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A New Type of Neptunyl(VI) Hydroxide which is Topologically Similar to α-$UO_2(OH)_2$

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A new type of neptunyl(VI) hydroxide α-$NpO_2(OH)_2$ **I** which is topologically similar to α-$UO_2(OH)_2$ has been synthesized from the thermal decomposition of the orthorhombic type $NpO_2(OH)_2 \cdot H_2O$ **II**. The powder X-ray diffraction patterns and ^{237}Np Mössbauer spectra have shown that properties of α-$NpO_2(OH)_2$ **I** are different from those of the reported β-$NpO_2(OH)_2$ **III**, which is similar to β-$UO_2(OH)_2$.

There is widespread interest in neptunium chemistry associated with the reprocessing of nuclear fuels and treatment of actinide wastes in the backend chemistry. The backend chemistry is very important today since many nuclear power plants operate everyday to produce actinide wastes as by-products. Within the group of uranyl(VI) hydroxides, various crystal structures have been reported.[1–10] It is considered that this polymorphism originates from the amphoterism of the valence(VI) of uranium.[11–13] For the valence(VI) of neptunium, since the amphoterism phenomenon also exists,[14–16] the polymorphism is expected to exist in neptunyl(VI) hydroxides equivalent to the uranyl(VI) hydroxides. However, few crystal structures have been reported up to now on neptunyl(VI) hydroxides,[17–20] and no systematic study has appeared. Based on the above assumption, we studied neptunyl(VI) hydroxides, and succeeded in the synthesis of a β type anhydrous hydroxide.[21]

The hydroxide compounds should be formulated as $NpO_2(OH)_2 \cdot nH_2O$, because the Mössbauer parameters[22] and the infra-red spectra[23] support the evidence of the existence of the cationic moiety $(NpO_2)^{2+}$. They were reported as those with $n = 0$, 1 and 3.[16] In the case of $n = 1$, three types of structures of the monohydrates $NpO_2(OH)_2 \cdot H_2O$ have been found in the orthorhombic type, the hexagonal type and the amorphous type.[17,18,21] In the case of $n = 0$, $NpO_2(OH)_2$, which is topologically similar to β-$UO_2(OH)_2$, was already obtained,[16,18,20,21] while $NpO_2(OH)_2$, which is topologically similar to α-$UO_2(OH)_2$, has not been synthesized. It is well-known that the crystallographic chemistry of the ions $Np^{VI}O_2^{2+}$ and $U^{VI}O_2^{2+}$ are remarkably similar so that some Np(VI) coordination compounds are isostructural to the corresponding U(VI) coordination compounds.

In the series of uranyl(VI) hydroxides, the α and β forms of $UO_2(OH)_2$, and the transformation from the β form to the α form, were reported.[1] The similarities between $Np^{VI}O_2^{2+}$ and $U^{VI}O_2^{2+}$ ions would indicate that α-$NpO_2(OH)_2$ would be obtained by new synthetic methods. We have attempted to synthesize α-$NpO_2(OH)_2$ **I** by using the thermal-decomposition of the orthorhombic type $NpO_2(OH)_2 \cdot H_2O$ **II**. We have succeeded to obtain α-$NpO_2(OH)_2$ **I** as confirmed by powder X-ray diffraction method (XRD) and ^{237}Np Mössbauer spectroscopy.

Experimental

The ^{237}Np powder crystals were dissolved in concentrated HNO_3 by heating to a slight boil to prepare the stock Np(VI) mother aqueous solution. The orthorhombic type $NpO_2(OH)_2 \cdot H_2O$ **II** was synthesized by the pyridine method.[21] Into the stock mother aqueous $NpO_2(NO_3)_2$ solution, a small amount of pyridine was added at 343 K. The chocolate-brown precipitate of **II** was obtained around pH 3.5. The thermal decomposition of orthorhombic type $NpO_2(OH)_2 \cdot H_2O$ **II** compounds was investigated in a dry atmosphere on a Satorius MP8 electric microbalance by recording the thermogravimetric (TG) curve. The TG curve suggests that the formula $NpO_2(OH)_2$ species corresponds to a plateau between 393–523 K, as shown in Fig. 1. We have

