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Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research A

journal homepage: www.elsevier.com/locate/nima

Effect of recrystallisation on the radioactive contamination of CaWO_4 crystal scintillators

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ARTICLE INFO

Article history:

Received 24 May 2010

Received in revised form

10 November 2010

Accepted 24 November 2010

Available online 7 December 2010

Keywords:

Rare events search

CaWO_4 crystal scintillators

Radioactive contamination

Crystal growth

ABSTRACT

Minimising intrinsic radioactivity of crystal scintillators is of particular importance for experiments searching for rare events. We studied the impact of the crystal production process (recrystallisation) on the level of radioactive contamination of CaWO_4 crystal scintillators. Several samples of single crystal scintillators were produced using the recrystallisation procedure. It is shown that this has a significant effect on the radioactive contamination of the crystals. Depending on the stage of recrystallisation the activity due to ^{210}Po (product of ^{210}Pb decay) varies in the range 0.03–1.32 Bq kg^{-1} while the activity of ^{238}U varies from 0.04 to 0.33 Bq kg^{-1} . We found that uranium is rejected by the crystal with a segregation coefficient ≈ 0.3 . The improvement in radiopurity of CaWO_4 by one order of magnitude due to recrystallisation has been demonstrated. The additional benefit of this process is the improvement in the energy resolution. A programme to develop radiopure CaWO_4 crystal scintillators is discussed briefly.

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1. Introduction

Search for rare events includes experiments on detection of non-baryonic dark matter, low energy neutrinos, neutrinoless double beta decay, radioactive decay of very long-lived nuclei, search for hypothetical decays and particles, etc. Scintillation targets have been widely used in these experiments, yielding important scientific results (see for instance Refs. [1–11]). Recently the application of scintillation targets has received further motivation, prompted by the development of cryogenic phonon scintillation detectors (CPSD) that combine high energy resolution and low threshold with the ability to discriminate different types of interactions [12,13]. Active background rejection, using a combination of phonon and scintillation responses, permits to have a clean signal down to low energies (≈ 10 keV). Evidence for the effectiveness of this technique comes from recent results obtained in experiments searching for dark matter [14] and in studies of very long-lived isotopes [15,16]. It would have been impossible to achieve these results without CPSD. Active background rejection helps also to identify the majority of spurious events. Nevertheless, the sensitivity of future ton-scale

experiments [17] could be limited by the residual counting rate of detectors, caused mainly by the intrinsic radioactivity of the scintillator material used as the target. Thus, reduction in the radioactive contamination of the material is an issue of primary importance.

Calcium tungstate (CaWO_4) was discovered as a scintillator sixty years ago [18,19]. In Ref. [20] CaWO_4 crystal scintillators, enriched with ^{48}Ca , have been proposed as a detector to search for double- β decay of ^{48}Ca . CaWO_4 is an appropriate material for CPSD and it is currently used by the CRESST experiment to search for dark matter particles [13,14,21–23]. It should be stressed that the radioactive background due to ^{210}Pb and ^{238}U might have more severe implications for dark matter experiments than that of ^{226}Ra , whereas the latter is one of the most dangerous radionuclides for double beta decay experiments. Although the intrinsic radioactivity of the calcium tungstate scintillators used by CRESST seems to be sufficiently low for the experiment to achieve its objectives [22,23] there is a noticeable variation in radiopurity between different CaWO_4 samples [24,25]. These results also show that the U radioactive chain is far from equilibrium: the intrinsic radioactivity of calcium tungstate scintillators is dominated by the decay of ^{210}Pb and daughters. Cebrian et al. [24] measured the intrinsic radioactive background of a CaWO_4 detector due to ^{210}Pb at the level of 900 ± 70 mBq kg^{-1} and ^{210}Po 780 ± 20 mBq kg^{-1} . Zdesenko et al. [25] reported that the α -activity

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of ^{210}Po in a sample of CaWO_4 accounts for $291 \pm 5 \text{ mBq kg}^{-1}$. At the same time the activities of the parent isotopes ^{238}U and ^{226}Ra were measured to be lower by at least one order of magnitude. This large difference in the concentrations of parent and daughter nuclides is clearly associated with the technology used for the production of raw materials and crystals.

It is well known that the production of raw materials and crystal growth can introduce or remove trace elements. This occurs to a major extent at the stage of chemical purification of the raw materials, which exploits for separation the differences in chemical reactivity of elements. This purification is an essential but least controllable production stage. Currently available techniques allow monitoring the content of ^{238}U and ^{232}Th close to $\sim 10^{-12} \text{ g g}^{-1}$ (inductively-coupled plasma mass spectrometry, ICP-MS) and the gamma component of the intrinsic radioactivity of the powder materials down to a level of $\sim 0.1\text{--}1 \text{ mBq kg}^{-1}$ (ultra low-level gamma-spectroscopy with high-purity germanium detectors, HPGe). Selected raw materials of 4N–5N grade used for the growth of CaWO_4 crystals might exhibit a concentration of U and Th close to the detection limits of ICP-MS. Measurements with HPGe detectors show that the activity of gamma-ray emitting radionuclides in such materials can vary from few tens to a few hundreds of mBq kg^{-1} . As further purification can occur during crystal growth [26] this might be considered as acceptable. However, there is uncertainty regarding the contamination of raw materials with specific isotopes, especially the progenies of the final stage of the ^{238}U decay chain, i.e. ^{210}Pb , ^{210}Bi and ^{210}Po . With these isotopes being γ - (low energy), β - and α -emitters, respectively, they are very difficult to detect when present in a powder sample even at 10 mBq kg^{-1} level. At the same time, to achieve the sensitivity levels required for probing currently favoured dark matter models, scintillators with intrinsic radioactivity below 0.1 mBq kg^{-1} are needed [27]. Furthermore, potential contamination cannot be assessed from the activities of the primordial nuclides (^{232}Th , ^{238}U , ^{226}Ra) owing to secular equilibrium being broken.

Conversely, provided the scintillation crystal has been produced already, this specific contamination as well as several other radionuclides can be identified by measuring α -particles from the radiative decay of ^{210}Po and other α -emitting isotopes (see, for instance Refs. [5,8,10,25,26,28,29]). This contamination can deteriorate the radiopurity of scintillation detectors but unfortunately this can be assessed only at the last stage after expensive, laborious and time-consuming efforts associated with the transformation of the raw materials into a crystal. Therefore, it is vitally important to use any opportunity of systematic study in order to gain insight into the origin and the generic features of the radioactive contaminations and to trace them at different stages of the crystal production.

Motivated by this, we endeavour to investigate the effects of recrystallisation on the radioactive contamination of CaWO_4 crystal scintillators. We present an analysis of the results of monitoring the intrinsic radioactivity of scintillating crystals at different stages of their production. This work was inspired by interesting but limited data that became available from what was initially commissioned as a pure production contract, aiming at procurement of a large quantity of CaWO_4 scintillators.

2. Raw materials for the production of CaWO_4 crystals

The raw material for growing the crystals – CaWO_4 powder – was purchased from the NeoChem company (Moscow, Russia), which specialises in the production of raw materials for scintillation crystals. The CaWO_4 powder was synthesised from high-purity grade reagents. All operations were performed using quartz or polypropylene lab-ware, materials with low levels of intrinsic

Table 1

Concentration of impurities in CaWO_4 raw material (batch 1) and CaWO_4 crystal 1-1 measured using ICP-MS.

Element	Concentration (10^{-6} g g^{-1})	
	in CaWO_4 raw material (batch 1)	in CaWO_4 crystal 1-1
Be	≤ 20	–
K	≤ 20	≤ 3
Fe	≤ 75	3.5
Rb	–	≤ 0.005
Sr	3	2.5
Ba	2	0.25
Pb	0.1	0.3
Th	≤ 0.001	≤ 0.0005
U	0.006	0.008

radioactive contamination. Water and acids were further distilled by laminar evaporation in quartz-ware.

