

# Ultrapurification of Isotopically Enriched Materials for $^{40}\text{Ca}^{100}\text{MoO}_4$ Crystal Growth

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**Abstract**—This paper describes ultrapurification of isotopically enriched calcium and molybdenum compounds and  $^{40}\text{Ca}^{100}\text{MoO}_4$  calcium molybdate growth charge in order to remove radioactive uranium, thorium, and radium impurities.  $^{40}\text{Ca}^{100}\text{MoO}_4$  single crystals grown from such charges are needed for the fabrication of scintillator elements of the cryogenic detector for the AMoRE project: a search for  $^{100}\text{Mo}$  neutrinoless double-beta decay.

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## INTRODUCTION

A search for neutrinoless double-beta decay ( $2\beta_0\nu$  decay) is a priority issue in modern experimental particle physics [1]. Promising detectors for this purpose are cryogenic scintillators [2]. Researchers involved in the AMoRE project are now preparing an experiment which will involve a search for  $^{100}\text{Mo}$   $2\beta_0\nu$  decay with the use of a cryogenic scintillator detector based on  $^{40}\text{Ca}^{100}\text{MoO}_4$  single crystals [3].

### *Requirements for the Purity of Raw Materials and $^{40}\text{Ca}^{100}\text{MoO}_4$ Growth Charge*

The sensitivity of the AMoRE detector is determined by the background in the region of the expected peak from the sought process. Among the main sources of such background are decays of natural radioactive isotopes present as impurities in the detector material: the isotopes  $^{208}\text{Tl}$  ( $^{232}\text{Th}$  series) and  $^{214}\text{Bi}$  ( $^{226}\text{Ra}$  decay product in the  $^{238}\text{U}$  series) [4]. As follows from the decay schemes of the  $^{238}\text{U}$  and  $^{232}\text{Th}$  series [4], the removal of these isotopes is ensured by removing three chemical elements: uranium, thorium, and radium. Particular attention should be paid to the removal of radium from the calcium-containing component because calcium and radium belong to the same subgroup of chemical elements. The content of radioactive radium isotopes ( $^{228}\text{Ra}$  and  $^{226}\text{Ra}$ ) can be determined by low-background gamma-spectrometry using low-background detectors located in underground laboratories [5].

The region of the  $2\beta_0\nu$  decay peak is also contributed by electrons resulting from the  $2\beta_2\nu$  decay of the  $^{48}\text{Ca}$  isotope, present in natural calcium. The contribution from  $^{48}\text{Ca}$  can be reduced by using calcium depleted in this isotope by at least 30 times [6].

According to calculations, the content of  $^{226}\text{Ra}$ , the most dangerous radionuclide, in a  $^{40}\text{Ca}^{100}\text{MoO}_4$  growth charge should not exceed 2 mBq/kg ( $5 \times 10^{-15}$  at %)

(which will correspond to a specific activity of  $\leq 0.05$  mBq/kg ( $0.12 \times 10^{-15}$  at %) in a  $^{40}\text{Ca}^{100}\text{MoO}_4$  single crystal grown from such a charge, with allowance for additional purification of the material due to double crystallization in the growth process [7]).

The purpose of this work was to develop methods for ultrapurification of isotopically enriched materials for the crystal growth of  $^{40}\text{Ca}^{100}\text{MoO}_4$  calcium molybdate.

### *Preparation of $^{100}\text{Mo}$ -Enriched Molybdenum and $^{48}\text{Ca}$ -Enriched Calcium*

**Isotopically enriched  $^{100}\text{Mo}$ .** Molybdenum 95+%-enriched in  $^{100}\text{Mo}$  is manufactured by Electrochemical Plant Production Association (Zelenogorsk, Krasnoyarsk krai, Russia) through centrifugation and is supplied in the form of  $^{100}\text{MoO}_3$  molybdenum oxide powder.

The  $^{100}\text{Mo}$  production process involves the following steps:

1. Synthesis of molybdenum hexafluoride,  $\text{MoF}_6$ , in flowing fluorine gas (accompanied by  $\text{UF}_6$  synthesis if the molybdenum contains uranium impurities) and purification of the  $\text{MoF}_6$  in order to remove chemical elements that do not form volatile fluorides.
2.  $\text{MoF}_6$  enrichment with the  $^{100}\text{Mo}$  isotope through centrifugation, accompanied by the removal of uranium impurities via the separation of some of the  $\text{UF}_6$ -containing heaviest fraction of the  $^{100}\text{MoF}_6$  working gas [8].
3.  $^{100}\text{MoO}_3$  hydrolysis and preparation of  $^{100}\text{MoO}_3$  via calcination.

