THERMAL PROPERTIES OF THE HYDROXIDES AND OXIDES OF LANTHANIDES AND ACTINIDES

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ABSTRACT

A review of the thermal properties of the hydroxides and oxides of lanthanides and actinides has been given with up-to-date contributions included.

INTRODUCTION

A number of studies on the thermal properties of the hydroxides and oxides of lanthanides and actinides has been carried out by earlier researchers. However, since no modern critical review on this subject exists, an up-to-date survey of the literature is given in the present paper.

LANTHANIDES

General information on the hydroxides and oxides of lanthanides

The +3 state of oxidation is characteristic of all lanthanides both in solid compounds and in solutions in water and other solvents. A few solid compounds exemplifying the +4 state have been prepared, but only tetrapositive cerium has a sufficiently long half-life with respect to reduction to be of importance in aqueous solution. Although all of the lanthanides have been obtained in the +2 state by trapping in solid alkaline earth halide matrices, dissolution in aqueous systems results in rapid oxidation to the +3 state of all the species except europium(II). Even europium(II) has only a comparatively short half-life with respect to oxidation in aqueous solution.

The oxides of lanthanides are obtained by oxidative ignition of the metals or their compounds. All of the lanthanide sesqui-oxides Ln_2O_3 are readily obtained and well characterized. Except

for the elements Ce, Pr, and Tb these compounds are the final pro-
ducts of ignition in air of the hydroxides with most containing oxo
anions (e.g. CO_3^{2-} and SO_4^{2-}, but not PO_4^{3-}) or of the direct reaction
of elemental oxygen with the metals. For these three elements,
sesquioxides are formed by reduction of the higher oxides that
result from these reactions.

Coordination numbers and coordination polyhedra characteriz-
ing the structures of the A-, B- and C-type oxides which are hex-
agonal, monoclinic and cubic, respectively, are influenced by
temperature and crystal radius at their regions of stability.
The oxides of lanthanides are all difficulty soluble in water and
alkaline medium but dissolve, often readily, even when strongly
ignited, in aqueous solutions of the strong mineral acids, unless
a precipitating anion is present. Ease of reaction increases with
decreasing cationic crystal radius, paralleling decreasing basicity.
For the lanthanide oxides, basicity decreases with decreasing
crystal radius which decreases with increasing atomic number of
lanthanide. Hydration of the oxides to hydroxides is a charac-
teristic property. Carbon dioxide is absorbed from the air, again
decreasingly with decreasing basicity, with the formation of basic
carbonate, ignition in air does not yield carbonate-free oxides un-
less the temperature exceeds 800°C.

The reactivity with water itself decreases somewhat with in-
creasing atomic number. Dry oxygen (or air) attacks the massive
metals only very slowly at room temperature, but at elevated
temperatures they may ignite and burn vigorously. In the presence
of moisture, the lighter lanthanides react with oxygen quite rapid-
ly at room temperature, but the heavier ones do not. Hydration of
the more basic sesquioxides is apparently a factor since the re-
sulting hydrous products are non-adherent and slough off rapidly
to expose fresh surfaces. The less basic sesquioxides have less
tendency to hydrate and probably form adherent protective layers.
Europium reacts much more rapidly than the other metals of the
series. Finely divided europium may ignite spontaneously when
exposed to the air. In the presence of water, the soluble, yel-
lowish compound $Eu(OH)_2 \cdot H_2O$ forms first and then absorbs more
oxygen to give the sesquioxide. Cerium, praseodymium, and terbium
are also very reactive toward elemental oxygen. It is probable
that formation of the non-stoichiometric phases $LnO(x < 2)$ which
are non-protective and allow the ready transport of oxygen across
the oxide layer is a factor of importance.

The hydroxides of lanthanides, $Ln(OH)_3$, are precipitated in hydrous form by aqueous ammonia, various amines, and the soluble alkalis. Hydrothermal crystallization from sodium hydroxide at 193-800°C and 12-1400 atm yields the crystalline hydroxides. These substances are characterized by hexagonal unit cells, although the anhydrous scandium hydroxide is cubic. Hydrothermal methods can be also used to prepare oxide-hydroxide compounds. $LnO(OH)$. These compounds crystallize in the monoclinic system. Both types of compound are soluble in acids and are converted thereby to salts. Colloidally dispersed lanthanum hydroxide is sufficiently basic to be converted completely to carbonate by dissolved or atmospheric carbon dioxide.
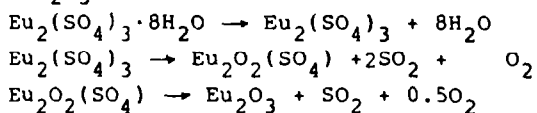
Thermal properties of the hydroxide and oxide of lanthanides

