I. Project Research

Project 13
Pr13  Chemical and electronic properties of Actinide compounds and their applications

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INTRODUCTION:
Actinide compounds shows a unique chemical and electronic nature due to the partial and insufficient shield of 5f orbital electrons as inner transition elements. We have a deep interest in the aspect of the electronic properties of the actinide compounds and formed the group consisting of three major fields: (1) inorganic and coordination chemistry, (2) electronic properties and (3) theoretical chemistry and its users. The methodology should have substantial applications to the issues of the 1F debris, the transmutation of the long-lived radioactive wastes. Also, since the epochal clinical effect of 225Ac nuclear medicine against the propagated prostate cancer, the demands for such actinide nuclides and for research environments are increasing. Such research environments as well as obtaining such actinide nuclides are extremely difficult to prepare in ordinary university institutes. The hot laboratory of the KURN S offers precious opportunities for the above-mentioned research group to carry out their characteristic research activities.

EXPERIMENTS:
The first fiscal year of the project has been devoted to the preparatory discussions on the equipment and the environment of the KURNS to start a series of researches. Each of research fields has made their progress as followings:
(1) K. Shirasaki has investigated the key separation step of 225Ac generation from 229Th. The fact that 229Th–225Ac system shows too many γ-ray emissions lead us difficulties in monitoring the separation factors, and improve the step. M. Nakase has synthesized the Zn-based porphyrin (ZnPc) complex as a prototype for the actinide porphyrins such as 225Ac complexes. T. Suzuki and M. Nogami has carried out the preparatory experiments on the extraction behavior of actinides, by using corresponding lanthanide ions and by using ICP-MS.
(2) The single-crystalline samples of a series of uranium intermetallic compounds were prepared and their magnetic and crystallographic properties were characterized.
(3) The calculation of the atomic orbitals for various uranium ions (e.g., U6+, U5+, and U4+) is crucial in chemical nature. The GRASP program [2] is used to calculate the radial distribution functions at the four-component relativistic method.

RESULTS:
(1) K. Shirasaki et al have proposed the use of 232Th–228Ac system and successfully revealed 40% of 228Ra remained in the starting 232Th. Figure 1 shows the synthesis of ZnPc.
(2) A newly synthesized compound U2Pt6Al15, characterized in a hexagonal crystal structure, shows disorder to have honey-comb structure. Also, a certain anomalous state of the conduction electron system in Th13U8Be13 was unveiled from the magnetization measurements (Fig. 2).
(3) From Fig. 3, the order of spread of 7s orbital is U6+ < U5+ < U4+, which indicates that 7s orbital becomes more spread as the number of 5f electrons is increased. Also, minor actinides (MA) phase diagrams for actinide transmutation based on CALPHAD is now underway by H. Shishido.

Fig. 1. Synthesis of the prototype Zn porphyrin complex.

Fig. 2. The U concentration dependence of the characteristic temperatures of Th13U8Be13.

Fig. 3. Radial distribution function of 6s orbitals in U6+, U5+, and U4+ ions.

REFERENCES:
INTRODUCTION: A series of ternary compounds having chemical composition close to 2:6:15 crystallizing in the hexagonal structure are known to form in rare earth [1,2] and actinide [3-5] intermetallics. Although an apparent structural disorder in the rare earth/actinide containing layer is observed in X-ray diffraction, a possible honeycomb arrangement of rare earth atom is suggested in earlier investigations on rare earth analogues [6]. In this paper, we report characterization of both crystallographic and magnetic properties of U$_2$Pt$_6$Al$_{15}$. [7]

EXPERIMENTS: The sample was prepared either by arc-melting the constituent elements or Al-flux method. Obtained samples were characterized by electron-probe microanalysis for stoichiometry and homogeneity. Crystal structure was investigated by the single-crystal X-ray diffraction using a tiny single crystal extracted from ingots. Magnetization was measured using a SQUID magnetometer.

RESULTS: X-ray diffraction successfully identified a hexagonal unit cell (P6$_3$/mmc, $a = 4.2957$ Å, $c = 16.2211$ Å). The structural disorder is reflected in the partial occupation on uranium 0.667(6) and one of the aluminum sites 0.33(2), in agreement with the previous report. Furthermore, additional weak peaks are observed at $(h/3 l/3 0)$ in the basal plane, corresponding to a superstructure with a larger lattice parameter. These superstructure peaks are elongated along the $c^*$ direction suggesting that the periodicity along the $c$-axis is lost. A honeycomb layer model with a planer disorder well describes experimental observation above. Similar model is also reported in rare earth analogue. A more complex superstructure is recently reported in europium analogue [8]. The present honeycomb arrangement of neighboring uranium layer is shown in Fig. 1. The neighboring uranium layers have a displacement (-1/3, 1/3) or equivalent directions in the hexagonal cell, keeping hexagonal symmetry in the average structure.

