

I-1. PROJECT RESEARCHES

Project 7

PR7 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. These studies will be also useful for application research area such as the handling of the 1F debris and developments of nuclear medicines.

Such research environments to handle actinides elements are extremely difficult to build in ordinary university institutes. The hot laboratory of the KURNS offers unique opportunities for the above-mentioned characteristic research activities.

EXPERIMENTS:

The second fiscal year of the project has been devoted to the setting up the experimental environment and initial test experiments. Each of research fields has made their progress as followings:

(1) T. Suzuki *et al.* has the investigated adsorption behaviors of actinides on polyvinylpyrrolidone (PVPP) in nitric acid and hydrochloric acid solutions. The adsorption behaviors were evaluated through measurements of the distribution coefficient.

(2) Y. Haga *et al.* has synthesized the novel uranium intermetallic compound $U_2Pt_6Ga_{15}$. The single-crystalline samples of this compound have been investigated by the measurements of crystallographic, thermodynamic, and transport properties.

(3) M. Nakase *et al.* has studied properties of Phthalocyanine (Pc) as a ligand for an effective extraction of U. First, they built an electrical furnace for purifications of complex materials. A test operation of the furnace was performed by using a Pc-Zn complex they synthesized.

(4) T. Yamamura *et al.* has studied the hydrothermal synthesis of actinide compounds for the U-Zr, U-Fe, and U-Si systems as the simulating-debris compounds. The conditions were (2) 150°C for 8 h, and (1) 450°C for 30 min, and an addition of acetaldehyde as organic additive. The characterization was carried out by using XRD.

RESULTS:

(1) From the distribution coefficients measured for uranyl ions on PVPP, T. Suzuki *et al.* confirmed that only actinides adsorb on PVPP and can separate the actinides from other elements such as alkaline earth elements. They concluded that the hexavalent actinide is adsorbed on PVPP both in the nitric acid solution and in the hydrochloric acid solution. They also revealed that the tetravalent actinide is not adsorbed on PVPP in the hydrochloric acid solution but adsorbed in the nitric acid solution.

(2) A newly synthesized compound $U_2Pt_6Al_{15}$ crystallizes in a layered structure of honeycomb planes with an inter-layer disorder. The average crystal structure belongs to the hexagonal space group. This compound was revealed to show a magnetic phase transition at approximately 25 K. The relatively sharp transition implicated by the magnetic susceptibility measurement the magnetic ordering is considered to be dominated by the in-plane correlations.

(3) The electric furnace for sublimation purifications (Fig. 1) has been built in the Hot Laboratory of KURNS. The test heating of the ZnPc yielded some impurities out of the crude product, indicating a sign for the purification. Currently the equipment is still being adjusted, and this setup will be fixed and systematic test is planned.



Fig. 1. Building the electric furnace for the sublimation purification method.

(4) Not only the very moderate hydrothermal condition (1), but also relatively severe condition (2), produced the diffractograms based on the UO_2 , independent from the metals coexisted. The result agrees well with our previous result without coexisting other metal ions [1]. The atmosphere is indicative of being reductive enough to transfer U(VI) to U(IV). An coexistence of other anions could result in the formation of new salt compounds such as silicates and phosphites [2-3]. The conditions are to be improved in future studies.

REFERENCES:

- [1] C. Tabata, K. Shirasaki, M. Konaka, Dexin Li, N. Sakai, T. Yamamura, Now in preparation for submission.
- [2] E.M. Villa, et al., *Inorg. Chem.*, 52 (2013) 965.
- [3] P. Estevenon, et al., *Dalton Trans.*, 49 (2020) 6434.

PR7-1 Antiferromagnetism in uranium intermetallic compound with structural modulation

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INTRODUCTION: Uranium ternary compounds having the chemical composition close to 2:6:15 are investigated. The detailed crystal structure investigation suggests the honeycomb arrangement of uranium atoms with the stacking modulation. [1,2] Among them, a new analogue $\text{U}_2\text{Pt}_6\text{Ga}_{15}$ has been successfully synthesized and magnetic property measurements identified the antiferromagnetic ordering.

EXPERIMENTS: The single crystal sample was grown by the gallium flux technique. Electron microprobe analysis ensured the homogeneity of the composition. The crystallographic parameters were determined by the single-crystal X-ray diffraction. The existence of streak scattering elongated along the c -axis suggests the stacking modulation as reported for the uranium [1] and rare earth analogues. Electrical resistivity, magnetization and specific heat as a function of temperature between 2 K and room temperature were measured to identify the magnetic phase transition.

