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Synthesis of americium trichloride by the reaction of americium nitride with cadmium chloride

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Abstract

Americium trichloride was synthesized by the reaction of americium nitride with cadmium chloride at 600–660 K in a dynamic vacuum. The product was hexagonal AmCl₃, of which lattice parameters were determined to be $a_0 = 0.7390$ and $c_0 = 0.4215$ nm. The results indicate that high purity AmCl₃ samples, in which the oxychloride was not found, were prepared without the use of corrosive reagents. The reaction of the nitrides with cadmium chloride is suitable for synthesis of high purity actinide and lanthanide chlorides. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Actinide chlorides are attractive materials in both basic chemistry and nuclear engineering. Some of the behaviors of the actinide compounds are significantly different from those of the lanthanide compounds though the elements in these two f-series show similarity in many aspects. One of the differences is the range of valence states of the ionic compounds including chlorides. Investigation of the behaviors of the actinide compounds is important to understand the role of 5f electrons.

Meanwhile, transuranium compounds are of particular interests in partitioning and transmutation strategy aiming to reduce the radiotoxicity of high level nuclear wastes containing transuranium elements. Pyrochemical separation process, one of the candidates for the partitioning process, consists of electrorefining and molten salt/liquid metal reductive extraction using molten salts (i.e., molten chlorides) as solvents. In the molten chlorides bathes, a typical chemical form of the actinides is the chloride. Therefore, thermodynamic data of actinide chlorides are needed not only for basic chemistry but also for development of the pyrochemical separation processes. However, the thermodynamic data (i.e., heat capacity and electrochemical data)

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of transuranium chlorides are limited because of difficulty of handling the samples with high radioactivity and instability in the atmosphere. The transuranium chlorides need to be synthesized and handled in the hot facilities (glove boxes or hot cells) maintained with inert atmosphere.

Americium trichloride, which is one of the transuranium chlorides, has been synthesized in a small scale by the reaction of the oxide with CCl₄ [1] or HCl [2,3] and by the ammonium chloride route [4–6]. In the ammonium chloride route, the anhydrous chloride was synthesized by the thermal decomposition of the complex chloride (NH₄)₃AmCl₆, which was synthesized by heating hydrochloric acid solutions containing americium ions and ammonium ions under HCl gas [5]. In all the literatures shown above, corrosive reagents such as HCl were used, and the samples were purified by sublimation to remove impurities such as oxychlorides; they are easily formed by the reaction of the chloride with moisture or oxygen in the atmosphere. The use of corrosive reagents may be a problem because they can corrode the materials of the hot facilities. A loss of the samples caused by sublimation could also be a problem when using a large amount of transuranium samples. A new method for synthesizing high purity transuranium chlorides without using corrosive reagents is needed.

On the other hand, to investigate the basic properties of Am in LiCl–KCl eutectic melt, Am metal dissolved in liquid cadmium were oxidized by $CdCl_2$ in the molten salt to form the chloride

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dissolved in the molten salt [7]. Furthermore, nitrides of some lanthanides and actinides were oxidized by CdCl₂ in LiCl–KCl eutectic melt to form their chlorides dissolved in the melt [8,9]. Adopting the methods shown above, the mixture of the transuranium chloride and alkaline chlorides can be obtained. However, it is difficult to separate the transuranium chloride from alkaline chlorides. If the reactions can occur without a molten salt bath as a solvent, they are adequate to prepare the transuranium chlorides solely without using corrosive reagents.

In the present study, americium trichloride was synthesized by the solid-state reaction of americium nitride with cadmium chloride in several hundreds milligrams scale. This method does not require the use of corrosive reagents and solvents.

2. Experimental

All the procedures were carried out in the module for TRU-High Temperature Chemistry (TRU-HITEC) installed in Nuclear Fuel Cycle Safety Engineering Research Facility (NUCEF), Japan Atomic Energy Agency (JAEA) [10]. The TRU-HITEC consists of a glove box and three hot cells maintained with a purified argon gas atmosphere. Typical impurities in the argon gas were $H_2O < 1$ ppm and $O_2 < 1$ ppm.

Starting material was ²⁴¹AmO₂ powder purchased from the Radiochemical Centre (UK) 35 years ago. Due to the decay of ²⁴¹Am ($T_{1/2}$ = 432 years) during 35 years of storage, the composition of the actinide elements was estimated to be 95% of ²⁴¹Am and 5% of ²³⁷Np. The oxide sample was heated at 923 K in an oxygen gas flow (0.5 L/min) for 1 h to remove organic contamination and moisture adsorbed on the sample and to adjust the oxidation state of the americium. The heated sample was identified as a single phase of the dioxide with the fluorite structure by X-ray diffraction analysis.

