Li_2MoO_4 Crystals Grown by Low-Thermal-Gradient Czochralski Technique

Veronika Grigorieva¹, Vladimir Shlegel¹, Tatyana Bekker^{2,3,4}, Nina Ivannikova¹, Andrea Giuliani^{5,6}, Pierre de Marcillac⁵, Stefanos Marnieros⁵, Valentina Novati⁵, Emiliano Olivieri⁵, Denys Poda^{5,7}, Claudia Nones⁶, Anastasiia Zolotarova⁶ and Fedor Danevich⁷

1. Nikolaev Institute of Inorganic Chemistry, Novosibirsk 630090, Russia

2. Sobolev Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Science, Novosibirsk 630090, Russia

3. Novosibirsk State University, Novosibirsk 630090, Russia

4. Novosibirsk State Academy of Architecture and Arts, Novosibirsk 630099, Russia

5. CSNSM, Univ. Paris-Sud, CNRS/IN2P3, Universite Paris-Saclay, Orsay 91405, France

6. CEA Saclay, DSM/IRFU, Gif-sur-Yvette Cedex 91191, France

7. Institute for Nuclear Research, Kyiv 03028, Ukraine

Abstract: For the first time Li_2MoO_4 crystals, including samples enriched with isotope molybdenum-100 (^{100}Mo), were grown by Czochralski technique at low-thermal-gradient conditions (LTG Cz), which allowed obtaining crystals of record size and quality. Dependence between growth rate, growth mechanism and crystal faceting was established. Low temperature tests of the produced Li_2MoO_4 and $\text{Li}_2^{100}\text{MoO}_4$ scintillating bolometers have demonstrated high performance of the detectors in terms of energy resolution and particle discrimination ability. Radioactive contamination of the Li_2MoO_4 and $\text{Li}_2^{100}\text{MoO}_4$ crystal scintillators produced from selected initial materials after double crystallization was tested in low background underground conditions. The achieved radiopurity level satisfies the requirements of the next generation large scale double beta decay experiments.

Key words: Low-Thermal-Gradient Czochralski technique, scintillation crystals, cryogenic bolometers, rare events search.

1. Introduction

Crystal scintillators are promising materials for detection of ionizing radiation and particles. They can be used for both practical (e.g. inspection systems, imaging) and basic research purposes. Despite large number of different compounds already approved as scintillators, there is an interest in new scintillation materials. In particular, next generation neutrinoless double beta ($0\nu2\beta$) decay experiments call for crystal scintillators containing certain elements. Search for $0\nu2\beta$ decay of atomic nuclei is considered as a unique way to study properties of neutrino and weak interactions, probe of physics beyond the Standard Model of particles [1-6].

Low temperature scintillating bolometers, based on crystal scintillators containing the element of interest, are promising detectors to search for $0\nu2\beta$ decay thanks to the high detection efficiency and energy resolution, effective particle discrimination to suppress background [7-9]. The intensive R&D in progress of molybdenum-containing scintillators is driven by the strong interest to the isotope ^{100}Mo , which is one of the most perspectives due to the high decay energy ($Q_{2\beta} = 3034.40(17)$ keV [10]), a possibility of mass scale isotopic enrichment (natural isotopic abundance $\delta = 9.744(65)\%$ [11]) and promising theoretical estimations of the decay probability (see, e.g., Ref. [6] and references therein). The CUPID Interest Group consider ^{100}Mo as one of the isotopes to realize a large scale cryogenic double

Corresponding author: Veronika Grigorieva, Ph.D. student, junior researcher, research field: crystal growth.

beta decay experiment with a sensitivity on the level of the inverted hierarchy of the neutrino mass pattern [12, 13].

An ideal crystal scintillator to be used as cryogenic scintillating bolometer in a high sensitivity ¹⁰⁰Mo double beta experiment should satisfy several requirements: as high as possible concentration of molybdenum (both in wt.%, and per crystal volume), high energy resolution and particle discrimination efficiency, as low as possible bulk and surface radioactive contamination (first of all by thorium and radium), cosmogenic radionuclides activity, and neutron-gamma cross section. The technology of scintillation elements mass production should provide maximal ready-to-use scintillation elements yield and molybdenum utilization, minimal losses of costly isotopically enriched molybdenum (the production cycle should include recovery of the enriched material) [14].

