Purification of CaF_2 Crystal for Double Beta Decay Experiments

K. Fushimi,[1, a)] K. Imagawa,[2] Y. Kishida,[3] S. Kurosawa,[4, 5, 6] R. Orito,[1] A. Sakaue,[3] Y. Takihira,[7] S. Umehara,[7] A.Yamaji,[8, 5] Y. Yamamoto,[1] K. Yasuda,[2] and T. Yoshida[9]

[1)]*Department of Physics, Tokushima University, 2-1 Minami Josanjima-cho, Tokushima city, Tokushima 770-8506, Japan*
[2)]*5-15-24 Torikai Honmachi, Settsu city, Osaka 566-0052, Japan*
[3)]*Graduate School of Science and Technology for Innovation, Tokushima University, 2-1 Minami Josanjima-cho, Tokushima city, Tokushima 770-8506, Japan*
[4)]*New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aza-Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan*
[5)]*Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan*
[6)]*Institute of Laser Engineering, Osaka University, 2-6 Yamadaoka, Suita, Osaka 565-0871, Japan*
[7)]*Research Center for Nuclear Physics, Osaka University, 10-1 Mihogaoka, Ibaraki city, Osaka 567-0047, Japan*
[8)]*New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aza-Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan*
[9)]*Graduate School of Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka city, Osaka 560-0043, Japan*

[a)]*Corresponding author: kfushimi@tokushima-u.ac.jp*

Abstract. We report on inorganic crystal purification for the search for the neutrinoless double-beta decay of ^{48}Ca using CaF_2 crystals. We are working on the purification of CaF_2 crystal, which is made from water-insoluble raw materials. The goal of the purity in this crystal is ≤ 1 μBq/kg. We measured the impurities in the crucible and CaF_2 powder before we made a molten product of the CaF_2. We will consider the correlation between the purity contained in the materials around the crystal growth and the purity of the molten product. The material-selection policy and prospects for the large-volume detector system will be discussed.

OUTLINE OF CANDLES PROJECT

Neutrinoless double-beta decay ($0\nu\beta\beta$) is one of the double-beta decay modes. It may occur when a neutrino has a finite mass, or a weak right-handed interaction exists. The search for $0\nu\beta\beta$ decay gives direct information for new particle physics because it violates lepton-number conservation. The half-life of $0\nu\beta\beta$ decay ($T^{0\nu}_{1/2}$) is directly related to the Majorana mass of the neutrino $\langle m_\nu \rangle$ as

$$\frac{\ln 2}{T^{0\nu}_{1/2}} = G^{0\nu} \left| M^{0\nu} \right|^2 \langle m_\nu \rangle^2. \tag{1}$$

The $0\nu\beta\beta$ decay has been investigated for several isotopes. The reported lower limits on half-lives are, for example, $T^{0\nu}_{1/2} \geq 1.07 \times 10^{26}$ yr (KamLAND-Zen [1]) for ^{136}Xe. The lower limit on the half-life is proportional to $1/\sqrt{BG}$, where BG is the background rate in the region of interest.

The CANDLES (CAlcium fluoride for studies of Neutrino and Dark matters by Low Energy Spectrometer) aims to search for $0\nu\beta\beta$ of ^{48}Ca. The $Q_{\beta\beta}$ value of ^{48}Ca (4.27 MeV) is the highest value among the double-beta decay nuclei, which reduces potential backgrounds.

The present CANDLES-III detector consists of modules of cubic CaF_2 (pure) crystals, whose dimension is 10 cm×10 cm×10 cm. It contains 350 g of ^{48}Ca in 96 crystals. We have performed the CANDLES-III experiment for a live time of 130.4 days in the Kamioka underground laboratory in Gifu prefecture, Japan. The present sensitivity to the $0\nu\beta\beta$ of ^{48}Ca was obtained as 5.6×10^{22} yr at the 90% confidence level [2].

