Doping a CaF_2 crystal with ^{229}Pa and the γ-ray measurement of ^{229m}Th

Y. Shigekawa,[*1] A. Nambu,[*1] X. Yin,[*1] Y. Kanayama,[*1] H. Shimizu,[*1] and H. Haba[*1]

The first excited state of the ^{229}Th nucleus (^{229m}Th) has an excitation energy of 8.36 eV (148 nm),[1)] which leads to an ultraprecise nuclear clock via nuclear laser excitation. In the nuclear clock, the internal conversion (IC) and electron bridge (EB) processes of ^{229m}Th, whose half-lives are much shorter than that of the γ-ray emission, must be suppressed to ensure a narrow natural linewidth of the nuclear transition. One of the ways to prohibit the IC and EB processes is doping fluoride compounds with ^{229m}Th. Recently, the γ rays of ^{229m}Th were observed with the ^{229}Th-doped CaF_2, MgF_2, and $LiSrAlF_6$ crystals[1–3)] and $^{229}ThF_4$ films.[4)] The half-life of ^{229m}Th varied with the material (150–630 s), although the underlying reasons are yet to be elucidated. It is not easy to prepare a variety of ^{229}Th compounds to investigate the half-life variation due to the small amount of ^{229}Th available in the world.

We have been aiming to observe the γ rays of ^{229m}Th by doping fluoride crystals with ^{229}Pa ($T_{1/2}$ = 1.50 d), which decays to ^{229m}Th by electron capture.[5–8)] A large quantity of ^{229}Pa can be produced by the $^{232}\mathrm{Th}(p,4n)^{229}\mathrm{Pa}$ reaction,[8)] which allows us to prepare various ^{229}Pa-doped crystals by ionizing ^{229}Pa and implanting it into crystals. This will enable us to study the half-life variation in various crystals and to determine the best crystal suitable for the nuclear clock. In this study, we prepared a ^{229}Pa-doped CaF_2 crystal and attempted to observe the γ rays of ^{229m}Th.

To produce ^{229}Pa, two ^{232}Th metallic foils (total thickness 0.12 mm) were irradiated with a 29.6-MeV proton beam at the RIKEN AVF cyclotron. The average beam current was 10.2 μA, and the irradiation time was 9.2 hours. The chemical separation of ^{229}Pa was performed in the previously developed method.[7)] The chemical yield of Pa was around 90%. The radioactivity of ^{229}Pa in the purified sample was 610(30) MBq at the end of the bombardment (EOB). The reaction by-products, ^{232}Pa ($T_{1/2}$ = 1.32 d) and ^{230}Pa ($T_{1/2}$ = 17.4 d), had radioactivities of 40(1) and 16.4(5) MBq at EOB, respectively. The purified ^{229}Pa sample was dissolved in 10 μL of 1 M HNO_3/0.4 M HF (Pa stock solution).

For the ^{229}Pa implantation (Fig. 1(a)), we first dropped 1 μL of the Pa stock solution on a Re filament coated with colloidal graphite.[6)] The filament was heated to ∼2000°C for 8 min. Here, Pa compounds were reduced to Pa atoms by the graphite, and Pa ions were produced by surface ionization. The Pa ions were accelerated to 30 keV and implanted into

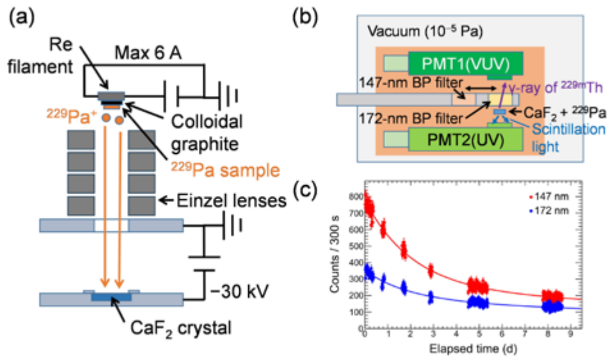

Fig. 1. (a) Schematic of the ionization and implantation of ^{229}Pa. (b) Schematic of the γ-ray measurement of ^{229m}Th. (c) Photon count rate as a function of the time for the 147-nm (red) and 172-nm (blue) BP filters, measured by PMT1. It is estimated that ^{229}Pa and ^{229m}Th were in radiative equilibrium at the measurement start time.

a CaF_2 crystal. The total efficiency for ionization and implantation was 0.32(1)%. The radioactivity of ^{229}Pa in the crystal was 91(5) kBq at the start time of the measurement of the ^{229m}Th γ rays. This radioactivity was close to the value we targeted (100 kBq) to obtain a sufficient count rate of ^{229m}Th γ rays (∼1 s^{-1}).[5)]

The crystal was then annealed at 400°C for 1 min to incorporate ^{229}Pa into appropriate crystal sites. After the crystal cooled down, it was placed in the apparatus shown in Fig. 1(b) and the γ-ray measurement started 14 min after the end of the annealing. The ^{229m}Th γ rays were measured with a photomultiplier (PMT1) through bandpass (BP) filters centered at 147 and 172 nm. The 147-nm filter passed the ^{229m}Th γ rays, while the 172-nm filter blocked them. Another photomultiplier (PMT2) was used to detect scintillation photons induced by high-energy radiation, enabling background photon reduction in PMT1 via anticoincidence. Figure 1(c) shows the measured photon count rates over time. The data for each BP filter was well fitted with the sum of the decay curves of ^{229}Pa, ^{232}Pa, and ^{230}Pa. From the fitting, the count rates of ^{229}Pa, ^{232}Pa, and ^{230}Pa at the measurement start time for the 147-nm BP filter were determined to be 1.0(3), 0.7(3), and 0.833(9) s^{-1}, respectively, while those for the 172-nm BP filter were 0.0(1), 0.59(1), and 0.581(4) s^{-1}, respectively. The count rate of ^{229}Pa for the 147-nm filter was much higher than that for the 172-nm BP filter, which could indicate the observation of the ^{229m}Th γ rays. For further confirmation,

*1 RIKEN Nishina Center

DOI:10.34448/RIKEN.APR.58-079

we need to reduce the amounts of ^{232}Pa and ^{230}Pa by mass separation. Moreover, the time from annealing to the measurement needs to be reduced to observe the growth curve and determine the half-life of ^{229m}Th.

References

1) J. Tiedau *et al.*, Phys. Rev. Lett. **132**, 182501 (2024).
2) S. Kraemer *et al.*, Nature **617**, 706 (2023).
3) R. Elwell *et al.*, Phys. Rev. Lett. **133**, 013201 (2024).
4) C. Zhang *et al.*, Nature **636**, 603 (2024).
5) Y. Shigekawa *et al.*, RIKEN Accel. Prog. Rep. **55**, 124 (2022).
6) Y. Shigekawa *et al.*, RIKEN Accel. Prog. Rep. **55**, 126 (2022).
7) Y. Shigekawa *et al.*, RIKEN Accel. Prog. Rep. **56**, 145 (2023).
8) Y. Shigekawa *et al.*, J. Radioanal. Nucl. Chem. **333**, 1479 (2024).