Two batches of CaWO_4 raw material were produced. A large lot of 16 kg (batch 1) was synthesised using conventional starting materials, techniques and lab-ware, which have previously been used also for the production of lead tungstate powder. This CaWO_4 powder was immediately dispatched to the crystal producing company to start the growth of the single crystals characterised in this study.

A small amount of the material (50 g, batch 2) was synthesised in new lab-ware, using a designated laboratory setup, from selected starting materials that have been purified further to reduce the level of impurities. This batch of CaWO_4 powder was subjected to extensive investigations in order to clarify how the changes in the synthesis process may affect the intrinsic radioactivity of the compound (see Section 5).

The content of impurities in the calcium tungstate powder from batch 1 and CaWO_4 crystal 1-1 was measured using high resolution ICP-MS (Thermo Fisher Scientific ELEMENT2) at the Gran Sasso National Laboratories of INFN (Italy). A sample of CaWO_4 was etched in a microwave device (using method EPA 3052) with 5 ml ultrapure HNO_3 and 0.5 ml of ultrapure HF. Then the sample was diluted to 40 ml and it was treated in an ultrasound bath at 80°C over two hours to reduce precipitation in the solution. The concentrations of K, Sr, Ba and Pb were measured in semiquantitative mode, while Fe, Th and U were quantified by standard addition technique with three levels of standard spiked to the sample. The uncertainty of the semiquantitative mode is of the order of 20%. The results of these measurements, presented in Table 1, suggest that the raw material can be classified as 4N grade, which is considered to be acceptable to begin with since we expected that recrystallisation should improve the purity of the crystal. Comparison of the results for the raw material and crystals shows that only Ba exhibits a substantial decrease (by one order of magnitude) while the concentration of other impurities (Sr, Th, U) remains effectively the same. One should note, though, that the concentration of Pb increased by a factor of three, which might be an indication of contamination of the crystal by lead at the stage of crystal production. We will get back to this issue in the Discussion section.

3. Production of CaWO_4 crystals

The CaWO_4 crystal scintillators were produced by the Scientific Research Company CARAT (Lviv, Ukraine) from crystal ingots grown using the Czochralski method in an iridium crucible with high frequency heating. Single, new crucible, new screen and new crystal holder were used to grow all crystals under study. The ingots were grown from the CaWO_4 powder of batch 1 and the samples of set 1 were produced. The flow of crystal production is

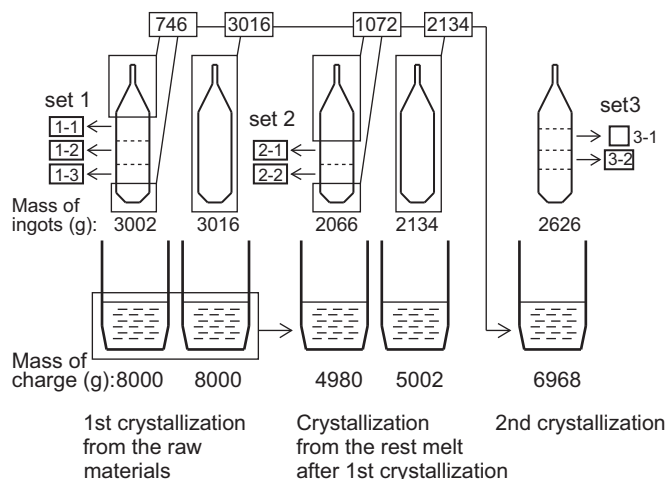


Fig. 1. Flow chart of CaWO₄ crystal growth (the masses of the initial charge for the crystals grown are listed below the sketches of the crucibles). The crystals of set 2 were produced from the ingot grown from the rest of the melt after the 1st crystallisation. The crystals of set 3 were grown from the ingots of sets 1 and 2 (the masses of crystals in grams used for the 2nd crystallisation are in boxes above the images of the crystal ingots). Samples of crystal scintillators are marked as 1-1, 1-2, 1-3 (set 1), 2-1, 2-2 (set 2) and 3-1, 3-2 (set 3).

displayed in Fig. 1. The crystals of set 2 were produced from the ingot grown from the rest of the melt after the 1st crystallisation. Since iridium is a highly brittle metal the rest of the CaWO₄ melt after crystal growth has been removed from the crucible by high-frequency heating. The melted CaWO₄ compound was collected in a ceramic cup. The samples of set 3 were produced from the crystal that was grown from the melted ingots obtained during the two consecutive stages of the 1st crystallisation.¹ A surface layer of about 1 cm of crystal 3-1 (set 3) was removed. The samples were subject to measurements of scintillation properties and radioactive contamination as discussed further.

4. Characterisation of the CaWO₄ scintillating crystals

4.1. Energy resolution to γ -quanta

The side surfaces of all crystals were made to reflect diffusely by applying fine grinding paper (standard ANSI grit size 600), while the upper and lower faces were polished. The crystals were optically connected to a 3" photomultiplier (PMT) Philips XP2412 using the Dow Corning Q2-3067 optical couplant and were covered by 3 layers of polytetrafluoroethylene (PTFE) reflector tape. The measurements were carried out using an ORTEC 572 spectrometric amplifier with 10 μ s shaping time. The crystals were irradiated by γ -quanta from a ¹³⁷Cs source. The best energy resolution was measured for the crystals of set 3. The energy spectrum measured with the crystal scintillator 3-1 is shown in Fig. 2. The energy resolution (full width at half maximum, FWHM) is 6.3% for the 662 keV γ -quanta of ¹³⁷Cs. It is worthwhile mentioning that Moszynski et al. [30] reported an energy resolution for small CaWO₄ samples for the 662 keV γ -quanta of ¹³⁷Cs equal to 6.6%.

¹ We remind the reader that the main goal of the crystal producer was the production of a maximum amount of CaWO₄ crystal scintillator rather than the investigation of effects that recrystallisation has on the radioactive contamination of CaWO₄ crystals. A minimum charge of the crucible of \approx 5 kg is required in the crystal growth procedure. To maximise the utilisation of raw material the melt from the 1st crystallisation was used to produce the second pair of ingots. The ingots obtained in these two growth processes were then melted and used in 2nd crystallisation.

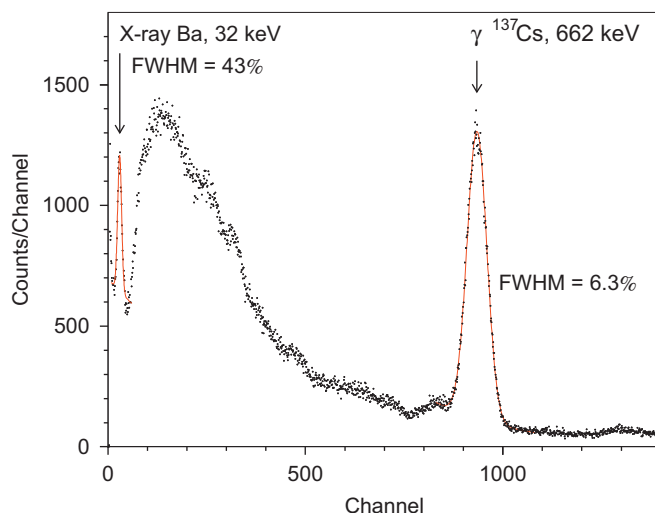


Fig. 2. Energy spectrum of ¹³⁷Cs γ -rays measured for a CaWO₄ scintillation crystal 3-1 (\varnothing 42 \times 40 mm). Fits of X-ray and γ -lines are shown by solid lines.