RESULTS: Figure 1 shows the temperature dependence of magnetic susceptibility with magnetic field applied along the principal directions of the hexagonal lattice, a and c -directions. A significant magnetic anisotropy with the magnetic easy axis along the c is observed. Paramagnetic behavior is observed between about 25 K and 60 K for the field along the c -axis. The paramagnetic effective moment is estimated as $3 \mu_B/\text{U}$, suggesting that uranium atoms carry magnetic moments. With lowering temperature, a peak appears in susceptibility, and, subsequently, a sudden drop is observed at 25.4 K. Susceptibility further decreases down to the lowest temperature of the measurement. On the other hand, susceptibility with the field along the a -axis is smaller and less temperature dependent, even below the susceptibility anomaly at 25.4 K. These observations are consistent with the occurrence of an antiferromagnetic ordering at the Néel temperature $T_N = 25.4$ K with the ordered moment along the c -axis. Electrical resistivity and specific heat measurements (not shown) also detected an anomaly related to the antiferromagnetic transition. Considering the stacking disorder mentioned above, such a relatively sharp phase transition seems unlikely, because of the modulated magnetic interaction due to partially disordered atomic arrangements. The present observation therefore suggests that the magnetic interaction within the honeycomb layer is dominant and (disordered) interlayer interaction plays only a secondary role.

It should be noted that there is an unusual behavior of magnetic susceptibility just above T_N . A broad maximum

appears at 27 K. Such anomaly is not seen in ordinary antiferromagnets. However, in uranium and other correlated magnets show similar anomalies in the paramagnetic state. To clarify the origin of the anomaly, we measured field dependence of magnetization in detail. It turned out that the position of the broad anomaly changes with magnetic field in exactly the same manner as that of T_N . On the contrary, the maximum appearing in the correlated magnets has different field dependence in general. It is therefore likely that the susceptibility maximum in $\text{U}_2\text{Pt}_6\text{Ga}_{15}$ is related to antiferromagnetism rather than the electronic correlation, namely, the structural modulation probably modulates magnetic interaction between the honeycomb layers leading to a distribution of the T_N resulting in relatively broad anomaly above the main antiferromagnetic transition.

To conclude this report, we found a new uranium intermetallic antiferromagnet with honeycomb arrangements. Considering the relatively sharp transition, antiferromagnetism within the honeycomb layer is likely. Further investigation on the magnetic structure and magnetic interaction are needed to clarify the magnetic characteristics.

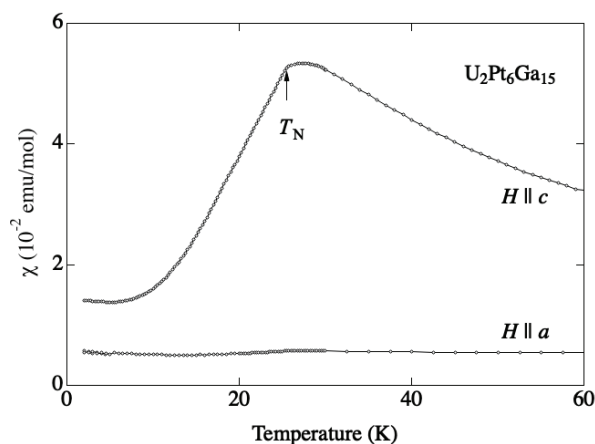


Fig. 1. Temperature dependence of magnetic susceptibility measured on a single crystal sample of $\text{U}_2\text{Pt}_6\text{Ga}_{15}$.

REFERENCES:

- [1] Y. Haga *et al.*, JPS Conf. Proc., **29** (2020) 013003.
- [2] Y. Matsumoto *et al.*, to be published in J. Phys. Soc. Jpn.

PR7-2 Adsorption Characterization of Actinide Chemical Species on Solid Adsorbents

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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. In addition, recently, the supply of α -nuclides for α -therapy is becoming increasingly important. Increase. For the purpose, the actinides separation from the decay series is required. In this year, the adsorption behaviors of actinides on polyvinylpyrrolidone (PVPP) were investigated in nitric acid and hydrochloric acid solutions. We use the uranyl ion as a representative of the hexavalent actinide ions, and the thorium ion as representative of the tetravalent actinide ions.