Despite the disordered structure, a relatively sharp magnetic phase transition due to uranium 5f electrons was observed. [7] Considering the fact that each honeycomb layer is separated by 8.1 Å and U-U distance (4.3 Å) within the layer is much shorter than that, magnetic interaction within the layer is considered to be primarily dominant. The disorder of the stacking between the layers less influences the magnetic transition.

In summary, we established the honeycomb uranium arrangements in a uranium compound U$_2$Pt$_6$Al$_{15}$. A well-defined magnetic ordering is found in this compound. The detailed magnetic property investigation is in progress.

REFERENCES:
PR13-2 Crossover between Fermi-liquid and non-Fermi-liquid states in Th_{1-x}U_xBe_{13} (0 \leq x \leq 1)

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\textbf{INTRODUCTION:} UBe\textsubscript{13} (the cubic NaZn\textsubscript{13} structure) is well known as the second heavy-electron superconductor discovered by Ott et al. in 1983 \cite{1}. It becomes superconducting (SC) at $T_c \sim 0.85$ K, where $C(T)$ shows a large jump ($\Delta C/\gamma T_c \sim 2.6$) followed by a non-exponential temperature dependence below $T_c$. Numerous experimental studies during the last three decades have revealed many anomalous SC properties which are incompatible with the BCS framework. Despite intensive efforts, however, the exact nature of the SC state, including the symmetry of order parameter, still remains unresolved. This puzzle may mainly stem from the difficulty in understanding the normal state of this system: Though many properties of UBe\textsubscript{13} at high temperature resemble those of typical Kondo lattice, the low-temperature behavior shows a significant deviation from Landau’s Fermi liquid theory. It is expected that the origin of this so-called “non-Fermi-liquid” (NFL) could be crucial to understand the unconventional SC of this system. Our previous studies on the diluted magnetic system Th\textsubscript{1-x}U\textsubscript{x}Be\textsubscript{13} (x \leq 0.11) revealed that the low-temperature properties in the dilute U limit is described as Fermi liquid (FL), and imply that the NFL state in the pure UBe\textsubscript{13} could be attributed to a quantum criticality due to the competition between the crystalline-electric-field (CEF) singlet state versus the Kondo-Yosida singlet and/or CEF triplet states \cite{2}.

\textbf{EXPERIMENTS:} In order to see how the low-temperature state changes from FL to NFL with x, we have performed magnetic susceptibility (\$\chi\$), specific heat (C), and electric resistivity ($\rho$) measurements on the Th\textsubscript{1-x}U\textsubscript{x}Be\textsubscript{13} single crystals in the entire range of U concentration: 0 \leq x \leq 1 for temperatures down to 0.1 K at Hokkaido University. A part of the crystal growth for x \leq 0.11 and the follow up experiments were done in MGML (https://mgml.eu/) at Charles University, Czech Republic.

\textbf{RESULTS and DISCUSSION:} Weiss temperatures derived from fitting the high-temperature susceptibility data by Curie-Weiss law are all negative in the whole range of x, and its absolute value increases with increasing x. The $\gamma$ value at low temperature also increases monotonically with increasing x. Interestingly, the characteristic temperature of the FL state estimated from $\chi(T)$ and $\rho(T)$ data decreases continuously and monotonically with increasing x, and shows a tendency to vanish at $x^* \sim 0.8$, above which the NFL behavior becomes significant in C(T)/T and $\rho(T)$ (Fig. 1). These results strongly suggest that a crossover of the low-T states between FL and NFL occurs around $x^*$. Together with our high-pressure $\rho(T)$ measurements for some concentrations, we suggest that the anomalous metallic state in UBe\textsubscript{13} is mainly ascribed to the inter-U-site electronic correlations. We plan to make further detailed discussion by checking the U concentration x using ICP-MS at the Institute for Integrated Radiation and Nuclear Science, Kyoto University.

