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Solid state reactions of CeO_2, ThO_2 and PuO_2 with ammonium sulphate

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Abstract

Solid state reactions of CeO_2, ThO_2 and PuO_2 with $(NH_4)_2SO_4$ were investigated by chemical, IR, thermal and X-ray diffraction methods. At 250°C, CeO_2, ThO_2 and PuO_2 formed tetrasulphate compounds i.e., $(NH_4)_4Ce(SO_4)_4$, $(NH_4)_4Th(SO_4)_4$ and $(NH_4)_4Pu(SO_4)_4$, respectively. On further heating $(NH_4)_4Ce(SO_4)_4$ decomposed to give $(NH_4)_2Ce(SO_4)_3$, $(NH_4)Ce(SO_4)_2$ and $Ce_2(SO_4)_3$; where, cerium undergoes change in oxidation state from +4 to +3. The decomposition of $(NH_4)_4M(SO_4)_4$ (M = Th or Pu) led to the formation of $(NH_4)_2M(SO_4)_3$ and $M(SO_4)_2$. Crystal data for solid reaction products were determined from their X-ray powder diffraction data. Dissolution of the products formed at 350–360°C during the reactions of CeO_2, ThO_2 and PuO_2 with $(NH_4)_2SO_4$ was also investigated. © 1999 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Dissolution of nuclear fuel materials is an essential requirement for fuel processing and for the accurate and precise determination of their constituents by chemical methods. Treating fuel materials with fused salts is one method for solubilizing them. For this purpose, fuel materials have been treated with alkali salts such as nitrates and carbonates of lithium and sodium [1], $NaNO_3$, $NaNO_3$–NaOH and $NaNO_3$–Na_2CO_3 [2], Na_2O_2–NaOH [3] and $Na_2S_2O_7$–$K_2S_2O_7$ [4]. Reacting spent nuclear fuels with fused alkali nitrates is a common pretreatment step in fuel processing. Reaction between UO_2 and nitrate melt forming soluble alkali uranates is fast and complete at 400–500°C [5]. In the sulphate medium, Brambilla et al. [6] considered molten alkaline sulphate eutectic mixtures at 500–600°C as a means of performing nuclear fuel dissolution for reprocessing irradiated fuel elements. Fusion of PuO_2, PuO_2–UO_2 and PuO_2–ThO_2 with ammonium bisulphate at 400°C has been developed for the dissolution of refractory materials in H_2SO_4 to produce a solution suitable for analysis by electrometric methods [3]. The molten salt method leaves a large amount of unreacted salt which leads to increase in the volume of high level waste. Fujino et al. [1] studied the reaction of UO_2 with various amounts of alkali salts to know the minimum amount of salts required to form soluble uranates.

On reaction with $(NH_4)_2SO_4$ at high temperature, metal oxides form various sulphates [7] and in an earlier study [8], it was observed that uranium oxides, when reacted with $(NH_4)_2SO_4$ at temperature above 250°C, formed double sulphates of uranium and ammonium. Excess of ammonium sulphate decomposes as volatile gaseous products above 350°C, leaving no unreacted salt.

Thorium and plutonium oxides are nuclear fuel materials and cerium is a structural and chemical homologue of plutonium and also a major fission product [9]. In the present work, solid state reactions of CeO_2, ThO_2 and PuO_2 with ammonium sulphate were carried out in order to identify the reaction products formed at various temperatures, and to examine their dissolution characteristics. The solid reaction products were characterized by chemical, IR, thermogravimetry and X-ray diffraction analysis.

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Preliminary studies had shown that the solid sulphate compounds formed during the solid state reactions of uranium oxides with $(NH_4)_2SO_4$ readily dissolved in 1–2 M HNO_3 or H_2SO_4 [10]. The products formed at 350–360°C during the reactions of CeO_2, ThO_2 and PuO_2 with $(NH_4)_2SO_4$ were also investigated for their dissolution behaviour.

2. Experimental

CeO_2, ThO_2 and PuO_2 were obtained by the decomposition of oxalates of cerium, thorium and plutonium, respectively at 800°C. All the three oxides were mixed separately with $(NH_4)_2SO_4$ (Analar grade) in various molar proportions.