EXPERIMENTS: We used the commercially available type PVPP (Alfa Aesar). The uranyl ion was used in ICP-MS standard solution (XSTC-289, SPEX). The other ions including thorium ion were used in XSTC-311. The adsorption behaviors were estimated by using distribution coefficient, K_d [mL/g]. The K_d s were obtained by batch experiment. The adsorption behaviors of alkali metal ions, alkaline earth ions, several transition metal ions such as Cr, Ni, Fe, Ag, etc. were also investigated.

RESULTS: The distribution coefficients of uranyl ion are shown in Fig.1. The uranyl ion in nitric acid solution is adsorbed on PVPP under the wide range of concentration. While in hydrochloric acid solution, the distribution coefficient increases with the concentration. In the case of thorium ion, the adsorption on PVPP was not observed in the hydrochloric acid solution, but was observed in the nitric acid solution as shown in Fig. 2. The distribution coefficient was confirmed to increase with the concentration of nitric acid. From results of distribution coefficients of uranyl ion and thorium ion, we concluded that the uranium and thorium can be separated in the both case of nitric acid and hydrochloric acid. It was not observed the adsorption of other elements on PVPP in nitric acid solution. While in hydrochloric acid solution, the slight adsorptions of iron and silver were observed. From these obtain data, we confirmed that we make only actinides adsorb on PVPP and can separate the actinides from other elements such as alkaline earth elements. In conclusion, the hexavalent actinide is adsorbed on PVPP both in the nitric acid solution and in the hydrochloric acid solution, and the tetravalent actinide is not adsorbed on PVPP in the hydrochloric acid solution but adsorbed

on PVPP in the nitric acid solution.

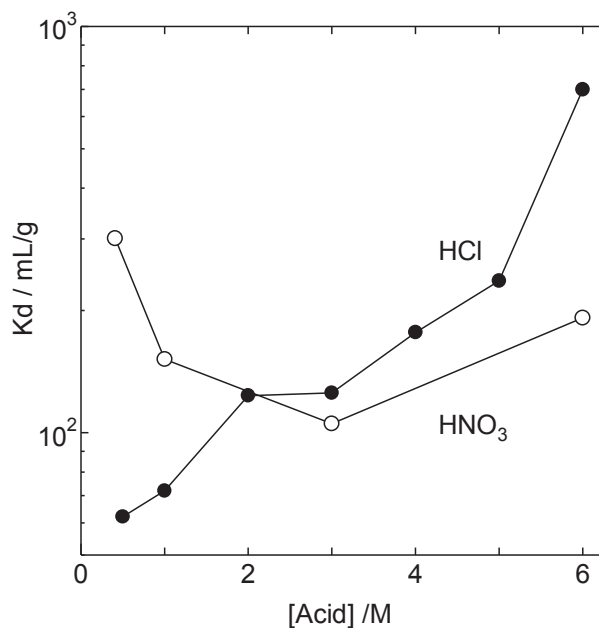


Fig. 1. Adsorption behaviors of uranyl ion on PVPP in nitric acid solution and hydrochloric acid solution.

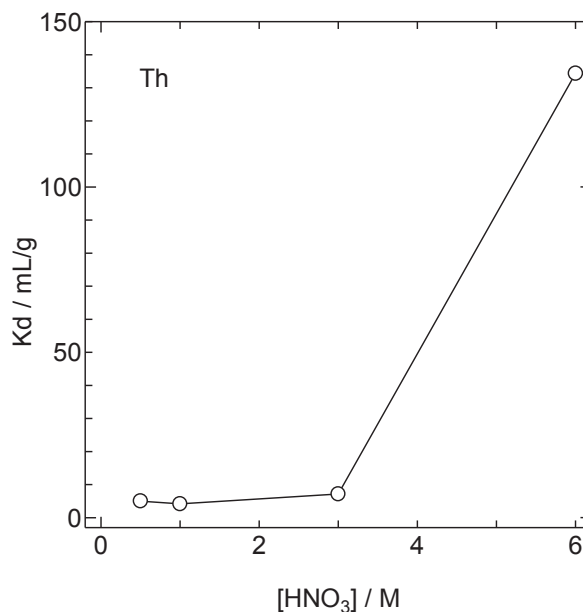


Fig. 2. Adsorption behaviors of thorium ion on PVPP in nitric acid solution.

