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Preparation, Phase Equilibria, and Crystal Chemistry of La, Pr, and Nd Hydroxide Bromides and Hydroxide Iodides*

EDWARD THEODORE LANCE-GÓMEZ
Argonne National Laboratory, Argonne, Illinois 60439

AND JOHN M. HASCHKE†
Rockwell International, Rocky Flats Plant, Building 779, P.O. Box 464, Golden, Colorado 80401

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Hydrothermal phase equilibria in the pseudoternary hydroxide bromide and hydroxide iodide systems of lanthanum, praseodymium, and neodymium have been investigated. The condensed products obtained by composition variation along isothermal (550–600°C) and isobaric (1330 atm) sections have been characterized by X-ray diffraction and thermogravimetry. The hexagonal UCl_3-type trihydroxides are stable in all cases. In the hydroxide bromide systems, the hexagonal $Ln_7(OH)_{18}Br_3$ and monoclinic $Ln(OH)_2Br$ (Ln = La, Pr, Nd) phases are found. A single hydroxide iodide, $Ln_7(OH)_{18}I_3$, is observed for La and Pr; hydroxide iodides are not found for Nd. Lattice parameters are reported for both the $Y(OH)_2Cl$- and $La_7(OH)_{18}I_3$-type phases. Quaternary $Ln_7O_7(OH)_4X$ phases (X = Br^-, I^-) are formed during thermal decomposition of the $Ln_7(OH)_{18}X_3$ phases. The phase equilibria and structural features of the hydroxide halides and hydroxide nitrates are discussed.

Introduction

Recent investigations (*1–6*) of several lanthanide + hydroxide + monovalent anion systems, $Ln(OH)_{3-x}X_x$ ($X = F^-, Cl^-, NO_3^-$) have contributed significantly to the understanding of their anion substitution processes. The accommodation of fluoride ions by the trihydroxide is adequately interpreted in terms of a solid solution (*1, 2*), but other work (*7*) has shown that the $Ln(OH)_2X$ ($X^- = Cl^-, NO_3^-$) phases are ordered derivatives of parent UCl_3- or $PuBr_3$-type structures and are described by alternating layers of $Ln(OH)_2^+$ and X^-. However, the lack of structural knowledge of the intermediate $Ln_7(OH)_{18}X_3$ phases (*6*) has limited the understanding of anion accommodation in the lanthanide systems.

The present investigation was undertaken in an effort to describe the phase equilibria of additional hydroxide halides and to define conditions for the growth of single crystals. Preliminary results showed marked similarities between the equilibria of the hydroxide chloride and hydroxide bromide systems; however, the bromides gave evidence of enhanced crystal growth rates. Consequently, the investigation was expanded to include the hydroxide iodides which are of particular importance for assessing size effects in anion accommodation.

Experimental

The hydroxide bromides and hydroxide iodides of La, Pr, and Nd were prepared by hydrothermal reaction of the respective oxide and the hydrated halide in a manner analogous to that used for the hydroxide chlorides (*6*).

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† To whom correspondence should be addressed.

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TABLE I

REFINED LATTICE PARAMETERS OF MONOCLINIC $Ln(OH)_2Br$ PHASES[a]

Ln	a (Å)	b (Å)	c (Å)	β (deg)
La	6.377(4)	4.030(2)	7.163(6)	113.15(4)
Pr	6.309(3)	3.942(3)	7.069(5)	112.44(3)
Nd	6.283(3)	3.910(2)	7.051(4)	112.12(3)

[a] Uncertainties in last digit appear in parentheses.

Hydroxide bromide samples were reacted at 550 ± 50°C and water pressures of 1330 ± 35 atm for 3 to 9 days; hydroxide iodides were reacted at 600 ± 50°C and 1330 ± 35 atm for 8 to 9 days. The solid products were washed with acetone and/or water and dried in air. Powder X-ray diffraction data were obtained with a 114.6-mm-diameter Guinier–Haegg camera with Cu$K\alpha_1$, radiation ($\lambda = 1.54051$) and silicon ($a_0 = 5.43062$ Å) as an internal standard. Thermal decomposition reactions were studied with a Perkin–Elmer TGS-1 thermobalance using nitrogen atmospheres and heating rates of 4° min^{-1} to a maximum of 850°C.

Crystal growth experiments for the hydroxide halides of lanthanum were conducted at the T–P conditions of the preparative work and with equilibration periods of up to one month. The sealed gold sample capsules were filled with a quantity of water (*8*) that would insure adequate fluid volume at a specific temperature and pressure, but would not cause rupture. The hydroxide to halide ratios were generally in the range 3 or 4 : 1.