Currently there are several molybdates considered as possible low temperature scintillating bolometers for high sensitivity 2 β experiments. The AMoRE collaboration utilizes calcium molybdate (CaMoO₄) crystal scintillators [15, 16]. Despite CaMoO₄ is the most efficient among the molybdate scintillators, the compound contains 2 β active isotope ⁴⁸Ca, which can produce background in the region of interest of the AMoRE experiment (and therefore, calcium depleted in isotope ⁴⁸Ca is requested for crystals production). Therefore, collaboration searches for an alternative molybdate for the final stage of the experiment. The LUMINEU collaboration has developed large volume high performance ZnMoO₄ cryogenic scintillating bolometers [17-19], including detectors enriched with ¹⁰⁰Mo [20]. An advantage of ZnMoO₄ is the absence of heavy and radioactive elements, high concentration of molybdenum (43 wt.%) and very low level of radioactive contamination [18]. However, there are some problems in the crystal growth due to the incongruent melting of ZnMoO₄ compound [19]. Lithium molybdate (Li₂MoO₄) is characterized by

even higher concentration of molybdenum (55 wt.%), a lower estimated contribution of cosmogenic radionuclides, and comparatively easy crystal growth process. After first studies of small size Li₂MoO₄ samples grown by conventional Czochralski technique [21, 22], excellent characteristics were demonstrated at milli-Kelvin temperature on large volume Li₂MoO₄ crystal scintillators produced by the low-thermal-gradient Czochralski technique [23]. Moreover, Li₂MoO₄ based detectors can be also used for neutron counting in low background conditions [22] and search for solar axions [24].

Li₂MoO₄ belongs to the phenakite Be₂(SiO₄) structure type with a space group $R\bar{3}$ and unit cell parameters $a = 9.590 \text{ \AA}$, $c = 16.659 \text{ \AA}$ [25]. The structure consists of a three-dimensional network of corner-linked MoO₄ tetrahedra and two types of slightly distorted LiO₄ tetrahedra. The compound melts congruently at 701 °C.

Barinova et al. [26] reported the growth of Li₂MoO₄ crystal by conventional Czochralski technique. Up to three luminescence bands with the maxima at 1.98, 2.08 and 2.25 eV were detected in the emission spectra of the crystals [27]. The size of grown Li₂MoO₄ crystals was up to 100 × 25 mm, but they contained visual defects. Recent publication presents the results on growth of Li₂MoO₄ crystals from aqueous solution activated by low-frequency vibrations [28].

A low thermal gradient version of the Czochralski technique (LTG Cz) has been successfully used for growing scintillating crystals [29-31]. The method allows one to grow crystals of superior optical quality because of the extremely low temperature gradient of 0.05-1.0 K/cm in the melt in comparison to the conventional Czochralski technique with the temperature gradient of up to 100 K/cm. Thus, LTG Cz was successfully adopted for growing high quality bismuth germinate Bi₄Ge₃O₁₂ (BGO) crystals with the weight of up to 75 kg [29], CdWO₄ and ZnWO₄ crystals with record-breaking optical transition with

the weight of up to 10 kg and 8 kg, respectively [30]. Application of LTG Cz allowed to obtain unique isotopically enriched crystals ¹⁰⁶CdWO₄ [31, 32], ¹¹⁶CdWO₄ [31, 33] and Zn¹⁰⁰MoO₄ [20, 31].

The purpose of the present work was development of large-sized Li₂MoO₄ single crystals of optical quality, suitable for application in low background cryogenic scintillating bolometers, by low thermal gradient Czochralski technique. Growth mechanisms and their influence on faceting and crystal quality have been investigated.