PR7-3 Synthesis of noble phthalocyanine derivatives and effect of substituent on recognition of light actinide and chemical property-2

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INTRODUCTION:

In Th fuel cycle, effective separation of U from Th and other fission products in spent Th fuels is needed. To enable that, thorium–uranium extraction (THOREX) process, similar to the plutonium–uranium redox extraction (PUREX) process, has been studied [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 ligand which consisted of C, H, O, N atoms (CHON principle) such as monoamide is recently reported for U/Th separation [2]. In this study, Phthalocyanine (Pc) was selected as the main structure of the ligand which also satisfy the CHON principle. To make the solubility of Pc in organic solvent higher, the Pc derivatives with substituent modification is ongoing. The Pc-metal complex in organic solvent itself is also interesting to investigate. In FY2020, some Pc complexes were synthesized. To obtain the complex with actinide, the purification technique with minimized waste production is highly desirable. Therefore, some of the purification technique is tested, and sublimation setup was equipped in the control area.

EXPERIMENTS AND RESULTS:

Synthesis of Pc was done at Tokyo Tech as shown in **Figure 1**. By ¹H-NMR measurement, successful synthesis of the desired products was confirmed but small amount of impurity was detected.

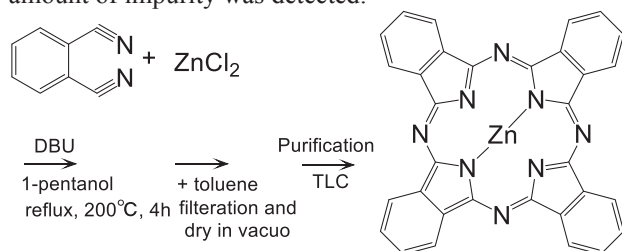


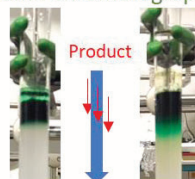
Figure 1 Synthetic scheme of Pc-Zn complex

To purify the product, recrystallization was firstly tested. As well known, the Pc-derivatives are not soluble into most of the solvents, hence, suitable noble solvent was not determined. In small scale, recrystallization seems to be well proceeded, but the purification was not successful once the scale becomes large. In FY2020, some of the purification methods were tested as shown in **Figure 2**. When the chromatography was implemented, the green product did not move much, indicating huge amount of organic solution is needed. The thin-layered chromatography also gave green product but this method is not suitable for the large-scale synthesis. The soxlet extrac-

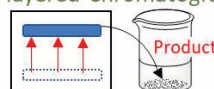
tion is convenient method to efficiently remove impurity. In our test, sometimes it is difficult to keep the product in the cylindrical filter equipped in the center position. The final attempt was sublimation method. This method was done intensively by T.Yamamura et al., for Pc-U or -Th complexes purification. The quartz tube was sealed and the tungsten wire was equipped inside the tube with changing the pitch. Currently the equipment is still adjusting but in FY2021, this setup will be fixed and systematic test will be done.

1. Chromatography

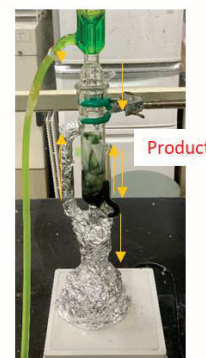
Column chromatography



Thin-layered Chromatography



2. Soxlet extraction



3. Sublimation



Figure 2 Purification methods tested in this study

CONCLUSIONS and FUTURE PLAN:

Purification of Pc-metal complexes were surveyed and some insight for waste minimization was obtained. The plan in FY2021 is listed;

1. Synthesis and purification of Pc derivatives with long alkyl chain to increase solubility in organic phase.
2. Upgrade the purification method.
3. Implement solvent extraction experiment
4. Survey of the synthetic scheme of Pc derivatives to make the Pc *N,O*-hybrid donor ligand

REFERENCES:

- [1] R.H.Rainey and J.G.Moore, *Nucl Sci Eng*, 10(4), 367–371, 1961.
- [2] P.N.Pathak, *Solv Ext Ion Exch*, 20(3), 293–311, 2002.

PR7-4 Hydrothermal synthesis of actinide mixed oxides for basic debris research

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INTRODUCTION: The Fukushima Daiichi Power Plant (1F) of Tokyo Electric Power Company, Incorporated (TEPCO) is characterized not only by the core meltdown but also by the formation of debris containing not only fuels and claddings but also containment vessels, concrete structures, and seawater salts. The composition of the debris is considered to be U-Zr-Fe(Ni,Cr)-Si-O-B-C-FP. Materials with different elemental compositions, structures, and electronic states are considered to be generated locally through cooling processes such as crystallization and amorphization as oxide or metallic phases.