The CANDLES-III experiment sensitivity suffered from a large number of background events that have been investigated previously [2, 3]. The main components of the background events in the region of interest (ROI) were external gamma rays produced by (n,γ) reactions, and internal beta rays and gamma rays from ^{208}Tl, which has the highest Q_β-value in the thorium-series. The summed energy of the beta and gamma rays reaches up to 5.001 MeV, which may provide a background.

We measured the concentrations of thorium-series isotopes in the CaF_2 crystals by the delayed-coincidence method, which identifies the sequential decays of ^{220}Rn ($T_{1/2} = 55.6$ s) and ^{216}Po ($T_{1/2} = 0.145$ s). The concentration of the

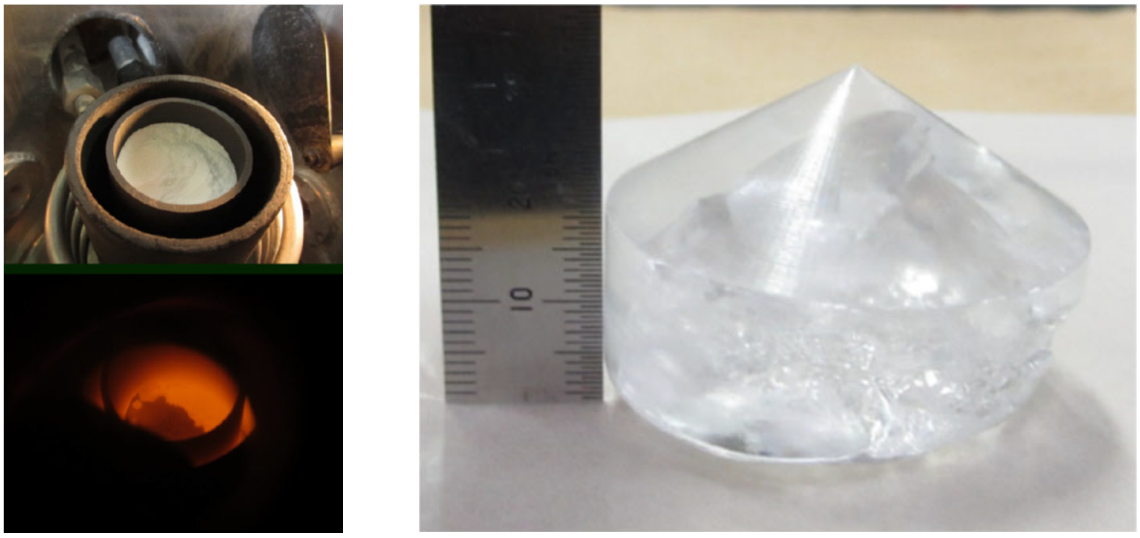

FIGURE 1. Left: Pictures of crucible after filling with CaF_2 powder and melting. **Right:** Produced crystal of CaF_2.

thorium-series isotopes was between 2 μBq/kg and 60 μBq/kg; the highly contaminated crystals caused most of the background.

We plan to upgrade the CANDLES detector with purer CaF_2 crystals enriched in ^{48}Ca. The concentration of the radioactive impurities (RIs) in the enriched crystal must be sufficiently small, a few μBq/kg. The purification of the raw materials of CaF_2 is an indispensable task for the future detector.

INVESTIGATION OF CONTAMINATION

Material selection and production

One can easily purify a material using ion-exchange resin and re-crystallization if the raw material is water-soluble. However, CaF_2 is not water-soluble, so purifying a CaF_2 crystal is problematic. Washing the CaF_2 powder with high-purity nitric acid achieved a relatively good result. However, the concentration of radioactive impurities (RIs) in the washed CaF_2 did not meet our requirements. We decided to control the surrounding and raw materials of CaF_2 to produce a purer crystal.

The first selection of materials involved the crucible used for crystallization. The purity of the crucible is essential since a dirty crucible causes contamination in a crystal [4]. We used three graphite crucibles as described below:

a) Normal graphite crucible;

b) High-purity graphite without polish;

c) High-purity graphite with a polished inner surface.

Each dimension was 45 mm in diameter and 72 mm in length. Melting and coagulation of the CaF_2 material were done with various conditions. Figure 1 shows the crucible and the the produced crystal.