Results

The Hydroxide Bromides

Polycrystalline products with the characteristic colors of the respective lanthanides salts were obtained for the hydroxide bromides. Three phases, which are isostructural with those of the hydroxide chloride systems, are observed for each lanthanide. The $Ln(OH)_3$, $Ln_7(OH)_{18}Br_3$, and $Ln(OH)_2Br$ phases (Ln = La, Pr, Nd) are readily identified from their powder X-ray diffraction data. The close agreement between the diffraction data for the hexagonal UCl_3-type trihydroxides in equilibrium with the $Ln_7(OH)_{18}Br_3$ phases and for trihydroxides obtained in halide-free systems indicate that the solubility level of bromide in the trihydroxide is very low. The $Ln(OH)_2Br$ and $Ln_7(OH)_{18}Br_3$ phases are previously uncharacterized, but are isostructural with the monoclinic $Y(OH)_2Cl$-type (*3, 9, 10*) and with the hexagonal $La_7(OH)_{18}I_3$-type (*11*) structures, respectively. The refined lattice parameters are presented in Tables I and II. Invariance of these parameters with bulk composition also indicates that the hydroxide bromides have narrow composition ranges.

The thermal decomposition reactions of $La_7(OH)_{18}Br_3$ and $La(OH)_2Br$ differ slightly from those of the corresponding hydroxide chlorides (*6*). Like its chloride analog, $La_7(OH)_{18}Br_3$ decomposes (360–415°C) to $La_7O_7(OH)_4Br_3$, but a second loss beginning at 530°C is not complete within the temperature range of the instrument. The products of two

TABLE II

REFINED LATTICE PARAMETERS OF THE HEXAGONAL $Ln(OH)_{18}X_3$ PHASES[a]

$Ln(OH)_{18}X_3$	a (Å)	c (Å)
$La_7(OH)_{18}Br_3$	17.874(8)	3.916(1)
$Pr_7(OH)_{18}Br_3$	17.709(6)	3.831(1)
$Nd_7(OH)_{18}Br_3$	17.62(2)	3.794(3)
$La_7(OH)_{18}I_3$	18.315(7)	3.928(1)
$Pr_7(OH)_{18}I_3$	18.17(1)	3.909(2)

[a] Uncertainties in last digit appear in parentheses.

possible secondary decomposition paths are: (a) 2 $La_2O_3(s)$ + 3 LaOBr(s) + 2 $H_2O(g)$, and (b) $\frac{7}{2}$ $La_2O_3(s)$ + 3 HBr(g) + $\frac{1}{2}$ $H_2O(g)$. Although pyrolysis of the chloride corresponds closely to path (a) (*6*), decomposition of the bromide intermediate apparently proceeds by both paths. It is unclear whether the reactions occur simultaneously or whether path (b) actually involves the reaction of LaOBr(s) and $H_2O(g)$ produced by path (a). Slow reaction of residual water could account for the gradual mass loss. Decomposition of $La(OH)_2Br$ is also similar to that of $La(OH)_2Cl$; the first loss (360–380°C) is to LaOBr, but the second loss, beginning at 780°C, shows partial conversion to the oxide. The temperature is substantially below that at which mass loss from incongruent sublimation to $La_2O_3(s)$ + $LaBr_3(g)$ would be expected (*12*), and the effect can only be attributed to slow oxidation by water and/or oxygen.

Large crystals (millimeter-sized platelets) of $Ln(OH)_2Br$ are readily produced by both the preparative and crystal growth procedures. Their growth habit is identical to that of $La(OH)_2Cl$ (*6*). Particles of $La_7(OH)_{18}Br_3$ were coarser in texture than those of $La_7(OH)_{18}Cl_3$. This result suggests a greater solubility for the bromide phase in hydrothermal media; however, the crystal growth experiments with long equilibration periods only produced a decided coarsening of the product.

The Hydroxide Iodides

The hydroxide iodide products also have the characteristic lanthanide colors and show a pronounced tendency toward mineralization and crystal growth. However, the number of phases observed is more limited than for the chloride- and bromide-containing systems. For La and Pr, only the $Ln(OH)_3$ and $Ln_7(OH)_{18}I_3$ phases are observed. The $Pr_7(OH)_{18}I_3$ phase has not been prepared pure; it is always observed to coexist with $Pr(OH)_3$. Refined lattice parameters for these hydroxide iodides appear in Table II. For Nd, only the trihydroxide is observed. Several attempts to prepare additional ternary phases at temperatures as low as 350°C and pressures as low as 1000 atm were unsuccessful.

