# Surface ionization of protactinium toward implanting $^{229}$Pa into a $CaF_2$ crystal

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The first excited state in the $^{229}$Th nucleus ($^{229m}$Th) has an excitation energy of ∼8.3 eV,[1] which may allow an ultraprecise nuclear clock. We aim to observe the $\gamma$ rays of $^{229m}$Th and to determine its half-life, which is an essential parameter to develop the nuclear clock, by doping a $CaF_2$ crystal with $^{229}$Pa, which decays to $^{229m}$Th with a negligibly small recoil energy.[2] The doping with $^{229}$Pa will be achieved by ionizing $^{229}$Pa, implanting $^{229}$Pa ions with high energy (>10 keV) into a $CaF_2$ crystal, and annealing the crystal. Ionizing $^{229}$Pa with high efficiency and implanting ∼100 kBq of $^{229}$Pa are important to clearly observe the $\gamma$ rays of $^{229m}$Th. Surface ionization, which is the ionization of atoms on the surface of a metal at a high temperature, is one of the methods that can realize a high ionization efficiency (0.1–100%); however, the ionization efficiency for Pa is as low as 0.001–0.01%[3] because of the high stability of Pa compounds such as $Pa_2O_5$. To overcome this difficulty, Pickett *et al.* developed a method to bring Pa compounds into contact with colloidal graphite on the surface of a Re filament, realizing an ionization efficiency of 0.3–0.7%.[4,5] Following this method, we performed experiments for ionizing $^{233}$Pa ($T_{1/2}$ = 26.975 d) in this study toward the ionization of $^{229}$Pa ($T_{1/2}$ = 1.5 d).

$^{233}$Pa was separated from its mother nuclide $^{237}$Np in the following procedure. First, 9 M HCl solution containing $^{237}$Np and $^{233}$Pa was fed onto a TK400 resin's column (TrisKem). Next, $^{237}$Np was eluted by pouring 9 M HCl, following which $^{233}$Pa was eluted by pouring 1 M HCl. The eluate contacting $^{233}$Pa was evaporated, dissolved with 0.1 M HCl/0.1 M HF, and fed onto an anion-exchange column (Muromac 1X8). After pouring 0.1 M HCl/0.1 M HF, $^{233}$Pa was eluted with 0.4 M HCl/0.1 M HF. Finally, we prepared a stock solution of $^{233}$Pa in 50 $\mu$L of 1 M $HNO_3$/0.4 M HF.

Figure 1 shows a schematic view of the setup for the surface ionization and implantation of Pa, performed in a high vacuum ($10^{-4}$–$10^{-5}$ Pa). A Re filament (0.0254 × 0.762 × 10 mm) was fixed by spot welding to two SUS316 wires ($\varphi$1.0 mm), which were connected to a vacuum feedthrough to apply a current for heating the filament. The temperature of the filament was measured using an infrared thermometer. An Al electrode, where −15 kV was applied, was placed 86.4 mm below the filament. We fixed a $CaF_2$ crystal ($\varphi$12 mm, 0.5 mm thickness) or a Cu foil ($\varphi$12 mm, 0.05 mm thickness) to the Al electrode. The Cu foil was used for optimizing the setup and conditions of surface ionization. According to our simulation, the collection efficiency of ions in the $CaF_2$ crystal or the Cu foil is ∼100%; therefore, the collection efficiency of Pa corresponds to the ionization efficiency.

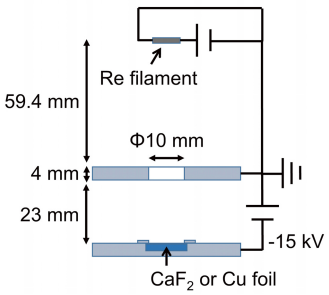


Fig. 1. Schematic view of the setup for the surface ionization and implantation of Pa.

The surface ionization and implantation of $^{233}$Pa were performed for the Cu foil (Run A) and the $CaF_2$ crystal (Run B) as follows. First, the Re filament was heated with a current of ∼5.5 A for 10 min to remove impurities on the filament. Next, 1 $\mu$L of water containing colloidal graphite (EM Science 12650) was dropped on the filament and evaporated by applying a current of 0.7 A to the filament. Then, 1 $\mu$L of the stock solution containing 19.1(2) kBq of $^{233}$Pa was dropped on the Re filament and evaporated with a current of 0.7 A. After the filament was placed in a vacuum chamber, the current applied to the filament was gradually increased. At a filament current of 2.5 A, we applied a voltage of −15 kV to the Al electrode (Fig. 1). The temperature of the filament exceeded 1960°C with a current of ∼5.5 A and increased to 2000°C in ∼20 min. The heating at ∼2000°C lasted until the filament was broken (79 and 127 min for Runs A and B, respectively).

The radioactivity of $^{233}$Pa collected in the Cu foil (Run A) was measured to be 121(2) Bq. Considering the solid angle between the filament and the foil, the radioactivity of $^{229}$Pa atoms deposited on the foil was calculated to be 15.8(2) Bq. Hence, the ionization efficiency was 0.55(1)%. The radioactivity of $^{233}$Pa remaining on the filament after heating was 4.3(1)% of that before heating, implying that highly stable $^{233}$Pa compounds were efficiently reduced and evaporated. For the case of the implantation into the $CaF_2$ crystal (Run B), the ionization efficiency was 0.53(1)%, which is close to the value for the Cu foil, although $CaF_2$ is a non-conducting material. We will be able to implant 100 kBq of $^{229}$Pa, which is expected to sufficient to clearly observe the $\gamma$ rays of $^{229m}$Th, by using a solution containing 19 MBq of $^{229}$Pa.

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References
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