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TECHNICAL REPORT

Reduction of radioactive elements in molybdenum trioxide powder by sublimation method and its technical performance

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Abstract: We studied the effectiveness of the purification of molybdenum trioxide (MoO_3) powder with the sublimation method. To utilize the method, we have designed sublimation apparatus to purify the powder and annealing apparatus to collect the fine powder, followed by the wet chemistry method. As part of purification R&D, MoO_3 powder was purified using a low vacuum sublimation method to remove radioactive elements such as Ra, Th, U, etc. The purification was performed at different temperatures to determine the optimum conditions for high decontamination factors and high recovery efficiencies. After applying the sublimation method, the powder was dissolved in aqueous ammonia; recrystallized to obtain polyammonium molybdate (PAM); and annealed to acquire MoO_3 fine powder. The phase of MoO_3 powder was studied by using X-ray diffraction (XRD) techniques. The effectiveness of the purification techniques was checked with inductively coupled plasma mass spectrometry (ICP-MS) measurements and the radioactivity from Ra, Th, and U were measured with high purity germanium (HPGe) detectors at Yangyang underground laboratory in Korea. The purified MoO_3 powder was used by the AMoRE (Advanced Mo-based Rare process Experiment) collaboration to grow scintillating crystals.

Keywords: Materials for solid-state detectors; Scintillators, scintillation and light emission processes (solid, gas and liquid scintillators)

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1 Introduction

The neutrinoless double beta decay ($0\nu\beta\beta$) is a promising, although very rare, process that can probe the Majorana nature of neutrinos. The observation of $0\nu\beta\beta$ would constrain an absolute value of the neutrino masses [1]. Many underground experiments are searching for $0\nu\beta\beta$ [2–6]. Several $0\nu\beta\beta$ candidate isotopes (^{76}Ge, ^{130}Te, ^{136}Xe, ^{82}Se, ^{150}Nd, ^{100}Mo, ^{48}Ca and ^{116}Cd) are studied in ref. [7]. The Advanced Mo-based Rare process Experiment (AMoRE) uses calcium molybdate ($CaMoO_4$) scintillating crystals with depleted ^{48}Ca and enriched ^{100}Mo [6]. The collaboration has chosen ^{100}Mo as the $0\nu\beta\beta$ source for the following reasons: the nucleus has a high Q value of 3034 keV, which provides background rejection for one of the main backgrounds such as ^{208}Tl (^{232}Th family), whose decays peak at 2615 keV; relatively large natural abundance of 9.8%; tens of kilograms of enriched ^{100}Mo can be produced with centrifugation techniques within one year; the estimated theoretical half-life is relatively short compared to other candidate isotopes [8–11].

In $0\nu\beta\beta$ search experiments, background events should be reduced as much as possible [12]. To reduce radioactive backgrounds sufficiently, materials used for the detector, shield and support structure need to have very low-level radioactive isotopes contamination [12, 13]. While the background arising from cosmic rays can be reduced through performing experiments deep underground, extensive efforts are required to limit and evaluate the inevitable presence of radioisotopes.

The radio purity of the scintillating-crystal detector required for $0\nu\beta\beta$ search experiments is beyond the range of industrial practices. The objective of present R&D is to develop the preliminary techniques for ultra-purification of radioactive contaminates from commercial MoO_3 powder, which is used for making Mo-containing crystal. Hence, the optimized techniques will be used in the future for purifying enriched $^{100}MoO_3$ powder. The enriched molybdenum powder will be used by

AMoRE in different phases of the experiment for growing $Li_2^{100}MoO_4$ [14] and $Na_2^{100}Mo_2O_7$ [15] single crystal.

There are several well-known techniques available for the purification of MoO_3 such as co-precipitation, re-crystallization, solvent extraction, sublimation, etc. Among these, sublimation could be the most effective technique for MoO_3 purification because of its low processing time, avoiding many more reagents, and its high yield efficiency. With this technique, the high-purity crystalline powder can be obtained by controlling the vaporization mechanism [16]. During the sublimation process, the solid is heated under the reduced pressure where it volatilizes and condenses as a purified compound on the cooled surface, leaving non-volatile impurities behind.