\textbf{ACKNOWLEDGEMENT:} We are grateful to Dr. J. Prchal for his assistance in the low-temperature experiments. The present work was supported by JSPS KAKENHI Grant Number JP15H05882, JP15H05885 and JP15K21732 (J-Physics), and the Strategic Young Researcher Overseas Visits Program for Accelerating Brain Circulation from the Japan Society for the Promotion of Science. The Prague group was supported by the Czech Science Foundation by the Grant No. P204/15/0377S.

\textbf{REFERENCES:}
Adsorption Characterization of Actinide Chemical Species on Solid Adsorbents
- Measurement of Rare Earth Elements by ICP-MS -

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INTRODUCTION: The accurate and precise analyses of actinides and many kinds of fission products in the spent fuels and/or nuclear debris are important issue for nuclear fuel management and the radioactive waste management. The separation or removal of the actinides is required before the above analyses. Especially, for the quantitative actinide analysis and the actinide isotope ratio analysis by using mass spectrometry such as ICP-MS (inductivity coupled plasma mass spectrometry) or TIMS (thermal ionization mass spectrometry), the mutual separation of actinides is highly important from the viewpoint of removal of isobaric interferences. And also, for the analyses of fission product nuclides, the removal of uranium and plutonium, which are dominant elements in the spent fuel or nuclear debris, is important. We have been studying the separation and removal of actinides by using the solid type absorbents such as amine type resin, amino type resin. By the way, the light actinides have many valences, and the adsorption behaviors of actinides on solid adsorbents depend on their valences. We must study the adsorption behaviors of each valences of actinides on solid adsorbents. For this study, the control and confirmation of actinide valences, the adsorption experiments, and the detection and measurement methods of actinides are necessary. However, now, the preparation for application of actinide analysis in Institute for Integrated Radiation and Nuclear Science (IRNS), Kyoto University, has not been readied enough to carried out the experiment. In consideration under such a situation, we confirmed the fundamental characteristics of ICP-MS set in hot laboratory of IRNS.

ICP-MS EXPERIMENTS: We use the ICP-MS (Analytik jena, Plasma Quant MS) set in a hot laboratory of IRNS. The standard solution of europium for ICP-MS (AccuStandard Inc.) was used as the sample. The lanthanides are one of the targets of our study. Some lanthanides are mono-isotope elements, and some lanthanides have many isotopes. Europium has two isotopes; ¹⁵¹Eu and ¹⁵³Eu. Number of isotopes is appropriate, because of not too many. It is also desirable that the mass number s of isotopes are alternate, that is, if the mass numbers are continuous, it is difficult to distinguish the mass of the heavier isotope ion and the mass of hydrate ion of lighter isotope. The confirmations in this year are the spectrum profile, the detection limitation, and the generation of molecular ions. The concentration of europium for the spectrum profile and the molecular ion generation was 1 ppb, and for the detection limitation was 1 ppb, 0.1 ppb, and lank. The upper limitation of sample concentration which can be feed into this ICP-MS is defined as 1 ppb. The repetition of measurements is 5.

RESULTS: Mass spectrum around mass number of 151 and 153 is shown in Fig. 1. The good peak curves on 151 and 153 are obtained. Although peak points are little difference from the real mass, the peaks are corrected by mass calibration. The relationship of europium sample concentration and cps is shown in Fig. 2. We confirmed that the cps of concentration of 0.1 ppt is same level of background. We confirmed the generation of molecular ions; hydrate ion, monoxide ion. We didn’t observed the dioxide ion. The generation ratios of molecular ions and atomic ion are about 10⁻³. However, the cps of every detected molecular ion was so small that we should carry out further precise measurement.

![Fig. 1. Mass spectrum of europium by ICP-MS.](image1)

![Fig. 2. Relationship of europium sample concentration and cps. Solid circles and open circles are data of ¹⁵¹Eu and ¹⁵³Eu, respectively. Datum of blank sample was set on 10⁻² ppt.](image2)
Preparation of $^{228}$Ra/$^{228}$Ac stock solution

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INTRODUCTION: In the past decade, $^{225}$Ac ($T_{1/2} = 10$ d) which decays through a chain of four $\alpha$-emissions and two $\beta$-emissions to the stable $^{209}$Bi, has been receiving constant attention as a targeted alpha therapy (TAT) nuclide due to its ability to kill considerably high efficiency of tumor cell [1]. By contrast, $\gamma$-rays of $^{225}$Ac suffer from low emission ratios and are often unresolved from the $\gamma$-emissions associated with its daughter nuclides. Thus $\gamma$-ray spectrometry, which is a convenient method for identification of radionuclides, has an uncertainty about the application to $^{225}$Ac. This fact makes it difficult to study chemical properties of actinium complexes using a tracer amount of $^{225}$Ac.