Thermograms of the reaction mixtures of CeO_2 and ThO_2 with $(NH_4)_2SO_4$ were recorded in platinum cups on a Setaram thermoanalyzer. Thermograms for PuO_2 and $(NH_4)_2SO_4$ mixtures were recorded on a Mettler thermoanalyser enclosed in the glove box for handling radioactive samples. A stream of dry air was used as the cover gas. For DTA studies, sintered alumina was used as a reference material. The X-ray diffraction patterns were recorded on a Diano X-ray diffractometer using CuKα radiation ($\lambda = 0.154178$ nm). The density of the compounds were determined pyknometrically by the displacement method using carbon tetrachloride solvent. The IR spectra of the samples were recorded in the range of 4000–400 cm^{-1} on a Pye Unicam spectrophotometer model PU 9512 with samples dispersed in nujol mulls and pressed in KBr discs.

Products were analyzed for Ce(III) and Ce(IV) contents by determining total cerium and Ce(IV) by redox titrimetric method. Total cerium content in the sample was determined by oxidising the weighed aliquots of the sample to Ce(IV) using 30 mg of AgO in 10 ml of 1M H_2SO_4 medium. Excess of AgO was destroyed selectively by adding 1M sulphamic acid. Ce(IV) in the solution was reduced to Ce(III) using known excess of standard Fe(II) solution and titrated against standard $K_2Cr_2O_7$ solution. For determining the amount of Ce(IV), weighed aliquot of the same sample was dissolved in 10 ml of 1M H_2SO_4 and Ce(IV) was reduced with known excess of standard Fe(II). The excess of Fe(II) was titrated against standard dichromate solution. Ce(III) content was calculated by subtracting the amount of Ce(IV) from total cerium content. For the determination of plutonium content, weighed amount of the reaction products dissolved in 1M H_2SO_4 were analysed by redox titrimetry using the method of Drummond and Grant [11].

Thorium content in reaction products was determined by the X-ray fluorescence method using tungsten target, scintillation counter and LiF[200] as dispersion crystal on a Diano X- ray spectrometer, using ThLα line for intensity measurement.

3. Results and discussion

3.1. Reactions with CeO_2

TG curves of reaction mixtures of CeO_2 and $(NH_4)_2SO_4$ in molar proportions of 1:4 and higher showed weight losses in the temperature range of 250–325°C, 325–350°C, 360–435°C, 435–510°C and 750–840°C, which were accompanied by the corresponding DTA endothermic peaks. Fig. 1 shows the TG and DTA thermogram of 1:4 mixture of CeO_2 with $(NH_4)_2SO_4$ recorded at a heating rate of 4°C/min. For the mixtures having ratios 1:5 and above, TG curves differed from that of 1:4 mixture only below 400°C indicating the loss of excess unreacted $(NH_4)_2SO_4$. On heating a 1:4 mixture of CeO_2 and $(NH_4)_2SO_4$ isothermally in a furnace at 250°C for 10 h, a mass loss of 15% was observed which corresponded to the formation of $(NH_4)_4Ce(SO_4)_4$ according to Eq. (1) given below:

$$CeO_2 + 4(NH_4)_2SO_4 \overset{250°C}{\rightarrow}$$

$$(NH_4)_4Ce(SO_4)_4 + 4NH_3 + 2H_2O, \quad (1)$$

Further isothermal heating of the reactants at 325°C, 360°C, 450°C and 775°C for 5–6 h led to the formation of the products $(NH_4)_2Ce(SO_4)_3$, $(NH_4)Ce(SO_4)_2$, $Ce_2(SO_4)_3$ and CeO_2, respectively. The mass losses observed during heating at different stages, were in agreement with the expected losses for the formation of the products as given in Table 1. The intermediate products were analysed by redox titrimetry to determine the oxidation state of cerium, which confirms the presence of cerium in +4 state in $(NH_4)_4Ce(SO_4)_4$ and $(NH_4)_2Ce(SO_4)_3$ and in +3 state in $(NH_4)Ce(SO_4)_2$ and $Ce_2(SO_4)_3$. The products, $(NH_4)Ce(SO_4)_2$ and