In this work, we present purification of MoO_3 powder with sublimation and annealing apparatus designed by ourselves. Both apparati can be used for laboratory scale and mass production of purified MoO_3 powder.

2 Purification study with sublimation method

2.1 Experimental apparatus

2.1.1 Sublimation machine

The sublimation apparatus was especially designed for the purification of MoO_3 powder. An image of the sublimation system is shown in figure 1. The apparatus consists of two layers of cylindrical quartz tubes: outer and inner quartz tubes which are within the sublimation retort. The outer quartz tube is the main sublimation tube for maintaining the vacuum of about 10 mTorr, and for supporting the different inner quartz tubes. Two flanges are on both sides of sublimation tube. These are used for loading and removing the inner quartz tubes. There are three different inner quartz canisters (see figure 2), which are placed inside the sublimation tube. These quartz tubes, having different diameters, are connected horizontally to each other. The middle quartz tube has different dimensions at the bottom and top. The sample is loaded inside this tube and is supported by another two quartz tubes, from the left and right sides. The right quartz tube is for collecting the powder after completing the sublimation process. The arrangement of the inner tubes are shown at the top of figure 1.

The apparatus consists of three zone furnaces that are adjacent to each other; their temperatures are controlled individually by three different temperature controllers. The temperature of each zone can be controlled from 0°C to 1000°C. Different zone temperatures are monitored using Nickel-chromium/Nickel-Alumel thermo elements. The vacuum is maintained using a rotatory pump. Two valves, soft and rough, are used for creating the vacuum. Initially, the rough valve is opened to create a vacuum up to 10 mTorr. Once the vacuum is below 10 mTorr, the rough valve is closed and the soft valve is opened. During sublimation, the soft valve remains open. The heating block and sublimation retort can be tilted from 0° to 60°. In normal operation, the sublimation retort is inclined at an angle of 20°, as shown in figure 3. To protect the O-ring, of the doors in the machine, water is continuously supplied through the water inlet. The initial weight charge of MoO_3 powder is 50 g to 1500 g.

2.1.2 Annealing furnace

The annealing machine was especially designed for the production of uniform stoichiometric MoO_3 powder for single crystal growth. An image of the annealing furnace is shown in figure 4. It consists a long quartz tube, for annealing the powder in a closed environment, and a quartz

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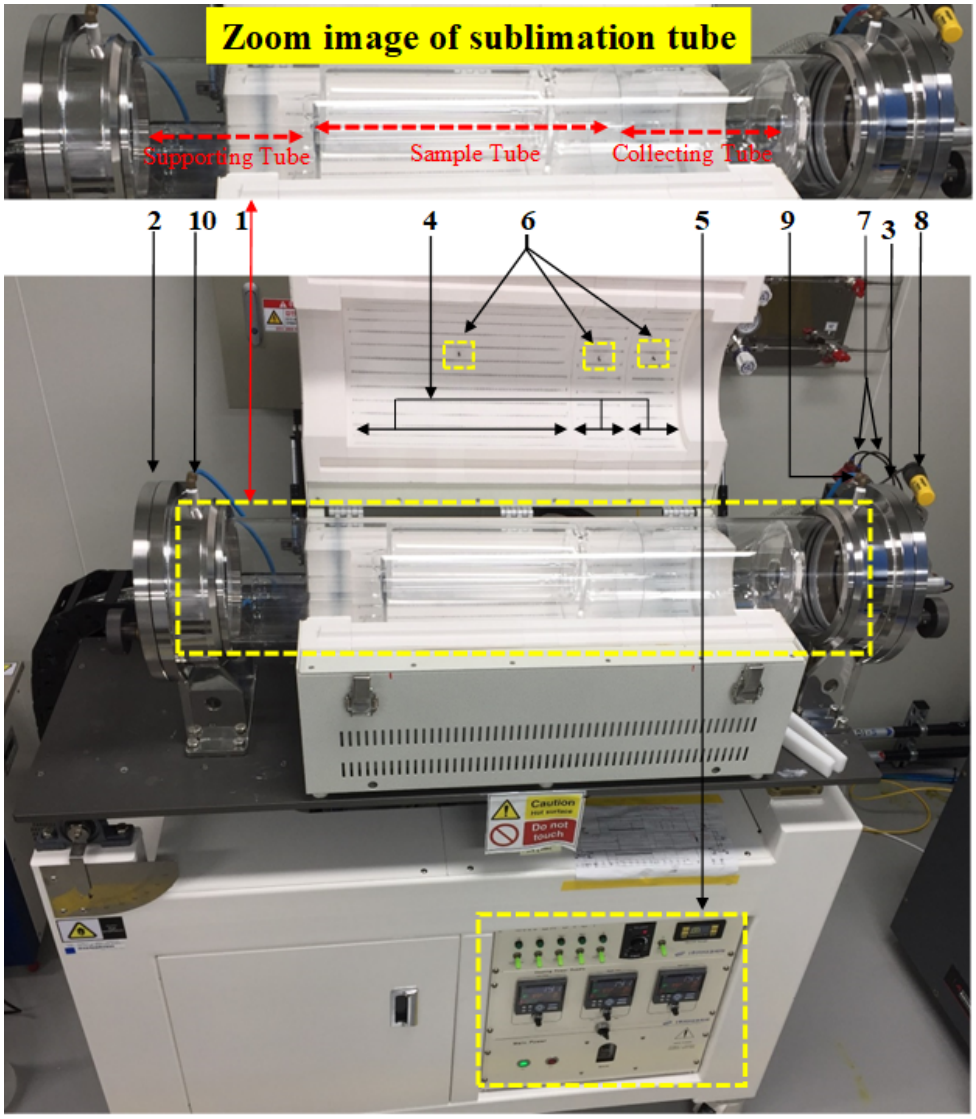