The temperature of solidification and phase transition of rare earth oxides have been studied by using a heliostat-type solar furnace. The solidification temperature above 2300°C for rare earth oxides increases with increasing ionic radius of the rare earth element in the compound. From the phase diagram of these oxides, Ln_2O_3, the rare earth oxides are classified as hexagonal (Ln=La, Pr, Nd), monoclinic (Ln=Sn, Eu, Gd) and cubic (Ln=Dy, Er, Tb and Ln) [1]. For the preparation of catalytically active forms of cerium oxide by slow thermal decomposition of amorphous $Ce(OH)_4$ at a constant rate and low water vapour pressure, it was found that although the precursors are amorphous, they become crystalline at temperature above 500°C [2].

Crystal field theory has been used to identify and locate the energy levels of low-lying (below 100000 cm^{-1}) states of the rare earth monoxides [3]. These states were then used to calculate the thermal functions, which were, in turn, used to derive accurate dissociation energies of the rare earth monoxides. These newly derived dissociation energies are discussed in terms of a model related to the promotion energies for $4f^{n+1}5d^0 \rightarrow 4f^n5d^1$, estimated as 0, 0, 53.1, 80.8, 216.3, 321.3, 0, 3.3, 90.4, 100.4, 85.8, 156.9, 277.4 and 0 for monoxides of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, respectively. On the contrary, the reduction of Ln_2O_3 (Ln=La,Nd and Dy) has been carried out at high temperature [4] : The minimum temperature of formation of Ln^{2+} is 500°C and at 700°C the amount of Ln^{2+} formed is maximum ; Ln^{2+} oxides are stable in media containing < 10^{-6} vol % oxygen, and at greater oxygen concentration the oxidation to Ln^{3+} occurs.

The thermal decomposition of hydrated europium sulphate,

$Eu_2(SO_4)_3 \cdot 8H_2O$, at temperatures up to 1450°C in air has been studied by high-resolution luminescence spectroscopy, X-ray diffraction study, thermogravimetry (TG) and differential thermal analysis (DTA) [5]. Information regarding the number of europium(III) species present in a particular material can be inferred from the fine structure within the europium(III) emission bands. Determination of the site symmetry of the europium(III) emitting species can be deduced from a complete analysis of the luminescence spectra. The application of this method has shown the presence of a multitude of partially dehydrated species in materials where the more conventional thermal analysis methods predict the presence of only pure anhydrous material. The data indicate the presence of an intermediate assumed to be $Eu_2O(SO_4)_2$. The presence of this intermediate has been suggested before, though never actually observed. Complete decomposition to $Eu_2O_2SO_4$ occurs by 800°C and finally to Eu_2O_3 by 1150°C, according to the following sequence :

$$Eu_2(SO_4)_3 \cdot 8H_2O \rightarrow Eu_2(SO_4)_3 + 8H_2O$$
$$Eu_2(SO_4)_3 \rightarrow Eu_2O_2(SO_4) + 2SO_2 + O_2$$
$$Eu_2O_2(SO_4) \rightarrow Eu_2O_3 + SO_2 + 0.5O_2$$

The kinetics on the thermal decomposition of hydrated neodymium(III) nitrate, $Nd(NO_3)_3 \cdot 6H_2O$, under a flow of argon, has been investigated by a diffusion mechanism [6]. The rate constant was found to be temperature dependent below 390°C with an apparent activation energy of 805 kJ mol^{-1} and almost temperature independent above 390°C with an apparent activation energy of 65 kJ mol^{-1}. The enthalpy of decomposition was estimated as 208.6 kJ mol^{-1} at atmospheric pressure and decreased to 187.3 kJ mol^{-1} at high pressure. The reaction studied $Nd(NO_3)_3 \cdot 6H_2O \rightarrow Nd(NO_3)_3 \rightarrow$ $NdO(NO_3)$ + oxides of nitrogen takes place in the temperature range at 380-430°C, because the $Nd(NO_3)_3$ is stable over a limited temperature range at 365-380°C. Similar studies on the thermal decomposition kinetics of anhydrous trivalent lanthanide nitrates of praseodymium and europium, $La(NO_3)_3$, $Pr(NO_3)_3$ and $Eu(NO_3)_3$, were carried out and compared with that of neodymium(III) nitrate [7]. The kinetics of the decomposition reaction of $La(NO_3)_3$ and $Pr(NO_3)_3$ are described by the contracting area and contracting volume mechanism, respectively. The enthalpy of decomposition amounts to 123.4 and 102.6 kJ mol^{-1}, respectively. No reversible changes were observed for these two nitrates. The decomposition reaction of $Eu(NO_3)_3$ is similar to that of $Nd(NO_3)_3$ in so far as a reversible change occurs simultaneously with the decomposition reaction,