2. Experimental Procedures

Deeply purified molybdenum oxide (MoO₃) [17] and commercial high purity lithium carbonate (Li₂CO₃, 99.99%) were used for solid-state synthesis of Li₂MoO₄ according to the reaction: MoO₃ + Li₂CO₃ = Li₂MoO₄ + CO₂ ↑. The compound was kept for 5-10 h at a temperature of 450 °C.

Li₂MoO₄ crystals were grown in air atmosphere from the synthesized powder by LTG Cz in the platinum crucible of 70 × 130 mm. The platinum crucible was placed into a three-zone resistance furnace with low thermal conductivity bottom and top thermal insulation (Fig. 1). The crucible was covered with a platinum lid furnished with a pipe socket through which the pull rod with the crystal holder was introduced into the inner space. During the entire process the grown crystal stayed inside the crucible. The heater and control system allows one to keep the axial and radial thermal gradients within 0.05-1.0 K/cm. Visual control is impossible in this growth system which stipulates the use of weighing control at all stages of the growing process including the seeding.

In different growth processes growth rates varied from 0.3 mm/h to 2.5 mm/h. Rotation velocity was 3 rounds per minute, duration of the growth process was from 10 to 12 days. Li₂¹⁰⁰MoO₄ crystals enriched in the isotope ¹⁰⁰Mo were grown.

The morphology of crystallization front was studied

visually and by using diffractometer DRON-3, Carl Zeiss Axioskop 40 microscope in polarized reflected light, MIRA3 TESCAN microscope in reverse electrons. Differential thermal analysis of the grown crystals was carried out with the help of derivatograph NETZSCH STA 449F1 STA449F1A-0161-M.

Quantitative chemical analysis of Li₂MoO₄ crystals was carried out at Analytic Laboratory at the NIIC SB RAS (Novosibirsk, Russia). Bolometric tests were carried out at the Centre de Sciences Nucléaires et de Sciences de la Matière (Orsay, France).

3. Results and Discussions

Growth mechanisms and crystal morphology. The quality of crystals grown at different growth rates was studied and compared.

At the growth rate of 1 mm/hour and higher both normal and tangential growth mechanisms coexisted. In this case crystallization front consisted of numerous small faceted and rounded areas. The quality of the crystals was relatively low due to the appearance and

Fig. 1 Scheme of the furnace for low thermal gradient version of the Czochralski technique.

increasing concentration of visually distinguishable inclusions during the growth run. Thus, the lower part of the crystal became cloudy (Fig. 2a). This may be explained by the capture of inclusions and formation of defects at the boundaries between the faceted and rounded areas on the front. The size of facets could reach 0.3-0.4 cm². Facets belonging to rhombohedron {101}, hexagonal prism {110} and pinacoid {001} simple forms were present. Reflection angles 2θ determined for the facets with the use of diffractometer DRON-3 corresponded to the X-ray data [25]. The steps and growth pyramids formed a complicated relief on the crystallization front with large number of benches and pits (Figs. 2b and 2c).

At the growth rate below 1 mm/hour normal growth mechanism was realized. The crystallization front was entirely rounded and the quality of the crystals was much higher (Fig. 3).

During the study of morphogenesis of crystallization front the value of Jackson's criterion for Li₂MoO₄ was calculated based on measured values of heat of fusion and melting temperature (34 kJ/mol and 974 K, respectively). Calculated value of Jackson's criterion was 4.2.

Previously LTG Cz was used for growing crystals with a high value of Jackson's criterion, e.g. Bi₄Ge₃O₁₂ (16), ZnWO₄ (9.1), CdWO₄ (9.6). As these crystals tend to be front-faceted, crystallization was carried out at a high speed in order to exclude the formation of rounded parts growing according to normal mechanism and to produce a fully faceted front [34]. Thus, crystallization front of Bi₄Ge₃O₁₂

crystals, grown at a rate of 3-12 mm/h, was formed by three large facets belonging to {112} simple form; whereas crystallization front of CdWO₄ grown at a rate of 3-12 mm/h—by one pinacoid facet {010}. This scheme cannot be realized with lithium molybdate due to the presence of the different facet families with similar values of reticular density which leads to a simultaneous growth of divergent facets. The relatively low value of Jackson criteria for Li₂MoO₃ evidences strengthening of atomic roughness and tendency to the normal growth mechanism. To grow Li₂MoO₄ crystals we stepped away from tangential growth mechanism and fully faceted front to normal growth mechanism and fully rounded front. In this way, Li₂MoO₄ single crystals of optical quality without any visual defects were obtained.