Figure 1. Image of the sublimation system showing different components: (1) sublimation tube (∅200 × 1138 mm^3); (2) flange (left side); (3) flange (right side); (4) heater; (5) control panel; (6) thermocouples; (7) vacuum valve; (8) vacuum gauge; (9) water inlet; (10) water outlet.

boat for loading the PAM powder. The maximum capacity of the quartz boat is 500 g. The apparatus is made up of a single zone cylindrical heating furnace. This furnace can be operated from room temperature up to 1000°C, and its temperature is monitored by a K-type thermocouple. Two inlet and outlet valves are placed on both ends of the flange. One set allows gas to flow for maintaining atmospheric pressure, while the other is for water flow to prevent the O-ring, in the flanges, from thermal shock. In addition to this, it also includes a vent to supply air for the oxidation of molybdenum oxide. A rotary pump provides the vacuum for trapping the excess ammonia gas and water. To protect the pump from the corrosive fume, the pump is connected to a cold trap and gas filter.

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Figure 2. Different inner quartz tubes. The left tube is for supporting the middle tube with $\varnothing 120 \times 320$ mm^3, the middle tube is for sample loading with $\varnothing 129 \times 300$ mm^3 (bottom side) and $\varnothing 172 \times 145$ mm^3 (top side), and the right tube is for sample collection with $\varnothing 180 \times 265$ mm^3.

