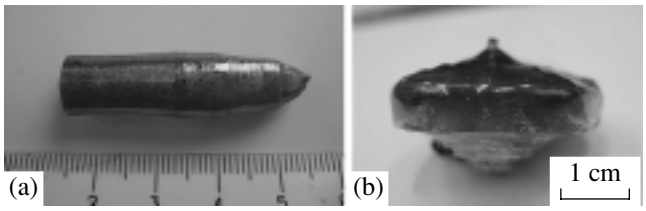

Fig. 2. Photographs of the $ZnMoO_4$ crystals grown by the (a) Czochralski and (b) Kyropoulos methods.

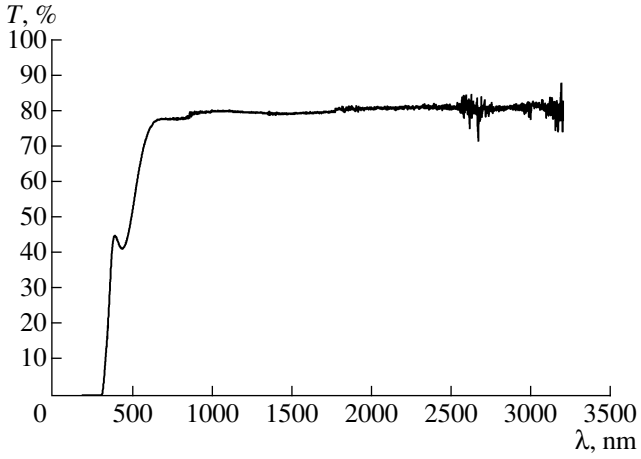

Fig. 3. Transmission spectrum of the $ZnMoO_4$ crystal in the range 200–3100 nm; the sample thickness is 2 mm.

perature of 1000°C. To decrease the MoO_3 loss, the flux overheating during charge melting into the crucible did not exceed 50°C and the temperature gradients in the crystallization zone were reduced to 60°/cm. When crystals were grown by the Czochralski method, the pulling rate was 3 mm/h and the rotation rate was 30 rpm. When the Kyropoulos method was used, the pulling rate did not exceed 1 mm/h and the rotation rate was 5 rpm. It is established that the bulk crystallization rate should not exceed 0.40 cm^3/h to obtain optically homogeneous crystals. The Czochralski-grown crystals were 40 mm in length and 15 mm in diameter. The crystals grown by the Kyropoulos method were 15 mm in length and 30 mm in diameter (Fig. 2). The crystals had an intense yellow color.

STUDY OF PHYSICOCHEMICAL CHARACTERISTICS

The optical quality of the grown crystals is characterized by the absence of bubbles, cracks, and inclusions of foreign phases. Bubbles were generally observed in the crystals grown at bulk crystallization rates exceeding 0.40 cm^3/h and excess MoO_33 concentrations in the flux above 7.0 wt %.

The transmission spectra of $ZnMoO_4$ crystals were recorded on a Shimadzu spectrophotometer in the range 200–3100 nm. They contain a broad absorption band peaking at 443 nm (Fig. 3). The nature of the intense yellow color of the crystals was not established; annealing in air at 800°C for 10 h does not eliminate it.

The X-ray analysis of the grown zinc molybdate crystals revealed that this material is crystallized into

Table 1. Unit-cell parameters and volume of $ZnMoO_4$ single crystals grown from fluxes of different composition. The data for stoichiometric $ZnMoO_4$ are taken from [5]

Unit-cell parameters	Flux composition		
	$ZnMoO_4$ + 6.5 wt % MoO_3	$ZnMoO_4$ + 5.2 wt % MoO_3	$ZnMoO_4$ stoichiometry
a, Å	6.9649(8)	6.968(1)	6.9661(6)
b, Å	8.371(1)	8.370(2)	8.3705(8)
c, Å	9.694(1)	9.694(2)	9.6850(9)
α, deg	96.723(9)	96.73(1)	96.736(7)
β, deg	106.881(7)	106.88(1)	106.871(7)
γ, deg	101.729(7)	101.72(1)	101.728(7)
V, Å^3	520.1(2)	520.2(2)	519.69

Table 2. X-ray spectral microanalysis data on the chemical composition of the crystals grown from a flux enriched with molybdenum oxide (the stoichiometric $ZnMoO_4$ composition is given for comparison)

Sample	Sample chemical composition, at %			
	Zn	Mo	O	W
$ZnMoO_4$ + 6.5 wt % MoO_3	15.60	17.19	67.20	
Crystal grown from a $ZnMoO_4$ + 6.5 wt % MoO_3 flux	16.51 ± 0.21	16.44 ± 0.25	66.74 ± 0.25	0.31 ± 0.11
Stoichiometric $ZnMoO_4$	16.67	16.67	66.67	

the triclinic system with the space group $P1^-$. The unit-cell parameters for the crystals grown from fluxes of different composition are listed in Table 1. These values indicate that the structural parameters of the samples under study practically coincide and are in good agreement with the data of [5]. The cleavage plane was experimentally determined to be (001). The single crystal density calculated from the X-ray data is 4.317 g/cm^3, while the density measured by the pyknometric method is 4.19 g/cm^3. The X-ray spectroscopic microanalysis of the sample grown from $ZnMoO_4$ + 6.5 wt % MoO_3 flux showed that the ratio of the main components and oxygen corresponds to the stoichiometric composition within the experimental error. Moreover, the $ZnMoO_4$ crystals contain a small amount of tungsten dopant, which is considered a concomitant impurity in molybdenum oxide (Table 2).