In terms of emission ratios of $\gamma$-rays, $^{228}$Ac ($T_{1/2} = 6.15$ h, daughter nuclide of $^{228}$Ra) has potential value because it emits well-defined and intense $\gamma$-rays that are easily resolved from the daughter nuclides. Aldrich et al. reported the preparation method of $^{228}$Ac generator from natural thorium salts in 2020 [2]. Their method was composed of two parts with the bulk thorium separation by the precipitation of thorium hydroxide, and purification of $^{228}$Ra by the column chromatography using ion-exchange resins. In the handling of thorium hydroxide, the voluminous slurry precipitate complicates the convenient separation from the daughter nuclides.

Hence, we studied simple bulk thorium separation by cation exchange chromatography.

EXPERIMENTS: The separation method was based on a technique used in conjunction with $^{222}$Ra separation from irradiated thorium [3]. Thorium oxide was dissolved in conc. HNO$_3$ spiked with a slight amount of conc. HF with heating (~230°C) for approximately 5 min. The solution was evaporated near dryness and added mili-Q water (18.2 MΩ, repeated two times). Then, the solution was brought to dryness and reconstituted in mili-Q water with citric acid. Finally, the solution volume was adjusted by the addition of mili-Q water.

The thorium citrate solution was processed according to the following steps. The solution passed through an ion exchange column containing 2.5 mL cation exchange resin, which was preconditioned with a 1 M (mol/L) citric acid solution. The eluate from the column was collected (fraction 1), then an additional 1 M citric acid solution was passed through for washing the column (fraction 2 and fraction 3). The column was then washed with 0.1 M HNO$_3$ to remove residual citric acid (fraction 4) and flowed 6M HNO$_3$ (fraction 5). These fractions were subjected to the $\gamma$-ray spectrometry using a high-pure Ge-detector (ORTEC). The $^{228}$Ac activity was determined by $\gamma$-emission of 911 keV. The distribution ratio ($D_i$) of $^{228}$Ra in each fraction ($i = 1$-5) was calculated by the equation:

$$D_i = A_i/ \left( \sum_{i=1}^{5} A_i \right) \quad (1).$$

Here, $A_i$ is an activity obtained from $\gamma$-ray spectrometry of fraction $i$.

RESULTS: As shown in Fig. 1, almost all of $^{232}$Th daughters were found in fraction 1, which was assumed to be contained thorium as a major eluted nuclide.

The initial $^{228}$Ra atomicity ($N_i$) of each fraction can be estimated by the equation:

$$N^*_i = \frac{A_i}{(\lambda_2 - \lambda_1)} \cdot \frac{N_1}{2} \left( e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) + N_2 e^{-\lambda_2 t} \quad (2).$$

Here, $N_2$ and $N_2^*$ are the number of $^{228}$Ac atom at initial and elapsed time $t$, respectively, $\lambda_1$ and $\lambda_2$ are the decay constant of $^{229}$Ra and $^{228}$Ac, respectively. The distribution ratios ($D_i$) of $^{228}$Ra in the fractions 1-5 were determined by $^{228}$Ac activities and summarized in Table 1. This result indicates that approximately 40% of $^{228}$Ra is remained in bulk thorium.

![Fig. 1. $\gamma$-ray spectra of a sample of fraction 1.](image)

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<th>Fraction no.</th>
<th>1</th>
<th>2</th>
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<th>4</th>
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REFERENCES:
INVESTIGATION ON COMPLEX FORMATION OF MONOAMIDE COMPOUNDS WITH ACTINYL IONS

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INTRODUCTION: Development of highly selective compounds for actinyl ions has been important. We have been focusing on monoamide compounds as promising candidates, considering the possibility of complete incineration of waste compounds (so-called “CHON principle”[1]). This year, as the first year of the project, we made a summary on various monoamides we have been investigating. In addition, some subjects which should be investigated during the next few years and environments necessary for experiments to be carried out in KUR were extracted.