From the standpoint of actinide science, the study on the physical and chemical mechanisms on their aging will contribute to the improvement of reliability in the storage of 1F molten debris. According to the knowledge of materials science, such micro-material and structural changes at grain boundaries and within grains due to lattice damage should be reflected in macroscopic properties such as shape and mechanical properties.

Specifically, we have found that the lattice parameter in the (U,Th)O₂ and (U,Np)O₂ system follows the Vegard's law, which decreases linearly with Np content, and that Na exists in a lattice position with good symmetry in the (U,Na)O₂ system by ²³Na NMR [1].

In this study, we investigated in the extension of our hydrothermal method to the U-Zr, U-Fe-Ni-Cr, U-Fe-Si, and U-B systems. For the study in the first year, we have carried out the hydrothermal experiments for the U-Zr, U-Fe, and U-Si systems.

EXPERIMENTS: We have developed techniques for hydrothermal synthesis by fabricating an ultra-small cell which can be used under the condition of 500°C-25 MPa. Uranium was initially used as hexavalent nitrate or chloride, but electrolytically reduced tetravalent was also used. In the hydrothermal synthesis, the salts and organic complexes of each element are added and dissolved to produce a homogeneous reaction, which may be closer to the actual condition of the simulated debris.

Hydrothermal experiments for the U-Zr, U-Fe, and U-Si systems were carried out by using UO₂(NO₃)₂ and Fe(NO₃)₃ as starting materials, zirconium nitrate dihydrate, sodium metasilicate dihydrate, (1) 150°C for 8 h, and (2) 450°C for 30 min, and an addition of acetaldehyde as organic additive, etc. The slurry was centrifuged and the solid phase was collected. The slurry was centrifuged, the solid phase was collected, dried, and XRD was obtained. The slurry was centrifuged and the solid phase was collected.

RESULTS: Not only the very moderate hydrothermal condition (1), but also relatively severe condition (2),

produced the diffractograms based on the UO₂ as shown in Fig. 1, independent from the metals coexisted. The result agrees well with our previous result without coexisting other metal ions [1]. The atmosphere is indicative of being reductive enough to transfer U(VI) to U(IV). An coexistence of other anions could result in the formation of new salt compounds such as silicates and phosphites [2-3].

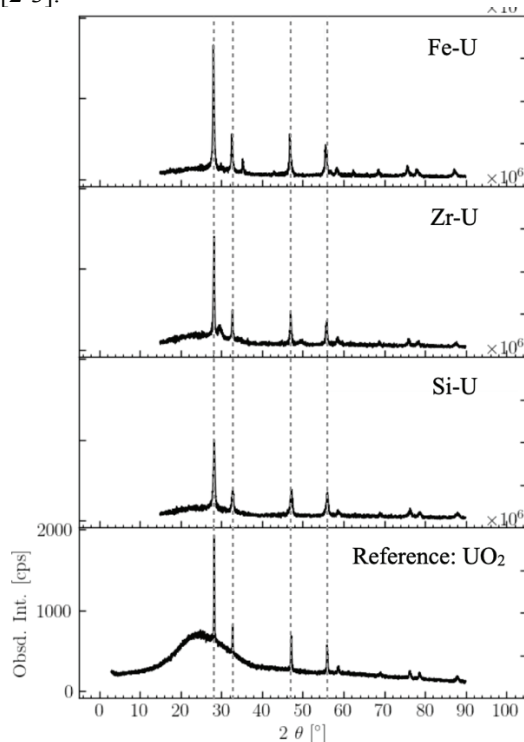


Fig. 1. X-ray diffractograms for samples obtained after hydrothermal synthesis at 450°C for 30 min. Starting materials are described in text.

By referring to recent researches by other researchers, hydrothermal synthesis of actinide compounds is challenging in some compounds. The phosphite salts of actinides(IV) are not extensively studied, but by using organic templates, some compounds with rare structures have been prepared [2]. On the other hand, the hydrothermal synthesis of silicates of rare earths and actinides such as ThSiO₄ and USiO₄ has been widely studied, but the synthesis was not reproducible. Eventually, the synthesis of PuSiO₄ has been done including calcination at 1350°C after pellet formation [3]. Thus, various developments could be necessary for hydrothermal synthesis of uranium salts.

The conditions are to be improved in future studies.

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- [1] C. Tabata, K. Shirasaki, M. Konaka, Dexin Li, N. Sakai, T. Yamamura, Now in preparation for submission.
- [2] E.M. Villa, et al., *Inorg. Chem.*, 52 (2013) 965.
- [3] P. Estevenon, et al., *Dalton Trans.*, 49 (2020) 6434.