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Hydrothermal Equilibria and Crystal Chemistry of Phases in the Oxide–Hydroxide–Sulfate Systems of La, Pr, and Nd

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Equilibria of the aqueous $Ln + O + SO_4$ (Ln = La, Pr, Nd) system have been investigated at water pressures of 120 ± 20 MPa and temperatures of 450 ± 50°C. At low sulfate contents, the UCl_3-type trihydroxides coexist with the orthorhombic dioxide monosulfates. A second two-phase region, $Ln_2O_2SO_4 + Ln(OH)SO_4$, appearing at higher sulfate concentrations is followed by a third two-phase region, $Ln(OH)SO_4 + Ln_2(SO_4)_3 \cdot nH_2O$. Whereas the monohydroxide monosulfates all have the same monoclinic structure, several new hydrate compositions and structures form in hydrothermal media. X-ray diffraction data indicate that the $n = 7$ hydrates of La and Pr and the monohydrate of La have closely related orthorhombic structures similar to that of the anhydrous $La_2(SO_4)_3$ phase obtained by decomposition of the hydrates at low temperature. The $n = 5$ sulfate hydrates of Pr and Nd have also been characterized, and a metastable $La_2(OH)_4SO_4$ phase has been identified. Lattice parameters and diffraction data obtained by powder and single crystal methods are reported, and the thermal decomposition reactions of the products are described.

Introduction

The hydrothermal phase equilibria and crystal chemistry of the anion substitution phases formed by the reaction of lanthanide oxides, Ln_2O_3 (Ln = La, Pr, Nd), with LnX_3 compounds containing monovalent anions, X, have been described in several reports. The general equilibrium behavior of systems with $X = NO_3^-$, Cl^-, Br^-, and I^- (*1–3*) is best described as pseudoternary, $Ln + OH + X$. Several of the stoichiometric hydroxide anion phases such as $Ln_7(OH)_{18}X_3$ and $Ln(OH)_2X$ have structures that are derivatives of UCl_3- or $PuBr_3$-type parents (*4–7*). Thermally induced polymorphism is observed in some instances (*4*), and a general tendency for the smaller lanthanide cations to form oxide-containing quatenary ($Ln + O + OH + X$) phases at high temperatures is evidenced by the formation of $Gd_3O(OH)_5Br_2$ (*8*). In some cases, such as the $Pr + OH + NO_3$ system at 850°C and 130 MPa water pressure, the nitrate ion reacts to form $PrO_2 + N_2$ (*9*). Additional studies of ternary systems containing stable anions are needed for a more complete definition of the chemistry and anion substitution processes of the lanthanide solids. Such results for commonly occurring anions may also enhance the understanding of lanthanide and actinide behavior in nuclear waste repositories having high water contents.

The present investigation was performed as the initial study of an effort to define the hydrothermal and crystal chemistry of Ln + OH + divalent anion systems. The sulfate ion was selected because of its importance and frequency of occurrence. Af-

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ter data for sulfate-rich preparations showed the presence of several new hydrated sulfate phases, the scope of the study was expanded to include a cursory investigation of sulfate chemistry in hydrothermal media.

Experimental Procedures

Hydrothermal equilibria of the *Ln* + O + SO_4 systems of La, Pr, and Nd were investigated along the 120 ± 20 MPa isobars and the 450 ± 50°C isotherms of the phase diagrams. The equipment and procedures used in the study are similar to those described previously (*9*). Anhydrous dilanthanide trisulfates were prepared by reacting the oxides of La, Pr, and Nd with excess H_2SO_4 and condensing the solutions before filtering the solid and drying at 350°C in air. Hydrothermal samples (0.1–0.5 g) were prepared by combining the anhydrous sulfates with the respective trivalent oxide in various stoichiometric ratios. For praseodymium, the sulfate was combined with $Pr(OH)_3$ prepared by the hydrothermal reaction of $Pr_{12}O_{22}$ with water (*9*). The ratios of oxide to sulfate varied from pure Ln_2O_3 to pure $Ln_2(SO_4)_3$. The solid reaction mixtures and distilled water were welded in containers constructed of thin-wall gold tubing. In each case the quantity of water was calculated using the density of water at the reaction conditions. In attempts to prepare certain products, reaction temperatures as low as 250°C were employed. The stability of the sulfate ion in hydrothermal media was investigated by heating selected samples to temperatures in excess of 850°C.