Thermal decomposition data for $La_7(OH)_{18}I_3$ are similar to those of $La_7(OH)_{18}Cl_3$ and $La_7(OH)_{18}Br_3$. An initial decomposition (360–415°C) to $La_7O_7(OH)_4I_3$ corresponds closely to the loss of seven moles of water (found 7.25%, theor. 7.60%). A second mass loss extends over a wide temperature range, and complete interpretation of the decomposition curve is impeded. The process is complex and may be due to an initial formation of LaOI(s) and $La_2O_3(s)$ and subsequent oxidation of the oxide iodide at high temperature.

Crystals of $La_7(OH)_{18}I_3$ were prepared by long-term equilibration procedures. Single-crystal data (*11*) permit indexing of the powder data and refinement of the lattice parameters for the $Ln_7(OH)_{18}X_3$ phases. The crystals grow as extremely fine needles; the needle axis is colinear with the hexagonal *c*-axis. Crystals frequently have lengths greater than 1 cm and diameters less than 0.001 cm and are so fine that they are easily bent by their own mass.

Discussion

The phase equilibria of hydroxide chloride, bromide iodide, and nitrate systems of La, Pr, and Nd are almost identical and only differ by the absence of the $Ln(OH)_2I$ and $Nd_7(OH)_{18}I_3$ phases. Minor structural differences between the hydroxide halides and hydroxide nitrates arise because the nitrate has multidentate capabilities and tends to disorder (*5, 11, 13*). For the high-temperature form of $La(OH)_2NO_3$, only a $PuBr_3$-type substructure is observed (*13*); long-range order of the nitrates is apparently not found because it is disordered over several monodentate and bidentate orientations and on the average behaves like a spherical ion. This interpretation is consistent with the inability to refine nitrate oxygens in both the $La(OH)_2NO_3$ (*13*) and $La_7(OH)_{18}NO_3$ (*11*) structures.

It is somewhat surprising that only the $Y(OH)_2Cl$- and $La_7(OH)_{18}I_3$-type structures are observed for a substantial range of anion size (Cl^- to I^-, NO_3^-). The layered $Y(OH)_2Cl$-type structure has been previously described and discussed for the hydroxide chloride and hydroxide nitrate systems (*6*). The absence of $Ln(OH)_2I$ phases is probably not attributable to an inability to form layers of $La(OH)_2^+$ and I^-, but rather to packing problems and to disruption of intralayer and interlayer (O–H–x) hydrogen bonding (*10*). Intralayer repulsion between iodides might be anticipated, and the formation of a structure type with a cation coordination number less than eight is not expected for the larger lanthanides (*14*). An unexpected observation is that the stability range of the $La_7(OH)_{18}I_3$-type structure extends from Cl^- to I^- and NO_3^-. The absence of $Nd_7(OH)_{18}I_3$ apparently marks the stability limit of this structure. A refinement of the structure shows that the larger anions are accommodated by ordered occupancy of vacant channels in the parent UCl_3-type structure (*13*). A thorough description and discussion of this new structure has been prepared for publication (*15*).

Under hydrothermal conditions, the $La_7(OH)_{18}X_3$ compositions appear to exhibit a solubility trend along the halide series.The formation of highly ordered $Ln_7(OH)_{18}Cl_3$ and $Ln_7(OH)_{18}Br_3$ phases is demonstrated by their powder diffraction data, but single crystals have not been grown. The somewhat coarser texture of $Ln_7(OH)_{18}Br_3$ products and the contrasting crystal growth of $La_7(OH)_{18}I_3$ suggest that the ionic mobilities in these phases increases substantially from Cl^- to I^-. However, the most important factor in the successful growth of $La_7(OH)_{18}I_3$ crystals may well be its phase equilibrium, i.e., the absence of a stable $La(OH)_2I$ composition. In the chloride and bromide systems at high halide contents, the $Ln(OH)_2Cl$ and $Ln(OH)_2Br$ phases are in equilibrium with halide-rich aqueous phases, and their crystal growth is rapid. The presence of these $Ln(OH)_2X$ phases prevents the coexistence of the $Ln_7(OH)_{18}X_3$ phases with halide-rich solutions, and crystal growth is unobserved. Coexistence of $La_7(OH)_{18}I_3$ with an iodide-rich aqueous phase apparently contributes substantially to promotion of crystal growth.

A definition of the hydrothermal hydroxide halide equilibrium systems for the lighter lanthanides is completed by this report. In addition, the observed stabilities of the hydroxide halides have been correlated with their structures and with the ability of these structures to accommodate monovalent anions of different size. The instability of hydroxide anion phases with variation of both the sizes of the trivalent cation and the second anion suggest that changes in structure type and/or composition are to be expected across the lanthanide series. An extension of equilibrium studies to the hydroxide halide systems of other lanthanides is being made in an effort to confirm these possibilities.

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