Thus, the preferable conditions for Li₂MoO₄ growth are those which lead to the formation of smooth, rounded crystallization front: low growth rate (1 mm/hour or lower), rotation velocity of 3 rounds per minute with slight changes of the temperature distribution in the zones to maintain equally convex front during the entire growth process.

Crystal size. In order to optimize the process of bolometer production, the length of grown Li₂MoO₄ crystals was increased so that two scintillation elements could be cut out from one crystal boule. Cylinder part of such crystals should be 96-100 mm. The problem we encountered while prolonging the growth process was the tendency of crystallization front to extend into the melt. To avoid this effect, the bottom and top heat zones were additionally heated

Fig. 2 Li₂MoO₄ crystal grown at a rate of 1 mm/hour (a) and typical view of crystallization front (b); SEM image of rhombohedron surface in reverse electrons (MIRA3 TESCAN) (c).

Fig. 3 Li₂MoO₄ crystal grown at a rate of 0.5 mm/hour.

Fig. 4 Li₂MoO₄ crystal of optical quality grown at a rate of 0.5 mm/hour by low-thermal-gradient Czochralski technique.

during the second part of the growth process. The obtained Li₂MoO₄ crystals were of optical quality up to 100 mm length and 55 mm in diameter (Fig. 4). Crystal yield was 80-85 wt.%. The losses of isotopically enriched molybdenum during the crystal growth and cutting out of the scintillation elements were less than 1-2%.

Crystal purity. Potassium is a typical contaminant of Li₂MoO₄ due to the chemical affinity between lithium and potassium. The potassium concentration in grown crystals was estimated to be on the level of $4 \cdot 10^{-4}$ wt.% which calls for additional purification of lithium carbonate used for lithium molybdate synthesis.

Distribution coefficient of potassium in Li₂MoO₄ was found to be below 1 which gave the opportunity to reduce potassium concentration in crystals by recrystallization. For this purpose, two Li₂MoO₄

crystals were grown from the original charge consisting of stoichiometric mix of Li₂CO₃ and MoO₃ powders. The upper parts of the crystals (expected to be less contaminated by potassium) were utilized to produce the final Li₂MoO₄ crystal. After that their upper and, correspondingly, less contaminated parts were taken and melted in platinum crucible and next generation Li₂MoO₄ crystal was grown from that melt. No potassium contamination was observed in the recrystallized crystal on the level of detection limit $1 \cdot 10^{-5}$ wt.%.

Characterization of Li₂MoO₄ based cryogenic scintillating bolometers. Several samples of Li₂MoO₄ crystal scintillators including the ones produced from enriched with ¹⁰⁰Mo were tested as cryogenic scintillating bolometers at milli-Kelvin temperature [35]. The detectors showed high performance in terms

of energy resolution (full width at the half of maximum, FWHM) 4 keV – 7 keV for gamma quanta of ²⁰⁸Tl with energy 2,615 keV, and excellent particle discrimination ability ($DP = 8 - 19$) between beta-particles (gamma-quanta) and alpha-particles above energy 2.5 MeV. The last characteristic can be expressed through average values (widths) of the alpha or beta/gamma distributions $\mu(\sigma)$ as following:

$$DP = (\mu_{\gamma(\beta)} - \mu_{\alpha}) / \sqrt{\sigma_{\gamma(\beta)}^2 + \sigma_{\alpha}^2}$$

The achieved energy resolution and particle discrimination are comparable to the characteristic of CdWO₄ scintillating bolometers [36] and substantially higher than that of ZnSe detectors [37].