Single crystals of several products were prepared by mineralization techniques. Crystals of certain hydrated sulfates and of products obtained at the $1Ln_2O_3 : 2Ln_2(SO_4)_3$ stoichiometric ratio were obtained by extending the reaction time to 3 weeks. For products at other stoichiometries, several mineralizer solutions (e.g., 1 *M* $(NH_4)_2SO_4$, 1 *M* NH_4NO_3, and 6 *M* HNO_3) were used for heating periods of up to 4 weeks.

The solid products were washed with distilled H_2O and were characterized by chemical analyses and by powder and single crystal X-ray diffraction. Powders were analyzed using a 114.6-mm-diameter Guinier-Haegg camera with Cu$K\alpha_1$ radiation and silicon (a_0 = 5.43062 Å) as internal standard. Single crystal diffraction data were obtained with an equi-inclination Weissenberg camera using Cu$K\alpha$ radiation; however, in one instance the crystal system and lattice dimensions were determined with a Syntex $P\bar{1}$ autodiffractometer. Compositions of crystallographically pure products were verified by gravimetric determination of H_2O loss on heating and of lanthanide and sulfate contents by oxalate and barium precipitation, respectively. Additional analyses were obtained from thermal decomposition data obtained with a Perkin–Elmer TGS-1 thermobalance. Samples (5–15 mg) were pyrolyzed in Pt containers under flowing dry N_2 at temperatures up to 900°C. Heating rates were linear at 2.5 or 4 K · min^{-1}. Since sulfate decomposition was slow at 900°C, that temperature was maintained until a constant mass was achieved.

Results and Discussion

Phase Equilibria

At 450°C and 120 MPa, the reactions of the oxide + sulfate mixtures with water were generally rapid. The products have colors characteristic of the respective trivalent lanthanides. Single phases are observed at the following four stoichiometries: pure oxide, $2Ln_2O_3 : 1Ln_2(SO_4)_3$, $1Ln_2O_3 : 2Ln_2(SO_4)_3$, and pure sulfate. Powder X-ray diffraction results show that the products at all other compositions are diphasic mixtures. Since these results are consistent with prior work (*9*) which shows

TABLE I

LATTICE PARAMETERS OBTAINED FROM POWDER X-RAY DIFFRACTION DATA[a]

Phase	Space group[b]	a (Å)	b (Å)	c (Å)	Degree
$La_2O_2SO_4$	*Immm*	13.720(6)	4.286(1)	4.191(1)	—
$Pr_2O_2SO_4$		13.429(4)	4.247(1)	4.141(1)	—
$Nd_2O_2SO_4$		13.333(6)	4.226(1)	4.116(1)	—
$La(OH)SO_4$	$P2_1/c$	4.542(4)	12.642(8)	7.198(5)	111.09(4)
$Pr(OH)SO_4$		4.500(5)	12.52(1)	7.117(8)	111.10(5)
$Nd(OH)SO_4$		4.469(1)	12.426(8)	7.066(2)	111.10(2)
$La_2(SO_4)_3 \cdot 7H_2O$	Unknown	9.971(4)	9.570(3)	17.384(6)	—
$Pr_2(SO_4)_3 \cdot 7H_2O$		9.918(9)	9.476(9)	17.31(2)	—
$La_2(SO_4)_3 \cdot H_2O$	*Pccn*	8.544(8)	6.856(5)	17.30(1)	—

[a] Uncertainty in the last digit is given in parentheses.

[b] Space groups were determined from single crystal data.

that the lighter lanthanide oxides form UCl_3-type trihydroxides at these conditions, only the results for sulfate-containing products are described.

$Ln_2O_2(SO_4)$ and $Ln_2(OH)_4SO_4$ Phases

The stable phases formed at the $2Ln_2O_3 : 1Ln_2(SO_4)_3$ ratios are the dioxide monosulfates. The $Ln_2O_2SO_4$ products were identified by their powder X-ray diffraction patterns and by single crystal diffraction data which showed orthorhombic symmetry. The lattice parameters presented in Table I agree with those reported for products prepared under anhydrous conditions (*10*).

The dioxide monosulfate structure has been investigated by single crystal X-ray diffraction methods. Rectangular crystals up to 1 × 1 × 0.1 mm in size were obtained by mineralizing powdered $Pr_2O_2SO_4$ in 6 *M* HNO_3 for 3 to 4 weeks at 400°C and 120 MPa and then cooling the product to room temperature in 1 to 2 h at constant pressure. Systematic absences consistent with space groups *Immm*, *Imm*2, $I2_12_12_1$, and *I*222 were observed. An attempt to fully refine the structure using an extensive intensity data set obtained with an autodiffractometer was unsuccessful (*11*). Refinement of the structure in space group *Immm* yielded metal, oxide, and sulfur positions similar to those derived by Fahey (*12*), but the positions of the sulfate oxygens could not be determined. Although the powder patterns were sharp, Weissenberg photographs showed streaks characteristic of disorder, and electron density maps showed that the oxygen charge was distributed over spherical shells surrounding the sulfur positions. The presence of rotational disorder is attributed to the quenching-in of sulfate positions existing at 400°C.

A metastable dilanthanum tetrahydroxide monosulfate formed when the $2La_2O_3 : 1La_2(SO_4)_3$ mixture was reacted for 25 h. Metastability of the $La_2(OH)_4SO_4$ was indicated by its conversion to pure $La_2O_2SO_4$ during attempts to prepare single crystals by mineralization in ammonium nitrate solution at 400°C. Results of thermal analysis show that $La_2O_2SO_4$ was formed by the loss of 2 moles of H_2O at approximately 350°C. The low-angle X-ray reflections observed for polycrystalline $La_2(OH)_4SO_4$ are presented in Table II. Attempts to index the reflections on an orthogonal crystal system or to identify an isostructural phase were unsuccessful. The products obtained in all efforts to prepare the Pr and Nd analogs of $La_2(OH)_4SO_4$ by heating reaction mixtures for short periods

TABLE II

LOW-ANGLE X-RAY REFLECTIONS OF $La_2(OH)_4SO_4$, $Nd_2(SO_4)_3 \cdot 5H_2O$ AND HIGH-TEMPERATURE $La_2(SO_4)_3$

$La_2(OH)_4SO_4$		$Nd_2(SO_4)_3 \cdot 5H_2O$		High-Temp. $La_2(SO_4)_3$	
Intensity[a]	*d* (Å)	Intensity[a]	*d* (Å)	Intensity[a]	*d* (Å)
w	8.509	w	9.052	w	7.280
s	6.956	m	6.945	w–m	6.187
w–m	6.432	s	6.109	s	5.010
m–s	5.057	m–s	6.041	w–m	4.921
m	4.436	w	5.966	w	4.845
m–s	3.296	m	5.299	w–m	4.374
w	3.233	m	4.828	w	4.128
m–s	3.197	m–s	4.504	w	4.039
w	3.058	m	3.805	w	3.875
m	2.981	s	3.728	vw	3.847
w–m	2.901	w	3.456	m–s	3.745
w	2.791	m	3.418	m–s	3.462
w	2.479	m	3.396	m	3.406
w	2.394	w	3.167	m	3.308
w–m	2.311	m–s	3.042	w–m	3.288
w–m	2.277	w	2.995	w	3.167
w–m	2.260	w	2.989	w	3.096
w	2.096	w	2.971	w–m	3.006
w–m	1.972	w–m	2.924	w	2.910
w–m	1.951	m	2.719	s	2.874

[a] s, strong; m, medium; w, weak; v, very.

of time at various temperatures and pressures were the dioxide monosulfates.

$Ln(OH)SO_4$ Phases

The products obtained for La, Pr, and Nd at the $1Ln_2O_3 : 2Ln_2(SO_4)_3$ stoichiometry are monohydroxide monosulfates. As shown by the lattice parameters presented in Table I, the products are isostructural. Polyhedral-shaped single crystals (<0.5 mm in diameter) of the La and Pr phases were obtained by mineralization in 6 M HNO_3 and in distilled water, respectively. The powder X-ray diffraction data were indexed on monoclinic symmetry with the aid of Weissenberg data which showed $P2_1/c$ symmetry. The composition of the lanthanum phase was established by the mass loss (3.7 ± 0.3 mass %, 3.57 mass % theoretical) observed on dehydration at 550°C and by the measured sulfate content (37.4 ± 0.4 mass %, 37.81 mass % theoretical) of the phase. As expected, X-ray analysis of the decomposition residue showed it to be a mixture of $La_2(SO_4)_3$ and $La_2O_2SO_4$.

The identity of $Pr(OH)SO_4$ has been verified by a full structural refinement which defined the coordinates of all atoms (*13*). Unlike the Ln + OH + X systems in which the structural backbone consists of infinite sheets of $[Ln(OH)_2^+]_m$ with m monovalent X ions inserted between the sheets, the $Pr(OH)SO_4$-type structure consists of infinite chains of $[Ln(OH)^{2+}]_m$ which are surrounded by m sulfate ions. Although the metal hydroxide chains may be viewed as fragments of the $[Ln(OH)_2^+]_m$ sheets, the results show that a simple anion substitution process is not operative with the divalent sulfate ion.

$Ln_2(SO_4)_3 \cdot nH_2O$ Phases

For samples in which the Ln_2O_3: $Ln_2(SO_4)_3$ ratio was less than 1 : 2 and for those prepared with pure sulfate, the products contained hydrated sulfate phases, $Ln_2(SO_4)_3 \cdot nH_2O$. Two different hydrates were observed for La and Pr and a single hydrate was found for Nd. Whereas $n = 7$ and $n = 1$ hydrates were identified for La, the $n = 7$ and $n = 5$ products were characterized for Pr. Only the $n = 5$ product was found for Nd. Unlike the hydrated sulfates obtained by condensation of aqueous solutions at room temperature, these products did not dissolve on repeated washing with distilled water. The morphologies of the products were unaltered by drying and extended storage in air. Although the formation of heptahydrate phases was generally correlated with higher hydrothermal pressures, the precise preparative conditions for the different hydrates are undefined and attempts to duplicate experiments did not always yield the same hydrate.

The $La_2(SO_4)_3 \cdot H_2O$ phase was obtained at water pressures less than 120 MPa. Polyhedral-shaped single crystals were prepared by mineralizing the product for 3 weeks in 6 *M* HNO_3 or in 1 *M* NH_4SO_4 at the same pressure. *Pccn* symmetry was indicated by Weissenberg data, and the orthorhombic parameters in Table I were obtained by refinement of the powder reflections. The monohydrate stoichiometry was verified by the measured lanthanum (48.1 ± 0.5 mass %, 47.57 mass % theoretical) and sulfate (49.1 ± 0.4 mass %, 49.35 mass % theoretical) contents and by the observed loss (3.1 ± 0.5 mass %, 3.08 mass % theoretical) on heating to constant mass at 550 or 700°C in air. Attempts to prepare the praseodymium analog over a wide range of temperatures were unsuccessful.

The $Ln_2(SO_4)_3 \cdot 7H_2O$ phases of La and Pr were obtained by heating the sulfate at water pressures near 140 MPa. Polyhedral crystals of the praseodymium product formed during the initial equilibration period of 1 week. The powder diffraction patterns for the products were indexed using orthorhombic parameters obtained from autodiffractometer data for a single crystal, but the space group was not determined. The refined lattice parameters presented in Table I are in close agreement with those reported for orthorhombic $Ce_2(SO_4)_3 \cdot 8H_2O$ (a = 9.91, b = 9.50, c = 17.30 Å, *Cmca*) (*14*). The presence of seven waters of hydration in the hydrothermal product was verified by heating samples of the lanthanum phase to constant mass at 200 and 850°C. The observed mass loss at the low temperature (16.1 ± 0.6 mass %, 15.62 mass % theoretical) indicated conversion to the monohydrate, which was identified by the X-ray diffraction pattern for the pyrolysis product. The heptahydrate composition was further evidenced by thermal decomposition to $La_2O_2SO_4$ (41.5 ± 0.4 mass %, 41.36 mass % theoretical) at 850°C.

$Ln_2(SO_4)_3 \cdot 5H_2O$ phases were identified for Pr and Nd. Since the pentahydrate of praseodymium sulfate was obtained at conditions which also yielded heptahydrate, the preparative procedures for these sulfate hydrates cannot be defined. Single crystals of the pentahydrates were not obtained, and the powder X-ray diffraction data for the isostructural phases have not been indexed. The low-angle reflections observed for the Nd product are listed in Table II. Comparison of these data with those reported for $Nd_2(SO_4)_3 \cdot 5H_2O$ prepared by condensation of aqueous sulfate solutions at room temperature (*15*, *16*) show that the hydrothermal product has a different structure. The pentahydrate composition was established by the results of thermogravimetric analysis described in a later section of this report.

Anhydrous $Ln_2(SO_4)_3$ Phases

Polycrystalline anhydrous sulfates of La, Pr, and Nd were obtained by thermal decomposition of the hydrates in the 300 to 700°C temperature range, but only the lanthanum products have been characterized. Powder diffraction data show that the $La_2(SO_4)_3$ product at 550 and 700°C differ. The low-angle reflections for the high-temperature product are presented in Table II and similar data for the low-temperature product are given in Table III. As indicated by asterisks, the more intense reflections have been reported previously for $La_2(SO_4)_3$ (*17*). All observed reflections are assignable to an orthorhombic cell with a = 9.86(1), b = 9.81(1), and c = 17.40(2) Å, but good agreement is also obtained with tetragonal cell having a = 9.84 and c = 17.40 Å.

As evidenced by the similarities between the reflection intensities of the powder diffraction data in Table III, and by the close agreement of the orthorhombic cell parameters for $La_2(SO_4)_3 \cdot 7H_2O$ and $La_2(SO_4)_3 \cdot H_2O$ in Table I, a structural relationship is suggested for the low-temperature anhydrous sulfate, the monohydrate, and the heptahydrate. In addition, the diffraction pattern for the trihydrate prepared by heat-

TABLE III

LOW-ANGLE X-RAY DIFFRACTION PATTERNS OF ANHYDROUS AND HYDRATED DILANTHANUM TRISULFATE PHASES

Low-temperature $La_2(SO_4)_3$[a,b]			$La_2(SO_4)_3 \cdot H_2O$			$La_2(SO_4)_3 \cdot 7H_2O$		
Intensity	*hkl*	*d* (Å)	Intensity	*hkl*	*d* (Å)	Intensity	*hkl*	*d* (Å)
m*	002	8.750	m	002	8.656	m	020	8.721
s*	011	6.464	m–s	011	6.377	w–m	111	6.412
m*	111	5.256	m–s	111	5.112	vs	121	5.414
w*	103	4.930	vw	112	4.558	w	200	4.989
w	013	4.452	w	013	4.425	w	002	4.784
w	004	4.352	w	004	4.329	w	012	4.616
w	201	4.155	w–m	201	4.147	w–m	131	4.434
w*	202	4.025	w–m	113	3.933	w	040	4.350
w	203	3.587	w	210	3.627	w–m	220	4.333
w–m*	005	3.493	w–m	211	3.549	w–m	202	4.453
w	020	3.456	s	020 203	3.434	w–m	051	3.281
m–s*	105	3.304				m–s	222 042	3.214
m*	120	3.254	—	—	—			
w	213	3.186	—	—	—	m	320	3.105
s*	122	3.060	s	213	3.072	w–m	311	3.090

[a] Sample prepared by decomposition of $La_2(SO_4)_3 \cdot H_2O$ in air at 550°C.

[b] Reflections listed for anhydrous $La_2(SO_4)_3$ in ASTM 3-0074 are marked with asterisks (*27*).

TABLE IV

COMPARISON OF OBSERVED AND THEORETICAL MASS LOSS PERCENTAGES FROM THERMAL ANALYSIS DATA FOR CRYSTALLOGRAPHICALLY PURE PRODUCTS

Hydrothermal product	Residue composition	Mass loss (%)	
		Observed	Theoretical
$La_2(SO_4)_3 : 7H_2O$	$La_2(SO_4)_3 : 3H_2O$	10.7	10.41
	$La_2(SO_4)_3 : H_2O$	15.9	15.62
	$La_2(SO_4)_3$	18.9	18.22
	$La_2O_2SO_4$	40.5	41.36
$La_2(SO_4)_3 : H_2O$	$La_2(SO_4)_3$	3.2	3.08
	$La_2O_2SO_4$	29.8	30.50
$La(OH)SO_4$	$\frac{1}{4}La_2(SO_4)_3 + \frac{1}{4}La_2O_2SO_4$	3.7	3.57
	$\frac{1}{2}La_2O_2SO_4$	19.7	19.46
$La_2(OH)_4SO_4$	$La_2O_2SO_4$	7.2	8.15
$Pr_2(SO_4)_3 \cdot 5H_2O$	$Pr_2(SO_4)_3 \cdot H_2O$	2.9	2.73
	$Pr_2(SO_4)_3$	13.9	13.65
	$Pr_2O_2SO_4$	36.0	37.90
$Nd_2O_2SO_4$	$Nd_2O_2SO_4$	0.0	0

ing the heptahydrate at 75 to 80°C is very similar to that of the monohydrate. These observations suggest that the waters of hydration are accommodated in a metal sulfate structure that remains essentially unchanged during dehydration. Except for $Ce_2(SO_4)_3 \cdot 8H_2O$ (*14*), hydrates with orthorhombic symmetries are apparently obtained only at hydrothermal conditions.

Although differential thermal analysis data for $La_2(SO_4)_3$ prepared by decomposition of the hydrate shows no evidence for a phase transition in the 500 to 800°C region (*18*), diffraction data for the anhydrous sulfate obtained at 200°C by Pitha *et al.* (*19*) suggests that other polymorphs exist. Two of the three strongest reflections reported by these authors have *d* values that are similar to those for the high-temperature product in Table II, but the correspondence of the two phases cannot be established. The present observations indicate the occurrence of polymorphism for $La_2(SO_4)_3$ and suggest that different forms of the anhydrous sulfate are obtained by decomposition of different hydrates.

Thermal Decomposition

Thermal decomposition curves for representative hydrothermal products are presented in Fig. 1. Dashed curves are shown for mass changes at temperatures less than 100°C because of uncertainties in the temperatures over this region. The behavior of $La_2(SO_4)_3 \cdot 7H_2O$ is particularly uncertain because the loss of water began when the flow of dry nitrogen was started. The decomposition reactions to form $Ln_2O_2SO_4$ products were generally incomplete at the maximum attainable temperature of 900°C, but that temperature was maintained until a constant mass was achieved. The final percentage of mass loss observed for each product is included in Fig. 1. The theoretical loss for each intermediate composition is indicated by the accompanying horizontal arrow. The observed and theoretical mass losses in Table IV confirm the stoichiometries established by other analyses. The results for $Nd_2O_2SO_4$ show that the hydrothermal products are free of both water and hydroxide.

The decomposition reactions of the hydrates obtained in hydrothermal media differ from those observed for hydrates prepared at room temperature (*20, 21*). Whereas the pentahydrate and dihydrate intermediates are obtained from the octahy-

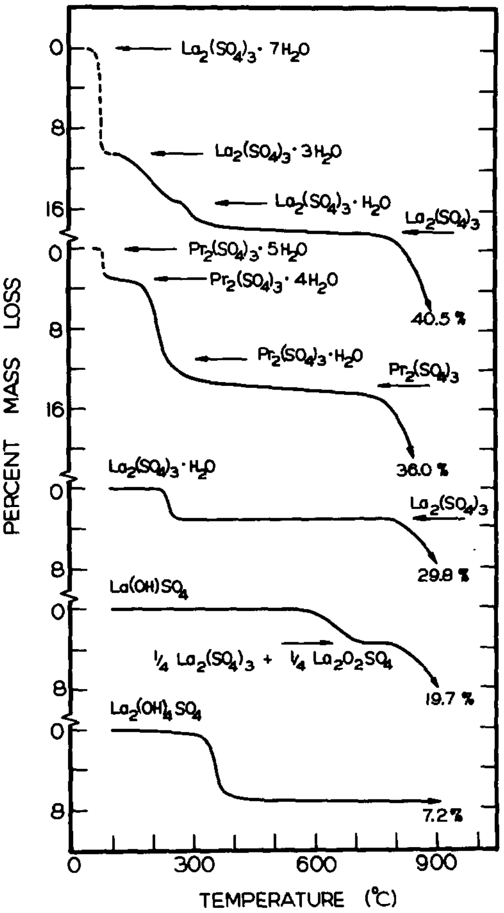

FIG. 1. Thermal decomposition curves for selected lanthanide hydroxide sulfates and hydrate sulfates obtained in hydrothermal media. (The theoretical mass losses for the indicated intermediate compositions are indicated by horizontal arrows. The constant mass losses attained at 900°C are shown in parentheses.)

drates, the heptahydrates form trihydrates and monohydrates. The possibility cannot be excluded that a higher hydrate than $n = 7$ was formed under hydrothermal conditions. The decomposition temperature of the heptahydrate is low and the sulfate structure can apparently lose water without large rearrangements. Since precautions were not taken to prevent dehydration of the product during storage, a higher hydrate may have been present initially. Although some uncertainty exists, the decomposition reactions further emphasize the differences indicated by the preparative results.

Conclusions

The equilibrium relationships and properties of the quatenary $Ln + O + OH + SO_4$ systems in supercritical water have been studied over a limited range of temperature and pressure. The sulfate ion is stable up to 850°C in water and does not oxidize trivalent praseodymium to the tetravalent state as occurs with nitrate (*9*).

Although the observed stability of the sulfate ion is not particularly surprising, the remarkable stabilities of the dioxide monosulfate phases in hydrothermal media were unanticipated. On the basis of chemical intuition, the formation of hydroxide sulfates might be expected, but only the metastable $La_2(OH)_4SO_4$ phase is observed at the $2Ln_2O_3 : 1Ln_2(SO_4)_3$ reaction stoichiometry. In contrast, the $Ln(OH)SO_4$ phases were formed at al $1Ln_2O_3 : 2Ln_2(SO_4)_3$ compositions. Insight into this behavior may be gained by comparing these observations with those for the $Ln + OH + X$ systems (*1, 2, 6*). Since X is monovalent, it can readily substitute into the UCl_3-type $Ln(OH)_3$ structures to form stable products with high hydroxide contents such as $Ln_7(OH)_{18}X_3$. In contrast, the divalent sulfate is not readily accommodated by the parent trihydroxide lattice and forms stable phases only at high sulfate contents where the structural framework of the UCl_3-type lattice is virtually destroyed. When the apparent stability of the $Ln_2O_2SO_4$ structure is combined with the instabilities of possible hydroxide sulfate structures, the oxide sulfate is favored. As the basicities of the oxides decrease across the lanthanide series, increases in stabilities of oxide-containing phases are to be anticipated.

Other unexpected observations of this study are the low solubilities of the hydrated sulfates in water at high temperature. Although the phases are very immobile in neutral media, mineralization is apparently promoted by acidic conditions. The behavior of the sulfates may well be altered by the appearance of new hydrates and polymorphs in hydrothermal media, but the equilibria and crystal chemistry of these materials remain largely uncharted.

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