causing a change in the temperature dependence of the rate con-
stant. The enthalpy of decomposition was estimated as 119.6 kJ
mol^{-1}. Decreasing ionic size of the metal ions appears to de-
crease the thermal stability of the nitrate, as manifested by the
values of the temperature of initiation of decomposition. The
thermal decomposition of anhydrous cerium(III) nitrate, $Ce(NO_3)_3$,
shows to be a single irreversible reaction with the enthalpy of
reaction 111.1 kJ mol^{-1} and the activation energy 104.4 kJ mol^{-1}
[8]. The additional data were also obtained on the thermal decom-
position of anhydrous trivalent gadolinium, holmium and erbium
nitrates, $Gd(NO_3)_3$, $Ho(NO_3)_3$ and $Er(NO_3)_3$: the enthalpies of Ln
$(NO_3)_3$ to $LnO(NO_3)$ where Ln=Gd, Ho and Er were estimated as 138.1,
119.9 and 197.2 kJ mol^{-1}, respectively [9].

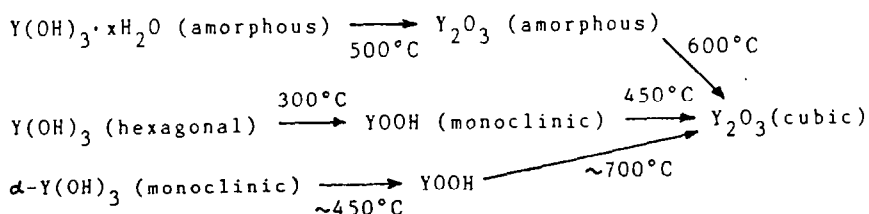The thermal decomposition of hydrated erbium(III) sulphite,
$Er_2(SO_3)_3$, has been studied by thermal analysis (TG and DTA)
[10]. The dehydration starts slowly above 150°C but the release of
water is rapid around 250°C. SO_2 gas is evolved slowly and sim-
ultaneously with H_2O. The anhydrous sulphite is formed below
300°C after which it decomposes through several reactions ac-
companied by a release of mainly SO_2, but also a small amount of
SO_3 near 650°C. In air, there is a clear plateau in the TG curve
between 600 and 800°C ; the weight loss involved depends strongly
on the sample size and heating rate, however. A plausible ex-
planation for the plateau is the formation of a mixture of Er_2-
$(SO_4)_3$, $Er_2O(SO_4)_2$ and $Er_2O_2SO_4$. The next plateau around 900-
1000°C corresponds to $Er_2O_2SO_4$. In nitrogen atmosphere, the first
plateau after the anhydrous sulphite appears later in the weight
scale as compared to air. Although the position of the
plateau corresponds to the sesquisulphide, it is according to X-
ray diffraction results a mixture of $Er_2O_2SO_4$ and Er_2O_3. In both
air and nitrogen, the final reaction step above 1000°C is the
formation of Er_2O_3. Further the thermal behaviour of $Ce_2(SO_3)_3 \cdot$
$3H_2O$, $Nd_2(SO_3)_3 \cdot 6H_2O$ and $Nd_2(SO_3)_3$ was studied by TG [11]. Cerium
sulphite first undergoes dehydration which is followed by de-
composition to CeO_2 in the temperature range 500-850°C. The de-
composition involves two intermediate phases both in air and
nitrogen. According to the TG curves, the phases in air are Ce_2
$(SO_3)_2SO_4$ and $Ce_2SO_3(SO_4)_2$ in nitrogen, $Ce_2O_2SO_4$. Neodymium
sulphite decomposes to $Nd_2O_2SO_4$ when heated in air or in nitrogen
up to 950°C. The intermediate levels observed do not correspond
to single phases, and the reaction mechanism depends strongly on