Inductively coupled plasma mass spectrometry (ICP MS) data for the  $^{100}\text{MoO}_3$  samples demonstrate that the chemical purity of the enriched material is 99.99% and that the  $^{238}\text{U}$  and  $^{232}\text{Th}$  concentrations in the oxide are within  $0.07 \times 10^{-7}$  and  $0.1 \times 10^{-7}$  wt %, respectively (to

improve the sensitivity to these impurities, specialized techniques were developed [9]).

Gamma spectrometric characterization with the use of a low-background semiconductor detector at the Baksan Neutrino Observatory, Institute for Nuclear Research, Russian Academy of Sciences (RAS), showed that the specific activity of  $^{226}\text{Ra}$  and its daughter isotope  $^{214}\text{Bi}$  was under 2.3 mBq/kg [10].

**Isotopically enriched  $^{40}\text{Ca}$  (depleted in  $^{48}\text{Ca}$ ).**  $^{40}\text{CaCO}_3$  calcium carbonate enriched in  $^{40}\text{Ca}$  (99.964–99.988 at %) and depleted in the  $^{48}\text{Ca}$  isotope ( $\leq 0.001$  at %) is manufactured by Elektrokhimpribor Plant (Lesnoi, Sverdlovsk oblast, Russia) using electromagnetic separation. The preparation of  $^{48}\text{Ca}$ -depleted calcium involves two steps: (1) isotope separation and capture in the receiving modules of the electromagnetic system; (2) removal of the isotopically enriched calcium from the receiving modules and chemical processing to the final product [11].

Processing at Elektrokhimpribor Plant yields isotopically enriched calcium in the form of calcium carbonate containing no more than 0.05 wt % impurities (70 elements) (Table 1).

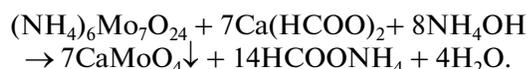
The  $^{238}\text{U}$  and  $^{232}\text{Th}$  concentrations in the enriched material are under  $0.2 \times 10^{-7}$  and  $0.8 \times 10^{-7}$  wt %, respectively. At the same time, gamma spectrometric characterization at the Baksan Neutrino Observatory, Institute for Nuclear Research, RAS, showed that the specific activity of  $^{226}\text{Ra}$  and its daughter isotope  $^{214}\text{Bi}$  was at a level of hundreds of mBq/kg [10]. The starting material was then further purified.

The best results were obtained through double recrystallization of calcium formate. We optimized the dissolution, recrystallization, and precipitate heat treatment conditions so as to achieve the desired chemical purity at minimal losses of the isotopically enriched calcium in all chemical processing steps.

As seen from Table 2, the new calcium purification technology, based on calcium formate recrystallization, ensures a reduction in  $^{40}\text{K}$ ,  $^{208}\text{Tl}$ ,  $^{228}\text{Ac}$ , and  $^{226}\text{Ra}$  ( $^{214}\text{Bi}$ ) concentrations by 20, more than 8, 160, and 5 times, respectively, as compared to a standard purification procedure. Nevertheless, the  $^{226}\text{Ra}$  ( $^{214}\text{Bi}$ ) content is 51 mBq/kg, so further purification is needed before growth charge synthesis.

#### *Further Purification of Raw Materials and $^{40}\text{Ca}^{100}\text{MoO}_4$ Growth Charge Synthesis*

The most attractive calcium molybdate growth charge synthesis process is precipitation from solution: first, we reliably obtain the stoichiometric composition; second, crystallization from solution may ensure further purification:



**Table 1.** ICP MS and ICP AES data for  $^{40}\text{CaCO}_3$  (measurements at the Analytical Certification Testing Center, Institute of Microelectronics Technology and High Purity Materials, RAS)