4.2. Low-background measurement of CaWO₄ crystal scintillators

The radioactive contamination of the crystals was measured in the low-background set-up installed at the Institute for Nuclear Research (INR, Kyiv, Ukraine). In the set-up, a scintillating CaWO₄ crystal covered by 3 layers of PTFE tape was optically connected to a 3" photomultiplier tube Philips XP2412 through a high purity polystyrene light-guide (\varnothing 66 \times 120 mm). The optical contact between the scintillation crystals, the light guide and the PMT was provided through the Dow Corning Q2-3067 optical couplant. The light-guide was wrapped with an aluminised Mylar[®]. The detector was surrounded by a passive shield made of oxygen-free high conductivity (OFHC) copper (5–12 cm thickness) and lead (5 cm thickness).

The energy scale and the resolution of the detectors were determined in calibration runs with ¹³⁷Cs and ²⁰⁷Pb γ -ray sources. The values of the energy resolution for 662 keV γ -quanta of ¹³⁷Cs and the 2615 keV γ -line of ²⁰⁸Tl (presented in background spectra, see Section 4.3) are listed in Table 2. The energy resolution becomes slightly worse due to the light-guide used in the low-background set-up. The energy calibration of the detector was checked with the γ -ray lines at 662 keV (¹³⁷Cs) and at 2615 keV (²⁰⁸Tl), present in the background spectra.

The response function to α -particles in a wide energy interval is given in Ref. [25]. Above α -particle energies of 2 MeV the α/β ratio² increases, following the relationship $\alpha/\beta = 0.129(12) + 0.021(3) \times E_{\alpha}$, where E_{α} is the energy of the α -particles in MeV.

In the present study the α/β ratio was measured for crystals 1-3 and 2-2 using collimated α -particles of an ²⁴¹Am source. The values of the α/β ratio for the two crystals, as well as the α/β ratios determined by analysis of the α -peaks from internal ²¹⁰Po (see Section 4.3), are presented in Table 2. Some difference in the α/β ratio for different detectors can be explained by different (and in most of the cases, irregular) shapes of the crystals. It should be noted that the α/β ratio is not only a property of a crystal, but more likely a certain characteristic of the scintillation detector, such as the shape, size, surface treatment, transparency, shaping time of electronics, etc. [31].

² The α/β ratio is defined as ratio of the α -peak position in the energy scale measured with γ -sources to the energy of α -particles. Because γ -quanta interact with the detector producing β -particles, we use the more convenient term of " α/β ratio".

Table 2
Properties of the CaWO₄ crystal scintillators (see text for details).

Set	Sample	Sizes (mm)	Mass (g)	FWHM (%) at 662 keV/2615 keV	α/β ratio		Live time of low-background measurements (h)
					External α-source	Internal ²¹⁰ Po	
1	1-1	∅60 × 42	740	11.3/6.6	–	0.241(5)	2.822
1	1-2	∅60 × 42	740	9.7/4.5	–	0.242(5)	2.583
1	1-3	∅60 × 42	740	10.0/4.6	0.23(1)	0.243(5)	2.672
2	2-1	Prism	473	9.8/4.9	–	0.26(1)	3.465
2	2-2	42 × 41 × 41	484	10.3/5.7	0.26(1)	0.25(1)	17.389
3	3-1	∅40 × 42	328	8.2/4.3	–	0.233(5)	18.644
3	3-2	∅60 × 42	740	8.3/4.4	–	0.231(5)	2.717

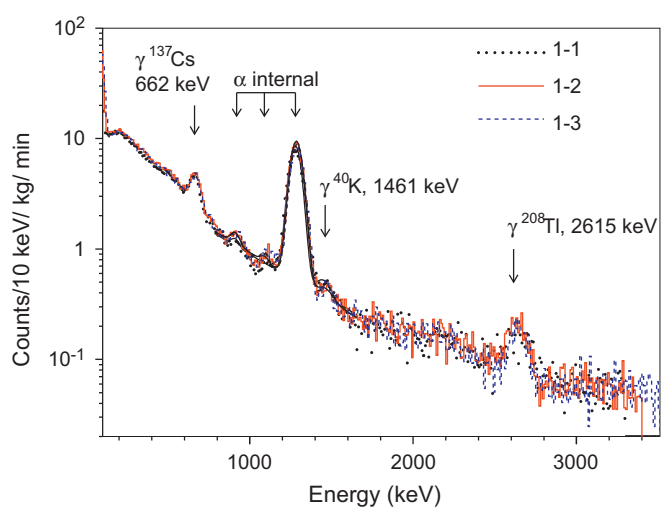


Fig. 3. Energy spectra of three CaWO₄ scintillators from set 1 measured in the low-background set-up. The levels of background for the crystals are within the statistical uncertainties indistinguishable from each other.

Finally, it is important to emphasise that the energy resolution of the crystals of set 3 is better (FWHM ≈ 8% at the 662 keV γ -line of ¹³⁷Cs) in comparison to set 1 (FWHM ≈ 10–11%). This demonstrates that the recrystallisation procedure improves the energy resolution of CaWO₄ crystal scintillators.

4.3. Radioactive contamination of the CaWO₄ crystal scintillators

In order to discriminate α -events from $\gamma(\beta)$ background, pulse shapes were measured with a 12 bit 20 MS/s transient digitizer developed in Ref. [32]. The technique of pulse-shape discrimination [25] allows determination of the origin of α -peaks in the background spectra of the CaWO₄ detectors.

The energy spectra of the three CaWO₄ crystals of set 1, normalised to their mass and live time of the measurements are shown in Fig. 3.

There are some peaks in the spectra caused by external γ -quanta: 662 keV of ¹³⁷Cs (contamination of the set-up due to the Chernobyl accident); 1461 keV of ⁴⁰K and 2615 keV of ²⁰⁸Tl (²³²Th family). The background count rates of all three detectors are practically the same. The peaks with energies in the energy interval 0.8–1.3 MeV can be attributed to an internal contamination with α -active U/Th nuclides. The α -nature of these peaks was confirmed through pulse-shape discrimination (see Fig. 4).

The peak in the energy spectra of the crystals of set 1 (see Fig. 5a) at the energy ≈ 1.28 MeV can be attributed to ²¹⁰Po pollution (daughter of ²³⁸U from the ²³⁸U family, $E_\alpha = 5304$ keV) with an activity of (1.32 ± 0.02) Bq kg⁻¹. The peak near 0.9 MeV is due to

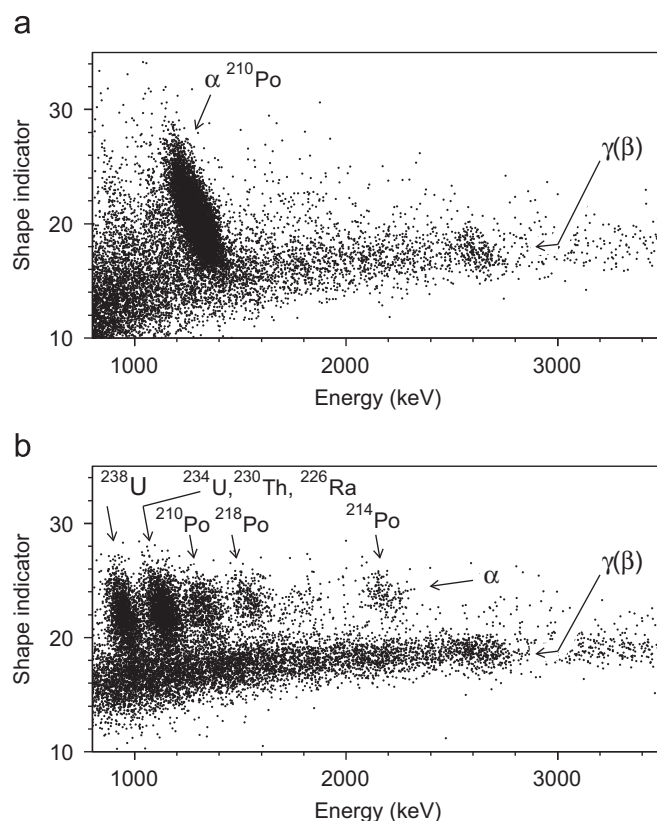


Fig. 4. Scatter plot of the shape indicator (see Ref. [25]) versus the energy for background exposure of CaWO₄ crystal scintillators. (a) Sample 1-2: live time of the measurement 2.12 h and (b) sample 2-2: measured for 1.10 h. The populations of α -events are well separated from the γ -quanta distributions. The difference in the energy distribution of α -events of the crystals from different sets is clearly visible.