Radioactive contamination of the Li₂MoO₄ and Li₂¹⁰⁰MoO₄ crystal scintillators was investigated in the Gran Sasso (Italy) and Modane (France) underground laboratories [35]. The tests have shown very high level of the crystals radiopurity. In particular, only limits were set on activity of the most harmful for the 0ν2β experiments radionuclides ²²⁶Ra and ²²⁸Th on the level of < (0.007 – 0.037) mBq/kg and < (0.006 – 0.021) mBq/kg, respectively. The activity of ⁴⁰K was not observed on the level of < (2 – 12) mBq/kg. However, a higher concentration of ⁴⁰K (62 mBq/kg) and ²²⁶Ra (0.13 mBq/kg) was detected in the Li₂MoO₄ samples produced from the Li₂CO₃ powder with higher activity of the radionuclides (measured by low background HPGe gamma spectrometry). Therefore, the issue of potassium and radium contamination should be addressed in the further development of Li₂MoO₄ crystals. An R&D is in progress to develop methods of lithium carbonate purification and screening aiming to decrease potassium and radium contamination. A clear indication of potassium and radium segregation was observed by comparison of the crystal samples produced by single and double crystallization. The radiopurity level of the crystals produced from the selected lithium carbonate by double crystallization is high enough to realize a pilot 0ν2β experiment in preparation with ~7 kg of

isotopically enriched molybdenum.

4. Conclusions

Li₂MoO₄ growth mechanisms, their dependence from growth rate and influence on crystal faceting were studied. At the growth rate 1 mm/hour and higher mixed growth mechanism is realized, while below 1 mm/hour normal growth mechanism is realized. High quality Li₂MoO₄ crystals were obtained in the processes in which normal growth mechanism was implemented. Large-size Ø55×100 mm² Li₂MoO₄ and enriched Li₂¹⁰⁰MoO₄ crystals of optical quality were grown. Low temperature tests of Li₂MoO₄ and Li₂¹⁰⁰MoO₄ crystals have demonstrated a high performance of the scintillating bolometers based on the produced scintillation elements in terms of energy resolution and particle discrimination ability. The radiopurity level of the produced Li₂MoO₄ and Li₂¹⁰⁰MoO₄ scintillation elements is very high on the level of < (0.007 – 0.037) mBq/kg and < (0.006 – 0.021) mBq/kg of ²²⁶Ra and ²²⁸Th, respectively. Altogether the tests have demonstrated that Li₂MoO₄ is a promising material for the next generation large scale double beta-decay experiments.

References

- [1] Cremonesi, O., and Pavan, M. 2014. "Challenges in Double Beta Decay." *Adv. High En. Phys.* Article ID 951432, 40 pages.
- [2] Päs, H., and Rodejohann, W. 2015. "Neutrinoless Double Beta Decay." *New J. Phys.* 17. Article ID 115010, 15 pages.
- [3] Bilenky, S. M., and Giunti, C. 2015. "Neutrinoless Double-Beta Decay: A Probe of Physics beyond the Standard Model." *Int. J. Mod. Phys. A* 30. Article ID 1530001, 55 pages.
- [4] Sarazin, X. 2015. "Review of Double Beta Experiments." *J. Phys. Conf. Ser.* 593. Article ID 012006.
- [5] Dell'Oro, S., Marcocci, S., Vie, M., and Vissani, F. 2016. "Neutrinoless Double Beta Decay: 2015 Review." *Adv. High En. Phys.* Article ID 2162659, 37 pages.
- [6] Vergados, J. D., Ejiri, H., and Simkovic, F. 2016. "Neutrinoless Double Beta Decay and Neutrino Mass." *Int. J. Mod. Phys. E* 25. Article ID 1630007, 59 pages.
- [7] Pirro, S. J., Beeman W., Capelli, S., Pavan, M., Previtali, E., and Gorla, P. 2006. "Scintillating Double-Beta-Decay Bolometers." *Phys. At. Nucl.* 69 (12): 2109-16.