We expected further purification by segregation during crystallization. We prepared a long crucible to test the position dependence of the RI concentration. We cut two 1.0-cm-long pieces from the 7.0-cm-long ingot, one from the lower part and one from the upper part. The ingot samples are shown in Figure 2.

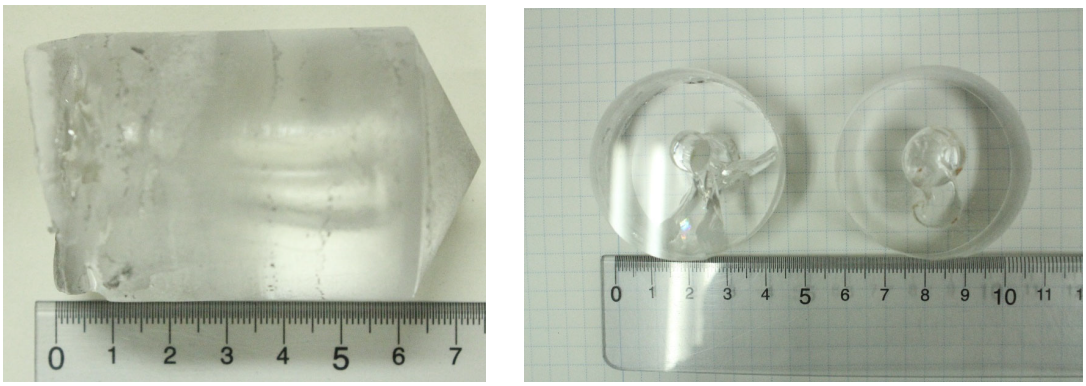

FIGURE 2. Left: Produced long crystal. The left side is the top of the ingot. **Right:** The pieces of the upper (left) and lower (right) sides of the ingot.

Purification of raw material

We tried to purify the raw materials of the CaF_2, especially the materials that contain calcium. We chose $CaCl_2$, which has a low cost and is well soluble in water. The water solution of the $CaCl_2$ is easily purified by our previous method for NaI purification [5].

The first step of the purification is the re-crystallization method. The solubility of $CaCl_2$ in water is 61.4 g at 100°C and 45.3 g at 25°C, where the solubility is defined as the mass of solute in 100 g of water solution. A significant difference in the solubility enables the removal of ^{40}K from $CaCl_2$. The insoluble impurities are removed by selecting ion-exchange resins. We selected an optimized resin that catches the thorium and uranium ions.

We will produce the pure CaF_2 powder through the chemical reaction,

$$CaCl_2 + 2HF \rightarrow CaF_2 + 2HCl. \tag{2}$$

We expect the purity of CaF_2 to be lower than 1 ppt by this method.

Measurement of radioactive impurity

The radioactive contamination was measured by counting alpha rays since this method is the most sensitive. The target isotopes are the progeny of the uranium and thorium series [6]. We assumed that all the isotopes in the thorium series are in secular equilibrium.

The parent of the thorium series is ^{232}Th ($T_{1/2} = 1.4 \times 10^{10}$ y). Although there are two progenies whose half-lives are longer than one year, one can assume that all the progenies are in secular equilibrium. We measured the sequential decays of ^{220}Rn ($T_{1/2} = 55.6$ s) and ^{216}Po ($T_{1/2} = 145$ ms), which directly indicate the radioactivity of ^{208}Tl. Both isotopes emit alpha rays whose energies are 6.288 MeV and 6.779 MeV, respectively.

The uranium series cannot be treated in the same manner since there is a long-lived progeny, ^{226}Ra ($T_{1/2} = 1600$ y). We measured the isotopes after ^{226}Ra since the progeny in the lower reaches emit high-energy beta rays, which may cause a background for the $2\nu\beta\beta$ of ^{48}Ca. We measured the sequential decays of ^{214}Bi ($T_{1/2} = 19.7$ m) and ^{214}Po ($T_{1/2} = 164\,\mu$s).