RESULTS: (1) Monoamide compounds: We have clarified that adsorptivity of various synthetic organic resins with a monoamide structure as the functional group to uranium(VI) species in acidic nitric acid solutions greatly differs depending on the chemical structure of the functional monoamide[2,3]. There seems to be two factors for interaction between monoamides and actinyl ions; one is “chelating effect” of the ring formed by polymer monoamides and actinyl ion(s), and the other is “flexibility” of monoamide. For chelating effect, it is well known that five- or six-membered rings are most stable for common metal complexes. While, situation seems different for our resins. For example, polymerized dimethylacrylamide (DMAA), one of resins with high adsorptivity and selectivity for U(VI) in HNO₃, is expected to form eight-membered ring when it adsorbs U(VI) (UO₂²⁺), where five carbon atoms and two carbonyl oxygen atoms of two DMAA molecules, and one uranium atom are composed of the ring (Fig.1)[2]. In addition, eight would be the minimum number for the chelating ring formed by our synthetic resins. These things suggest that detailed investigations on chelating effect for resins with a larger ring than common complexes are necessary.

For chelating effect, it is well known that five- or six-membered rings are most stable for common metal complexes. While, situation seems different for our resins. For example, polymerized dimethylacrylamide (DMAA), one of resins with high adsorptivity and selectivity for U(VI) in HNO₃, is expected to form eight-membered ring when it adsorbs U(VI) (UO₂²⁺), where five carbon atoms and two carbonyl oxygen atoms of two DMAA molecules, and one uranium atom are composed of the ring (Fig.1)[2]. In addition, eight would be the minimum number for the chelating ring formed by our synthetic resins. These things suggest that detailed investigations on chelating effect for resins with a larger ring than common complexes are necessary.

Flexibility is somewhat an opposite relationship to chelating effect. Functional groups are expected to improve the ability to capture metal ions more easily with an increase in flexibility, i.e., the length between the functional group and the main polymer chain. Flexibility would be very effective in case that adsorption occurs by, e.g., ion exchange, namely, the approach of plural ions with positive and negative charges, respectively. On the other hand, for monoamide resins, two monoamide carbonyl groups are in general necessary to capture one UO₂²⁺ ion, as can be seen in, e.g., Fig. 1. Effect of flexibility of monoamide resins might be, therefore, suppressed compared with that of ion exchange resins. Moreover, functional groups with longer chains must be disadvantageous from the viewpoint of chelating effect, because the number of atoms consisting of chelating rings becomes larger as mentioned above.

We have been accumulating adsorption data of our monoamide resins for U(VI), but we have not found any clear tendency between the chemical structure of functional monoamide and the adsorptivity. We have also taken into account the fact adsorption of U(VI) by monoamide resins occurs not only at oxygen atom of monoamide but also at other sites, which was clarified by the Scatchard plot analysis[4].

(2) Future studies for monoamide compounds: The above things were examples on resins. Current status for the development of our monoamide resins was introduced at the symposium held at KUR on Feb. 7, 2020, and fruitful discussions were made.

We have also been developing monoamide extractants and precipitants as well as resins. Based on the above knowledge, we will carry out the following studies at KUR.

Experimental areas treating actinide species are under preparation. Determination of concentration of actinide species is essential for our study, and an ICP-MS instrument has been introduced. We would like to establish the determination condition for ICP-MS with our colleagues.

Theoretical approach would also be necessary for understanding the interaction between monoamide compounds and actinyl ions. We would like to make frequent discussions with our colleagues in this regard.

REFERENCES:

Fig. 1. Expected bond style between DMAA resin and UO₂²⁺.
INTRODUCTION: Theoretical calculations of actinide compounds are very important to understand or predict new phenomenon in these compounds. We have developed computational methods based on the relativistic quantum chemistry and applied it to uranium (U) isotope fractionation, which is widely discussed in geochemistry [1]. In the present work, we evaluated equilibrium isotope fractionation coefficient $\ln K_{\text{env}}$ for 54 U species in U(VI), U(V), and U(IV) states with various ligands (e.g., H$_2$O, CO$_2$, CH$_3$COO$,\text{Cl}_2$, NO$_3$, etc.) using accurate relativistic quantum chemical methods to verify the accuracy of the computational results and predict $\varepsilon$ for new species.

