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Preparation and Characterization of Lanthanum Hydroxide Bromide Hydrates

J. SUN, T. KYOTANI, AND A. TOMITA*

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980, Japan

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The preparation of lanthanum hydroxide bromide and its hydrates, $La(OH)_2Br \cdot nH_2O$ (n = 0.0, 1.0, 1.5) is described. Crystal data for these compounds are $La(OH)_2Br \cdot 1.5H_2O$: hexagonal, a = 8.435 ± 0.001, b = 4.230 ± 0.001 Å, space group $P6mm$ or $P6/mmm$; $La(OH)_2Br$: monoclinic, a = 6.374 ± 0.001, b = 4.031 ± 0.001, c = 7.160 ± 0.001 Å, β = 113.12 ± 0.01°, space group $P2_1$ or $P2_1/m$. The infrared spectra of these compounds are presented, and they are discussed in relation to their structures. The thermal decomposition behaviors are determined with a thermobalance.

Introduction

LaOBr, when doped with Tm^{3+}, is an important phosphor in X-ray radiography (*1–3*). This compound is unfortunately hygroscopic, and therefore it is essential to understand the hydrolysis reaction of LaOBr to develop moisture-resistant phosphors. In the previous study, we found that $La(OH)_2Br$ was an intermediate product and $La(OH)_2Br \cdot H_2O$ was a final product (*4*) in the hydrolysis reaction between LaOBr and water vapor. For the reaction with a limited amount of liquid water, $La(OH)_2Br \cdot 1.5H_2O$ was obtained and with an excess amount of water $La(OH)_3$ and $LaBr_3$ were obtained as a final product (*5*).

The formation, the crystal structure, and the thermal decomposition of $Ln(OH)_2X$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Y; X = F, Cl) have been studied by many workers (*6–10*). Lance and Haschke (*11*) reported the formation of $La(OH)_2Br$ and its crystal parameter. However, few data on the hydrates, $Ln(OH)_2X \cdot nH_2O$, are available at present. The present investigation was undertaken in an effort to establish the preparation method for $La(OH)_2Br \cdot 1.5H_2O$ and $La(OH)_2Br \cdot H_2O$ by means of hydrolysis reaction of LaOBr at an ambient pressure. Their structural data were determined by X-ray powder diffraction. The thermal behavior was studied with thermogravimetry (TG) and differential thermal analysis (DTA).

Experimental

Preparation of sample. The starting material, LaOBr, was prepared according to the method of Rabatin (*2*) from La_2O_3 which was obtained from Yuelong Chemical Plant, China, the purity being >99.95%.

$La(OH)_2Br \cdot 1.5H_2O$ was prepared by hy-

* To whom correspondence should be addressed.

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drolyzing LaOBr with an appropriate quantity of H_2O. For example, 30 g of LaOBr was added to 10 ml of deionized water in a beaker. The beaker was placed in a closed vessel together with another beaker containing some water to maintain the saturation pressure of water vapor. The air in the vessel was replaced with CO_2-free air, and the temperature was maintained at 318 K for 60 hr. The product was almost dry and it was further dried at the same temperature over silica gel for a week. The molar ratio of liquid H_2O to LaOBr is very important in this reaction. The product was $La(OH)_2Br \cdot 1.5H_2O$ when the ratio was between 3 and 6. If the ratio was smaller than 3, a mixture of $La(OH)_2Br \cdot 1.5H_2O$ and $La(OH)_2Br \cdot H_2O$ was obtained. In the presence of an excess amount of H_2O, a further hydrolysis to $La(OH)_3$ took place (*5*).

$La(OH)_2Br \cdot H_2O$ was prepared by the reaction of LaOBr with water vapor. LaOBr (20 g) was allowed to react with water vapor for 2 days in a glass dish of a 70-mm diam under a saturated vapor pressure of water at 343 K. Then the product was dried *in vacuo* at 343 K for 24 hr.