- [8] Giuliani, A. 2012. "Neutrino Physics with Low-Temperature Detectors." *J. Low Temp. Phys.* 167: 991-1003.
- [9] Artusa, D. R., Avignone, F. T., Azzolini, O. et al. 2014. "Exploring the Neutrinoless Double Beta Decay in the Inverted Neutrino Hierarchy with Bolometric Detectors." *Eur. Phys. J. C* 74: 3096.
- [10] Rahaman, S. et al. 2008. "Q Values of the ⁷⁶Ge and ¹⁰⁰Modouble-Beta Decays." *Phys. Lett. B* 622: 111-6.
- [11] Meija, J., Coplen, T. B., Berglund, M., Brand, W. A., Bièvre, P., Gröning, M., Holden, N. E., Irrgeher, J., Loss, R. D., Walczyk, T., and Prohaska T. 2016. "Isotopic Compositions of the Elements 2013 IUPAC Technical Report." *Pure Appl. Chem.* 88 (3): 293-306.
- [12] Wang, G. et al. 2017. "CUPID: CUORE (Cryogenic Underground Observatory for Rare Events) Upgrade with Particle IDentification." arXiv:1504.03599v1 [physics.ins-det].
- [13] Wang, G. et al. 2017 "R&D towards CUPID (CUORE Upgrade with Particle IDentification)." arXiv:1504.03612v1 [physics.ins-det].
- [14] Danevich, F. A. 2012. "Development of crystal Scintillators from Enriched Isotopes for Double β Decay Experiments." *IEEE Trans. Nucl. Sci.* 59 (5): 2207-13.
- [15] Kim, G. B. et al. 2015. "A CaMoO₄ Crystal Low Temperature Detector for the AMoRE Neu-trinoless Double Beta Decay Search." *Adv. High En. Phys.* Article ID 817530, 7 pages.
- [16] Alenkov, V. et al. 2017. "Technical Design Report for the AMoRE $0\nu\beta\beta$ Decay Search Experiment." arXiv:1512.05957v1 [physics.ins-det].
- [17] Bergé, L. et al. 2014. "Purification of Molybdenum, Growth and Characterization of Medium Volume ZnMoO₄ Crystals for the LUMINEU Program." *JINST.* 9, P06004.
- [18] Armengaud, E. et al. 2015. "Development and Underground Test of Radiopure ZnMoO₄ Scintillating Bolometers for the LUMINEU $0\nu2\beta$ Project." *JINST.* 10, P05007.
- [19] Chernyak, D. M. et al. 2015. "Effect of Tungsten Doping on ZnMoO₄ Scintillating Bolometer Performance." *Opt. Mater.* 49: 67-74.
- [20] Barabash, A. S. et al. 2014. "Enriched Zn¹⁰⁰MoO₄ Scintillating Bolometers to Search for $0\nu2\beta$ Decay of ¹⁰⁰Mo with the LUMINEU Experiment." *Eur. Phys. J. C* 74: 3133, 7 pages.
- [21] Barinova, O. P. et al. 2009. "Intrinsic Radiopurity of a Li₂MoO₄ Crystal." *Nucl. Instr. Meth. Phys. Res. A* 607: 573-5.
- [22] Cardani, L. et al. 2013. "Development of a Li₂MoO₄ Scintillating Bolometer for Low Background Physics." *JINST.* 8, P10002.
- [23] Bekker, T. B. et al. 2016. "Aboveground Test of an Advanced Li₂MoO₄ Scintillating Bolometer to Search for Neutrinoless Double Beta Decay of Mo-100." *Astropart. Phys.* 72: 38-45.
- [24] Belli, P. et al. 2012. "Search for 7Li Solar Axions Using Resonant Absorption in LiF Crystal: Final Results." *Phys. Lett. B* 711: 41-5.
- [25] Kolitsch, U. 2001. "The Crystal Structures of Phenacite-Type Li₂(MoO₄), and Scheelite-Type LiY(MoO₄)₂ and LiNd(MoO₄)₂." *Z. Kristallogr.* 216: 449-54.