Americium nitride was prepared from the oxide by the carbothermic reduction method [11]. The oxide sample was ground and mixed with carbon powder at a molar ratio (C/oxide) of 3.2. The mixture was pressed to pellets; each pellet had about 100 mg of the oxide. Several pellets were placed in a tungsten crucible and heated at 1423–1823 K for about 8 h in a nitrogen gas flow (2.5 L/min). The CO gas release was monitored continuously by an infrared spectrometer to observe the conversion from the oxide to the nitride. The formation of the nitride is expressed by

$$AmO_2 + \frac{1}{2}N_2 = AmN + 2CO \uparrow .$$
⁽¹⁾

After the CO gas release subsided, the sample was additionally heated at 1823 K for more than 8 h in N_2 + 4% H_2 gas flow (2.5 L/min) to remove residual carbon.

Americium trichloride was synthesized by the reaction of the nitride with cadmium chloride; the amounts of the reactants used in two runs are shown in Table 1. This reaction can be expressed by

$$AmN + \frac{3}{2}CdCl_2 = AmCl_3 + \frac{3}{2}Cd\uparrow + \frac{1}{2}N_2\uparrow$$
(2)

The nitride was ground and mixed with CdCl₂ (APL, 99.99%) powder at a molar ratio (CdCl₂/AmN) of 1.75. The mixture was pressed to pellets; each pellet had about 100 mg of the nitride. Several pellets were placed in an alumina crucible and heated up stepwise from room temperature to 723 K in a dynamic vacuum kept with a turbo-molecular pump. The pressure in the vacuum system



Fig. 1. The evolution of the pressure while heating the mixture of the nitride and $CdCl_2$ on run #2.

was monitored by a pressure gauge. The heating equipment has a water-cooled cold finger set in the furnace to trap cadmium vapor produced by reaction (2). Heating was stopped after the monitored pressure became low; it suggested the termination of the release of nitrogen gas by reaction (2).

Each of the obtained samples was ground and mounted on a sample holder made of platinum for X-ray diffraction analysis. The XRD profiles were obtained at room temperature typically by 0.02° step scanning between 5° and 80° in 2θ using Mo K α radiation (Rigaku RINT Ultima⁺) to determine both the chemical form and the lattice parameters.

3. Results and discussion

3.1. Synthesis of the nitride from the oxide

The obtained nitride sample was determined as a single cubic phase with $a_0 = 0.49973 \pm 0.00001$ nm. The lattice parameter was close to the reported value $a_0(\text{AmN}) = 0.4998 \pm 0.0001$ nm [11] and obviously larger than $a_0(\text{NpN}) = 0.48987 \pm 0.00001$ nm [12]. The sample was considered to be a solid solution (Am_{0.95}Np_{0.05})N, of which lattice parameter was expected to be 0.4993 nm adopting the Vegard's law to the reported values of AmN and NpN [11,12]. The observed lattice parameter was 0.09% larger than the expected value. The lattice expansion could be attributed to the self-irradiation damage [13].

3.2. Synthesis of the chloride from the nitride

Behaviors of the pressure monitored during heating of the mixture of the nitride and $CdCl_2$ were essentially same on two runs. Fig. 1 shows the evolution of the pressure observed on

Table 1

The amounts of the reactants and the product, the yield of the reaction and the lattice parameters of the products (AmCl₃) by the reaction of americium nitride with cadmium chloride

Run#	Reactants		Product (mg)	Yield (%)	Lattice parameters	
	Nitride (mg)	CdCl ₂ (mg)			$a_0 (nm)$	<i>c</i> ₀ (nm)
1	176.3	221.9	233.8	97	0.7391 ± 0.0002	0.4214 ± 0.0003
2	211.9	279.4	289.0	100	0.7388 ± 0.0003	0.4215 ± 0.0004



Fig. 2. Temperature dependence of the pressure while heating the mixture of the nitride and CdCl₂.

run#2. The behavior of the pressure can be categorized into three temperature regions. At temperatures lower than 600 K (region I), the pressure increased up to about 10^{-4} Pa just after the temperature was raised stepwise, and then decreased gradually at each temperature. At 600 K < T < 660 K (region II), the pressure reached constant at each temperature and the pressure increased with temperature. At 660 K < T < 723 K (region III), the pressure increased gradually at each temperature was raised stepwise and then decreased gradually at each temperature.