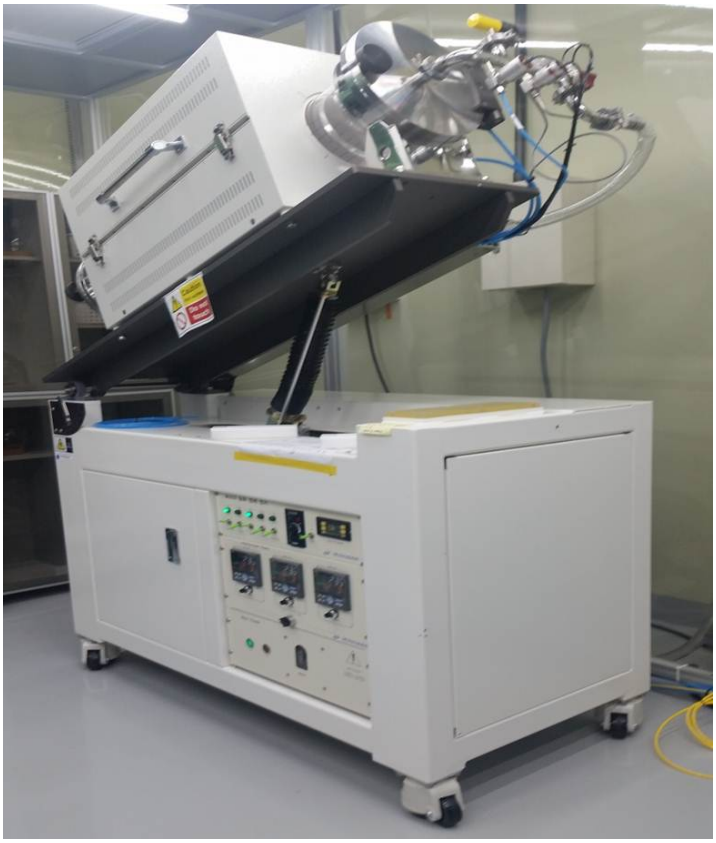

Figure 3. Sublimation machine during operation.

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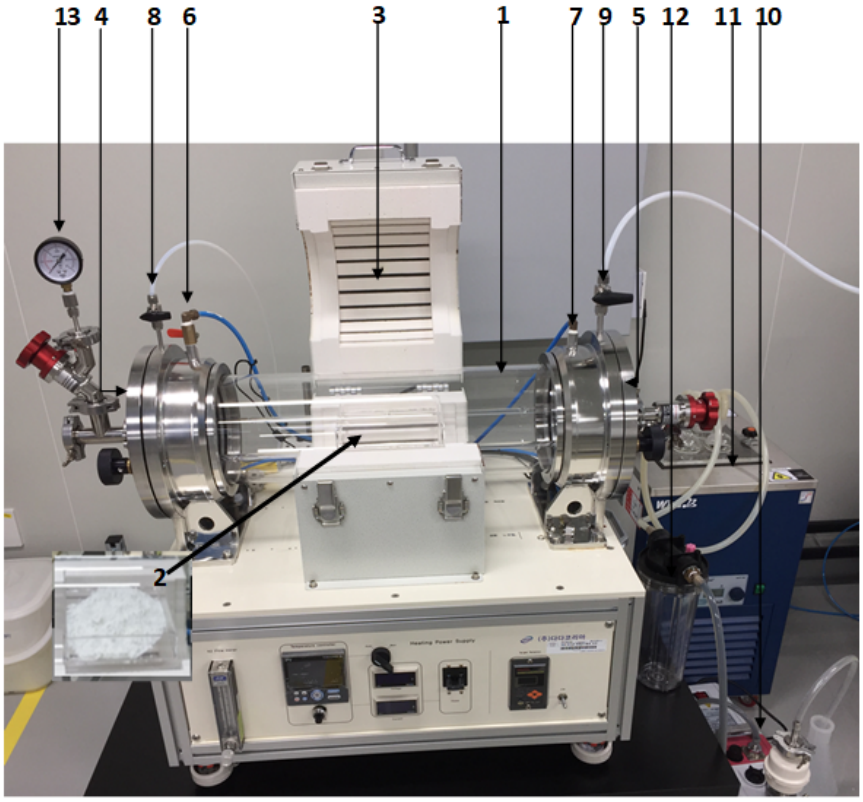

Figure 4. Image of the annealing furnace: (1) quartz tube with ∅180 × 620 mm^3; (2) quartz boat with thickness of 3 mm and the dimensions of 166 × 160 × 27 mm^3; (3) thermocouple; (4) flange (left); (5) flange (right); (6) water inlet; (7) water outlet; (8) gas inlet; (9) gas outlet; (10) vacuum pump; (11) cold trap; (12) pump protector from water; (13) vacuum gauge.

2.2 Purification study

All apparatus were tested in a clean room of class 1,000. A vertical laminar flow hood, providing a class 10 environment, was used for sample preparation. Commercial MoO_3 powder, with purity grade of 99.95% produced by Alfa-Aesar, was used to check purification of the powder. To find out the optimal temperature for the powder purification, the sublimation method was applied at various temperatures from 670°C to 800°C, using 50 g of MoO_3 powder in a low vacuum (< 10 mTorr). Because the melting point of MoO_3 is 795°C, low vacuum helps to sublimate the MoO_3 powder at a lower temperature, leaving the non-volatile impurities in solid phase. The temperature of the coldest part of the sublimation retort was about 500°C to 600°C, where purified MoO_3 vapor was de-sublimated and collected. The operating temperatures of the furnace was reached within ~30 min after the furnace was turned on and was kept constant until the entire sublimation process finished. After this, the furnace was switched off and left to cool back down to room temperature. Pure nitrogen gas was purged inside the sublimation tube to maintain atmospheric pressure, before removing the MoO_3 powder. The powder was collected in a plastic bottle to check the collection efficiency and purification factor.