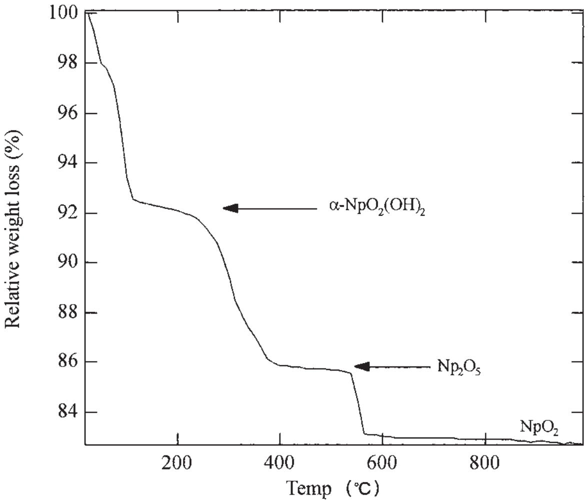

Fig. 1. Thermogravimetric curve of the orthorhombic-type $NpO_2(OH)_2 \cdot H_2O$ **II**.

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obtained a new type of neptunyl(VI) hydroxide $NpO_2(OH)_2$ **I** by heating **II** at 403 K for 90 minutes. The products were examined by the powder X-ray diffraction patterns using a diffractometer, model RAD-3C (Rigaku Co., Cu $K\alpha$ radiation). ^{237}Np Mössbauer spectra were measured using a cryostat equipped with a driving system (WissEL GmbH, System MS II) with an assembled ^{241}Am metal source.[24] The Mössbauer data obtained were least square fitted to Lorentzian lines by using "IGOR" (Wave metrics, Lake Oswego, Oregon) software.

Results and Discussion

$NpO_2(OH)_2$ **I** as the powder crystals is synthesized by the thermal decomposition of the orthorhombic type $NpO_2(OH)_2{\cdot}H_2O$ **II**. It is very difficult to obtain single crystals of **I** suitable for X-ray structure determination. The powder X-ray pattern at room temperature indicates the structure of **I** is isostructural to that reported on α-$UO_2(OH)_2$, as shown in Fig. 2. That can be indexed in the orthorhombic crystal system with the lattice parameters $a = 0.418(2)$, $b = 1.017(3)$, and $c = 0.697(3)$ nm, very close to that of α-$UO_2(OH)_2$.[7] Refinement of the crystal structure of α-$NpO_2(OH)_2$ has been tried by X-ray powder Rietveld analysis using the atomic position parameters of α-$UO_2(OH)_2$ and the space group *Cmca* (No. 64). The Rietveld analysis has been done using free software of RIETAN-97β.[25] The refinement results ($R_{wp} = 26.35\%$, $R_p = 20.21\%$, $S = 1.18$) are not enough to decide accurately the atomic distances and angles in α-$NpO_2(OH)_2$ due to the poor powder XRD data. The Ritevelt results also show that the layered structure of **I** is similar to that of α-$UO_2(OH)_2$.[7] As α-$NpO_2(OH)_2$ is a layered compound consisting of parallel infinite $NpO_2(OH)_2$ subunits where the Np atom coordinates to eight O atoms, the $NpO_2(OH)_2{\cdot}H_2O$ **II** compound can be considered as an intercalation compound which is built up by infinite two-dimensional $NpO_2(OH)_2$ host frameworks and guest H_2O molecules between the layers. Figure 1 suggests the material **II** may contain the larger amount of intercalated water molecules into the interlayer space and/or some amount of absorbed water molecules on the surface. The thermal induced water-guest release reaction in $NpO_2(OH)_2{\cdot}H_2O$ **II** allows for the formation of α-$NpO_2(OH)_2$ **I**. Since the Mössbauer spectra of compounds α-$NpO_2(OH)_2$ **I**, the orthorhombic type $NpO_2(OH)_2{\cdot}H_2O$ **II**, and β-$NpO_2(OH)_2$ **III** have been obtained, those are shown in Fig. 3, and the Mössbauer parameters are listed in Table 1. We have found that the Mössbauer spectrum of compound **I** is clearly different from that of **III**, and slightly different from that of **II**. The results from Mössbauer spectroscopy agree with the X-ray structural data. While the thermally induced guest-release reaction is described as $NpO_2(OH)_2{\cdot}H_2O \rightarrow \alpha\text{-}NpO_2(OH)_2 + H_2O$, the ^{237}Np Mössbauer data indicate a change in the environment around the Np atom occurs in the host layer since the water molecules in the host layer are lost. The crystal structure of α-$NpO_2(OH)_2$ **I** is different from that of β-$NpO_2(OH)_2$ **III** because the Np(VI) atom of **I** is coordinated by eight O atoms and that of **III** by six O atoms.