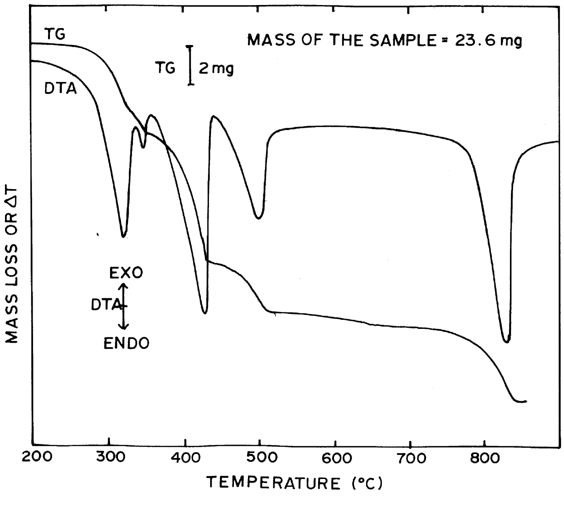

Fig. 1. TG and DTA curves of 1:4 mixture of CeO_2 with $(NH_4)_2SO_4$.

Table 1
Reaction products of $(NH_4)_2SO_4$ with CeO_2, ThO_2 and PuO_2 formed at different temperatures

Reaction mixtures	Temperature (°C) ± 10	Mass loss (%)		Products identified
		Measured [a]	Calculated	
$4(NH_4)_2SO_4+CeO_2$	250	15.2 ± 0.1	14.9	$(NH_4)_4Ce(SO_4)_4$
	325	33.9 ± 0.1	33.7	$(NH_4)_2Ce(SO_4)_3$
	360	51.2 ± 0.2	50.0	$(NH_4)Ce(SO_4)_2$
	450	59.8 ± 0.2	59.4	$Ce_2(SO_4)_3$
	775	76.0 ± 0.3	75.4	CeO_2
$4(NH_4)_2SO_4+ThO_2$	250	13.2 ± 0.1	13.1	$(NH_4)_4Th(SO_4)_4$
	350	28.8 ± 0.1	29.8	$(NH_4)_2Th(SO_4)_3$
	450	46.5 ± 0.2	46.5	$Th(SO_4)_2$
	760	67.7 ± 0.2	66.7	ThO_2
$4(NH_4)_2SO_4+PuO_2$	250	12.9 ± 0.1	13.0	$(NH_4)_4Pu(SO_4)_4$
	350	30.4 ± 0.1	29.5	$(NH_4)_2Pu(SO_4)_3$
	450	46.3 ± 0.2	46.1	$Pu(SO_4)_2$
	760	66.6 ± 0.2	66.1	PuO_2

[a] Mean of two measurements with their deviations.

$Ce_2(SO_4)_3$, identified in these reactions are in agreement with the decomposition scheme of $(NH_4)_4Ce(SO_4)_4$ given in the literature [12,13], where, the magnetic susceptibility and XPS measurments were used for the characterisation of oxidation states in the products.

Thus, cerium undergoes two successive changes of oxidation state, Ce(IV) → Ce(III) → Ce(IV). The mechanism of such double valency change in cerium during the thermal decomposition of their compounds has not been well understood. The reduction of cerium from +4 to +3 oxidation state in $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ and $(NH_4)_2Ce(NO_3)_6$ has been explained by Pokol et al. [12] due to the reducing effect of ammonium ions. But it is probably not the sole reducing agent since this phenomenon is also observed during the thermal decomposition of $Ce(SO_4)_2 \cdot 4H_2O$ [14] and various cesium cerium sulphates [15], and also for $K_2Ce(NO_3)_6$ and $Rb_2Ce(NO_3)_6$ [16].

The identification of the intermediate $(NH_4)_2Ce(SO_4)_3$ in these reactions has not been reported before. The intermediate product of the composition $(NH_4)_3HCe(III)(SO_4)_{3.5}$ reported by Sharma et al. [17] could not be isolated in these reactions.

The IR spectra of $(NH_4)_2Ce(SO_4)_3$ and $(NH_4)Ce(SO_4)_2$, given in Fig. 2, show characteristic frequencies in the region of 3350–3100 cm^{-1} due to ammonium ions and in the region of 1250–950 cm^{-1} and 680–580 cm^{-1} due to sulphate ions. The IR spectrum of $Ce_2(SO_4)_3$ showed absorption frequencies in the region of sulphate ions only. The IR spectra and X-ray data on $(NH_4)_4Ce(SO_4)_4$ could not be recorded due to its hygroscopic nature.

