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HIGH-PURE ZINC FOR GROWING $Zn^{82}Se$ SCINTILLATION CRYSTALS

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A process has been developed to produce high-purity granular zinc for growing $Zn^{82}Se$ scintillation crystals designed to study the neutrinoless double beta decay (0ν2β) of the selenium isotope ^{82}Se in the CUPID-0 experiment. The chemical and isotopic compositions of high-purity zinc were studied and its radioactive purity was evaluated. At a level less than mBq·kg^{-1} in the background spectrum of high-purity zinc, measured by a germanium detector, no peaks were observed for natural radionuclides ^{40}K, ^{60}Co, ^{137}Cs and the uranium-thorium decay chain. An increased activity of such nuclides as ^{54}Mn, ^{56}Co, ^{57}Co, ^{58}Co and ^{65}Zn, formed mainly due to cosmogenous effects, was noted.

INTRODUCTION

The interest in 0ν2β-decay is primarily associated with the ascertainment of the nature of neutrinos and the presence or absence of neutrino mass. In particular, understanding whether neutrinos are "Majorana" or "Dirac" particles is a critical step to get a clearer picture of our universe. The only way to reveal the property of this neutrino is to look for the so-called neutrinoless double beta decay, a very rare nuclear transformation that is forbidden in the current standard model of particle physics.

Currently, a series of experiments is being performed on the search for neutrinoless double beta decay of (0ν2β) [1]. The interest in 0ν2β-decay significantly increased after the detection of neutrino oscillations, which indirectly confirms the availability of mass in neutrino. However, oscillation experiments are not sensitive to the nature of the neutrino mass (Dirac or Majorana) and do not provide information about the absolute neutrino mass scale. The discovery of at least one example of the neutrino-free mode 0ν2β will be direct evidence that the neutrino is a massive Majorana particle and the lepton number conservation law can be violated.

The main difficulty encountered in carrying out experiments on the study of 0ν2β-decay is caused by the low probability of the event, the need for long-term experiments and the maximum reduction in background impacts, as well as by the thorough analysis of the experimental results. Current and planned experiments are aimed at achieving sensitivity on the value of the half-life of $T_{1/2}(0\nu)$ at a level of more than 10^{25} years. To achieve this goal, a detector with an extremely low background level and high experimental sensitivity is needed. Cryogenic bolometric technique [2] is one of the most promising experimental approaches in this area because of its excellent energy resolution, registration efficiency and flexibility in using an absorber. A cryogenic bolometer consists of an absorbing material being cooled to a very low temperature (about 10…20 mK), and a thermometer capable to measure the temperature increase at a very low energy of the transfer of interacting particles to the absorber. But the bolometric method has a drawback, because such a detector cannot distinguish between different particles that release the same amount of energy in the absorber. However, if the absorbing material is also a scintillator, the application of a second reading channel and simultaneous measurement of bolometric and scintillation signals makes it possible to distinguish interacting particles of various types at the expense of changing the ratio of light to heat.

CUPID-0 is the first project aimed to demonstrate the possibilities of scintillation bolometric techniques [3] to search for 0ν2β-decay using an enriched isotope. The ^{82}Se isotope included in the composition of $Zn^{82}Se$ scintillation crystals was chosen as the nuclide of interest. To ensure the detection of 0ν2β-decay of ^{82}Se, it is desirable to have a background index of ~ 10^{-3} count/keV/kg/year, and in this case the careful selection of the material is obligatory.

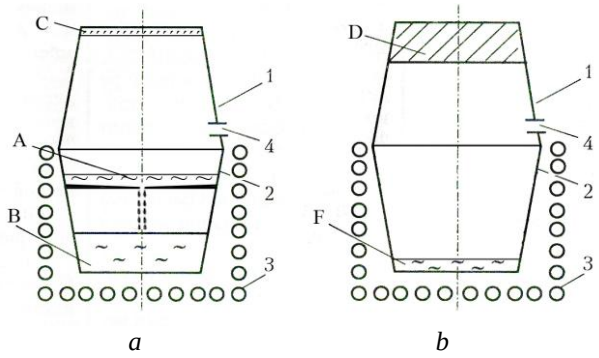
The high purity of the initial metals Zn and ^{82}Se used for the synthesis of $Zn^{82}Se$ and further crystal production is especially important in this regard. So, the content of impurity elements Fe, Cr, V, Ni, As, Cu, Mo, Si, and S, affecting the scintillation characteristics of ZnSe crystals, should be less than 1 ppm. Even more stringent requirements are imposed on the radioactive purity of the detector. To reduce the natural background radiation, the concentration of natural radionuclides ^{40}K, ^{60}Co, ^{137}Cs in ZnSe crystals should be less than (0.1…0.01) ppb, and that of the uranium-thorium chain did less than (1.0…0.1) ppt.