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Large chunks of crystalline MoO_3 powder were formed at the end of the sublimation process, containing molybdenum oxides of different composition and color [5]. To acquire uniform MoO_3 powder for growing crystals containing molybdenum, all of the sublimated powder was dissolved in excess aqueous ammonia to make ammonium molybdate solution. Ammonium molybdate solution was completely evaporated to recrystallize the PAM crystals. The obtained PAM crystals were annealed in two steps to obtain fine MoO_3 powder. First, preheating at 250°C for releasing the excess amount of ammonia and water under vacuum; and second, annealing at 675°C in air to produce a stoichiometric MoO_3 compound.

An Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS) was used to measure impurities such as Sr, Ba, Pb, Th, and U. The contents of radioactivity were measured using a high purity germanium (HPGe) detector at the deep underground laboratory in Yangyang, Korea. In particular, ^{226}Ra is one of the major backgrounds for the $0\nu\beta\beta$ experiment. Because Ra, Sr, and Ba are in the same group of the periodic table, reductions of Sr and Ba indicate a reduction of ^{226}Ra. The crystalline phases were verified using a Philips XPERT-MED X-ray diffractometer in the 2θ range from CuKα radiation (λ= 0.154 nm), at a scanning step of 0.025° and rate of 3 sec per step, where θ is the Bragg angle.

3 Results and discussions

3.1 Yield efficiency

To evaluate the feasibility of the sublimation method, yield efficiency (Y) and processing time at various temperatures were calculated. The yield efficiency of the method (in %) is defined as follows,

$$Y = \frac{\text{Weight of } MoO_3 \text{ powder after sublimation}}{\text{Weight of } MoO_3 \text{ powder before sublimation}} \times 100 \tag{3.1}$$

The yield efficiency and processing time at various temperatures are shown in figure 5. The graph indicates that the yield efficiency of MoO_3 is approximately 92% to 94% below 700°C, which is low compared to the high temperature region. At low temperature, the volatilization rate is low, and it takes longer to complete sublimation. Conversely, at high temperature the rate is elevated and it takes less time to complete sublimation [16, 17]. In this study, the rate of vaporization at high temperature (>700 °C) is ~3.30 g/h, while it is ~0.70 g/h at lower temperatures (<700 °C). The yield efficiency was ~96 % in the temperature range of 700°C to 760°C. The yield at a higher temperature (800°C) decreased. This can be explained by the melting of MoO_3 [18]. Our study shows that the highest recovery of MoO_3 powder was obtained in the range from 700° C to 730° C.

3.2 Purification factor

The concentration of the impurities in the initial and purified sample was measured with the ICP-MS, as shown in table 1. Of note, the concentration of impurities for U and Th after sublimation is at the trace level. Hence, these elements are at the detection limit of the ICP-MS measurement. The effectiveness of purification was evaluated by decontamination factors ($D.F.$) using the equation below,

$$D.F. = \frac{C_0}{C_f} \tag{3.2}$$

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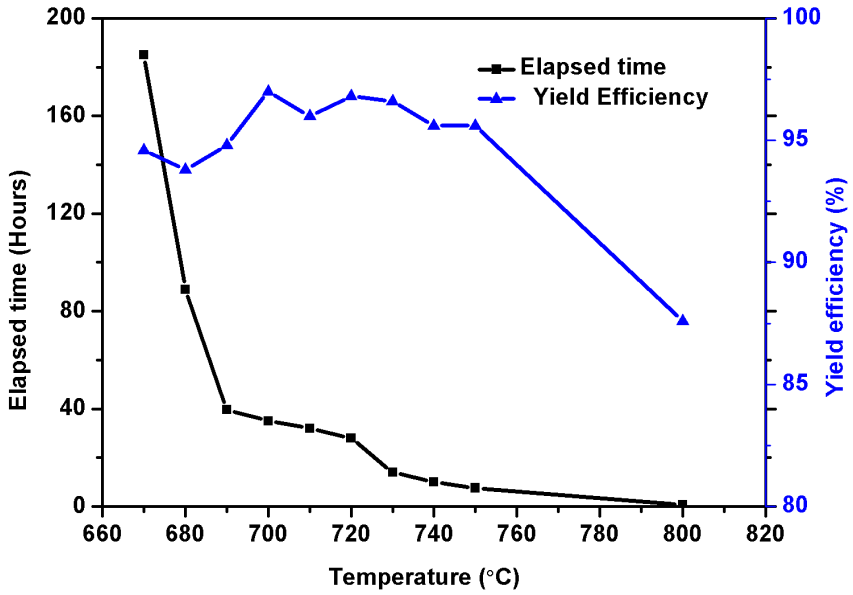