The X-ray powder data of $(NH_4)_2Ce(SO_4)_3$, $(NH_4)Ce(SO_4)_2$ and $Ce_2(SO_4)_3$ were indexed on monoclinic, monoclinic and orthorhombic crystal systems, respectively. The cell parameters refined by the least-squares method using a computer programm [18] are given in Table 2. The indexed X-ray powder data of $(NH_4)_2Ce(SO_4)_3$ and $(NH_4)Ce(SO_4)_2$ are given in Table 3 and for $Ce_2(SO_4)_3$ in Table 4, respectively. The similarity in the crystal data of $(NH_4)_2Ce(SO_4)_3$ with that of $(NH_4)_2U(SO_4)_3$ [8] indicates that both the compounds are isostructural. The crystal data on $(NH_4)Ce(SO_4)_2$ had been reported by Sarukhanyan et al. [19], i.e., $a = 0.7119$ nm, $b = 0.5424$ nm, $c = 0.9295$ nm, $\beta = 98.58°$ and $Z = 2$, whereas the X-ray powder data of $(NH_4)Ce(SO_4)_2$ obtained in the present studies could be indexed on cell parameters given in Table 2. The differences in both the crystal data of $(NH_4)Ce(SO_4)_2$ suggest its existence in two different polymormphs which may reflect different methods of preparation of the compound. $(NH_4)Ce(SO_4)_2$ was prepared by Sarukhanyan et al. by the isothermal evaporation of the solution of $(NH_4)_2SO_4$ and $Ce_2(SO_4)_3$ at 70°C, whereas in the present studies it is formed as a decomposition product at 360°C. The unit cell parameter '*b*' is nearly doubled for the high temperature phase, whereas '*a*' and '*c*' values for both polymorphs do not differ significantly.

3.2. Reactions with ThO_2 and PuO_2

Thermograms of the reaction mixtures of ThO_2–$(NH_4)_2SO_4$, PuO_2–$(NH_4)_2SO_4$ in molar ratios of 1:4 and higher were recorded in a thermoanalyser up to 850°C at a heating rate of 4°C/min. TG and DTA curves of the mixture of ThO_2 and $(NH_4)_2SO_4$ were similar in nature to those of PuO_2 and $(NH_4)_2SO_4$. TG and DTA curves of mixture of ThO_2 and $(NH_4)_2SO_4$ in 1:4 molar ratio have been shown in Fig. 3. For the mixtures of ThO_2 or

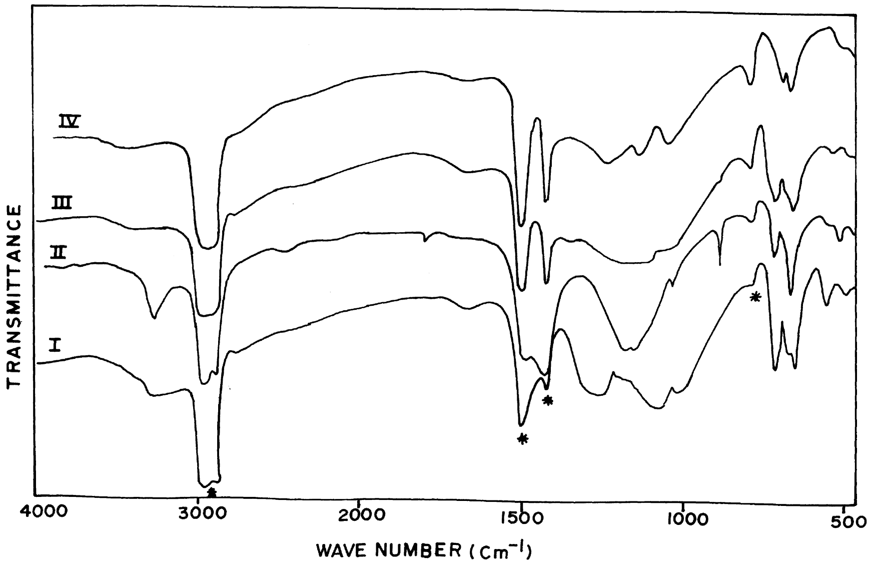

Fig. 2. IR spectra I - $(NH_4)_2Ce(SO_4)_3$, II - $(NH_4)Ce(SO_4)_2$, III - $Ce_2(SO_4)_3$, IV - $Th(SO_4)_2$. Absorption bands from nujol are marked with an asterisk.