The aim of this work is to develop a process of producing high-purity zinc, suitable for growing scintillation crystals of zinc selenide to study rare nuclear events in the CUPID-0 experiment, and investigation of its chemical and isotopic compositions, radioactive contamination.

EXPERIMENTAL SECTION

For deep refining of zinc at the NSC KIPT a new comprehensive method for zinc refining as well as a special device for its implementation have been developed [4–6]. The temperature and time regimes of zinc purification are described in [6]. Refining of zinc was performed in two stages (Fig. 1). At a first stage, the highly volatile impurities (Na, K, S, P, Cl, etc.) were

distilled off with their condensation on the surface of condenser C (see Fig. 1,a). At the same time, to remove oxide and other slags, the refined metal was filtered in the same device using a "filter" plate having a small taper and a hole in the middle. After removal a condensate containing highly volatile impurities, the second stage of the process was carried out – the removal of low-volatile impurities (Fe, Ni, Si, Al, Cu, Pb, etc.) by distillation of metal, poured into the crucible, onto a condenser with a distillation fraction up to 95% (see Fig. 1,b).



a *b*

Fig. 1. Scheme of a device for zinc distillation: a – the stage of filtration and distillation of highly volatile impurities; b – the stage of removal of low-volatile impurities by distillation of the metal on a heated condenser. A – initial metal; B – filtered metal; C – a thin layer of condensate with highly volatile impurities; D – distillate; F – residue in a crucible with low-volatile impurities; 1 – condenser; 2 – crucible; 3 – heater; 4 – hole

To grow zinc selenide single crystals, it was necessary to have high-purity zinc in the form of granules with a diameter of 3…5 mm. For this purpose, distilled zinc was further subjected to a granulation process in a specially designed device by dropping molten purified metal into cooled bidistilled water (Fig. 2) [7]. The final product was zinc granules with a diameter of 3…5 mm (Fig. 3).

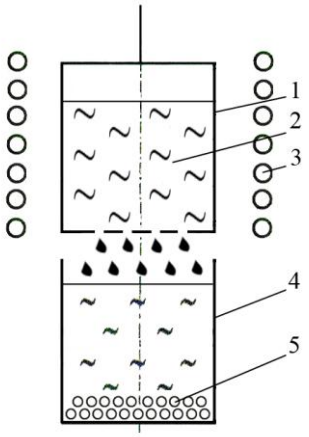


Fig. 2. Scheme of the device for granulating zinc, cadmium and lead: 1 – container with holes; 2 – molten metal; 3 – heater; 4 – container with a coolant; 5 – granular metal

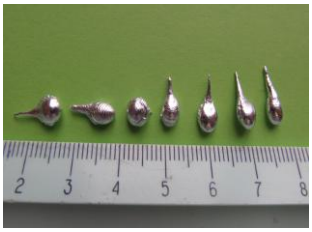


Fig. 3. The samples of zinc granules after pouring

RESULTS AND DISCUSSION

Table 1 shows the results of the analysis of the content of impurities in the initial and high-purity granular zinc. A quantitative analysis of the content of impurity elements in the initial and purified granular zinc was performed by laser mass spectrometry – LMS (NSC KIPT, Kharkiv, Ukraine). A comparative analysis of impurity elements in zinc was also performed by inductively coupled plasma mass spectrometry – ICP-MS at the Laboratori Nazionali del Gran Sasso (LNGS, Assergy, Italia). A good agreement was observed between the values of impurity concentrations determined by different methods.

Table 1

The concentration of impurities in zinc before and after purification and granulation

Element	$C_{initial}$, ppmw	$C_{purified}$, ppmw	Element	$C_{initial}$, ppmw	$C_{purified}$, ppmw
Na	1.0	0.03	As	3.0	<0.04
Mg	<0.05	0.038	Y	<0.05	<0.05
Al	4.0	0.035	Mo	<0.3	<0.3
Si	7.0	0.04	Cd	20.0	4.3
P	1.0	<0.01	Sn	15.0	<0.3
S	1.0	<0.01	Sb	<0.2	<0.2
K	3.0	0.035	Te	<0.3	<0.3
Ca	2.0	0.07	W	<0.5	<0.5
V	<0.03	<0.03	Hg	<0.4	<0.4
Cr	<0.04	<0.04	Tl	<0.3	0.18
Mn	<0.03	<0.03	Pb	30.0	0.29
Fe	30.0	0.056	Bi	<0.1	<0.1
Co	<0.03	<0.03	Ag	<0.1	<0.1
Ni	<0.05	<0.04	In	<0.09	<0.09
Cu	10.0	0.11	Se	<0.09	<0.09