METHODS: We calculated $\varepsilon$ between $^{235}$U and $^{238}$U as the sum of the nuclear volume term ($\ln K_{\text{nv}}$) and the nuclear mass term ($\ln K_{\text{nm}}$) [2-4]. $\ln K_{\text{nv}}$ is due to the electronic energy difference caused by the different size and shape of nucleus of isotopes [2,3], while $\ln K_{\text{nm}}$ is due to the vibrational level caused by the different reduced mass of isotopologues [4]. In the heavy element system, $\ln K_{\text{nv}}$ is dominant in $\varepsilon$. Because $\ln K_{\text{nv}}$ is highly affected by relativity, we used the exact two-component (X2C) relativistic method with the Gaussian finite nucleus model, implemented in the DIRAC16 program.

RESULTS: As a calibration, we calculated $\varepsilon$ for U(IV)-U(VI) in chlorides and obtained as 1.72‰, which agrees well with the experimentally reported $\varepsilon$ (1.64‰) [5]. As shown in Fig. 1, $\varepsilon$ strongly depends on the uranium valence state, and its general order is $U(\text{VI}) > U(\text{V}) > U(\text{IV})$. Also, we can confirm that the magnitude of $\ln K_{\text{nv}}$ is much larger than $\ln K_{\text{nm}}$ from Fig.1. This is consistent with the fact that $\ln K_{\text{nv}}$ is the dominant term in U isotope fractionation. To explain the strong dependence of $\varepsilon$ on U valence, we depicted the radial distribution function of 6s orbital of U$^{6+}$, U$^{5+}$, and U$^{4+}$ atomic ions (Fig. 2) because this orbital significantly affects the magnitude of $\ln K_{\text{nv}}$. The order of spread of 6s orbital is U$^{6+} < U^{5+} < U^{4+}$, indicating that 6s orbital is more spread as more 5f electrons are added. This causes the decrease in electron density at the nucleus, leading to the large $\ln K_{\text{nv}}$ [3], and consequently, $\varepsilon$ shows large value. Besides, the largest difference in $\varepsilon$ between U(VI) and U(IV) is about 3‰, which indicates that the U speciation significantly affects isotope fractionation. The present theoretical data set of $\varepsilon$ including various specification would be very helpful for the accurate discussions of U isotope fractionation in geochemistry.

REFERENCES:
INTRODUCTION: Partitioning and transmuting is presently regarded as an effective method to address the issue of high-level radioactive waste disposal. The most efficient way to transmute minor actinide (MA) nuclides is to cause fission reactions with neutrons, and such studies have been reported since almost the beginning of the use of nuclear energy [1]. Neutrons generated by fusion reactors are most preferred for transmutation because of their high energy and monochromaticity. We have proposed to transmute MA rather moderately, namely with a low fission reaction rate to avoid imposing severe engineering challenges on the system design [2].

In this concept, MA mixed oxides (e.g., Am–Cm–O) are loaded into limited space in fusion reactors, where sufficient neutron flux can be secured with relatively lower heat flux. Whereas some studies have reported the phase diagram of U or Pu based MA oxides, no reports have provided the diagrams of the MA-only mixed oxides. It is vital to reveal the properties and construct a database for realization of the transmutation system.

The objective of this study is to evaluate the phase diagram of the MA-only mixed oxides. Measurement of the phase diagrams is not a straightforward task because the toxicity, radioactivity, scarcity and the short lifetime of many actinides impede experimental studies. Thus, we aim to develop a method to evaluate the phase diagrams. In the first year, we discussed the research direction and important issues to be solved each other. We also examined the phase diagrams of MA from earlier studies.

DISCUSSION: We had a meeting at Research Reactor Institute in Kyoto University and the concept of this research and important issues have been confirmed each other. The most focused point was the idea of MA transmutation to Plutonium even number nuclides in the research concept. We have proposed a rather moderately transmuting MA in a fusion reactor to reduce the heat generation from fission reactions [2], which results in the production of many Pu-238 nuclides. However, one important issue—the decay heat from Pu-238—was indicated in the meeting. The nuclide Pu-238 has large decay heat and is utilized as a heat source in radioisotope thermoelectric generators. We have concerned a possibility to handle the large quantity of the targets having large and continuously decay heat in a huge fusion reactor system. The research direction is still under debate and we proceed with the research from a general point of view to solve the crucial issue.

RESEARCH REVIEW: The term CALPHAD (Calculation of PHAs Diagram) means calculating phase diagrams from thermodynamic models with parameters adjusted to available measured data. Few researches have evaluated the phase diagrams and thermodynamic models of the MA mixed oxides (U–Pu–Np–O, Pu–Am–O) [3-5]. These studies were based on very limited experimental values to derive the thermodynamic models. Unfortunately, there are no thermodynamic data of the MA-only mixed oxides; thus, ab initio calculation needs to be performed to provide inputs for CALPHAD.