Table 2
Crystal data of the reaction products of solid state reactions of CeO_2, ThO_2 and PuO_2 with $(NH_4)_2SO_4$

Compound	Crystal system	Cell Parameters [a]	Density (g cm^{-3})		Z
			Measured	Calculated	
$(NH_4)_2Ce(SO_4)_3$	Monoclinic	$a = 0.9412(2)$ $b = 1.6417$ (4) $c = 2.3041$ (6) $\beta(°) = 114.71$ (3)	2.84	2.86	12
$(NH_4)_2Th(SO_4)_3$	Monoclinic	$a = 0.9414$ (1) $b = 1.6507$ (3) $c = 2.2990$ (3) $\beta(°) = 113.61$ (1)	3.35	3.38	12
$(NH_4)_2Pu(SO_4)_3$	Monoclinic	$a = 0.9348$ (2) $b = 1.6408$ (4) $c = 2.2851$ (5) $\beta(°) = 114.29$ (2)	–	3.51	12
$(NH_4)Ce(SO_4)_2$	Monoclinic	$a = 0.7118$ (2) $b = 1.0751$ (4) $c = 0.9253$ (3) $\beta(°) = 99.14$ (3)	3.20	3.32	4
$Ce_2(SO_4)_3$	Orthorhombic	$a = 1.0186$ (2) $b = 1.0383$ (1) $c = 1.6775$ (2)	3.22	3.20	6
$Th(SO_4)_2$	Hexagonal	$a = 0.9392$ (1) $c = 1.1611$ (4)	4.68	4.76	6
$Pu(SO_4)_2$	Hexagonal	$a = 0.9146$ (3) $c = 1.1428$ (5)	–	5.18	6

[a] a, b and c values are in nm.
Numbers in parentheses correspond to e.s.d.s.

Table 3
X-ray powder diffraction data of $(NH_4)_2Ce(SO_4)_3$ and $(NH_4)Ce(SO_4)_2$ ($\lambda = 0.154178$ nm)

h	*k*	*l*	*d* (Observed) (nm)	*d* (Calculated) (nm)	*I*/*I*$_o$
$(NH_4)_2Ce(SO_4)_3$					
−1	1	1	0.8160	0.8165	10
1	1	0	0.7583	0.7583	10
0	0	3	0.6947	0.6977	100
1	0	1	0.6947	0.6962	
0	1	3	0.6435	0.6421	5
1	1	2	0.5271	0.5281	5
−1	0	5	0.4581	0.4594	15
−2	0	1		0.4581	
−1	3	3	0.4316	0.4319	5
0	3	3		0.4306	
0	0	6	0.3485	0.3489	45
2	0	2		0.3481	
1	5	0	0.3065	0.3065	5
0	6	1	0.2713	0.2713	15
−3	3	2		0.2711	
1	3	6	0.2524	0.2524	15
3	3	2	0.2274	0.2272	10
4	0	0	0.2137	0.2138	10
3	3	3		0.2136	
0	5	8	0.2048	0.2046	5
−5	1	7	0.1843	0.1844	5
0	8	5		0.1843	
2	6	6	0.1749	0.1750	5
2	1	9		0.1748	
4	4	3	0.1679	0.1679	5
2	9	0		0.1678	
2	8	6	0.1524	0.1524	5
5	3	2		0.1523	
$(NH_4)Ce(SO_4)_2$					
0	1	1	0.6959	0.6957	100
0	0	2	0.4564	0.4563	15
2	0	0	0.3512	0.3514	10
−2	0	1	0.3469	0.3468	40
0	4	0	0.2687	0.2688	10
1	4	0	0.2511	0.2509	10
−2	3	1	0.2495	0.2496	10
−3	1	1	0.2305	0.2304	5
−1	0	4	0.2280	0.2282	10
0	1	4	0.2235	0.2234	5
2	0	3	0.2138	0.2138	5
0	2	4	0.2102	0.2100	5
0	4	3	0.2014	0.2014	<5
−4	1	1	0.1755	0.1755	<5
3	0	3	0.1729	0.1729	10
1	1	5	0.1683	0.1683	<5