As can be seen from the data shown in Table 1, a comprehensive refining method is very effective one for the entire range of impurity elements. The concentration of the most impurity elements was reduced by one or two orders of magnitude or more. For example, the concentration of Fe is reduced by about 500 times, and Al, Si, K, Cu, Bi did by ~ 100 times.

In addition to the high level of chemical purity of the materials used, a correct determination of the sensitivity to the 0ν2β-decay requires knowledge of the actual isotopic composition of zinc and the internal radiation background of the material. Knowing the actual isotopic composition of zinc allows one to reduce the uncertainty in the final values of half-life, especially in the case of low isotopic occurrence, for example, for the isotope ^{70}Zn. To verify the isotope composition of zinc, the additional ICP-MS measurements were performed. The results are presented in Table 2.

Table 2

Isotope composition of the sample of high-purity zinc in comparison with the values established in [8]

Isotope	Isotopic composition of zinc, established in [8], %	Isotopic composition of high purity zinc, %
^{64}Zn	49.17	47.55
^{66}Zn	27.73	27.95
^{67}Zn	4.04	4.23
^{68}Zn	18.45	19.59
^{70}Zn	0.61	0.68

As can be seen from the data given in Table 2, deviations of the isotopic composition of high-purity zinc were found at a level of several percent, compared with the values recommended in [8]. The differences between the natural zinc isotopes make it possible to determine the origin of starting materials chosen for growth of the ZnSe crystal and to evaluate the degree of influence of isotope content on the radionuclides activity arising from the activation by cosmic rays. On the other hand, knowledge of the actual isotopic composition of zinc, or, in other words, of the number of nuclei of a particular isotope, is required in the search for double beta decay which can occur in the ^{64}Zn isotope. Accurate knowledge of the actual isotopes composition allows not only to reduce the error in the final result but also to improve the half-life limits, if the isotope of interest is present in a larger amount than in the recommended “natural” mixture of isotopes.

In the low-energy region, there are two main sources of detector radiative background: the natural radioactivity of the uranium and thorium families and the cosmic radiation. The problem of natural radioactivity is solved by creating a detector made from very pure materials. To reduce a cosmic influence, the measurements must be carried out deep underground.

The measurements of internal radiation background of high-purity zinc for radioactive contaminants other than uranium and thorium, and especially for their daughter nuclides, were performed using gamma spectrometry with ultra-low-background high-purity germanium (ULB-HPGe) detectors. To enable shielding of cosmic rays, the measurements were carried out by a Stella device (SubTerranean Low Level Assay) deep underground (3600 m water equivalent) at the Gran Sasso National Laboratory of the Institute for Nuclear Research (Italy) [9–12].

The energy spectra were processed using the MaGe code of the Monte Carlo simulation method based on the GEANT4 software package [13]. The values of limits were obtained using the procedure presented in paper [14].

Although the peaks of natural radionuclides ^{40}K, ^{60}Co, ^{137}Cs and of uranium and thorium chains were not observed on the background spectrum of the high-purity zinc sample, a significant activity of some specific nuclides, such as ^{54}Mn, ^{56}Co, ^{57}Co, ^{58}Co, and ^{65}Zn, was observed at the levels of tenths and several units mBq·kg^{-1}. All these isotopes were generated in a zinc sample due to irradiation with cosmic rays during the entire period of storage of the initial zinc material on the ground.

While the ^{65}Zn isotope is formed by the capture of neutrons with the natural zinc isotope ^{64}Zn, the other nuclides: ^{54}Mn ($T_{1/2}$ = 312.12 days), ^{56}Co ($T_{1/2}$ = 77.27 days), ^{57}Co ($T_{1/2}$ = 271.79 days), and ^{58}Co ($T_{1/2}$ = 9.15 hours) can be obtained by neutron fission. The activity of ^{56}Co and ^{58}Co nuclides can be reduced by storing purified zinc underground, as well as by minimizing the time required to synthesize and grow ZnSe crystals, and by quick delivering ZnSe crystals to underground storage. For the other two isotopes, ^{54}Mn and ^{57}Co, a significant decrease of their activity during storage underground and optimization of their storage time is not expected due to the relatively long half-life decay.