Temperature dependence of the observed pressure is shown in Fig. 2. Plotted data are the peak values for the regions I and III, and the constant values for the region II. The behavior in the region I can be attributed to the release of the gas adsorbed on the sample or the apparatus. The pressure of the nitrogen gas generated by reaction (2) would be very low in the region I. The pressure in the region II increased as the temperature increased. This result suggests that reaction (2) proceeds in the region II. The temperature dependence of the pressure is expressed as $P = P_0 \exp(-E_a/RT)$, where E_a is the apparent activation energy of the reaction; E_a was calculated to be 191 kJ/mol with the results of run #2. The pressure decrease in the region III could be due to the termination of reaction (2).

Dark yellow fine powder was obtained by the reaction. The amounts of the product and the yield of the reaction are shown



Fig. 3. The XRD pattern of the obtained chloride sample with the reported data of $AmCl_3$ [15]. The peaks assigned to the Pt sample holder are marked with (×).

in Table 1. The color of the cold finger became black; cadmium metal from reaction (2) seems to be trapped. Residual $CdCl_2$ could be vaporized and also trapped on the cold finger while heating the sample around 700 K, at which vapor pressure of $CdCl_2$ reaches to 2 Pa [14].

Fig. 3 shows both the XRD pattern of the obtained chloride and the reported XRD peaks of AmCl₃ [15]. All the observed peaks except those assigned to the Pt sample holder were assigned to the hexagonal trichloride. No peaks which can be assigned to the oxides or the oxychlorides were found. Table 1 shows the lattice parameters of the hexagonal americium trichloride refined by the least square fitting with the software CellCalc [16]. Table 2 compares the averaged lattice parameters for two samples obtained in this study with the reported ones of AmCl₃ [1–5,17] and NpCl₃ [17–19]. The lattice parameters obtained in this study are close to those reported for AmCl₃ prepared by other methods, and obviously smaller than those of NpCl₃. The sample was considered to be $(Am_{0.95}Np_{0.05})Cl_3$, of which lattice parameters are expected to be $a_0 = 0.7384$ and $c_0 = 0.4217$ nm adopting the Vegard's law to the reported values of AmCl₃ [3,15] and NpCl₃ [17,18]. The observed lattice parameters agree with those expected for (Am_{0.95}Np_{0.05})Cl₃ within the experimental uncertainties.

The results show that high purity transuranium chloride samples can be prepared without using corrosive reagents by the method described in this paper. In addition, this method does

Table 2

The averaged lattice parameters of two samples in this study and the reported lattice parameters of $AmCl_3$ and $NpCl_3$

Sample	Scale	Method of syntheses	<i>a</i> ₂ (nm)	<i>c</i> ₀ (nm)	Reference
Sample	Seale	Wethod of syntheses			Kelefellee
²⁴¹ AmCl ₃ ^a	200-300 mg	Nitride + $CdCl_2$	0.7390	0.4215	This work (average)
²⁴¹ AmCl ₃	\sim µg	$AmO_2 + CCl_4^{b}$	0.7385 ± 0.001	0.4248 ± 0.001	[1,17]
²⁴¹ AmCl ₃	20-30 mg	$AmO_2 + HCl^b$	0.7384 ± 0.0004	0.4225 ± 0.0004	[2]
²⁴³ AmCl ₃	-	$AmO_2 + HCl^b$	0.7382 ± 0.0001	0.4214 ± 0.0001	[3]
²⁴³ AmCl ₃	multi-mg	Ammonium chloride route ^b	0.7390 ± 0.0003	0.4234 ± 0.0002	[4]
²⁴³ AmCl ₃	$\sim 20 \mathrm{mg}$	Ammonium chloride route ^b	0.73880 ± 0.00005	0.42235 ± 0.00005	[5]
²³⁷ NpCl ₃	$\sim \mu g$		0.7420 ± 0.001	0.42815 ± 0.0005	[17–19]

^a The composition of the sample is estimated to be (²⁴¹Am_{0.95}²³⁷Np_{0.05})Cl₃.

^b The samples were purified by sublimation after the syntheses.

not require additional purification by sublimation because the obtained sample did not contain impurities such as the oxychlorides and the oxides. It could be due to the fact that the reactants, the nitride and $CdCl_2$, do not contain oxygen atoms in principle. The reagents containing oxygen can easily react with chlorides to form stable by-products, the oxychlorides and the oxides. Therefore, this method is suitable for synthesizing not only transuranium chlorides but also the chlorides of other actinides and lanthanides.

4. Conclusion

Americium trichloride has been successfully synthesized by the reaction of americium nitride with cadmium chloride at 600–660 K in a dynamic vacuum. The product is hexagonal AmCl₃; its averaged lattice parameters for two samples prepared with a nearly identical manner are $a_0 = 0.7390$ and $c_0 = 0.4215$ nm. The results indicate that high purity AmCl₃ samples, in which the oxychloride was not found, were prepared without the use of corrosive reagents and purification by sublimation.

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