PuO_2 with $(NH_4)_2SO_4$ in proportions higher than 1:4, unreacted $(NH_4)_2SO_4$ gets decomposed below 400°C as observed in the reactions with CeO_2. TG and DTA curves show mass loss in the region of 250–320°C, 355–400°C, 400–460°C and 720–815°C. Mass loss in the temperature range of 355–400°C is accompanied by two DTA endothermic peaks, whereas all other mass losses show single DTA endothermic peak. In order to isolate the products formed during the reactions, 1:4 mixtures of MO_2 + $(NH_4)_2SO_4$ (where M = Th and Pu) were heated isothermally at 250°C, 360°C, 450°C and 760°C for 6–8 h in a furnace. The observed mass losses at different temperatures given in Table 1 correspond to the formation of products $(NH_4)_2M(SO_4)_3$, $M(SO_4)_2$ and MO_2. Thus the reaction sequence of ThO_2 or PuO_2 with $(NH_4)_2SO_4$ can be given by Eqs. (2)–(5).

Table 4
X-ray powder diffraction data of $Ce_2(SO_4)_3$ ($\lambda = 0.154178$ nm)

h	*k*	*l*	*d* (Observed) (nm)	*d* (Calculated) (nm)	I/I_o
1	0	1	0.8706	0.8707	10
1	0	2	0.6473	0.6475	100
0	2	0	0.5191	0.5191	50
0	2	2	0.4415	0.4414	90
2	1	3	0.3539	0.3540	70
0	3	0	0.3460	0.3461	10
0	3	1	0.3395	0.3390	85
2	2	3	0.3048	0.3048	90
1	1	5		0.3046	
2	3	0	0.2862	0.2862	25
3	2	1	0.2801	0.2802	60
0	0	6		0.2796	
3	2	5	0.2168	0.2168	35
0	4	6	0.1902	0.1902	10
4	3	4	0.1843	0.1843	15
2	1	9	0.1726	0.1726	20

$$MO_2 + 4(NH_4)_2SO_4 \xrightarrow{250°C} (NH_4)_4M(SO_4)_4 + 4NH_3 + 2H_2O \tag{2}$$

$$(NH_4)_4M(SO_4)_4 \xrightarrow{350°C} (NH_4)_2M(SO_4)_3 + 2NH_3 + H_2O + SO_3, \tag{3}$$

$$(NH_4)_2M(SO_4)_3 \xrightarrow{450°C} M(SO_4)_2 + 2NH_3 + H_2O + SO_3, \tag{4}$$

$$M(SO_4)_2 \xrightarrow{760°C} MO_2 + 2SO_3. \tag{5}$$

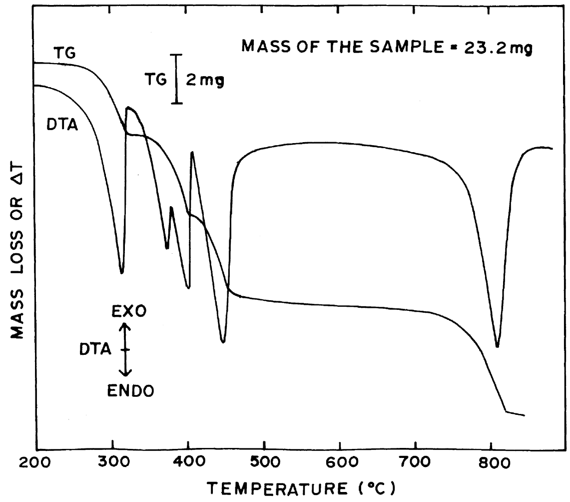

Fig. 3. TG and DTA curves of 1:4 mixture of ThO_2 with $(NH_4)_2SO_4$.