$La(OH)_2Br$ was obtained by dehydrating either $La(OH)_2Br \cdot 1.5H_2O$ or $La(OH)_2Br \cdot H_2O$ at 413 K *in vacuo*.

Characterization of products. To determine La content, the product was dissolved in a dilute HNO_3 solution (0.2 mole/liter). It was titrated with EDTA solution by using hexamethylenetetramine as a buffer and xylenol orange as an indicator. The Br content was determined by titrating with silver nitrate solution, acetic acid being used as a buffer and eosine Y as an indicator. The H content was determined with a Perkin-Elmer 240B analyzer. Table I shows the results of elemental analysis for three compounds prepared in this study. The experimental data agree fairly well with the calculated values.

The thermal decomposition reaction was studied with a differential thermal microbalance (Shinku Riko, TGD-3000). The sample of 20 mg was heated in N_2 up to 900 K at a rate of 20 K $\cdot$ min^{-1}.

TABLE I

ELEMENTAL ANALYSIS OF $La(OH)_2Br$ AND ITS HYDRATES

Compound	Found (%)			Calculated (%)		
	La	Br	H	La	Br	H
$La(OH)_2Br \cdot 1.5H_2O$	49.7	28.5	1.73	49.6	28.6	1.79
$La(OH)_2Br \cdot H_2O$	50.9	29.7	1.44	51.3	29.5	1.49
$La(OH)_2Br$	54.9	31.3	0.83	54.9	31.6	0.79

Infrared spectra of the samples in KBr-pellet were recorded in the range between 330 and 5000 cm^{-1} with a Japan Spectroscopic Co., A-3 infrared spectrometer. Powder X-ray diffraction data were obtained by using Shimadzu VD-1 diffractometer with nickel-filtered Cu$K\alpha$ radiation (λ = 1.5418 Å).

The apparent density of the sample was measured by a pycnometric method using carbon tetrachloride as a displacing fluid.

Results and Discussion

Figure 1 shows the TG and DTA curves for the thermal decomposition of three compounds. The TG curve for $La(OH)_2Br \cdot 1.5H_2O$ has three stages as is seen in Fig. 1a. The first two stages in the range from 360 to 480 K are not clearly separated, but it is clear from the DTA curve that there are two stages in this region. The total weight loss in this region was 9.60%. This value corresponds well to the loss of 1.5 moles of crystal water (Calc., 9.66%). The dehydration from hydroxide groups took place at 580–660 K. The weight loss of this stage, 6.40%, also agreed with the theoretical value (6.44%).

Figure 1b shows the dehydration of $La(OH)_2Br \cdot H_2O$. The weight loss at 360–500 and 580–660 K corresponds to the loss

of crystal water and water from two OH groups, respectively. The decomposition of $La(OH)_2Br$ is illustrated in Fig. 1c. This curve is quite similar to the pattern of the last stage for the two hydrate compounds. The temperature of the endothermic peak of DTA was in all cases at around 640 K. The thermal decomposition reactions can be summarized as follows:

$$La(OH)_2Br \cdot 1.5H_2O \xrightarrow{360\text{–}480\ K} La(OH)_2Br \xrightarrow{580\text{–}660\ K} LaOBr \quad (1)$$

$$La(OH)_2Br \cdot H_2O \xrightarrow{360\text{–}500\ K} La(OH)_2Br \xrightarrow{580\text{–}660\ K} LaOBr \quad (2)$$

$$La(OH)_2Br \xrightarrow{580\text{–}660\ K} LaOBr \quad (3)$$

Figure 2 illustrates the infrared spectra of $La(OH)_2Br$ and its hydrates. The spectrum of $La(OH)_2Br$ is similar to those of $La(OH)_2Cl$(7) and $Y(OH)_2Cl$(8). The absorption bands at 3550 and 3525 cm^{-1} were assigned to OH stretching vibrations. The presence of two peaks in this region may suggest that the two OH groups in $La(OH)_2Br$ are in different environments. The OH stretching frequencies are somewhat lower than those of $La(OH)_3$ at 3609 cm^{-1} (*12*), and this may be due to the presence of hydrogen bonding between OH and Br. A similar hydrogen bonding has been proposed for $La(OH)_2Cl$(7). The absorption bands at 700 and 570 cm^{-1} can be ascribed to OH deformation bands, and those at 430 and 360 cm^{-1} to La–O stretching vibration.