Figure 1 schematically depicts the situation of ab initio with respect to CALPHAD [6]. The ab initio calculation can provide energetics and phase diagram information. The energetics (structural energies, heats formation) of existing or hypothetical compounds can be easily evaluated and directly input in a CALPHAD database. The ab initio outputs can be also converted to a Redlich–Kister format and combined with the thermodynamics database in use with CALPHAD. This procedure has been successfully applied to some cases of binary metal alloys [7]. We consider that the phase diagrams of the MA-only mixed oxides can be predicted with a certain accuracy based on the examination above.

FUTURE TASKS: We move forward with the ab initio calculations to evaluate the energetics of the MA oxides. It is important, as well known, that the values provided by ab initio calculations must be assessed critically because the values depend on the methods and approximations used and they scatter similarly to how experimental values do. Because we do not have expert knowledge that guarantees the best results for the issues, prudent and critical study is under way.

REFERENCES:
INTRODUCTION: In Th fuel cycle, effective separation of U from Th and other fission products in spent Th fuels is needed. To enable that, an extraction method similar to plutonium–uranium redox extraction (PUREX) has been studied, namely, thorium–uranium extraction (THOREX)[1]. In the THOREX process, UO$_2$$^{2+}$ is extracted by tri-n-butyl phosphate (TBP) with the aid of Al(NO$_3$)$_3$. Some of the other ligands such as monoamide is recently reported for U/Th separation [2]. In both the cases, extractability of UO$_2$$^{2+}$ is high, but that of Th$^{4+}$ is also high, leading to low selectivity of UO$_2$$^{2+}$ over Th$^{4+}$. Therefore, study on highly selective ligands to specific light actinide is needed. In this study, Phthalocyanine (Pc) was selected as the main structure of the ligand. Pc is known as forming stable complex with U and there are many reports on mechanism and characterization study. However, the Pc has low solubility in organic solvent which limit the utilization in solvent extraction. Therefore, the Pc derivatives with substituent modification was planned and metal free Pc and Pc-Zn complex were synthesized in fiscal year of 2019. Zinc was selected because of the relatively weak interaction of Zn and N of Pc. One of the most famous complexes of Pc is Pc-Cu complex but the covalent bond of Cu and N of Pc is too strong to exchange to other metal ions. Also, N is easily protonated under acidic condition, hence the O-derivatized Pc will also be synthesized. During this study, applicability of Pc derivatives to solvent extraction will be surveyed.

EXPERIMENTS AND RESULTS: Synthesis of Pc was done at Tokyo Tech and test-run of hydrothermal synthesis of U-complex was done at Koyo University. To synthesize the Pc, literature survey was firstly done and some preliminary experiments were conducted. The simple metal free Pc and Pc-Zinc complex were synthesized as following schemes in (1) and (2) of Figure 1. In both the schemes, the starting building block of phthalonitrile can be replaced into derivatized one and the combination of different building blocks can make the synthesis of other Pc derivatives easily possible. Also, Zn in the Pc-Zn complex can be easily replaced into other metals. For purification of metal free Pc and Pc-Zn, Soxhlet extractor and thin layer chromatography (TLC) were used respectively. The color of metal free Pc and Pc-Zn were white and dark blue, respectively as shown in Figure 2. By $^1$H-NMR measurement, successful synthesis of the desired products was confirmed. The purities of both products were not high enough for characterization study, hence, further purification methods such as distillation will be tested and the synthetic scale will also be enlarged.

Figure 1 Synthetic scheme of (1) metal free Pc and (2)Pc-Zn

Figure 2 Pictures of synthesized chemicals, (1) metal free Pc and (2)Pc-Zn

FUTURE PLAN: From next fiscal year, the following experiments are planned:
1. Synthesis of Pc derivatives with long alkyl chain to increase solubility in organic phase.
2. Survey of the synthetic scheme of Pc derivatives-U complexes.
3. Survey of the synthetic scheme of Pc derivatives to make the Pc N,O-hybrid donor ligand
4. Trial of single crystal synthesis of Pc derivatives and some metals and their characterization

CONCLUSIONS: The synthetic schemes of metal free Pc and Pc-Zn complex were established and the further synthetic strategy was made clear. The characterization study will also be started from next fiscal year.

REFERENCES: