Preparation and Characterization of Lanthanum Carbonate Hydroxide

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Two polymorphs of $LaCO_3OH$ were prepared from either $La_2(CO_3)_3$ or $LaBr(OH)_2$ at an ambient pressure. The first one was the same as reported before by several workers who prepared it by the hydrothermal technique. The second one is a new polymorph of $LaCO_3OH$. The infrared spectra and thermogravimetric curves of these two polymorphs were determined and compared. Its crystal data were determined by X-ray powder diffraction: orthorhombic, $a = 5.033(3)$ Å, $b = 8.598(5)$ Å, $c = 7.401(3)$ Å. All data support that the structure of this new modification is similar to that of ancylite.
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Introduction

Lanthanum bromide oxide has been widely used as an X-ray phosphor (*1*), the disadvantage of this compound being that it readily reacts with water vapor and carbon dioxide in ambient atmosphere (*2*). In the first paper of this series the authors studied the reaction between LaBrO and H_2O (*3*). During the course of that study several new compounds were identified, and their characteristics were reported in the preceding paper (*4*). We are now investigating the reaction between LaBrO and a mixture of H_2O vapor and CO_2, and we obtained two polymorphs of $LaCO_3OH$ at an ambient pressure.

Aumont et al. (*5*), Christensen (*6*), and Haschke (*7*) have prepared $LaCO_3OH$ by using a hydrothermal technique, and its crystal structure was analyzed. The former two groups have proposed the hexagonal structures: $a = 12.57(9)$ Å, $c = 10.02(2)$ Å (*5*), and $a = 12.616(8)$ Å, $c = 10.022(5)$ Å (*6*). Haschke also indexed his X-ray diffraction data using a hexagonal cell: $a = 12.634(2)$ Å and $c = 10.048(2)$ Å (*7*). However, from a more detailed analysis he concluded that $LaCO_3OH$ is an orthorhombic phase ($a = 21.891(5)$ Å, $b = 12.639(3)$ Å, and $c = 10.047(2)$ Å), and the parameters for orthorhombic cell is related to those of hexagonal subcell by simple equations (*7*). The crystal parameters of one polymorph we prepared in this study were very similar to these known parameters. The structure of another polymorph was completely different from the above. The main subject of this paper is to describe the crystal data, infrared spectrum, and thermal behavior of this new $LaCO_3OH$.

Caro and his colleagues characterized

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many $LnCO_3OH$ compounds and classified them into two groups (8–13). The structure of A-type and B-type $LnCO_3OH$ are similar to those of ancylite and bastnaesite, respectively. $LaCO_3OH$ which has been reported before has been ascribed to B-type, but A-type $LaCO_3OH$ has not been reported so far. It may be interesting to check whether the new modification prepared in this study is A-type $LaCO_3OH$ or not.

Experimental

Preparation of the sample. Two different procedures were employed for preparing $LaCO_3OH$. In the first method we utilized $La_2(CO_3)_3$ as a starting material. A hydrolysis reaction was performed by weighing 25 g of $La_2(CO_3)_3$ into a flask, adding 500 cm^3 of deionized water, heating at 350 K for 20 hr and then at 370 K for 1.5 hr. The product was separated from the solution by filtration and then dried at 410 K. This procedure gives the first polymorph which we term here $LaCO_3OH(I)$. Aumont *et al.* (5) and Haschke (7) also prepared this compound from $La_2(CO_3)_3$, but the reaction conditions were totally different; the temperature and pressure used by Haschke, for example, was 773 K and 100 MPa.

$LaBr(OH)_2$ was used in the second procedure in place of $La_2(CO_3)_3$. About 3 g of $LaBr(OH)_2$ was mixed with 6 cm^3 of deionized water, and then was allowed to react with CO_2 at 343 K for 1 day in the presence of saturated water vapor at this temperature. The product was washed with deionized water to remove La and Br ions. The reaction was continued for another day with 20 cm^3 of fresh water. This procedure was repeated twice. The product was washed thoroughly with water and dried at 403 K for 3 hr. The product is termed La $CO_3OH(II)$.
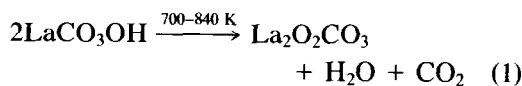
It should be worthwhile to mention some variations from the above fundamental procedures. $La_2(CO_3)_3$ used in the first method

was prepared by contacting a $La(OH)_3$ slurry with CO_2, followed by filtration and further displacement of OH groups with CO_2 by the gas phase reaction at 320 K. This $La_2(CO_3)_3$ contained a small amount of unreacted $La(OH)_3$. This impurity might have some essential roles in the later step. When pure $La_2(CO_3)_3$ was used, the resulting product was a mixture of $LaCO_3OH(I)$ and (II). In the second method LaBrO can also be used as a starting material to obtain $LaCO_3OH(II)$. The experimental procedure is the same as in the case of $LaBr(OH)_2$.

Characterization of the product. The elemental analysis was conducted by the method described in the preceding paper (4): Found for $LaCO_3OH(I)$; La, 62.82; C, 5.80; H, 0.68%: Calc. for $LaCO_3OH \cdot 0.25H_2O$; La, 63.02; C, 5.45; H, 0.69%: Found for $LaCO_3OH(II)$; La, 62.06; Br, 0.79; C, 5.34; H, 0.86%: Calc. for La $Br_{0.02}CO_3(OH)_{0.98} \cdot 0.4H_2O$; La, 61.90; Br, 0.71; C, 5.35; H, 0.80%. This compound has small amounts of water of crystallization and also some Br-containing impurities. Infrared spectra and thermogravimetric curves were recorded by the same procedures as reported before (4).

Results and Discussion

Figure 1 shows TG curves for both types of $LaCO_3OH$. DTA curves are not shown here, but two endothermic peaks were observed for both. The decomposition mainly took place in the following two stages.

$$2LaCO_3OH \xrightarrow{700-840 \text{ K}} La_2O_2CO_3 + H_2O + CO_2 \quad (1)$$

$$La_2O_2CO_3 \xrightarrow{980-1110 \text{ K}} La_2O_3 + CO_2. \quad (2)$$

The observed weight losses for the respective stages for $LaCO_3OH(I)$ were 16.2 and 10.1%. Theoretical values for La $CO_3OH \cdot 0.25H_2O$ are 16.1 and 10.0%. The observed weight losses, for $LaCO_3OH(II)$,
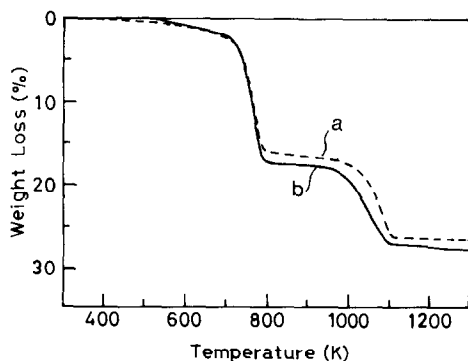
FIG. 1. TG curves for the thermal decomposition of two polymorphs in air, the heating rate being 10 K min^{-1}. (a) LaCO$_3$OH(I), (b) LaCO$_3$OH(II).

17.3 and 9.8%, agree with the theoretical values for LaBr$_{0.02}$CO$_3$(OH)$_{0.98}$ · 0.4H$_2$O, 17.0 and 9.8%. A slight weight decrease was observed for the latter case at a high-temperature range above 1200 K. This weight change corresponds to the release of Br from the impurity in LaCO$_3$OH(II). It can be said that the agreement between elemental analysis and thermogravimetric analysis is fairly good for both polymorphs. Decomposition temperatures reported by Aumont et al. (5) were 690–790 K for the first stage and 1020–1130 K for the second stage followed by a small weight loss at 1270–1320 K. The temperature ranges determined by Haschke (7) were 700–800 K and 900–1070 K. Although there are some discrepancies among these temperature ranges, it may be concluded that our two compounds and those reported earlier are very similar from the viewpoint of thermal behavior.