The most remarkable difference in the infrared spectra of the hydrates (Figs. 2a,b) from those of $La(OH)_2Br$ are the appearance of an H–O–H bending vibration band at around 1660 cm^{-1} and a hydrogen bonded OH stretching band at 3450 cm^{-1}. Both of these can be assigned to crystal water. In addition several new bands were observed in the low-frequency region. The weak broad bands at 2500, 1080, and 850 cm^{-1} in Fig. 2a may be overtones or combi-

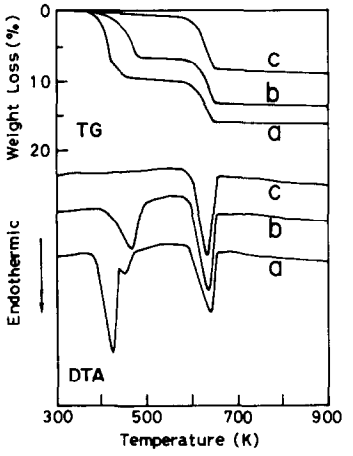

FIG. 1. TG and DTA curves for thermal decomposition of $La(OH)_2Br \cdot nH_2O$ in N_2 at the heating rate of 20 K · min^{-1}. (a) $La(OH)_2Br \cdot 1.5H_2O$, (b) $La(OH)_2Br \cdot H_2O$, (c) $La(OH)_2Br$.

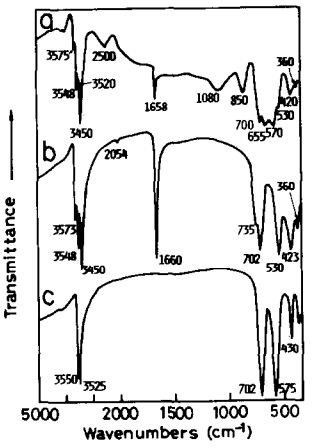

FIG. 2. Infrared spectra of $La(OH)_2Br \cdot nH_2O$. (a) $La(OH)_2Br \cdot 1.5H_2O$, (b) $La(OH)_2Br \cdot H_2O$, (c) $La(OH)_2Br$.

nation bands of fundamentals, but final assignment remains to be elucidated.

The powder X-ray diffraction patterns are shown in Fig. 3. It is evident from this figure that the three compounds have totally different structures from each other. The unit cell parameters were calculated for $La(OH)_2Br \cdot 1.5H_2O$ according to the following manner. The diffraction lines at 7.28 and 4.23 Å were first assigned to (100) and (001) planes of the hexagonal crystal system, respectively. Then the cell parameters were determined approximately as a = 8.41, c = 4.23 Å. The d spacings were calculated by slightly modifying these parameters until a reasonable agreement was obtained between the calculated and the experimental values. The final values were as follows: hexagonal, $a = 8.435 \pm 0.001$, $c = 4.230 \pm 0.001$ Å. The lines of the X-ray pattern were indexed with these parameters and the result is presented in Table II. No lines were systematically absent in this hexagonal crystal. This is similar to the diffraction pattern of hexagonal gold(I) cyanide which belongs to space group *P6mm* (No. 183) or *P6/mmm* (No. 191) (*13*). Therefore the probable space group for $La(OH)_2Br \cdot 1.5H_2O$ may be one of the above two.

The number of molecules in a unit cell, Z, can be calculated by using the observed value of density, D_{exp} (3.7 g · cm^{-3}). Estimated lattice parameters were considered to be reasonable because the calculated value of Z (2.07) is very close to a small integer, 2, and also the calculated diffraction parameters are consistent with the observed pattern. The density was calculated as 3.565 g · cm^{-3} from the estimated number of molecules in a unit cell and the volume of unit cell.