Jove et al. reported that Np(VI) compounds can belong to one of three distinct isomer-shift areas depending on their co-

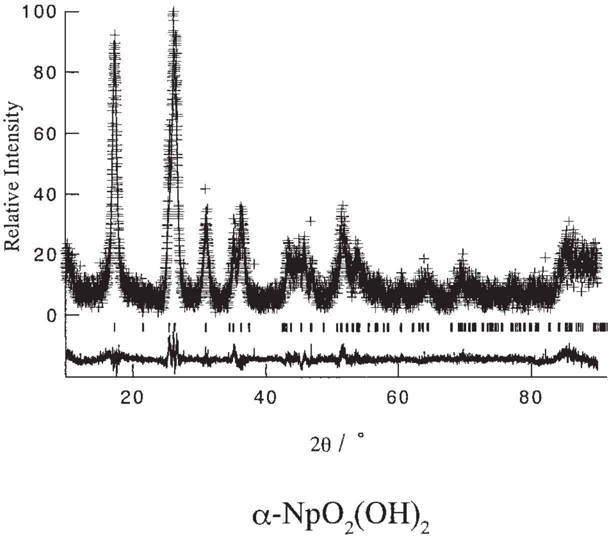

Fig. 2. Result of the Rietveld refinement for the α-$NpO_2(OH)_2$ **I**. Plus mark is observed and solid line is calculated.

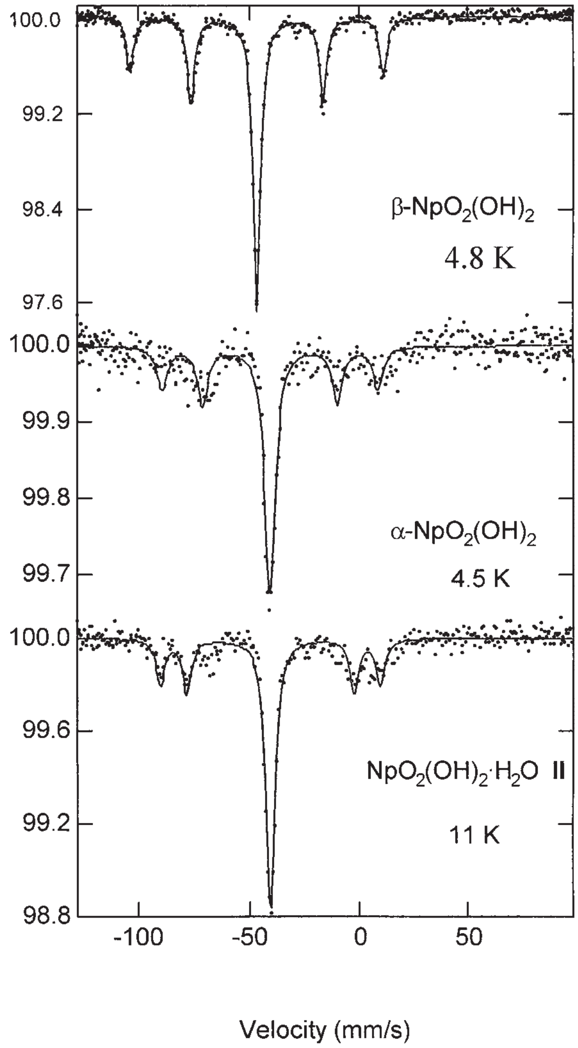

Fig. 3. ^{237}Np Mössbauer spectra for the α-$NpO_2(OH)_2$ **I**, the orthorhombic type $NpO_2(OH)_2{\cdot}H_2O$ **II** and the β-$NpO_2(OH)_2$ **III**.