Figure 5. Elapsed time and yield efficiency of MoO_3powder versus temperature for sublimation.

where C_0 and C_f are concentration of impurities in the initial and final product, respectively. The $D.F.$ for various elements at different temperatures is shown in table 2. Thus, the calculated $D.F.$ for Sr is 26 to at least 165; for Ba, 87 to 114; and for Th and U, at least 4.4 and 84, respectively. The variation in $D.F.$ for each element is due to differences in melting points. The melting points of SrO, BaO, ThO_2, and UO_2 are above 2000°C [19], while the melting point of MoO_3 (795°C) is very low compared to these compounds. Because of the low melting point of MoO_3, it vaporizes while other elements are in the solid phase. The impurity level of Pb remains constant (before and after sublimation) owing to its low melting point (400°C), and it vaporizes first [20], before the MoO_3 powder.

The contents of radioactive elements cannot be measured using the ICP-MS technique. Instead, these elements were measured using a HPGe detector at the deep underground laboratory. Table 3 shows the HPGe measurement results of commercial MoO_3powder, as well as the sublimated powder, at various temperatures (710°C, 720°C, and 730°C). As in the earlier studies from our group [13], the $D.F.$'s of Sr and Ba correlates with the reduction factor for Ra. However, in this study, because of the very limited size of the HPGe sample (50 g), the uncertainties of the measurements are high.

The results show that the low vacuum sublimation process is quite efficient for the removal of the ^{226}Ra, ^{40}K and ^{228}Ac radioactive elements. The limits shown in the table indicate that the resulting sample is purer than the untreated powder. From the numbers and limits listed in table 3, the $D.F.$ for ^{226}Ra, ^{40}K and ^{228}Ac were calculated and are shown in table 4.

3.3 Structural analysis

The typical XRD patterns of the MoO_3 powder, after annealing PAM powder, is shown in figure 6. The peaks observed for pure MoO_3 powder can be indexed as single-phase orthorhombic crystal

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Table 1. Concentration of various impurities in MoO_3 powder before and after sublimation at various temperatures.

	Concentration(ppb)				
Elements	Sr	Ba	Pb	Th	U
Inital MoO_3	6.6	1366.5	15.8	0.22	4.2
670 °C	0.1	14.6	10.9	<0.05	<0.05
680 °C	0.05	14.5	11.0	<0.05	<0.05
690 °C	0.25	13.8	13.2	<0.05	<0.05
700 °C	<0.04	12.2	11.8	<0.05	<0.05
710 °C	<0.04	15.7	11.6	<0.05	<0.05
720 °C	<0.04	11.9	13.7	<0.05	<0.05
730 °C	<0.04	14.7	13.1	<0.05	<0.05
740 °C	<0.04	15.0	11.4	<0.05	<0.05
750 °C	<0.04	15.8	12.8	<0.05	<0.05

Table 2. Decontamination of different impurities at different temperatures.

	Decontamination factor ($D.F.$)				
Elements	Sr	Ba	Pb	Th	U
Temperature					
670 °C	66	93.6	1.4	>4.4	>84
680 °C	132	92.2	1.4	>4.4	>84
690 °C	26.4	99	1.2	>4.4	>84
700 °C	>165	112	1.3	>4.4	>84
710 °C	>165	87	1.3	>4.4	>84
720 °C	>165	115	1.1	>4.4	>84
730 °C	>165	92.5	1.2	>4.4	>84
740 °C	>165	91.1	1.4	>4.4	>84
750 °C	>165	86.5	1.2	>4.4	>84

structure. The lattice parameters were all consistent with standard ICDC card number 00-005-0508. No extra phases of Molybdenum were obtained.