²³⁸U with an activity of (0.05 ± 0.01) Bq kg⁻¹, while ²³⁴U, ²³⁰Th and ²²⁶Ra contribute to the peak at 1.08 MeV with the area corresponding to the activity of (0.03 ± 0.02) Bq kg⁻¹. The total α -activity in the crystal is (1.40 ± 0.03) Bq kg⁻¹. A fit of the energy spectra in the energy region, 0.74–1.65 MeV, by a model consisting of Gaussians (to describe the α -peaks) and exponentials (in order to simulate background from external γ -rays)³ is shown in Fig. 5a. The activity of ²²⁶Ra can be estimated by analysing the α -peak of ²¹⁸Po ($E_\alpha = 6002$ keV): one should observe an α -peak with an energy of

³ It is known that the exponential function describes radioactive background of scintillation detectors adequately. Nevertheless we have been trying to apply a more sophisticated method of the background simulation (see below and Fig. 6). As a result the calculated areas of α peaks were similar (within uncertainties) to those obtained from the exponential approximation. Besides, the fit of background by an exponent is simpler and less dependant on the choice of the fitting interval.

1.53 MeV on the γ -scale. However, there is no visible peak at this energy in the spectra of set 1, whereas the peak of ^{218}Po is identified in the spectra of the crystals of set 2 (see Figs. 4b and 5b). Thus one can only set an upper detection limit on the activity of ^{226}Ra (see Table 3). Similarly, an α -peak with energy in the γ -scale near 0.78 MeV is expected for ^{232}Th . The fit of the energy spectra gives only an upper detection limit on the ^{232}Th activity in all the crystals. Since the equilibrium in the thorium chain can be broken between ^{232}Th and ^{228}Th , we estimated the activity of ^{228}Th by analysing the

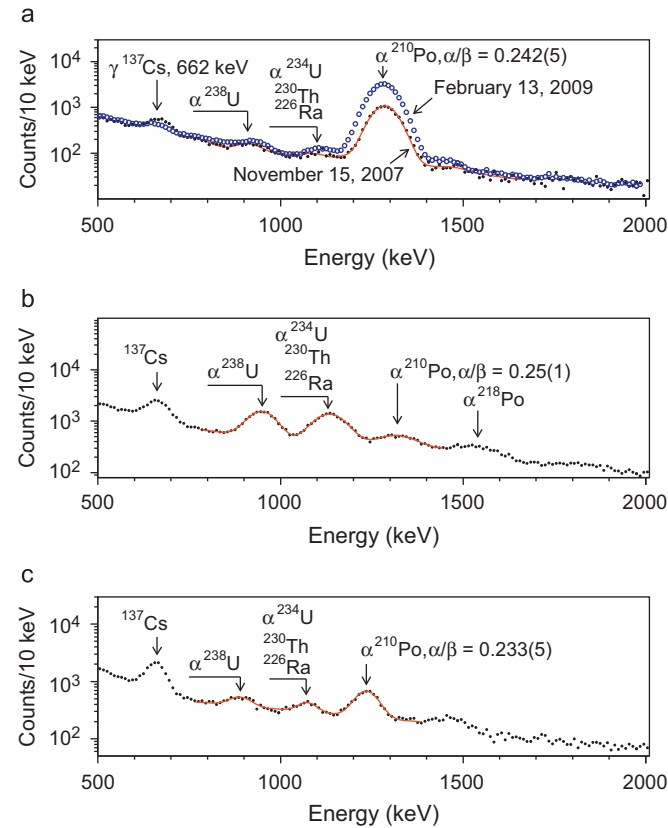


Fig. 5. Part of the energy spectra of CaWO_4 crystal scintillators of set 1, 2 and 3 measured in the low-background set-up (a) 1-2: 2.583 h, (b) 2-2: 17.389 h and (c) 3-1: 18.644 h. Fits of alpha-peaks are shown as solid lines. (a) Energy spectrum accumulated 454 days after the first measurement with the CaWO_4 crystal 1-2 is shown by circles (time of measurement is 22.289 h). One can clearly identify an increase in the ^{210}Po activity in the sample.

Table 3
Radioactive contamination of the CaWO_4 crystals. Upper limits given with $k=1$ and ca. 68% confidence level. Data for CaWO_4 from Ref. [25] and for CaMoO_4 from Ref. [37] are given for comparison.

Nuclide	Activity (mBq kg^{-1}) in crystal								[25]	[37]
	1-1	1-2	1-3	2-1	2-2	3-1	3-2			
^{232}Th	≤ 9	≤ 14	≤ 22	≤ 48	≤ 25	≤ 30	≤ 34	0.7(1)	≤ 1.5	
^{228}Th	≤ 6	≤ 14	≤ 11	≤ 10	≤ 12	≤ 8	≤ 13	0.6(2)	0.04(2)	
^{238}U	38(14)	54(12)	67(14)	330(17)	268(20)	51(8)	48(11)	14(5)	≤ 1.5	
Sum of ^{234}U , ^{230}Th , and ^{226}Ra	29(14)	26(17)	39(16)	321(14)	260(16)	37(6)	40(10)	–	–	
^{226}Ra	≤ 10	≤ 11	≤ 37	72(16)	107(11)	≤ 21	≤ 15	5.6(5)	0.13(4)	
$^{210}\text{Pb}^a$	4500(200)	4800(200)	4500(200)	≤ 190	≤ 360	≤ 590	≤ 690	≤ 430	≤ 17	
^{210}Po	1244(17)	1316(17)	1243(16)	26(9)	55(6)	151(8)	176(10)	291(50)	≤ 8	
Total α -activity U/Th	1310(30)	1400(30)	1340(30)	670(30)	580(30)	240(20)	260(20)	400	–	
^{40}K	≤ 37	≤ 40	≤ 39	≤ 44	≤ 98	≤ 21	≤ 33	< 12	≤ 3	
^{90}Sr – ^{90}Y	≤ 44	≤ 48	≤ 48	≤ 50	≤ 114	≤ 26	≤ 38	< 70	≤ 23	

^a Activity of ^{210}Pb in the crystals of set 1 was calculated on the basis of the measured ^{210}Po activity. It is assumed that accumulation of ^{210}Po follows the behaviour observed for the CaWO_4 crystal sample 1-2 (see text and Fig. 7). The limits on the activity of ^{210}Pb in the crystals of sets 2 and 3 were calculated following the same consideration (see text).

α -spectra in the energy region where two α -peaks with energies 1.65 (^{220}Rn , $E_\alpha=6228$ keV) and 1.83 MeV (^{216}Po , $E_\alpha=6778$ keV) are expected. The results of these estimates for ^{232}Th and ^{238}U in the crystals of set 1 are listed in Table 3.

The energy spectrum of the CaWO_4 scintillator 2-2 is shown in Fig. 5b. The activities of ^{210}Po , ^{238}U and the sum of ^{234}U , ^{230}Th and ^{226}Ra are substantially different from those observed in set 1 (see Table 3). The ^{238}U activity is much larger than what can be attributed to accumulation of U (an activity of 0.3 Bq kg^{-1} corresponds to $\approx 0.02 \times 10^{-6} \text{ g g}^{-1}$ of U). We recall that the crystals of set 2 were grown from the melt that was collected after the production of set 1 of CaWO_4 crystals. In order to remove the rest of the CaWO_4 compound after the crystal growth, the crucible was heated by high-frequency, and the melt left flowing into a ceramic cup. It is well known that ceramics can be contaminated by U/Th (see Ref. [33]), which may explain the increased uranium contamination in the crystals of set 2. Interestingly, the activity of ^{210}Po is one order of magnitude lower than that of the crystals of set 1. Finally, set 3 of the crystals exhibits an increase in the activity of ^{210}Po and a decrease in the activity of U and Th (see Fig. 5c and Table 3).

