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Growth and characterization of isotopically enriched $^{40}Ca^{100}MoO_4$ single crystals for rare event search experiments

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Calcium molybdate is considered as a very promising scintillator material for experimental studies of rare processes. This paper reports on the production and characterization of a $^{40}Ca^{100}MoO_4$ scintillator. Using the Czochralski technique, a crystal of high optical quality with total mass 0.55 kg, 42 mm diameter (minimum) and 53 mm length of the cylindrical section was produced from isotopically enriched raw materials, containing 96.1% of ^{100}Mo and 99.964% of ^{40}Ca. To satisfy the requirement of low intrinsic radioactivity the purity of the materials was monitored at different stages of the production process and it is shown that the concentration of ^{238}U and ^{232}Th in the final crystal does not exceed 0.05 ppb. The scintillation properties of $^{40}Ca^{100}MoO_4$ were measured over the 8 – 300 K temperature range and it is found that the light yield of the $^{40}Ca^{100}MoO_4$ crystal is very similar to that of the $CaMoO_4$ reference scintillator.

1 Introduction

One of the major achievements in particle physics during the last decade was the discovery of neutrino oscillation, evidencing that neutrinos have non-zero mass [1]. Finding the actual value and establishing whether neutrinos are Dirac or Majorana particles are the next great challenges for experimental particle physics. This has caused an increase in research activity on neutrinoless double beta decay (0νDBD) of some even-even nuclei. Experimental observation of 0νDBD would prove the Majorana character of neutrinos and give a handle on absolute neutrino mass values.

The scintillation method of detection offers very competitive and efficient ways of achieving high sensitivity in 0νDBD experiments. An example is the study of 0νDBD in a $^{116}CdWO_4$ scintillating crystal [2] that gave a very competitive limit for the electron neutrino mass (<1.7 eV) when compared with results from other experiments (see e.g. [3] and reference herein). Modern experiments aiming much higher sensitivity use cryogenic phonon-scintillation detectors that offer both high energy resolution and event discrimination capability [4-6]. Therefore there is currently worldwide interest in pursuing this technique.

^{100}Mo is considered as a very promising double beta decay nucleus due to its high transition energy (Q=3034 keV) and considerable natural abundance (9.63%). Within the range of inorganic Mo-containing materials, $CaMoO_4$ shows relatively bright scintillation at room temperature [7]. Other molybdates of the $AMoO_4$ family either exhibit practical scintillation only upon cooling ($PbMoO_4$, $SrMoO_4$, $CdMoO_4$) [7-10] or

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remain fairly dull ($MgMoO_4$, $ZnMoO_4$) [7,11,12]. This motivated the development of calcium molybdate scintillators for the 0νDBD experiment that has been initiated by some of the authors a few years ago. The work demonstrated the feasibility of production of large $CaMoO_4$ crystals with good optical and scintillation characteristics as well as low intrinsic radioactivity [13,14].

The objective of achieving better sensitivity in the experimental search for rare processes calls for an increase of the total number of nuclei subject to such process. This in turns entails the use of specific and potentially expensive isotopes. Large natural abundance of ^{100}Mo permits the production of up to 95% enriched material for reasonable price by centrifugation. Conversely it is acknowledged that the two-neutrino double beta decay of ^{48}Ca, albeit very rare, will impose unavoidable background, limiting the sensitivity of the experiment, searching for 0νDBD in enriched $Ca^{100}MoO_4$ [14]. ^{48}Ca is present in natural Ca with an abundance of 0.187%. The only possibility to eliminate this background it the use of Ca depleted of ^{48}Ca to a level of $\leq 10^{-5}$. These considerations motivated the development of calcium molybdate scintillators from isotopically enriched material.

The aim of this work was the production of a large-volume $^{40}Ca^{100}MoO_4$ scintillation crystal (diameter 40–50 mm, height 40–55 mm) with high light yield (more than 5,000 photons/MeV at room temperature) and low intrinsic radioactivity. In this paper we describe the progress achieved in the growth of these crystals and report the results of scintillation characterization of the sample over a wide temperature range (8 – 300 K).

2 Synthesis of $^{40}Ca^{100}MoO_4$ raw material

The isotope ^{100}Mo was produced by the JSC Production Association Electrochemical plant, (Zelenogorsk, Krasnoyarsk region, Russia). The total amount of ^{100}Mo enriched to 96.1% supplied in the form of $^{100}MoO_3$ oxide was 2.5 kg. The enriched material is very pure with respect to problematic radionuclides; the results of ICP-MS measurements show that concentrations of U and Th in the oxide do not exceed 0.07 and 0.1 ppb, respectively. 3.125 kg of calcium carbonate enriched in ^{40}Ca (99.964±0.005%) and depleted of the ^{48}Ca isotope by more than two order of magnitudes ($\leq 10^{-5}$) was produced by FSUE Electrochimprobor (Lesnoy, Sverdlovsk region, Russia). The fraction of ^{238}U and ^{232}Th in the powder measured by ICP-MS is below 0.2 and 0.8 ppb, respectively. However it was found that the powder contains substantial amounts of Sr (25 ppm) and Ba (26 ppm), indicating that there might be a noticeable presence of Ra impurity. This assumption was later confirmed through γ-spectroscopy analysis of the initial $^{40}CaCO_3$ powder; the activity due to Ra and progenies was found to be at the level of a few hundreds of mBq/kg. Therefore both $^{40}CaCO_3$ and $^{100}MoO_3$ were subjected to additional purification at the JSC NeoChem Company (Moscow, Russia) who are specialists in the production of high-purity raw materials for scintillation crystals.

Two commonly used techniques for the synthesis of the $CaMoO_4$ raw material (charge) are solid-phase synthesis and co-precipitation reaction. The co-precipitation reaction method offers essential advantages: the possibility of additional purification of the starting compounds and better control of stochiometry of the final product. Co-precipitation involves a liquid phase process and thus requires soluble ingredients. Insoluble oxides and carbonates are converted into acid-soluble salts (usually nitrates and ammoniates) and subjected to multiple filtering. This stage is very important when high purity of the final product is required. It was found that the use of calcium formate $Ca(HCOO)_2$ is better due to the much higher generic purity of this compound when compared with $Ca(NO_3)_2$. The synthesis reaction proceeds according to the following equation:

$$(NH_4)_6Mo_7O_{24} + 7\ Ca(HCOO)_2 + 8\ NH_4OH \rightarrow 7\ CaMoO_4 + 14\ NH_4\ (HCOO) + 4\ H_2O.$$

The analysis of the obtained powder $^{40}Ca^{100}MoO_4$ raw material showed significant improvement regarding purity (see table 1). The concentration of Sr and Ba decreased substantially while uranium and thorium are below the detection limit of 0.3 and 0.9 ppb, respectively.

3 Sample analysis

Samples of ^{40}Ca and ^{100}Mo enriched material, $^{40}Ca^{100}MoO_4$ raw material, and $^{40}Ca^{100}MoO_4$ single crystals where analyzed with inductively coupled plasma mass spectrometry ICP-MS (X-7, Thermo Elemental, USA) and inductively coupled plasma atomic emission spectroscopy ICP-AES (ICAP-61, Thermo Jarrell Ash, USA). To improve the sensitivity of ICP-MS to the impurities of ^{238}U and ^{232}Th in molybdenum compounds a new analytical technique was developed [15]. The technique includes decomposition of the sample in an acid solution and selective extraction of the molybdenum matrix from the solution using an organic extracting agent. A process like this increases the quantity of impurity ions in the sample , which in turn improves the sensitivity of the analysis. This allowed achieving a detection limit of 0.01 ppb both for ^{238}U and ^{232}Th when analysing samples of the single crystals produced.

Table 1 Content of controlled impurities in the enriched materials and crystals measured by ICP-MS and ICP-AES.

Element	$^{40}CaCO_3$	$^{100}MoO_3$	$^{40}Ca^{100}MoO_4$ raw material	$^{40}Ca^{100}MoO_4$ raw single crystal	$^{40}Ca^{100}MoO_4$ single crystal
	Concentration / Detection limit, ppm	Concentration / Detection limit, ppm	Concentration / Detection limit, ppm	Concentration / Detection limit, ppm	Concentration / Detection limit, ppm
Sr	24–27/0.06	<0.3/0.3	3.0/0.2	2.0–2.2/0.1	1.5–2.9/0.1
Ba	24–28/0.05	<0.9/0.3	8.4/0.6	<0.3/0.3	<0.3/0.3
^{238}U	<0.0002/0.0002	<0.0004/0.0004	<0.0003/0.0003	<0.00005/0.00005	<0.00001/0.00001
^{232}Th	<0.0008/0.0008	<0.001/0.001	<0.0009/0.0009	<0.00005/0.00005	<0.00001/0.00001

4 Crystal growth

The Czochralski technique is a universal method commonly used in the production of high-quality tungstates and molybdates [10,11,13,14]. The melting temperature of $CaMoO_4$ (T=1445 °C) permits pulling the crystals in air atmosphere using a crucible made of platinum (T_{melt} = 1769 °C) or in an oxygen-free atmosphere using an iridium crucible (T_{melt} = 2454 °C). Both approaches were investigated during preliminary tests. After analysis of the results obtained it was decided to pull the crystal in air from a platinum crucible with diameter 90 mm and height 70 mm. These experiments also allowed optimization of the direction of the growth relative to the crystallographic axis of the crystal. X-ray diffraction measurements of the synthetic crystal proves that it is of the scheelite type with tetragonal symmetry (space group of $I4_1/a$). The structure of the crystal consists of complex layers perpendicular to the c-axis. Each layer has a two-dimensional CsCl arrangement of a Ca cation and an anion complex (MoO_4) surrounded by eight ions of opposite sign (see fig. 1 in [16]). There are at least two optimal directions for seeding and further growth of the $CaMoO_4$ crystal. Crystals of similar quality can be pulled in directions close to the *a* or the *c* axis. Nonetheless, the crystals grown along the *a*-axis exhibit an elliptical cross section with a diameter ratio of ~1.3. Tilting the *a*-axis by ~25 degrees allowed improving this ratio to 1.15.

The finalized technology of $^{40}Ca^{100}MoO_4$ single crystal production can be presented as a sequence of the following steps. The charge of $^{40}Ca^{100}MoO_4$ in powder form is loaded into a crucible and heated to the melting temperature. Then the seeding starts at a rotation speed of 5-12 min^{-1} and the raw crystal is produced at high pulling speed (3-5 mm/h). The raw crystals produced in such way are then loaded into the crucible, melted and the final crystal is pulled at smaller speed (2-3 mm/h). After completion of the growth process the crystal is heat treated in the setup for 12 h. The $^{40}Ca^{100}MoO_4$ crystal ingot produced in this way has a total mass of 0.55 kg, diameters 49 mm (maximum) and 42 mm (minimum), and length of the cylindrical part 53 mm, with overall length 103 mm. The as-grown crystal has strong blue coloration due to oxygen depletion and reduction of Mo^{6+} ions. It has been shown that this coloration can be removed by extended annealing in an oxygen atmosphere [13,17]. This procedure was applied and finally a colourless $^{40}Ca^{100}MoO_4$ crystal was obtained (Fig. 1).

5 Characterization of $^{40}Ca^{100}MoO_4$ crystal

The transmittance spectrum of the 10x10x10 mm^3 sample of $^{40}Ca^{100}MoO_4$ crystal is displayed in figure 2. The absorption edge of the crystals is at 330 nm. At 540 nm (maximum of the luminescence band of calcium molybdate [7]) the transmittance reaches 78%. The spectrum shows no sign of absorption bands over a wide spectral region, evidencing good optical quality of the produced single-crystal. The studies of scintillation characteristics of the isotopically enriched $^{40}Ca^{100}MoO_4$ crystal were carried out using the multi-photon counting (MPC) technique [18]. The technique allows measuring the light output and decay curves of scintillation crystals over a wide temperature range. It has been extensively used for characterization of tungstates and molybdates proving to be a robust and reliable experimental method [7]. For the purpose of consistency we used the sample geometry (5×5×1 mm^3), setup (^{241}Am source, 9124A Electron Tube photomultiplier) and analysis procedure very similar to those described in ref. [17] where temperature dependences of scintillation properties of a $CaMoO_4$ crystal scintillator have been presented for the first time. Furthermore, to perform direct comparison, we carried out measurements of two samples: i) the reference sample of $CaMoO_4$ and ii) the sample made from the isotopically enriched $^{40}Ca^{100}MoO_4$ crystal produced in this work.

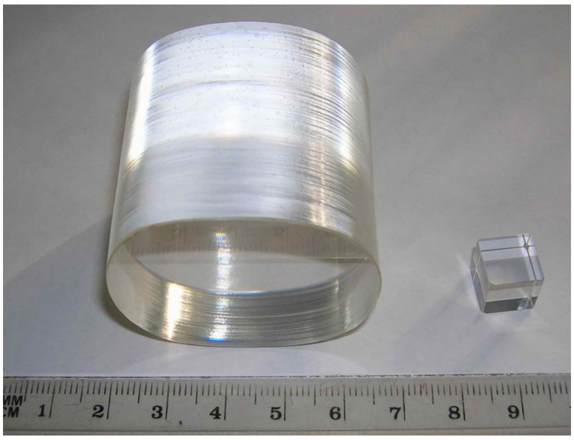

Fig. 1 Final $^{40}Ca^{100}MoO_4$ single crystal after annealing in oxygen and cubic sample cut from the same crystal.

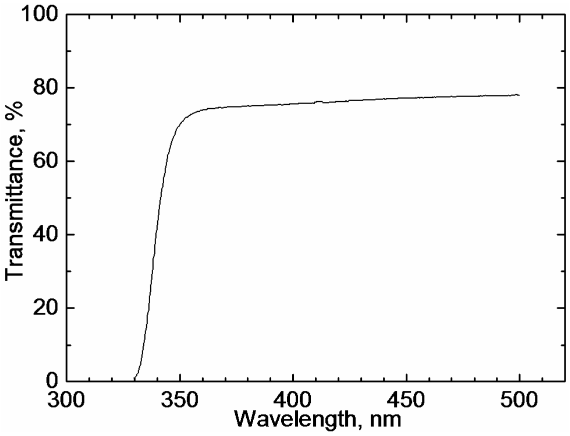

Fig. 2 Transmittance spectrum of $^{40}Ca^{100}MoO_4$ single crystals measured for the 10 mm cubic sample shown in figure 1.