the experimental conditions. Additionally, the thermal decomposi-
tion of hydrated scandium(III) sulphite, $Sc_2(SO_3)_3$ $5H_2O$, was
studied by TG [12]. The anhydrous scandium sulphite is formed up
to 200°C but it starts to decompose immediately after its forma-
tion. The decomposition leads to an intermediate phase which is
stable up to 700°C in nitrogen and air atmospheres. Although the
weight-loss between 43 and 58 % depending on experimental condi-
tions still remains as the formation of the intermediate, it
cannot be assigned to a single compound such as $Sc_2O_2SO_4$ or Sc_2-
O_2SO_3. The intermediate phase is amorphous to X-rays but IR
spectra indicate the presence of both sulphite and sulphate ions
pointing to a mixture. In the atmospheres in air and nitrogen,
however, the final decomposition step is the formation of scandi-
um sesquioxide.

For the thermal decomposition of hydrated ytterbium(III)
acetate, it has been reported that $Yb(CH_3COO)_3$ $4H_2O$ dehydrates at 70°C
in air to $Yb(CH_3COO)_3$ which undergoes a reversible phase transi-
tion at 240-255°C ; at 300-600°C $YbO(CH_3COO)$ is formed and de-
composed to $Yb_2O_2(CO_3)$ and then Yb_2O_3 + CO_2 [13].

On the one hand, some lanthanide oxides such as La_2O_3, CeO_2,
Sm_2O_3, Dy_2O_3, and Yb_2O_3 were obtained by calcining, in air, phases
prepared by precipitation with ammonia from solutions of the cor-
responding nitrates [14]. During the calcination to oxides, under
the experimental conditions used, the nitrate ions are removed to
an extent which cannot be detected by temperature programmed
desorption-mass spectrometry or IR spectroscopy, contradictory to
the existing literature. In contrast, the reaction between
aqueous solutions of yttrium salts (chloride and nitrate) at a
constant concentration and alkaline solutions (sodium and ammonium
hydroxides) has been investigated under various conditions [15].
As the result, amorphous and hexagonal yttrium hydroxides, $Y(OH)_3$·
xH_2O and $Y(OH)_3$, are obtained : although the composition of the
precipitates does not depend on the kind of the yttrium salt, the
basic yttrium salt is precipitated when the amount of alkali is
not enough in comparison with the concentration of yttrium salt,
and amorphous yttrium hydroxide, $Y(OH)_3$·xH_2O, is formed in the
presence of excess alkali. Amorphous yttrium hydroxide goes to
hexagonal yttrium hydroxide, $Y(OH)_3$, by ageing for 9 days at 80°C
in sodium hydroxide solutions at [NaOH] > 6 mol dm^{-3}, in addition
monoclinic yttrium hydroxide, α-$Y(OH)_3$, was prepared hydrothermal-
ly from amorphous yttrium hydroxide for 20 h at 300°C. The ma-

terials so obtained were examined by TG and DTA, and yttrium hydroxides and their thermal decomposition products by X-ray diffraction study and infrared (IR) spectrophotometry. The sequence for the thermal decomposition of those materials is proposed as follows [15] :

$$Y(OH)_3 \cdot xH_2O \text{ (amorphous)} \xrightarrow[500°C]{} Y_2O_3 \text{ (amorphous)} \searrow^{600°C}$$

$$Y(OH)_3 \text{ (hexagonal)} \xrightarrow[]{300°C} YOOH \text{ (monoclinic)} \xrightarrow[]{450°C} Y_2O_3 \text{(cubic)}$$

$$\alpha\text{-}Y(OH)_3 \text{ (monoclinic)} \xrightarrow[\sim450°C]{} YOOH \xrightarrow{\sim700°C}$$

ACTINIDES

General information on hydroxides and/or hydrous oxides and oxides of actinides

The binary oxides, MO_x, of the actinide elements form an interesting but complex class of compounds. In addition to the stoichiometric oxides, a wide range of intermediate oxide phases exists, sometimes with remarkable phase widths. The most important actinide oxides are the dioxides, MO_2, which crystallize with the calcium fluorite structure, and which are known for the elements thorium to californium, inclusive. With the exception of PaO_2, which has not been investigated in detail, these dioxides lose oxygen at high temperatures and form sub-stoichiometric oxides, MO_{2-x}, with oxygen vacancies in the anionic part of the unit cell. Protactinium and uranium dioxide also take up additional oxygen to give superstoichiometric oxides, MO_{2+x}, even on standing in air at room temperature. Most actinide oxides occur in several crystal modifications, e.g. at least five Pa_2O_5, seven UO_3, and five Cm_2O_3 modifications are known.

The lattice constants of the three best known lanthanide and acitinide sesquioxide modifications (hexagonal, monoclinic and cubic) and of the actinide dioxides can be shown as a function of the atomic number. The lattice constants of the lanthanide sesquioxides and those of the actinide dioxides show a constant decrease with increasing atomic number, i.e. with decreasing ionic radius, whereas distinct irregularities not associated with any crystal-chemical factors occur in the case of the actinide sesquioxides. This effect may be attributed to radiation damage to the crystal lattice by the inherent high α-activity or to non-stoichiometric oxides. In this connection it should be remembered that the investigations of curium and transcurium oxides

have involved only micro- or ultra-micro-quantities of sometimes
relatively short-lived isotopes. Further investigations with
long-lived isotopes (e.g. ^{248}Cm instead of ^{244}Cm or ^{254}Es instead
of ^{253}Es) in quantities sufficient for the analytical determina-
tion of the exact composition are obviously desirable.

As actinium oxide, the only known actinium oxide, hexagonal
AcO_3, has been obtained by thermal decomposition of the oxalate
$Ac_2(C_2O_4)_3$ aq at 1100°C. As thorium oxide, thorium dioxide
(thoria), ThO_2, the only compound in the thorium-oxygen system,
exists up to its melting point of 3390°C (the highest known for
an oxide) as a single cubic phase with the fluorite structure.
As protactinium oxides, the dioxide, PaO_2, and at least five
modifications of the pentoxide, Pa_2O_5, and four intermediate
oxides have been identified in the PaO_2 - Pa_2O_5 region by X-ray
powder diffraction methods. As uranium oxides, the binary oxides
$UO_{2\pm x}$, U_4O_9, U_3O_7, U_3O_8 and UO_3 (α, β, γ, δ and ϵ) have been
reported in the uranium-oxygen system together with several other
intermediates which have not been investigated to the same extent.
The uranium-oxygen system is one of the most complex oxide
systems known. Despite a number of investigations, contra-
dictory results have often been obtained and many questions still
remain, not only concerning chemical and physical properties, but
also the phase diagram. As neptunium, plutonium, americium and
curium oxides, the following binary oxides have been indicated :
NpO, Np_3O_8, Np_2O_5 and NpO_2 ; PuO, $C-Pu_2O_{3(+x)}$ ($= PuO_{1.51(1.52)}$),
$C'- Pu_2O_{3(+x)}$ ($= PuO_{62+x}$), $A-Pu_2O_3$ ($= \beta -Pu_2O_3$), $Pu_{1.995}$ ($PuO_{1.98}$)
and PuO_2 ; $AmO_{2(-x)}$, $AmO_{1.59}$ ($C-AmO_{1.5+x}$), $AmO_{1.62+x}$ ($C'-Am_2O_3$),
Am_2O_3 (A and B) and AmO ; CmO_2, CmO_{2-x} (α), $CmO_{1.82}$ (δ), $CmO_{1.72}$ (τ),
$CmO_{1.5+x}$ (σ) Cm_2O_3 (A,B,C,X and H). As the oxides of the trans-
curium elements, all oxides have been prepared with only micro-
gram or nanogram quantities of the isotopes ^{249}Bk, ^{249}Cf and
^{253}Es for the following binary ones : BkO_2, Bk_2O_3 (A and C), CfO_2,
Cf_2O_3 (A,B and C) and $C-Es_2O_3$.

The hydroxides of actinides are prepared for tri-, tetra-,
penta-, hexa- and heptavalent actinides. As trivalent actinides,
crystalline $Am(OH)_3$ is formed at 90°C by prolonged digestion
of the amorphous precipitate which forms when ammonia is added to
a solution of an Am(III) salt. Similar precipitates are
obtained as $Cm(OH)_3$, $Bk(OH)_3$ and $Cf(OH)_3$ but these compounds have
been studied in small amounts only. As tetravalent actinides,
the precipitates which are obtained by the addition of a base to
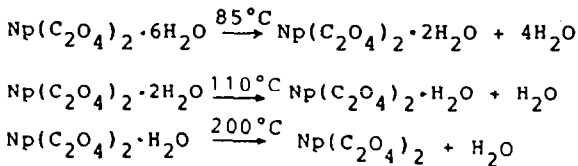an actinide(IV) solution are hydrous oxides, MO_2·aq, with varying

amounts of adsorbed water rather than distinct compounds such as $M(OH)_4$. As pentavalent actinides, the precipitate obtained by the addition of ammonia or an alkali hydroxide to a Pa(V) solution is $Pa_2O_5 \cdot aq$ rather than a compound with a well-defined water:oxide ratio. $Pa_2O_5 H_2O$, however, is prepared by the thermal decomposition of the Pa-peroxide $Pa_2O_9 \cdot 3H_2O$ at 200°C. $Pa(OH)_5$ has been postulated to exist in aqueous solution, despite the fact that the hydrolysis of pentavalent protactinium is extremely complicated and is by no means fully understood. In addition Neptunium(V) hydroxide, $NpO_2(OH)$, and plutonium(V) hydroxide, $PuO_2(OH)$, are obtained by the addition of ammonia to Np(V) or Pu(V) solutions. The following hydrated oxide of hexavalent actinides have been reported for uranium, neptunium and plutonium : $UO_2 \cdot 2H_2O(= UO_2 (OH)_2 \cdot H_2O)$, $UO_3 \cdot H_2O$, $UO_3 \cdot 0.8H_2O$ and $UO_3 \cdot 0.5H_2O$; $NpO_3 \cdot 2H_2O$ and $NpO_3 \cdot H_2O$; $PuO_3 \cdot 0.8H_2O$ and $PuO_3 \cdot H_2O$. As heptavalent actinides, $NpO_2(OH)_3 \cdot aq$, which is the only known heptavalent hydroxide, is precipitated at pH 5-6 from an aqueous solution containing Np(VII).

Thermal properties of the hydroxides and/or hydrous oxides and oxides of actinides
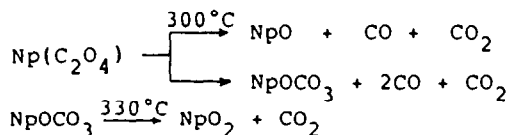
Heat capacities of β-UO_3 and γ-UO_3 have been measured from 5 to 350 K using an adiabatic calorimeter, and from 350 to 700 K by enthalpy increment drop calorimetry [16]. As the result, it was found that values for the thermodynamic properties at the standard reference temperature 298.15 K, the molar heat capacities, molar entropies and molar enthalpy increments are as follows: for β-UO_3, 81.34 JK^{-1} mol^{-1}, 96.32 JK^{-1} mol^{-1} and 14682 $J\ mol^{-1}$; for γ-UO_3, 81.67 JK^{-1} mol^{-1}, 96.11 JK^{-1} mol^{-1} and 14585 $J\ mol^{-1}$. Similarly three calorimetric methods, viz., low-temperature adiabatic, high-temperature drop and solution-reaction, were used to determine as a function of temperature the key chemical thermodynamic properties of $UO_2(OH)_2 \cdot H_2O$ [17]. The following results were obtained at 298.15 K : 172.02 JK^{-1} mol^{-1}, 188.54 JK mol and 29261 mol^{-1} for the molar heat capacity, molar entropy and molar enthalpy increment, respectively.

The thermal decomposition of the ammonium uranate precipitated from uranyl nitrate solution using gaseous ammonia led to amorphous UO_3, β-UO_3, $UO_{2.9}$ and U_3O_8 at different temperatures[18]. The results indicated that ammonium uranate expresed as $UO_2(OH)_{2-x}(ONH_4)_x \cdot yH_2O$ is a continuous non-stoichiometric system with no intermediate stoichiometric compounds and its composition varies according to mode of preparation, and also that the rate of heating and formation of hydrates are important factors for the

formation of $UO_{2.9}$ and U_3O_8. In addition, the thermal decomposition of ammonium uranates precipitated from uranyl nitrate solution on the addition of aqueous ammonium hydroxide and hexamine under various conditions has been studied by means of TG, DTA, IR spectroscopy and X-ray diffraction study [19,20]. Although all precipitates show the composition corresponding to $UO_3 \cdot NH_3 \cdot H_2O$, the precipitates with hexamine give X-ray diffraction patterns designed as types I and II, in which type I is similar to the precipitates with ammonia. As a result, it is concluded that ammonium uranates thermally decompose to amorphous UO_x ($3 \leqslant x \leqslant 3.5$) at about 400°C, and transform to U_3O_8 via β-UO_3 and/or α-UO_3, the latter being formed in the case of type II only. Similar examinations have reported that the thermal decomposition behaviour of ammonium uranates includes five decomposed steps : the first two for dehydration, the third for ammonia removal, the fourth for ammonia oxidation and the last step for UO_3 recrystallization [21,22]. Further the thermal decomposition of ammonium uranyl carbonate has been carried out in relation to the preparation of UO_2. By electron microscopy, it was observed that the reaction in the reduction of ammonium uranyl carbonate to UO_2 forms amorphous UO_3 as the first intermediate, depending on the experimental conditions, either crystalline UO_2 was formed directly from this phase or several other intermediates were indicated[23]. It has been found, however, that when ammonium uranyl carbonate is thermally decomposed, gases such as CO_2, NH_3 and H_2O are evolved, and that the produced amorphous UO_3 matrix contains besides UO_3 also carbon, nitrogen and H_2O [24].

By IR spectroscopy, it has been confirmed that the thermal decomposition of uranyl acetate, $UO_2(CH_3COO)_2$, proceeds by primary fission into UO_2 and acetate radicals, followed by oxidation of UO_2 to U_{38} and pyrolytic fission of the acetate radicals into various secondary products [25]. In the thermal decomposition of hydrated neptunium oxalate, $Np(C_2O_4)_2 \cdot 6H_2O$, the following process has been proposed [26] :

$$Np(C_2O_4)_2 \cdot 6H_2O \xrightarrow{85°C} Np(C_2O_4)_2 \cdot 2H_2O + 4H_2O$$

$$Np(C_2O_4)_2 \cdot 2H_2O \xrightarrow{110°C} Np(C_2O_4)_2 \cdot H_2O + H_2O$$

$$Np(C_2O_4)_2 \cdot H_2O \xrightarrow{200°C} Np(C_2O_4)_2 + H_2O$$

$$Np(C_2O_4) \xrightarrow{300°C} \begin{cases} NpO + CO + CO_2 \\ NpOCO_3 + 2CO + CO_2 \end{cases}$$

$$NpOCO_3 \xrightarrow{330°C} NpO_2 + CO_2$$

The complexes, $(R_3NH)_2UO_2Cl_4$ and $(R_3R'N)_2UO_2Cl_4$, prepared by drying in vacua the organic solutions from the extraction of aqueous UO_2Cl_2 solution with trioctylamine (TOA, R_3N) and trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) in benzene have been examined by TG and DTA under an atomophere of N_2, and their thermally decomposed products such as volatile matters and residues by gas chromatography, X-ray diffraction study and IR spectroscopy [27-29]. As the result, it was found that the complexes with TOA and TOMAC thermally decompose to UO_2 at 320-360 and 280-325°C via UO_2Cl_2 formed by cracking of the complexes at 205-320 and 200-280°C, respectively.

Moreover, the thermal decomposition of some complexes of uranium(VI) and thorium(IV) has been examined in order to check their compositions : $UO_2(NO_3)_2 \cdot 2tmu$ (tmu=tetramethylurea) [30] ; $[UO_2 L_2] \cdot 3H_2O$, $[UO_2 L_2 B_2] \cdot 2H_2O$ and $[Th X_2 L_2 B_2] \cdot 2H_2O$ (where X= SCN, B=pyridine and L=chalcones and their oximes) [31] ; Thorium (IV) benzenedicarboxylates such as $Th(C_8H_4O_4)_2 \cdot 2H_2O$, $Th(C_8H_4O_4)_2 \cdot 2H_2O$, $Th_3(OH)_5 (C_8H_4O_4)_2(C_8H_5O_4)_3 \cdot 5H_2O$ and $Th_5(OH)_{14}(C_8H_4O_4)_3 \cdot 7H_2O$ [32].

CONCLUSIONS

From this report it is deduced that the up-to-date contributions on the thermal properties of hydroxides and oxides of lanthanides are limited despite the publication of much literature on the preparation of superconductors, and that most studies on those of actinides are related to uranium.

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