In order to estimate the presence of β -active isotopes (^{40}K , ^{90}Sr and ^{90}Y , some U/Th daughters such as $^{234\text{m}}\text{Pa}$, ^{214}Pb , ^{214}Bi , ^{210}Pb , ^{210}Bi , ^{228}Ac , ^{212}Bi , ^{208}Tl) in the samples the measured background spectra of the CaWO_4 detectors were simulated with the GEANT4 package [34,35]. The initial kinematics of particles emitted in β -decays of nuclei and subsequent nuclear de-excitation processes were generated with the DECAY0 event generator [36]. There are no clear features in the spectra, which could be identified as internal trace contamination of the β -active nuclides. Thus, only upper detection limits on activities of β -active isotopes can be determined on the basis of the experimental data. The background spectra were fitted in the energy interval 0.1–3.0 MeV by the model, which also includes Monte Carlo simulated distributions able to describe the external γ -background from the materials of the set-up. Upper detection limits of activities from the β -active radionuclides ^{40}K and ^{90}Sr – ^{90}Y in the CaWO_4 crystals are listed in Table 3. The fit of the background spectrum of crystal 3-2 by this model in the energy interval 0.1–3.0 MeV and the main components of the background are shown in Fig. 6.

The complete summary of the measured radioactive contamination of the CaWO_4 crystals is given in Table 3. The table also includes the data for CaWO_4 from Ref. [25] and CaMoO_4 [37].

It should be stressed that we observed no difference in radioactive contamination of the crystals of set 3 (crystal 3-1 with removal of ≈ 1 cm surface layer and crystal 3-2 with no machining

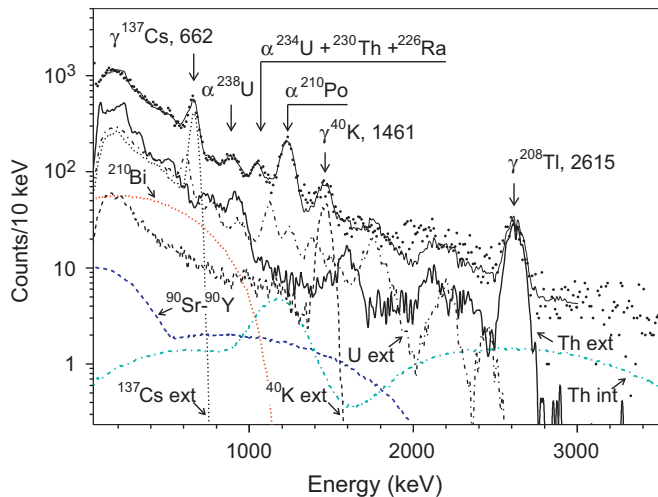


Fig. 6. Energy spectrum accumulated in the low-background set-up with CaWO₄ crystal scintillator 3-2 ∅ 60 × 42 mm over 2.717 h together with the model of the background. The main components of the external (¹³⁷Cs ext, ⁴⁰K ext, U ext, Th ext) and internal backgrounds (²¹⁰Bi, ⁹⁰Sr–⁹⁰Y, Th int) are shown (see text for details). The fit of the spectrum is shown by the solid line. Energies of γ-lines are given in keV.

of the side surface). Similarly, no significant difference was noticed in the contamination of samples from different parts of the ingot, though such effects were clearly observed in CdWO₄ crystal scintillators [38].

The radioactive contamination of a sample cut from CaWO₄ crystal 1-1 (with mass 142.2 g) was also tested at the Laboratoire Souterrain de Modane (LSM) with a germanium detector for gamma-ray spectrometry at a depth of 4700 m w.e. The rock overburden attenuates the muon flux by about a factor of 10⁶ compared to sea level.

The low-background planar Ge-detector was developed by the LSM and built by Canberra-Eurysis. In order to reduce the intrinsic background, all materials used for detector construction were carefully selected. The planar crystal geometry, 80 mm diameter and 30 mm thickness, provides good efficiency and good resolution for energies below 600 keV. The detector is shielded against environmental gamma-rays by a lead shield. The airborne Rn is suppressed by continuously flushing the sample chamber with air from a radon-trapping facility.

There is a clear 46.5 keV peak of ²¹⁰Pb in the energy spectrum accumulated over 115.12 h with the crystal sample, which corresponds to the activity of this radionuclide at the level of 4740 ± 570 mBq kg⁻¹. We have also observed some excess of events (in comparison to data of background measurements) in the 352 keV γ-line of ²¹⁴Pb, which indicates presence of ²²⁶Ra in the sample with activity of 4 ± 2 mBq kg⁻¹. The concentration of radioisotopes in the CaWO₄ crystal sample is determined from the intensities of the relevant gamma-lines in the energy spectrum. Monte Carlo simulations using the GEANT3.21 code are used to account for the detector counting efficiency. The accuracy of the simulation results has been tested with the certified standard material RGU of the IAEA. The agreement between the simulated and the experimental results is better than 5%. For other radionuclides of the ²³²Th and ²³⁸U families, as well as for ⁴⁰K and ⁶⁰Co, we have obtained only limits. In order to calculate the limits on activities that have not been observed (the minimum detectable activities, MDA) the relations derived by Hurtgen et al. [39] were used, which take into account low counting rates. The limits are reported with a coverage factor *k*=2. The summary of the measurements are presented in Table 4.

Juxtaposition of the data on the activity of ²¹⁰Pb with the results of earlier measurements of the radioactive contamination in sample 1-1

Table 4

Activity concentration of primordial radionuclides for the CaWO₄ sample cut from the crystal 1-1 measured by ultra-low background HPGe γ-spectrometry. The uncertainties given are expanded combined standard uncertainties and the limits are determined with *k*=2.

Chain	Isotope	Activity or MDA (mBq kg ⁻¹)
²³⁸ U	²³⁴ Th	< 165
	²²⁶ Ra	4 ± 2
	²¹⁰ Pb	4740 ± 570
²³² Th	²²⁸ Ra	< 6
	²²⁸ Th	< 7
	⁴⁰ K	< 36
	⁶⁰ Co	< 4

from Table 3 indicates that the progeny (²¹⁰Po) had much lower activity than the parent nuclide (²¹⁰Pb) at the time of that measurement. Given that the equilibrium in the chain of radioactive decay is usually broken during material purification and production of crystals, this is expected. Such difference demonstrates that the as-grown crystal contains essentially a lower amount of ²¹⁰Po. Since the half-life time of ²¹⁰Pb (*T*_{1/2}=22.3 years [40]) is much longer than that of ²¹⁰Po (138.376 days [40]) the increase in ²¹⁰Po activity with time is due to the accumulation of this isotope following the decay of ²¹⁰Pb. Hence, it is sensible to state that the measurements of the change of ²¹⁰Po activity with time give the possibility to evaluate the initial activity of ²¹⁰Pb in the sample.

To verify this assumption the CaWO₄ crystal scintillator 1-2 was examined 454 and 809 days after the first measurement in the scintillation low-background set-up in Kyiv. The energy spectrum (accumulated over 22.289 h) 454 days after the first measurement is displayed in Fig. 5a. The spectrum shows clearly the increase in the ²¹⁰Po activity in the sample. The time dependence of ²¹⁰Po activity was determined using the sum of exponential functions that describe the decay of initial ²¹⁰Po and the accumulation of ²¹⁰Po after the decays of ²¹⁰Pb and ²¹⁰Bi:

$$A(^{210}\text{Po}) = A_0(^{210}\text{Po})e^{-t\lambda_3} + N_0(^{210}\text{Pb})(a_1e^{-t\lambda_1} + a_2e^{-t\lambda_2} + a_3e^{-t\lambda_3}) \quad (1)$$

where

$$a_1 = \frac{\lambda_1 \lambda_2}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)}, \quad a_2 = \frac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} \quad \text{and} \\ a_3 = \frac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)}$$

A(²¹⁰Po) is the time dependant activity of ²¹⁰Po in the crystal, *A*₀(²¹⁰Po) is the initial activity of ²¹⁰Po in the crystal at the time of crystal production, *N*₀(²¹⁰Pb) is the initial quantity of ²¹⁰Pb in the crystal at the time of the crystal production, λ₁ is the decay constant of ²¹⁰Pb, λ₂ is the decay constant of ²¹⁰Bi (*T*_{1/2}=5.013 days [40]) and λ₃ is the decay constant of ²¹⁰Po.

The fit of the data presented in Fig. 7 shows that the activity of ²¹⁰Po in the crystal at the time of its production was less than 0.05 Bq kg⁻¹. Therefore, ²¹⁰Po appeared in the crystals mainly as a product of ²¹⁰Pb decay and the activity of ²¹⁰Po observed in the sample is directly linked to the contamination of the crystals by ²¹⁰Pb. Based on this it is possible to calculate the initial activity of ²¹⁰Pb in the CaWO₄ scintillator at the time of crystal production as (4.8 ± 0.2) Bq kg⁻¹. The value is in good agreement with the result of measurements by ultra-low background HPGe γ-spectrometry, which gives 5.0 ± 0.6 Bq kg⁻¹ as activity of ²¹⁰Pb in crystal 1-2 at the time of production. Finally, assuming such a relation between ²¹⁰Pb and ²¹⁰Po in the crystals of set 1, we made respective estimates of the ²¹⁰Pb activity in the samples. We do not know the activity of initial ²¹⁰Po in other crystals; therefore we set only

limits on the activity of ^{210}Pb in the samples of sets 2 and 3 under test (see Table 3).

5. Radioactive contamination of advanced CaWO_4 powder

5.1. γ -ray spectrometry of advanced CaWO_4 raw material

Radioactive contamination of a sample of CaWO_4 powder (batch 2) was tested at the LSM with the same germanium detector used to screen the CaWO_4 crystal (see Section 4.3).

The measured sample of the CaWO_4 powder was placed in a plastic box of 80 mm diameter and 4 mm powder thickness (the mass of the CaWO_4 sample was 45.72 g). The measurements were carried out for over 133.814 h.

The results are summarised in Table 5. The ^{226}Ra , ^{228}Ra and ^{228}Th activity concentrations are determined using the gamma-emitters given in the 3rd column. For the ^{232}Th daughters only upper detection limits could be determined: the ^{228}Ra concentration is $< 19 \text{ mBq kg}^{-1}$ and that of ^{228}Th is $< 7 \text{ mBq kg}^{-1}$. Regarding the ^{238}U decay chain, for ^{234}Th a limit on activity of $< 31 \text{ mBq kg}^{-1}$ is set and for ^{226}Ra the activity $(19 \pm 5) \text{ mBq kg}^{-1}$ has been measured. The large uncertainty in the specific activity of ^{226}Ra is caused by low statistics.

The ^{210}Pb concentration is of particular importance in this work. The number of counts measured for the 46.5 keV γ -line of ^{210}Pb is 5.5 ± 3.5 counts. As the number of counts is compatible with the

intrinsic background of the detector, the minimum detectable activity has been obtained. The calculated full peak efficiency for 46.5 keV is 18.4% (normalised to 100% emission probability). A concentration of $< 47 \text{ mBq kg}^{-1}$ was determined for ^{210}Pb .

5.2. Measurements of the α -activity of CaWO_4 powder

The measurement of the activity of weakly radioactive α -emitting solid state materials requires the application of special techniques because of the short range of α -particles. We obtained a first estimate of the activity due to radionuclide contamination using a 'thick-source' alpha counting technique that was originally developed for application in medical physics [41], and is a fairly sensitive and low-cost method for the measurements of low-level alpha radioactivity [42].

A thick layer of a powder sample from batch 2, total weight of 14 g, was placed on a prefabricated zinc sulphide scintillation screen (diameter 42 mm). Alpha particles from the sample passing through ZnS produce scintillation light that is detected by a photomultiplier positioned directly below the screen. After deduction of background $(0.04 \pm 0.02) \times 10^{-3} \text{ s}^{-1}$ the measured count rate induced by alpha particles from the sample was found to be $(0.15 \pm 0.02) \times 10^{-3} \text{ s}^{-1}$. On the basis of the examination of the spectra obtained by high resolution gamma spectroscopy for the sample, it was hypothesised that it contains only a single radionuclide source, probably ^{210}Po . If this was the case, the measured activity due to α -particles, converted to a specific activity, assuming an alpha energy of 5 MeV, a range of $1.21 \times 10^{-2} \text{ g cm}^{-2}$ [43] and a uniform distribution of sources within the material, would be $3.6 \pm 0.4 \text{ Bq kg}^{-1}$. The uncertainty (standard deviation) was assessed on the basis of the counting statistics and includes a nominal allowance for the uncertainty in the value of the range of α -particles in CaWO_4 .

In order to have independent confirmation of this estimate, another measurement was done at the Laboratori Nazionali del Gran Sasso (LNGS) in Italy using commercial detectors for α -spectroscopy [Canberra-Eurysis alpha spectrometer, model 7401VR, with a 1200 mm^2 Passivated Implanted Planar Silicon (PIPS[®]) detector]. This detector has a background count rate of (8 ± 1) counts per day (the uncertainty given is a combined standard uncertainty) in the region of interest of 1.0–5.4 MeV. A sample of CaWO_4 powder weighing $5.9 \pm 0.1 \text{ g}$ was placed on a polystyrene disc with dimensions $\varnothing 38 \times 2 \text{ mm}$. The distance to the PIPS[®] detector was 8 mm. The measurement was carried out over 14.03 days. The detector efficiency was determined with a Monte Carlo simulation using the GEANT3.21 package. The results are listed in Table 6.

The alpha activity of the CaWO_4 powder from batch 2 was re-measured two years after the first measurements. The test was

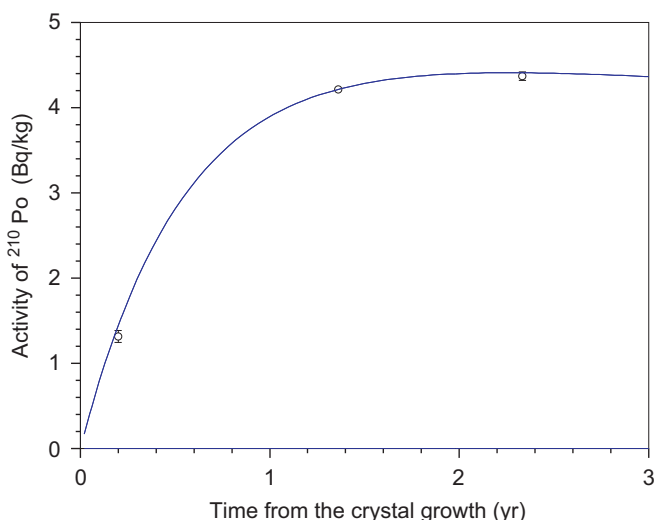


Fig. 7. Dependence of ^{210}Po activity in CaWO_4 crystal scintillator 1–2 on time after crystal growth (circles). The fit of the data by an exponential function, describing the increase in ^{210}Po due to the decay of ^{210}Pb , is shown as solid line.

Table 5
Activity concentration of primordial radionuclides for the CaWO_4 powder sample (batch 2). The uncertainties given are expanded combined standard uncertainties, the MDA is determined with $k=2$. GE stands for gamma-emitters used to determine the activity of ^{226}Ra , ^{228}Ra and ^{228}Th isotopes.

Chain	Isotope	GE	E (keV)	Counts	Counts in background	Activity or MDA (mBq kg ⁻¹)
^{238}U	^{234}Th	–	63	5.5 ± 2.9	< 1.9	< 31
	^{226}Ra	^{214}Pb	352	14.9 ± 4.2	1.7 ± 0.7	19 ± 5
	^{210}Pb	–	46.5	5.5 ± 3.5	7.4 ± 0.8	< 47
^{232}Th	^{228}Ra	^{228}Ac	338	< 2.3	< 1.4	< 19
	^{228}Th	^{212}Pb	238	6.0 ± 3.7	3.4 ± 1.0	< 7
	^{40}K	–	1461	4.5 ± 2.7	2.7 ± 0.8	< 120
	^{60}Co	–	1173	< 2.1	0.4 ± 0.3	< 7
	–	–	1332	< 2.1	0.7 ± 0.3	–

Table 6

Activity of ^{210}Po for CaWO_4 powder sample (batch 2) determined in a measurement at the LNGS (the uncertainties given are combined standard uncertainties). The absolute number of counts in the sample measurements and the background measurement has been normalised for the duration of the sample measurement (14.03 days).

Isotope	E (MeV)	Gross counts in the energy interval 1.0–5.4 MeV	Background counts in the energy interval 1.0–5.4 MeV	Net counts	Activity (Bq kg^{-1})
^{210}Po	5.3	156 ± 12	117 ± 11	39 ± 16	5 ± 2

performed at the LSM using a low background PIN diode α -spectrometer with an area of 400 mm^2 . First, the 3.7 g sample of CaWO_4 powder was measured directly over 112.55 h. The detection efficiency was evaluated using the GEANT3.21 code to be 2%. This direct measurement gave a limit on the ^{210}Po activity in the sample of $< 1.8 \text{ Bq kg}^{-1}$. As a next step a chemical deposition of polonium on a silver plate [44] was carried out in order to improve the sensitivity of measurement. After 165.53 h of obtaining data a limit could be set on the activity of ^{210}Po in the CaWO_4 powder of $< 0.2 \text{ Bq kg}^{-1}$ (the MDA is determined with $k=2$). This result can be explained by the decay of ^{210}Po over two years. Since the content of parent nuclide ^{210}Pb in this batch is very low, decaying ^{210}Po nuclei are not replenished. Taking into account the half-life of this isotope, its activity at the time of the last measurements should be in the range $0.1 - 0.18 \text{ Bq kg}^{-1}$, which is below the sensitivity of the method.

Comparing the results of α -spectrometry (Table 6) with the ones of γ -ray spectrometry (Table 5) one can see that the activity of ^{210}Po in the CaWO_4 powder was at least hundred times higher than the activity of its parent radionuclide ^{210}Pb . One may conclude that the purification process that had been used to produce batch 2 of the CaWO_4 powder is quite efficient in removing ^{210}Pb , which is the main source of contamination of the crystals produced from batch 1. Therefore the purification process can be used to produce starting material to grow radiopure CaWO_4 crystals via recrystallisation.

6. Discussion

The variation in activities of U daughters in the crystals from different sets is presented in Fig. 8. The striking feature of this plot is the anti-correlation between the activities of ^{210}Po and other alpha emitters from the ^{238}U chain in samples from different experimental sets. It has been demonstrated that the contamination of the crystals by ^{210}Po is predominantly due to the decay of ^{210}Pb . We suggest that ^{210}Pb is produced in the crystals owing to the decay of ^{238}U and not due to external contamination⁴. In this case, the activity of ^{210}Pb derived from that of ^{210}Po should show the same trend.

The analysis of the diagram from Fig. 8 suggests that ^{210}Pb and U impurities exhibit different tendencies during recrystallisation, U in particular is most likely to remain in the melt. The physical and chemical properties of the elements govern the propensity for their accumulation in the CaWO_4 crystals. It should be noted that PbWO_4 and CaWO_4 have the same structure (scheelite). These compounds exhibit good reciprocal solubility and can form complex crystal

⁴ Natural lead is usually contaminated by ^{210}Pb at a level of $10^2 - 10^3 \text{ Bq kg}^{-1}$. To explain the measured activity of ^{210}Pb in the crystals of set 1 it is necessary to include that the concentration of lead in the samples is at the level of $\sim 50 - 500 \text{ ppm}$. The results of ICP-MS measurements give a concentration of Pb that is by more than two orders of magnitude lower.

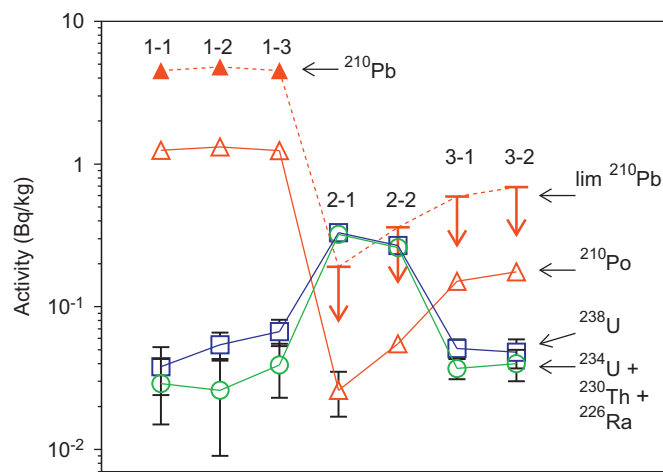


Fig. 8. Dependence of radioactive contamination of CaWO_4 crystals on growing conditions. Data for the samples are marked as 1-1, 1-2, 1-3 (set 1), 2-1, 2-2 (set 2) and 3-1, 3-2 (set 3). The activity of ^{210}Pb in the samples of set 1 is derived from the activity of ^{210}Po assuming that the accumulation of this nuclide in all samples of set 1 has the same trend as that in sample 1-2 (see text). Upper limits on activity of ^{210}Pb in the samples of sets 2 and 3 are shown by arrows.

mixtures such as $\text{Ca}_x\text{Pb}_{1-x}\text{WO}_4$ [45]. The ionic radius of $^{\text{VIII}}\text{Pb}^{2+}$ (0.143 nm) albeit larger than $^{\text{VIII}}\text{Ca}^{2+}$ (0.126 nm) permits accommodation of the impurity at a relatively big eight-coordinated site of the calcium ion in the scheelite structure of CaWO_4 .

On the other hand uranium forms four phases with tungstate: $\text{U}(\text{WO}_4)_2$, UW_3O_{11} , UW_4O_{14} and UW_5O_{17} , but not UWO_4 [46]. These alien phases are rejected by crystal during the growth. Thorium, exhibiting chemical properties fairly similar to uranium, is expected to behave in the same way. The ionic radius of $^{\text{VIII}}\text{Ra}^{2+}$ is too large (0.162 nm) [47], which precludes accommodation of this ion at Ca site.

The assumption that U is rejected by the crystals received support from the data obtained for set 3. These samples were produced from a mixture of the crystals taken from the 1st (low U content) and 2nd (high U content) set. Certain parts of the 1st and 2nd set crystals were mixed, which allowed to estimate the activity of ^{238}U in the melt as $A_0(^{238}\text{U}) \approx 0.17 \text{ Bq/kg}$. The activity of ^{238}U in the crystals of set 3 was reduced to the level of $A(^{238}\text{U}) \approx 0.05 \text{ Bq/kg}$. Using the simple formula

$$A(^{238}\text{U}) = s_U A_0(^{238}\text{U}) \quad (2)$$

we estimate the segregation coefficient for uranium $s_U \approx 0.3$.