Selective chemical etching of the $ZnMoO_4$ samples in a KOH aqueous solution (30%) revealed dislocations in the form of irregularly shaped etching pits ~0.03 mm in size with a density of (1–2) × 10^4 cm^{-2} (Fig. 4a). Thermal etching of a $ZnMoO_4$ polished cut is observed upon annealing in air at 800°C (Fig. 4b).

SPECTRAL-LUMINESCENT PROPERTIES

The luminescence spectra of $ZnMoO_4$ crystals, excited by synchrotron radiation, were measured in the temperature range 10–300 K on a SUPERLUMI setup located in a channel of the DORIS III positron storage (DESY, Hamburg) [6].

The luminescence spectrum of $ZnMoO_4$ crystals is a broad band peaking at 605 nm at a temperature of 10 K and excitation energy of 6.5 eV. A broad luminescence band in the case of band-to-band excitation is generally observed in molybdates with different crystal structure (scheelites, $MgMoO_4$, Li_2MoO_4) and is attributed to the luminescence of autolocalized excitons at the MoO_4 complex. Radiation with an energy of 6.5 eV allows one to separate electrons and holes in $ZnMoO_4$ crystals because this value exceeds the energy of the first reflection peak (5.35 eV). The luminescence decay time in $ZnMoO_4$ exceeds 10^{-6} s, which is characteristic for molybdates. Analysis of the reflection and excitation luminescence spectra and the specific features of temperature luminescence quenching in the range 10–300 K is under way.

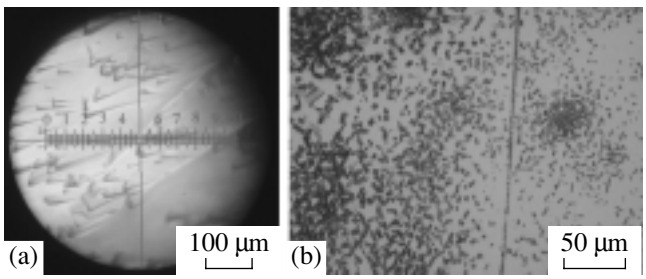

Fig. 4. Patterns of (a) chemical and (b) thermal etching of $ZnMoO_4$ plates.

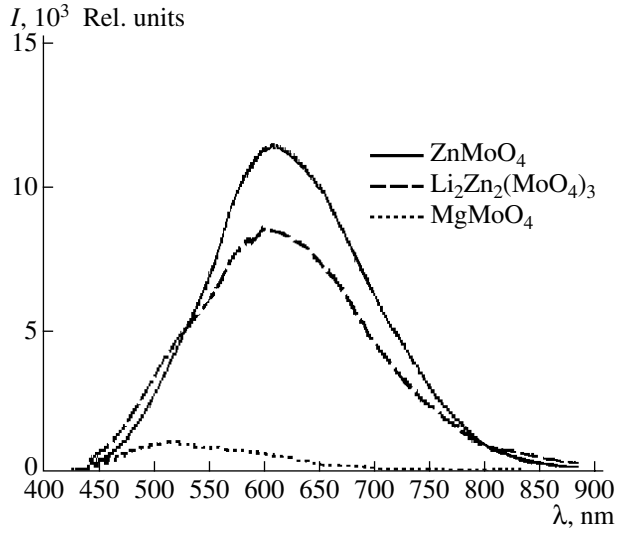

Fig. 5. Luminescence spectra of the molybdate crystals with light cations ($ZnMoO_4$, $Li_2Zn_2(MoO_4)_3$, and $MgMoO_4$) at 10 K.

The luminescence spectra of molybdate crystals of different structural types with light cations containing no radioactive isotopes ($ZnMoO_4$, $Li_2Zn_2(MoO_4)_3$, and $MgMoO_4$) are shown in Fig. 5. Examination of these spectra reveals that zinc molybdate exhibits the highest luminescence intensity at 10 K in comparison with other molybdates under study. Note that the synthesis of large $ZnMoO_4$ crystals and the possibilities of optimizing their optical quality make them promising for practical application in cryogenic scintillation detectors.

SPELL: ok

CONCLUSIONS

Large $ZnMoO_4$ single crystals were grown for the first time by crystallization from flux. The conditions for growing crystals of optical quality by the Czochralski and Kyropoulos methods have been determined. The lattice parameters of stoichiometric single crystals were measured. The spectral-luminescent characteristics of the grown crystals were studied. This material is shown to be promising for cryogenic scintillators.

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