Noteworthy is the situation, in terms of radioactive purity, with the isotope ^{65}Zn ($T_{1/2}$ = 244.26 days). Due to the method of its formation with neutron capture by the isotope ^{64}Zn, the most widely-spread natural isotope ^{64}Zn (49.17%), activity of ^{65}Zn is more than an order of magnitude higher than that of other cosmogenously activated nuclides. This should be taken into account when the task is to achieve the low background levels of about 10^{-3} pulses/keV/kg/year. One of the effective ways to reduce its contribution is choosing the initial metal zinc with the lowest activity of the ^{65}Zn nuclide, followed by storage for a long time underground. Then, when refining and growing ZnSe crystals, it should be to exclude any possibility of reactivation of this nucleus, in particular by carrying out these operations underground.

CONCLUSIONS

The process has been developed to produce high-purity granular zinc for growing Zn^{82}Se scintillation crystals designed to study the neutrinoless double beta decay (0ν2β) of ^{82}Se isotope in the CUPID-0 experiment. A pilot batch of granular zinc with a purity of more than 99.999%, intended for further research in the Gran Sasso underground laboratory, was produced. In addition to a detailed chemical analysis of high-purity zinc, the isotopic composition of zinc was studied, and the radiation background caused by residual radioactive nuclides was measured. Whereas the high-purity zinc sample turned out to be very pure with respect to the

natural radionuclides ^{40}K, ^{60}Co, ^{137}Cs and uranium and thorium chains (only the upper limits were established), the significant activity of some specific nuclides, such as ^{54}Mn, ^{56}Co, ^{57}Co, ^{58}Co and ^{65}Zn was noted at the level from tenths to several units of mBq·kg^{-1}. The attention is drawn to the need to take into account the contribution of cosmogenously activated nuclides, in particular the ^{65}Zn isotope, to the background level. Possible methods for decreasing the activities of cosmogenous activated nuclides are discussed. One of the cardinal ways to decrease cosmogenous effect is to perform the processes of zinc purification, synthesis and growth of ZnSe crystals at underground laboratories.

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ВЫСОКОЧИСТЫЙ ЦИНК ДЛЯ ВЫРАЩИВАНИЯ СЦИНТИЛЛЯЦИОННЫХ КРИСТАЛЛОВ $Zn^{82}Se$

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Разработан процесс получения высокочистого гранулированного цинка для выращивания сцинтилляционных кристаллов $Zn^{82}Se$, предназначенных для изучения безнейтринного двойного бета-распада ($0\nu2\beta$) изотопа селена ^{82}Se в эксперименте CUPID-0. Изучены химический и изотопный составы высокочистого цинка и проведена оценка его радиоактивной чистоты. На уровне менее чем мБк·кг$^{-1}$ в фоновом спектре высокочистого цинка не наблюдались пики от природных радионуклидов ^{40}K, ^{60}Co, ^{137}Cs и ураноториевой цепочки распада, измеренные германиевым детектором. Отмечена повышенная активность таких нуклидов, как ^{54}Mn, ^{56}Co, ^{57}Co, ^{58}Co и ^{65}Zn, образованных в основном в результате космогенных воздействий.

ВИСОКОЧИСТИЙ ЦИНК ДЛЯ ВИРОЩУВАННЯ СЦИНТИЛЯЦІЙНИХ КРИСТАЛІВ $Zn^{82}Se$

Г.П. Ковтун, О.П. Щербань, Д.О. Солопіхін, В.Д. Вірич, Ю.В. Горбенко

Розроблено процес отримання високочистого гранульованого цинку для вирощування сцинтиляційних кристалів $Zn^{82}Se$, призначених для вивчення безнейтринного подвійного бета-розпаду ($0\nu2\beta$) ізотопу селена ^{82}Se в експерименті CUPID-0. Вивчено хімічний і ізотопний склади високочистого цинку і проведена оцінка його радіоактивної чистоти. На рівні менш ніж мБк·кг$^{-1}$ у фоновому спектрі високочистого цинку не спостерігалися піки від природних радіонуклідів ^{40}K, ^{60}Co, ^{137}Cs і ураноторієвого ланцюжка розпаду, які виміряно германієвим детектором. Відзначена підвищена активність таких нуклідів, як ^{54}Mn, ^{56}Co, ^{57}Co, ^{58}Co і ^{65}Zn, утворених в основному за рахунок космогенних впливів.