These sequential-decay events were extracted from the background events by the delayed-coincidence method [7, 8]. The delayed-coincidence method extracts the time-correlated events, such as the sequential decay of two nuclei. The typical energy spectrum of alpha rays is shown in Fig. 3. In the energy spectra, we show the sequential decays of ^{220}Rn (blue) and ^{216}Po (red). The black line shows the expectation for accidental-coincidence events, as estimated from the beta-ray energy spectrum and event rate. The measured concentrations of the uranium and thorium series are listed in Table I.

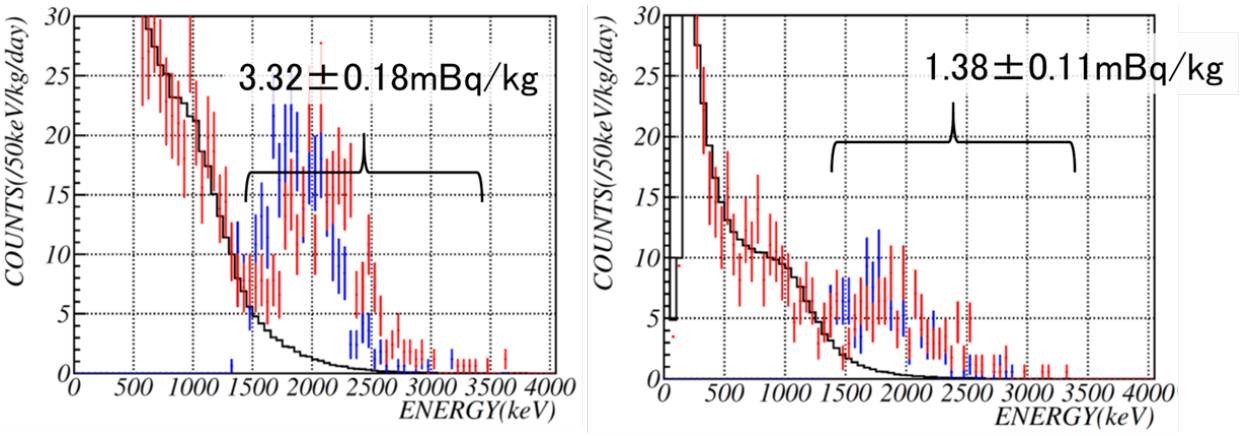

FIGURE 3. The energy spectra of extracted alpha-ray events emitted in the sequential decays of ^{220}Rn ($T_{1/2} = 55.6$ s, blue) and ^{216}Po ($T_{1/2} = 145$ ms, red) taken from the long ingot, compared to the expectation for accidental-coincidence events (black). **Left:** Data from the upper part of the ingot. **Right:** Data from the lower part.

TABLE I. Results of sample measurement in units of mBq/kg.

Sample Types	U-series (^{214}Po)	Th-series (^{216}Po)
High-purity polished	2.45 ± 0.25	2.20 ± 0.28
High-purity unpolished	3.37 ± 0.18	2.53 ± 0.18
Upper sample	2.14 ± 0.19	3.33 ± 0.18
Lower sample	0.88 ± 0.09	1.38 ± 0.11

DISCUSSION

We have investigated the method of CaF_2 purification. First, we selected the crucible material. The concentrations of RIs were not significantly different whether from the polished or non-polished crucible. We selected the high-purity, non-polished crucible since we were afraid of possible contamination while polishing the inner side of the crucible. We successfully confirmed the segregation effect in a small piece of the ingot. The zone-refining method in a long ingot worked well even though it was a small piece.

Further purification of CaF_2 will be projected by purifying the raw material. The $CaCl_2$ is one of the best raw materials because it is water-soluble and has low cost. We will purify the raw material by re-crystallization and optimized resin. The effectiveness of the resin usage was already confirmed by purification of NaI. The same method will be applied to purify the $CaCl_2$ powder.

ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant-in-Aid for Scientific Research on Innovative Areas No. 22H04575 and Grant-in-Aid for Scientific Research(A) No. 19H00688. This work was performed under the GIMRT Program of the Institute for Materials Research, Tohoku University (Proposal No. 202011-RDKGE-0005).

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