It should be noted though that we do not exclude additional contamination of the crystals of set 2 by U due to contact with the ceramic cup used to collect the rest of the melt after the 1st crystallisation. Furthermore, analysis of U contamination in the crystals of sets 1 and 2 have demonstrated that the high activity of ^{238}U in the crystals of set 2 cannot be explained without considering some intake of U. Contamination through the environment could be caused by the contact of the melt with ceramics at high temperature.

It is obvious that the equilibrium of the ^{238}U chain in the CaWO_4 crystals is broken: the activities of ^{238}U and ^{226}Ra as well as of initial ^{210}Po in the crystals are substantially lower than that of ^{210}Pb . These data agree with the results of other numerous studies of radioactive contamination of scintillation crystals (see, for instance, [5,8,10,16,25,26,28,29,37,48]).

Behaviour of ^{210}Pb is much more complicated and cannot be explained only by segregation. The possibility of evaporation of lead oxide from the melt during the growing process must also be taken into account. Indeed, the vapour pressure of PbO is $\approx 4.6 \text{ mm Hg}$, whereas uranium (U_2O_4) and thorium oxides (ThO_2) have

vapour pressures of 1.1 and 2.4 mm Hg, respectively (all data at 1000 °C) [49]. Hence lead can evaporate from the melt (the melting temperature of calcium tungstate is ≈ 1600 °C), which leads to a decrease in its concentration in the melt. Therefore segregation of lead needs further study. Both ICP-MS analysis of lead contamination and low-counting measurements of ^{210}Pb activity in powder and grown crystals can be applied.

Recrystallisation can be useful for reducing the concentration of U and Ra. But in order to use this approach the raw materials should be clear of ^{210}Pb . Given the technical difficulties of detection of this elusive element, the best recommendation may be to ensure that no traces of ^{210}Pb are detected in the raw materials by any of the accessible techniques. One of the most sensitive tests for estimating the contamination of the raw material with ^{210}Pb could be the growth of small samples of CaWO_4 crystal scintillators with subsequent measurements (in low background conditions) of the ^{210}Po activity during several months using pulse-shape discrimination. This method can provide sensitivity to ^{210}Pb in CaWO_4 crystal scintillators at a level of ≈ 0.1 mBq kg $^{-1}$. Only if the activity of ^{210}Pb in raw materials is sufficiently low one may expect that the crystals produced from such raw materials have a chance to satisfy the severe requirements of rare events search experiments. A promising result of specially produced CaWO_4 powder of batch 2 demonstrates a possibility to improve the radiopurity related to ^{210}Pb by two orders of magnitude.

Finally, additional care should be taken to avoid external contamination during crystal growth and processing. First of all, the ceramic parts of facilities used for crystal production can be a source of ^{40}K , U and Th contamination. Currently we cannot completely exclude the possibility of some external contamination of CaWO_4 crystals by U and ^{210}Pb (as well as by any other detrimental impurities) during the stages of crystal growth, handling and annealing. These issues must be carefully addressed and examined in future studies.

In summary we suggest a programme of research and development aiming to deliver CaWO_4 scintillation detectors of high purity for low count rate experiments. The principal stages of this programme are identified as follows:

1. Deep purification of the raw materials is the primary concern that needs addressing. Metal purification by vacuum distillation, zone melting and filtering are very promising approaches (see, Refs. [50,51]), while further study is necessary for the purification of Ca in order to achieve the required low level of radioactive contamination.⁵
2. Screening of the raw materials for crystal growth through ICP-MS and ultra low background γ -, β - and α -spectroscopy must be done as a compulsory stage of material selection and preparation process.
3. Two- to four-step recrystallisation is required, which also includes inspection of the produced scintillators after each stage.
4. All work should be done using highly pure reagents, lab-wares and water. All chemical processes should be carried out in a clean room, and as far as possible, in radon-free nitrogen atmosphere. Protection from radon has to be foreseen, especially during the final stage of the detector production and storage in order to avoid the plating-out of radon daughters.

Finally, it is worthwhile stressing that the recrystallisation procedure with the main aim to reach higher levels of radiopurity

will also improve the energy resolution of CaWO_4 crystal scintillators.

7. Conclusions

Seven CaWO_4 scintillation crystals were fabricated from three ingots that have been grown using the recrystallisation procedure. The radioactive contamination of the crystals was investigated and it was found that ^{210}Po and ^{238}U constitute the dominant fraction of the intrinsic α -background. The equilibrium of the ^{238}U chain in the crystals is broken.

It is demonstrated that the recrystallisation process causes significant changes in the radioactive contamination of CaWO_4 crystals. It leads to a significant variation in the activity of ^{210}Po (in the range 0.03–1.32 Bq kg $^{-1}$) and ^{238}U (0.04–0.33 Bq kg $^{-1}$) in the crystals. The increase in ^{210}Po activity with time evidenced that ^{210}Po is mainly produced due to ^{210}Pb decay. This finding permitted to carry out the quantitative assessment of the contamination of CaWO_4 crystals by ^{210}Pb .

Unfortunately it is rather difficult to derive clear conclusions regarding the behaviour of ^{210}Pb from the present study. First of all our investigation was based on limited data being a by-product of a production cycle performed by crystal manufacturers that resulted in some weaknesses in sample availability. In addition some contamination could occur in the course of production. As for the other alpha emitters from the ^{238}U chain, they show a tendency to remain in the melt. We have estimated the segregation coefficient for U to be ≈ 0.3 . The possible role of different processes that can cause build-up or depletion of specific impurities in the crystals was briefly discussed. In particular we have found an indication of U contamination in CaWO_4 crystals produced from a CaWO_4 charge that has been in direct contact with ceramics at high temperature. Therefore the rest of the melt after crystal growth cannot be used for production of radiopure scintillators without development of an appropriate method of melt collection.

The radioactive contamination of CaWO_4 powder prepared in special conditions was studied by low-background α - and γ -spectroscopy. The sample was produced using a modified procedure of synthesis, i.e. new lab-ware, an improved laboratory setup, pre-selected and additionally purified initial raw materials. The initial contamination of the powder by ^{210}Po was found to be at the level of (5 ± 2) Bq kg $^{-1}$. In the same batch, for ^{210}Pb only an upper detection limit of < 47 mBq kg $^{-1}$ could be given. We also observed an essential decrease in the activity of the ^{210}Pb daughter (^{210}Po) with time, which is in line with this finding. Altogether, this demonstrates that the optimised procedure used to produce the CaWO_4 compound can facilitate efficient removal of ^{210}Pb and offers a possibility for improving the radiopurity of CaWO_4 crystal scintillators.

Based on the results of this study we propose a programme of research and development, aimed to obtain radiopure calcium tungstate crystal scintillators for future experiments searching for rare events. The four principal components of the programme are: (i) careful screening of materials at all stages by ICP-MS and ultra low background α -, β - and γ -spectrometry, (ii) deep purification of raw materials, (iii) a few-step recrystallisation of the crystals and (iv) use of radiopure reagents, lab-ware, equipment and installations.

Acknowledgments

This study was supported in part by a grant from the Royal Society (London) "Development of advanced scintillation detectors for cryogenic dark matter search" and by the Science and Technology

⁵ An encouraging result [6] should be mentioned where a level of radiopurity ≈ 0.05 – 0.1 mBq kg $^{-1}$ of ^{228}Th and ^{226}Ra in $\text{CaF}_2(\text{Eu})$ crystals was detected. Another way to purify calcium (which is the main "carrier" of radioactivity in CaWO_4) could be use of organic compounds (like e.g. calcium gluconate) [52].

Facilities Council (STFC). The support for the group from the Institute for Nuclear Research (Kyiv, Ukraine) through the project “Kosmofizyka-2” (Astroparticle Physics) of the National Academy of Sciences of Ukraine is gratefully acknowledged. The authors would like to express gratitude to the referees for their careful reading of the manuscript and their useful comments.

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