Element	DL, $\mu\text{g/g}$	C, $\mu\text{g/g}$	Element	DL, $\mu\text{g/g}$	C, $\mu\text{g/g}$
Li	0.009	<DL	Ag	0.004	<DL
Be	0.006	<DL	Cd	0.02	<DL
B	3	<DL	Sn	0.05	<DL
Na	7	<DL	Sb	0.04	<DL
Mg	2	<DL	Te	0.01	<DL
Al	2	<DL	Cs	0.003	<DL
Si	16	<DL	Ba	0.05	23.7
P	27	<DL	La	0.002	0.037
S	24	<DL	Ce	0.002	0.30
K	21	<DL	Pr	0.0003	0.0019
Ca	6	Host	Nd	0.002	0.0072
Sc	0.2	<DL	Sm	0.001	0.0021
Ti	0.6	<DL	Eu	0.003	<DL
V	0.1	<DL	Gd	0.001	<DL
Cr	0.5	<DL	Tb	0.0005	<DL
Mn	0.03	10.6	Dy	0.0009	<DL
Fe	3	<DL	Ho	0.0002	<DL
Co	1	<DL	Er	0.0008	<DL
Ni	0.3	<DL	Tm	0.0003	<DL
Cu	0.2	<DL	Yb	0.0009	<DL
Zn	1	<DL	Lu	0.0006	<DL
Ga	0.04	<DL	Hf	0.02	<DL
Ge	0.04	<DL	Ta	0.002	<DL
As	0.09	<DL	W	0.04	<DL
Se	0.5	<DL	Re	0.001	<DL
Br	8	<DL	Os	0.001	<DL
Rb	0.008	<DL	Ir	0.0003	<DL
Sr	0.06	24.0	Pt	0.001	<DL
Y	0.008	<DL	Au	0.002	<DL
Zr	0.2	<DL	Hg	0.009	<DL
Nb	0.003	<DL	Tl	0.001	<DL
Mo	0.01	<DL	Pb	0.007	0.21
Ru	0.003	<DL	Bi	0.001	0.013
Rh	0.008	<DL	Th	0.0008	<DL
Pd	0.005	<DL	U	0.0002	<DL

Note: AES = atomic emission spectroscopy; DL = detection limit.

**Table 2.** Content of radioactive impurities in  $^{40}\text{CaCO}_3$  calcium carbonate (sample 1) and  $^{40}\text{Ca}(\text{HCOO})_2$  calcium formate (sample 2)

Isotope	Activity, Bq/kg	
	sample 1 (standard procedure, November 2009)	sample 2 (October 2011)
$^{40}\text{K}$	$(7.3 \pm 3.1) \times 10^{-2}$	$(3.6 \pm 2.7) \times 10^{-3}$
$^{208}\text{Tl}$ [ $^{228}\text{Th}$ ]	$(4.4 \times 3.6) \pm 10^{-3}$ [ $(1.2 \pm 1.0) \times 10^{-2}$ ]	$\leq 5.2 \times 10^{-4}$
$^{226}\text{Ra}$ ( $^{214}\text{Bi}$ )	$(2.6 \pm 0.2) \times 10^{-1}$	$(5.1 \pm 0.2) \times 10^{-2}$
$^{228}\text{Ac}$ [ $^{228}\text{Th}$ ]	$(1.6 \pm 0.2) \times 10^{-1}$	$(1.0 \pm 0.8) \times 10^{-3}$

Note: Low-background gamma spectrometry data (Baksan Neutrino Observatory, Institute for Nuclear Research, RAS).

The growth charge was synthesized and the isotopically enriched components were further purified as necessary at ZAO NeoKhim (Moscow).

**Preparation of ammonium paramolybdate.** Ammonium paramolybdate can be prepared by dissolving molybdenum oxide in aqueous ammonia. If further purification is necessary, a sorbent and complexing agent are added, and the solution is then thoroughly filtered.

**Preparation of calcium formate.** Calcium formate is additionally purified through several recrystallization steps. In this process, the pH of the medium is adjusted by nitric acid and aqueous ammonia.

The required purity is usually ensured by two or three recrystallization cycles, depending on the initial contamination of the material.

Using this approach, we were able to reduce the radium ( $^{226}\text{Ra}$ ) content of calcium formate from 51 to 1.4 mBq/kg (Table 2).

To prepare calcium formate for calcium molybdate growth charge synthesis, a saturated aqueous calcium formate solution should be prepared.

**Calcium molybdate growth charge synthesis.** Calcium molybdate was synthesized at a temperature of 50–60°C. The resultant calcium molybdate precipitate was heat-treated at a temperature of 800°C for 4 h in a silica crucible placed in a muffle furnace.