As observed with cerium, the oxidation state of plutonium does not change during the reaction of PuO_2 with $(NH_4)_2SO_4$. No change in the oxidation state of plutonium was observed during the thermal decomposition of $(NH_4)_4Pu(SO_4)_4{\cdot}3H_2O$ [20], $K_4Pu(SO_4)_4{\cdot}2H_2O$ and $Rb_4Pu(SO_4)_4{\cdot}2H_2O$ [21]. The reduction potential values (vs. NHE) of 1.44 V for Ce(IV)/Ce(III) couple and of 0.77 V for Pu(IV)/Pu(III) couple, show that Ce(IV) is a stronger oxidant. Though these values are in 1M H_2SO_4, they suggest that Pu(IV) is not easily reduced to Pu(III), as compared to the reduction of Ce(IV) to Ce(III).

The IR spectra of $(NH_4)_2Th(SO_4)_3$ and $(NH_4)_2Pu(SO_4)_3$ were similar to spectrum of $(NH_4)_2Ce(SO_4)_3$ shown in Fig. 2. The IR spectra of $Th(SO_4)_2$ and $Pu(SO_4)_2$ were also similar. The IR spectrum of $Th(SO_4)_2$ is included in Fig. 1, which shows the absorption frequencies in the region of 1200–1000 cm^{-1} and 750–600 cm^{-1} corresponding to sulphate ions. In case of $(NH_4)_4Ce(SO_4)_4$ the IR, and for the $(NH_4)_4M(SO_4)_4$ X-ray data could not be recorded due to their hygroscopic nature in air.

The X-ray powder data of $(NH_4)_2Th(SO_4)_3$ and $(NH_4)_2Pu(SO_4)_3$ were indexed on cell parameters similar to that of $(NH_4)_2Ce(SO_4)_3$, thus, suggesting that all the three compounds are isostructural. The refined cell parameters for $(NH_4)_2Ce(SO_4)_3$, $(NH_4)_2Th(SO_4)_3$ and $(NH_4)_2Pu(SO_4)_3$ are given in Table 2. The X-ray powder data of $Th(SO_4)_2$ and $Pu(SO_4)_2$ were also similar suggesting that they are isostructural. The least-squares refined crystal data of both $Th(SO_4)_2$ and $Pu(SO_4)_2$ are given in Table 2. The indexed X-ray data of $Th(SO_4)_2$ are presented in Table 5.

3.3. Dissolution studies

During the treatment of fuel materials with various salts for solubilizing them, identification of solid products formed has helped: (i) to know the minimum temperature of reactions [5] and (ii) to determine the

Table 5
X-ray powder diffraction data of $Th(SO_4)_2$ ($\lambda = 0.154178$ nm)

h	*k*	*l*	*d* (Observed) (nm)	*d* (Calculated) (nm)	I/I_o
1	0	2	0.4720	0.4725	100
1	1	2	0.3657	0.3651	25
2	0	2	0.3335	0.3331	60
0	0	4	0.2906	0.2903	15
2	1	2	0.2719	0.2717	50
2	2	0	0.2351	0.2348	20
2	1	4	0.2109	0.2111	30
1	0	6	0.1883	0.1883	10
2	3	2	0.1778	0.1776	30
5	0	2	0.1567	0.1566	15

minimum amount of salt required for complete reaction [1]. Earlier [8] as well as present studies have shown that $(NH_4)_2SO_4$ reacts with metal oxides at 250°C and above to form their sulphate compounds. All the sulphates formed during the reactions found to be readily soluble in 1–2M HNO_3 or H_2SO_4. $(NH_4)_2SO_4$, present in more than the required stoichiometric amount, decomposes as volatile gases above 350°C, leaving no unreacted salt, thus making it possible to solubilize the metal oxides in minimum amount of acid.

In order to study the quantitativeness of dissolution of the oxides, weighed amounts of CeO_2, ThO_2 and PuO_2 (50–100 mg) were mixed separately with $(NH_4)_2SO_4$ in 1:6 molar proportions and heated at 350–360°C for 2–3 h. Since the excess of $(NH_4)_2SO_4$ is decomposed as volatile gaseous products, it was taken in more than the required stoichiometric amount to complete the formation of soluble products i.e., $(NH_4)_2Ce(SO_4)_3$, $(NH_4)_2Th(SO_4)_3$ and $(NH_4)_2Pu(SO_4)_3$ faster. Solid residues were dissolved in 1M HNO_3 and analysed for cerium, thorium and plutonium content in solutions. Cerium and plutonium were determined by the titrimetric method and thorium was determined by the X-ray fluorescence. Each oxide was dissolved in duplicate. The mean of the analyzed values agreed within ±1% with the expected values. The result of analyses are given in Table 6, which show CeO_2, ThO_2 and PuO_2 can be quantitatively dissolved on reacting with $(NH_4)_2SO_4$ at 350–360°C.