The variation of the principal (long) scintillation decay time constant of $^{40}Ca^{100}MoO_4$ as function of temperature is shown in figure 3. This dependence, as well as numerical values (see table 2), reproduces those observed for the reference $CaMoO_4$ crystal [17]. The increase of the decay time constant with cooling from room temperature is largely governed by the processes of thermal quenching. However at very low temperatures (<20 K) the main reason of this increase is the capture of electrons at the metastable level of the emitting centre.

Table 2 Scintillation characteristics of $^{40}Ca^{100}MoO_4$ crystal at T=295 and 8 K.

Parameter	T=295 K	T=8 K
Decay constant, µs	16.5±0.3	345±25
Light output (relative to reference $CaMoO_4$), %	105±39	106±32

Figure 4 shows the temperature dependence of the light output for two samples of calcium molybdate crystals. The result indicates that for the isotopically enriched $^{40}Ca^{100}MoO_4$ crystal the variation of the light output with temperature follows the very same pattern as displayed by the reference $CaMoO_4$ crystal. It can also be seen that throughout the whole examined temperature range the light output of $^{40}Ca^{100}MoO_4$ is very similar to that of the reference calcium molybdate crystal taking into account the error of the measurements.

6 Summary

Isotopically enriched materials are important for particle physics experiments searching for rare events. Motivated by this we initiated a program aiming at the development of a production technology for

^{40}Ca^{100}MoO$_4$ crystals with ultra-low intrinsic radioactive background and high scintillation light yield. The level of enrichment of ^{100}Mo and ^{40}Ca used for crystal growth is 96.1% and 99.964% respectively. The starting materials were subjected to extensive purification that allowed reducing the concentration of natural radioactive isotopes of U and Th to below 0.05 ppb. It should be mentioned that the study of intrinsic radioactivity of this crystal were carried out when this paper was under reviewing and they will be published soon.

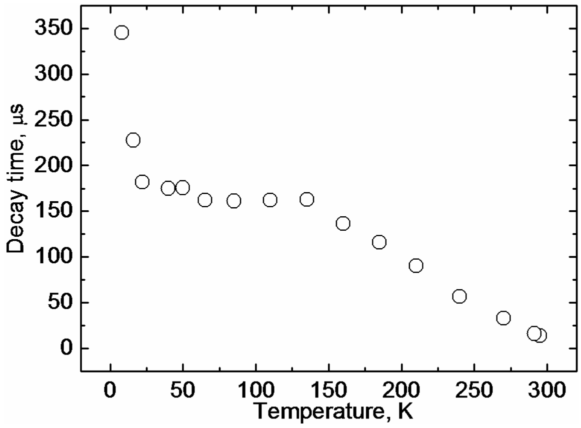

Fig. 3 Temperature dependence of long scintillation decay constant of ^{40}Ca^{100}MoO$_4$ crystal. Excitation with 5.5 MeV α-particles (^{241}Am source).

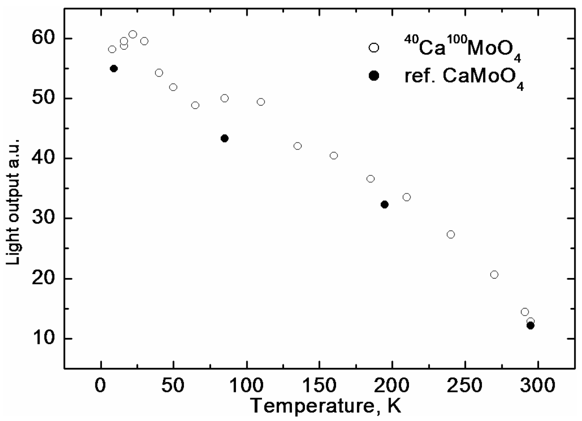

Fig. 4 Temperature dependence of light output of ^{40}Ca^{100}MoO$_4$ and reference CaMoO$_4$ crystals measured for excitation with 5.5 MeV α-particles (^{241}Am source).

For the first time a large (0.55 kg) ^{40}Ca^{100}MoO$_4$ crystal of good optical quality was produced and characterized. The light yield of the crystal is shown to be comparable with the reference CaMoO$_4$ scintillators throughout the wide temperature range down to 8 K. These promising results as well as the availability of production capacities for enriched materials, ultra-pure raw materials and large crystals form an important capability, underpinning the application of this material in large-scale experimental searches for neutrinoless double beta decay [19].

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