The results presented in Table 3 demonstrate that all of the impurities were almost completely removed from the material. The uranium and thorium contents determined by a more sensitive technique [9] were  $0.3 \times 10^{-7}$  and  $0.9 \times 10^{-7}$  wt %, respectively. These

**Table 3.** Impurity content of  $^{40}\text{Ca}^{100}\text{MoO}_4$  growth charge (ICP MS and ICP AES data, measurements at the Analytical Certification Testing Center, Institute of Microelectronics Technology and High Purity Materials, RAS)

Element	DL, $\mu\text{g/g}$	C, $\mu\text{g/g}$	Element	DL, $\mu\text{g/g}$	C, $\mu\text{g/g}$
Li	0.05	<DL	Te	0.4	<DL
Be	0.003	<DL	Cs	0.1	<DL
Na	25	<DL	Ba	0.6	8.4
Mg	2	<DL	La	0.007	<DL
Al	4	<DL	Ce	0.1	<DL
K	90	<DL	Pr	0.002	<DL
Ca	58	Host	Nd	0.01	<DL
Sc	0.2	<DL	Sm	0.03	<DL
Ti	9	<DL	Eu	0.05	<DL
Cr	1	<DL	Gd	0.004	<DL
Mn	0.3	3.3	Tb	0.004	<DL
Fe	22	<DL	Dy	0.003	<DL
Co	0.2	<DL	Ho	0.001	<DL
Ni	2	<DL	Er	0.003	<DL
Cu	1	<DL	Tm	0.005	<DL
Zn	1	4.1	Yb	0.006	<DL
Ga	0.1	<DL	Lu	0.02	<DL
As	0.2	<DL	Hf	0.009	<DL
Se	0.4	<DL	Ta	0.005	<DL
Rb	0.1	<DL	W	0.006	0.70
Sr	0.2	3.0	Re	0.001	<DL
Y	0.002	<DL	Ir	0.002	<DL
Zr	0.08	<DL	Pt	0.002	0.16
Nb	0.04	<DL	Au	0.008	<DL
Mo		Host	Hg	0.02	<DL
Rh	0.004	<DL	Tl	0.002	<DL
Pd	0.02	<DL	Pb	0.08	<DL
Ag	0.03	<DL	Bi	0.001	<DL
Cd	7	<DL	Th	0.0009	<DL
Sn	0.2	<DL	U	0.0003	<DL
Sb	0.02	<DL			

**Table 4.** Content of radioactive impurities in different raw materials and  $^{40}\text{Ca}^{100}\text{MoO}_4$  growth charge

Isotope	Activity, Bq/kg		
	$^{100}\text{MoO}_3$	$^{40}\text{Ca}(\text{HCOO})_2$ (purification at NeoKhim)	$^{40}\text{Ca}^{100}\text{MoO}_4$ growth charge
$^{40}\text{K}$	$(5.3 \pm 0.8) \times 10^{-2}$	$\leq 8.6 \times 10^{-3}$	$\leq 9.4 \times 10^{-3}$
$^{228}\text{Ac}$ [ $^{232}\text{Th}$ ]	$\leq 3.8 \times 10^{-3}$	$(1.3 \pm 1.1) \times 10^{-3}$	$(1.9 \pm 1.3) \times 10^{-3}$
$^{208}\text{Tl}$ [ $^{232}\text{Th}$ ]	$\leq 1.0 \times 10^{-3}$ [ $\leq 2.8 \times 10^{-3}$ ]	$\leq 1.3 \times 10^{-3}$	$\leq 1.1 \times 10^{-3}$
$^{226}\text{Ra}$ ( $^{214}\text{Bi}$ )	$\leq 2.3 \times 10^{-3}$	$(1.4 \pm 0.9) \times 10^{-3}$	$\leq 1.6 \times 10^{-3}$

Note: Low-background gamma spectrometry data (Baksan Neutrino Observatory, Institute for Nuclear Research, RAS).

levels meet the requirements for the concentration of these impurities in the growth charge.

It follows from the data in Table 4 that, at the sensitivity level of our analytical facility, the content of radioactive impurities is acceptable, except for  $^{226}\text{Ra}$ , whose content in the sample was determined to be 1.6 mBq/kg. At the same time, with allowance for further removal of  $^{226}\text{Ra}$  ( $K \geq 35$ ) due to double recrystallization during crystal growth [7], we expect that the content of the  $^{226}\text{Ra}$  isotope will be at a level of 0.04 mBq/kg.

## CONCLUSIONS

We developed a technique for ultrapurification of isotopically enriched calcium formate and obtained a product with a  $^{226}\text{Ra}$  ( $^{214}\text{Bi}$ ) content of 1.4 mBq/kg.

A  $^{40}\text{Ca}^{100}\text{MoO}_4$  calcium molybdate growth charge was prepared through precipitation from aqueous solution. Its purity was as follows:  $0.3 \times 10^{-7}$  wt % U,  $0.9 \times 10^{-7}$  wt % Th, and 1.6 mBq/kg  $^{226}\text{Ra}$ .

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