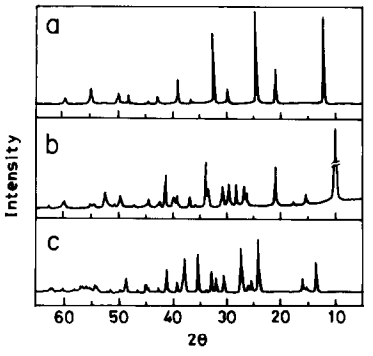

FIG. 3. X-ray diffraction patterns of $La(OH)_2Br \cdot nH_2O$. (a) $La(OH)_2Br \cdot 1.5H_2O$, (b) $La(OH)_2Br \cdot H_2O$, (c) $La(OH)_2Br$.

TABLE II

POWDER X-RAY DIFFRACTION DATA FOR $La(OH)_2Br \cdot 1.5H_2O$[a]

2θ (deg)	d_{exp} (Å)	I/I_1	d_{cal} (Å)	$h\ k\ l$
12.16	7.28	92	7.3049	1 0 0
21.00	4.23	38	4.2300	0 0 1
24.40	3.65	100	3.6606	1 0 1
			2.6525	2 0 0
29.86	2.992	17	2.9866	1 1 1
32.40	2.763	73	2.7645	2 0 1
			2.7610	2 1 0
36.90	2.436	3	2.4350	3 0 0
38.94	2.313	28	2.3121	2 1 1
42.80	2.113	8	2.1150	0 0 2
			2.1103	3 0 1
44.50	2.036	3	2.0316	1 0 2
48.10	1.8916	12	1.8906	1 1 2
48.20	1.8879	10	1.8872	2 2 1
49.82	1.8303	13	1.8303	2 0 2
49.92	1.8268	11	1.8272	3 1 1
			1.8262	4 0 0
54.65	1.6794	11	1.6790	2 1 2
54.80	1.6751	18	1.6759	3 2 0
59.35	1.5571	7	1.5580	3 2 1
62.15	1.4935	2	1.4933	2 2 2
67.65	1.3849	4	1.3845	1 0 3
67.85	1.3813	5	1.3823	4 0 2
			1.3809	5 0 1
			1.3805	4 2 0
70.40	1.3374	3	1.3373	1 1 3
70.55	1.3349	3	1.3341	3 3 1
71.75	1.3155	4	1.3154	2 0 3
71.85	1.3139	5	1.3135	3 2 2
71.96	1.3122	4	1.3124	4 2 1
			1.3120	5 1 0
75.72	1.2561	3	1.2557	2 1 3
75.92	1.2533	2	1.2531	5 1 1

[a] Hexagonal: $a = 8.435 \pm 0.001$, $c = 4.230 \pm 0.001$ Å, $Z = 2$, $D_x = 3.565$ g · cm^{-3}.

The analysis of the X-ray powder diffraction pattern of $La(OH)_2Br \cdot H_2O$ is complicated and therefore only its diffraction data are shown in Table III. The structural data of $La(OH)_2Br$ was determined by Lance *et al.* (*11*) who concluded a monoclinic structure with lattice parameters of $a = 6.377$, $b = 4.030$, $c = 7.164$ Å, $\beta = 113.15°$. We also reached the same conclusion, and the results are shown in Table IV. These are in good agreement with the data by Lance *et al.* The refined lattice parameters are $a = 6.374 + 0.001$, $b = 4.031 \pm 0.001$, $c = 7.160 \pm 0.001$ Å, $\beta = 113.12 \pm 0.01°$. The only systematically observed conditions for reflection ($0k0$, $k = 2n$) are consistent with space groups $P2_1$ (No. 4) and $P2_1/m$ (No.