CeO_2 and ThO_2 sintered at 1600°C could not be dissolved quantitatively under the same conditions. Thermogram of the 1:4 mixture of sintered ThO_2 and $(NH_4)_2SO_4$ at heating rate of 4°C/min showed much higher mass loss (39.5%) than the expected value of 29.8% for the formation of $(NH_4)_2Th(SO_4)_3$ in the temperature range of 350–380°C. Part of $(NH_4)_2SO_4$ decomposes before completely reacting with the sintered oxide. Nearly 75% of sintered CeO_2 and ThO_2 could be solubilized by reacting them with $(NH_4)_2SO_4$ in 1:10 molar proportion at 350°C. Solid products identified by the X-ray diffraction patterns were mixtures of unreacted oxides and $(NH_4)Ce(SO_4)_2$ and $(NH_4)_2Th(SO_4)_3$. Due to slower rate of reaction, $(NH_4)Ce(SO_4)_2$ and $(NH_4)_2Th(SO_4)_3$ formed initially made a coating over the partly unreacted sintered CeO_2 and ThO_2, respectively, thus preventing further reaction with $(NH_4)_2SO_4$. The more reactive oxides which were prepared at lower temperature of 800°C, reacted completely during the decomposition of $(NH_4)_2SO_4$. However, by dissolving soluble sulphates in 1M HNO_3 and reacting the residual oxides with $(NH_4)_2SO_4$ for two more times it was possible to dissolve nearly 95% of the sintered oxides.

Table 6
Dissolution data of the products formed at 350–360°C by reactions of CeO_2, ThO_2 and PuO_2 with $(NH_4)_2SO_4$

Oxide	Metal content (%)		Deviation (%)
	Measured [a]	Calculated	
CeO_2	80.7 ± 0.7	81.4	−0.7
ThO_2	86.8 ± 0.8	87.9	−1.0
PuO_2	87.9 ± 0.6	88.2	−0.4

[a] Mean of two measurements with their deviations.

4. Conclusion

Reactions of CeO_2 with $(NH_4)_2SO_4$ form $(NH_4)_4Ce(SO_4)_4$, $(NH_4)_2Ce(SO_4)_3$, $(NH_4)Ce(SO_4)_2$ and $Ce_2(SO_4)_3$ at 250°C, 325°C, 360°C and 450°C, respectively. The oxidation state of cerium as +4 in $(NH_4)_4Ce(SO_4)_4$ and $(NH_4)_2Ce(SO_4)_3$ and as +3 state in $(NH_4)Ce(SO_4)_2$ and $Ce_2(SO_4)_3$ was established by redox titrimetry. The X-ray powder data of $(NH_4)_2Ce(SO_4)_3$, $(NH_4)Ce(SO_4)_2$ and $Ce_2(SO_4)_3$ were indexed on monoclinic, monoclinic and orthorhombic crystal systems, respectively.

Solid state reactions of MO_2 (M = Th or Pu) with $(NH_4)_2SO_4$ led to the formation of $(NH_4)_4M(SO_4)_4$, $(NH_4)_2M(SO_4)_3$ and $M(SO_4)_2$ at 250°C, 360°C and 450°C, respectively. The X-ray powder data of $(NH_4)_2M(SO_4)_3$ and $M(SO_4)_2$ were indexed on monoclinic and hexagonal systems, respectively.

Reaction products of CeO_2, ThO_2 and PuO_2 with $(NH_4)_2SO_4$ at 350–360°C were found to be easily soluble in dilute acids, thus suggesting the usefulness of these reactions for their dissolution. Excess of $(NH_4)_2SO_4$ decomposes as volatile gases leaving no unreacted salt.

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