4 Conclusion

A low vacuum sublimation apparatus was designed, and successfully tested, for the purification of MoO_3 powder. The optimum temperature for sublimation of MoO_3 powder, at ~10 mTorr,

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Table 3. Content of radioactive impurities in initial MoO_3 powder and purified MoO_3 powder at three different temperatures.

Sample/Source	Unpurified MoO_3 powder (mBq/kg)	Purified MoO_3 powder (710 °C) (mBq/kg)	Purified MoO_3 powder (720 °C) (mBq/kg)	Purified MoO_3 powder (730 °C) (mBq/kg)
MoO_3mass(g)	50	44	43	45
Exposure (h)	89.76	180	264	151.2
^{226}Ra	9570 ± 2020	420 ± 154	605 ± 162	<130
^{40}K	3520 ± 802	218 ± 155	386 ± 144	307 ± 157
^{228}Ac	1991 ± 309	<15	<21.5	<48

Table 4. Effectiveness of sublimation process at different temperatures.

Temperature	Reduction factor for the impurities		
	^{226}Ra	^{40}K	^{228}Ac
710 °C	23	16	>133
720 °C	16	9.1	>92.6
730 °C	>74	11.4	>41.4

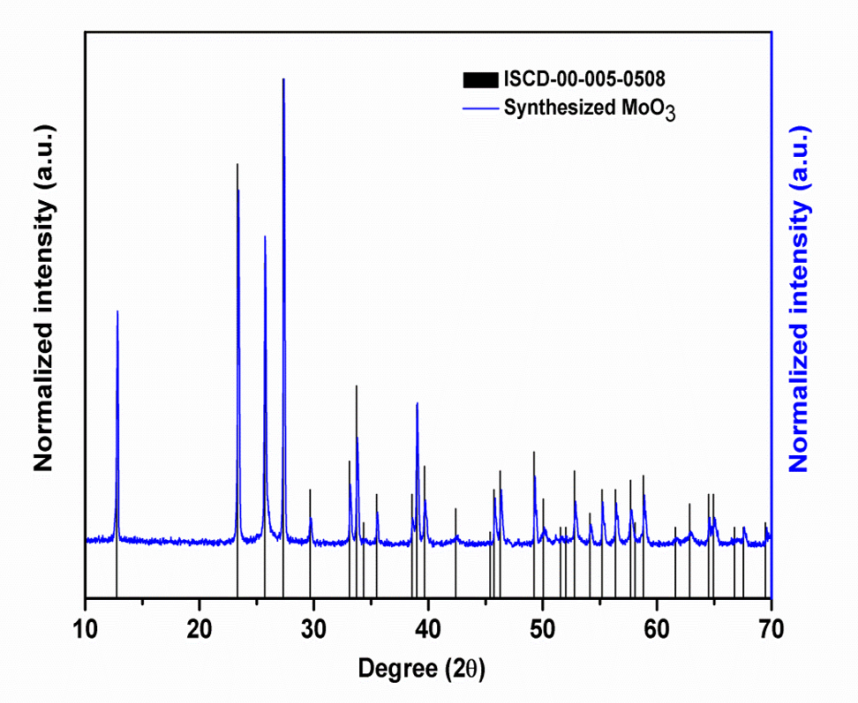

Figure 6. X-Ray diffraction patterns of MoO_3 powder after PAM annealing, where θ is the Bragg angle.

was found in the range of 710°C to 730°C. At these temperatures, the reduction factor of various elements is high relative to temperatures outside this range. Additionally, the recovery efficiency of molybdenum is high and the processing time for sublimation is low. Similarly, the HPGe results show that the reduction process of the various radioactive elements is quite efficient. Furthermore, a single zone heating furnace was designed for annealing the polyammonium molybdate compound to acquire the single phase of MoO_3. An X-ray diffraction analysis confirms that the powder obtained after the annealing process was MoO_3 powder, without any extra phases of molybdenum oxides. The optimized techniques, with the help of our custom designed sublimation and annealing machines, are used for production of pure MoO_3 powder for the AMoRE project.

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