- [26] Barinova, O. P., Danevich, F. A., Degoda, V. Ya., Kirsanova, S. V., Kudovenko, V. M., Pirro, S., and Tretyak, V. I. 2010. "First Test of Li₂MoO₄ Crystal as a Cryogenic Scintillating Bolometer." *Nucl. Instrum. Methods Phys. Res. A* 613 (1): 54-7.
- [27] Spassky, D. A., Nagirnyi, V., Savon, A. E., Kamenskikh, I. A., Barinova, O. P., Kirsanova, S. V., Grigorieva, V. D., Ivannikova, N. V., Shlegel, V. N., Aleksanyan, E., Yelisseyev, A. P., and Belsky, A. 2015. "Low Temperature Luminescence and Charge Carrier Trapping in a Cryogenic Scintillator Li₂MoO₄." *J. Lumin.* 166: 195-202.
- [28] Barinova, O., Sadovskiy, A., Ermochenkova, I., Kirsanova, S., Sukhanova, E., Kostikov, V., Belov, S., Mozhevitina, E., Khomyakov, A., Kuchuk, Z., Zharikov, E., and Avetissov, I. 2017. "Li₂MoO₄ Crystal Growth from Solution Activated by Low-Frequency Vibrations." *J. Cryst. Growth* 457: 151-7.
- [29] Pavlyuk, A. A., Vasiliev, Ya. V., Kharchenko, L. Yu., and Kuznetsov F. A. 1992. "Low Thermal Gradient Technique and Method for Large Oxide Crystals Growth from Melt and Flux." *Proc. of APSAM-92 (Asia Pacific Society for Advanced Materials)*, 164-71.
- [30] Borovlev, Yu. A., Ivannikova, N. V., Shlegel, V. N., Vasiliev, Ya. V., and Gusev V. A. 2001. "Progress in Growth of Large Sized BGO Crystals by the Low Thermal Gradient Czochralski Technique." *J. Cryst. Growth* 229 (1-4): 305-11.
- [31] Galashov, E. N., Denisova, T. M., Ivanov, I. M., Makarov, E. P., Mamontov, V. N., Shlegel, V. N., Stenin, Yu. G., Vasiliev, Ya. V., and Zhdankov, V. N. 2010. "Growing of ¹⁰⁶CdWO₄, ZnWO₄, and ZnMoO₄ Scintillation Crystals for Rare Events Search by Low Thermal Gradient Czochralski Technique." *Funct. Mater.* 17: 504-8.
- [32] Belli, P. et al. 2010. "Development of Enriched ¹⁰⁶CdWO₄ Crystal Scintillators to Search for Double β Decay Processes in ¹⁰⁶Cd." *Nuclear Instruments and Methods in Physics Research A* 615: 301-6.
- [33] Barabash, A. S. et al. 2011. "Low Background Detector with Enriched ¹¹⁶CdWO₄ Crystal Scintillators to Search for Double β Decay of ¹¹⁶Cd." *JINST.* 6, P08011.

- [34] Ivannikova, N. V., Shlegel, V. N., and Vasiliev, Ya. V. 2014. "Optimization of the Crystallization Rate in Growing Bi₄Ge₃O₁₂ Crystals by the LTG CZ Technique." *Crystallogr. Rep.* 59 (4): 612-5.
- [35] Armengaud, E. et al. 2017. "Development of ¹⁰⁰Mo-based Scintillating Bolometers for High-Sensitivity 0ν2β Decay Search." *Eur. Phys. J. C* (submitted).
- [36] Arnaboldi, C. et al. 2010. "CdWO₄ Scintillating Bolometer for Double Beta Decay: Light and Heat Anticorrelation, Light Yield and Quenching Factors." *Astropart. Phys.* 34: 143-50.
- [37] Beeman, J. W. et al. 2013. "Performances of a Large Mass ZnSe Bolometer to Search for Rare Events." *JINST.* 8, P05021.