TABLE III

POWDER DIFFRACTION DATA FOR $La(OH)_2Br \cdot H_2O$

2θ (deg)	d_{exp} (Å)	I/I_1
10.10	8.76	100
15.19	5.83	8
17.42	5.09	2
20.70	4.29	25
24.90	3.58	2
26.09	3.41	8
26.55	3.36	11
28.10	3.18	13
29.10	3.07	3
29.41	3.04	12
30.60	2.922	10
33.20	2.698	9
33.70	2.659	21
35.75	2.512	1
36.72	2.447	5
38.99	2.310	6
39.65	2.273	5
41.23	2.189	13
42.40	2.132	4
44.35	2.042	5
45.00	2.014	2
45.60	1.989	1
46.95	1.935	3
49.50	1.841	6
50.65	1.802	3
51.15	1.786	2
51.80	1.765	4
52.25	1.751	7
54.20	1.692	3
54.90	1.672	3
59.50	1.554	3
59.80	1.547	3

TABLE IV

POWDER X-RAY DIFFRACTION DATA FOR $La(OH)_2Br$[a]

2θ (deg)	d_{exp} (Å)	I/I_1	d_{cal} (Å)	$h\ k\ l$
13.50	6.56	56	6.5849	0 0 1
15.14	5.85	11	5.8621	1 0 0
15.84	5.59	25	5.6061	1 0 $\bar{1}$
24.00	3.71	100	3.7137	1 0 1
25.35	3.51	24	3.5211	1 0 $\bar{2}$
25.94	3.43	14	3.4380	0 1 1
27.25	3.27	81	3.2728	1 1 $\bar{1}$
30.50	2.931	32	2.9310	2 0 0
31.94	2.802	30	2.8031	2 0 $\bar{2}$
32.76	2.734	39	2.7313	1 1 1
33.82	2.650	8	2.6518	1 1 $\bar{2}$
35.22	2.548	70	2.5500	0 1 2
37.76	2.382	61	2.3862	1 0 $\bar{3}$
39.16	2.300	19	2.3014	2 1 $\bar{2}$
41.14	2.194	44	2.1950	0 0 3
42.76	2.115	9	2.1132	3 0 $\bar{1}$
43.55	2.078	4	2.0758	3 0 $\bar{2}$
44.10	2.053	4	2.0534	1 1 $\bar{3}$
44.53	2.035	11	2.0341	2 1 1
44.98	2.015	15	2.0155	0 2 0
46.60	1.9489	7	1.9483	2 1 $\bar{3}$
48.72	1.8690	28	1.8687	3 0 $\bar{3}$
49.78	1.8316	9	1.8328	1 0 3
51.60	1.7712	8	1.7714	1 2 1
52.32	1.7485	4	1.7492	1 2 $\bar{2}$
53.30	1.7187	3	1.7190	0 2 2
53.90	1.7010	10	1.7001	3 0 1
54.40	1.6865	14	1.6865	2 1 2
55.05	1.6681	8	1.6684	1 1 3
55.32	1.6606	7	1.6608	2 2 0
55.85	1.6461	12	1.6462	0 0 4
56.60	1.6261	11	1.6260	1 1 $\bar{4}$
57.07	1.6138	10	1.6133	2 1 $\bar{4}$
57.95	1.5913	6	1.5909	4 0 $\bar{2}$
60.10	1.5395	8	1.5398	1 2 $\bar{3}$
60.75	1.5245	4	1.5240	0 1 4
61.96	1.4976	8	1.4973	2 0 3

[a] Monoclinic: $a = 6.374 \pm 0.001$, $b = 4.030 \pm 0.001$, $c = 7.160 \pm 0.001$ Å, $\beta = 113.12 \pm 0.01°$, $Z = 2$, $D_x = 4.963$ g · cm^{-3}.

11). The crystal structure of $La(OH)_2Br$ thus belongs to the monoclinic $Y(OH)_2Cl$-type (*7*). The number of molecules in a unit cell was calculated by substituting the measured density, 4.6 g · cm^{-3}, and above lattice parameters. It was found to be around 1.85. Thus the calculated density from X-ray diffraction data was 4.963 g · cm^{-3}, by assuming $Z = 2$.

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