Table 1. ^{237}Np Mössbauer Parameters of Neptunyl(Ⅵ) Hydroxides

Compounds	Temperature /K	Isomer Shift (NpAl$_2$) /mm s^{-1}	e^2qQ /mm s^{-1}	η	Reference
$NpO_2(OH)_2 \cdot H_2O$ (orthorhombic type)	11	−39.9(1)	179(1)	0.69(1)	21
α-$NpO_2(OH)_2$	4.5	−40.2(1)	170(1)	0.44(1)	This work
β-$NpO_2(OH)_2$	4.8	−46.2(1)	193(1)	0.16(1)	21

ordination number (six-fold, seven-fold and eight-fold), and, likewise, the electric field gradient values can be subclassified in three distinct groups.[26] The isomer shift value of compound **I** is clearly in the range of eight-fold coordination, as can be seen in Fig. 4, where the compounds **7–10** are eight-fold coordination. The isomer-shift value of β-$NpO_2(OH)_2$ **Ⅲ**, which has six-fold coordination, is much less negative than compounds **1–6** with six coordination, as has already been discussed in the previous report.[21] However, the linear correlation between the isomer shift values and the mean Np–O bond distances is confirmed for **I** and **Ⅲ**. Since the mean Np–O bond distance may be deduced from the reported isostructural U(Ⅵ) compound data obtained by single crystal X-ray structural determination, the plot of **Ⅱ** is not found in Fig. 4 due to a lack of single crystal data of the isostructural U(Ⅵ) compound.

While the α and β forms of $UO_2(OH)_2$ and the transformation from the β form to the α form on cooling were found in the series of uranyl(Ⅵ) hydroxides,[7,23] the β-$NpO_2(OH)_2$ do not transform to α-$NpO_2(OH)_2$ on cooling in the same way as β-$UO_2(OH)_2$ because the ^{237}Np Mössbauer spectra of **I** and **Ⅲ** were measured at 4.5 K and 4.8 K, and the powder XRD data were obtained at room temperatures. This is an example that some properties of Np(Ⅵ) ions are slightly different from those of U(Ⅵ) ions, while the resemblances between U and Np atoms are sometimes useful in research on the Np compounds. It should be noted that the synthesis method to obtain α-$UO_2(OH)_2$ did not allow the formation of α-$NpO_2(OH)_2$ **I**.

In conclusion, we have found that α-$NpO_2(OH)_2$ **I** can be obtained by thermal decomposition of the orthorhombic-type $NpO_2(OH)_2 \cdot H_2O$ **Ⅱ**. The powder X-ray diffraction pattern of α-$NpO_2(OH)_2$ **I** indicates that the crystal structure of α-$NpO_2(OH)_2$ is similar to the reported structure of α-$UO_2(OH)_2$, having eight-fold coordination. The ^{237}Np Mössbauer parameters indicate the Np environment of **I** is different from that of **Ⅱ** and **Ⅲ**. The results suggest that the ^{237}Np Mössbauer parameters can give useful information about the coordination environment around the Np(Ⅵ) atom. ^{237}Np Mössbauer spectroscopy is also a very powerful tool for checking the materials in the family of Np(Ⅵ) hydroxides.

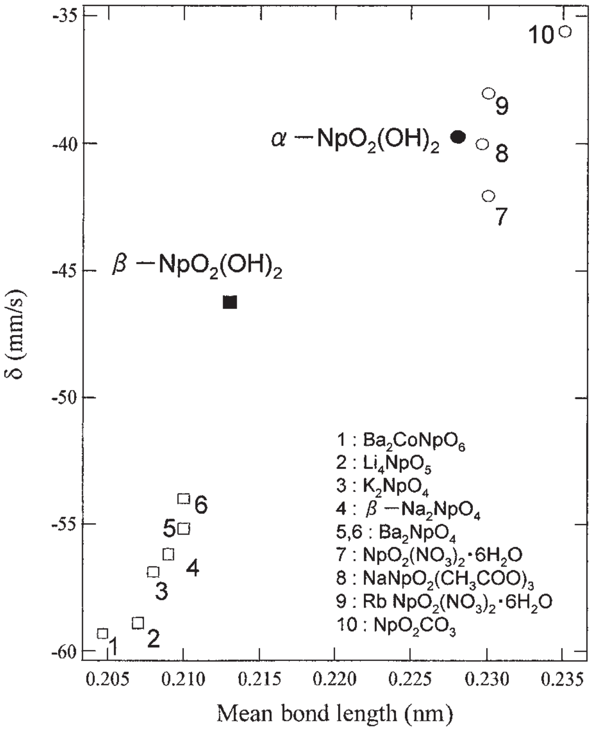

Fig. 4. Plot of isomer shift against mean Np–O bond distance for the oxygen-coordinated Np(Ⅵ) compounds. The mean Np–O bond distance may be deduced from isostructural U(Ⅵ) compounds. The data 1–10 are from Ref. 26.

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