Infrared spectra of LaCO$_3$OH(I) and (II) are illustrated in Fig. 2. Four modes of CO$_3^{2-}$ ion appeared at 1070–1100 cm^{-1} (ν_1), 850–880 cm^{-1} (ν_2), 1400–1510 cm^{-1} (ν_3), and 690–730 cm^{-1} (ν_4) (5, 14). The sharp band above 3610 cm^{-1} can be assigned to the stretching vibration of free OH group. Klevtsov et al. (15) studied the infrared spectrum of Ln(OH)$_2$Cl and assigned the

peaks between 500–800 cm^{-1} as OH-deformation bands. The absorption bands at around 600 and 800 cm^{-1} in Fig. 2 may be ascribed to this mode.

Spectrum a for LaCO$_3$OH(I) is very similar to those reported earlier (5, 6), which were identified as B-type according to Caro's classification (10). In other words the structure of this compound is similar to that of bastnaesite. The CO$_3^{2-}$ group in bastnaesite is located perpendicular to (LaOH)$^{2+}$ plane. The presence of two peaks in the ν_2 mode (nondegenerate) and three peaks in the ν_3 mode is an indication of nonequivalent CO$_3^{2-}$ groups in the structure, and these are characteristics for B-type compounds (5, 6, 13). The presence of several OH bands both in stretching and deformation regions suggests the presence of nonequivalent OH groups. This is also characteristic for B-type, although the number of OH-stretching bands in Fig. 2a are somewhat different from those reported in the literature. We observed three bands at 3487, 3618, and 3631 cm^{-1} and one broad band below 3480 cm^{-1}, whereas Aumont et al. (5) reported six peaks for B-LaCO$_3$OH, and Dexpert et al. (13) found four peaks for B-NdCO$_3$OH in this region. As a whole
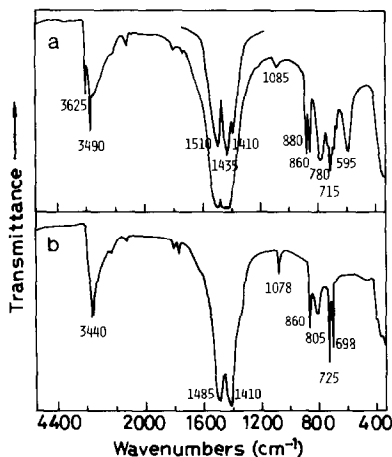

FIG. 2. IR spectra of two polymorphs. (a) La CO$_3$OH(I), (b) LaCO$_3$OH(II).

TABLE I

INFRARED ABSORPTION FREQUENCIES (cm^{-1})

	CO_3^{2-}							OH^-			
	ν_3	ν_1	ν_2		ν_4			ν		δ	
A-LaCO$_3$OH	1485	1416	1074	858	804	712	696	3444		723	
A-NdCO$_3$OH[a]	1495	1450	1081	858	820	718	700	3450		729	
B-LaCO$_3$OH	1512	1435	(1080)	872	777	727	706	3631	3487	(684)	590
		1408		849				3618		(663)	
B-NdCO$_3$OH[a]	1500	1440	(1100)	877	788	(743)	694	3635	3485	(668)	620
		1410	(1087)	850		732		3615	3465		

[a] From Ref. (13).

characteristic points shown in Fig. 2a are well consistent with the structure for B-La CO$_3$OH.

On the other hand, spectrum b for La CO$_3$OH(II) is less complicated. Only two-fold splitting of the degenerate modes of CO_3^{2-} ions (ν_3 and ν_4) were observed, and only one stretching band of hydrogen-bonded OH group was seen at 3440 cm^{-1}. It is highly probable that all CO_3^{2-} ions occupy more or less identical sites in the crystal lattice. Although the presence of A-La CO$_3$OH has not been reported, this spectrum can be compared with those for a-Nd CO$_3$OH and its homologs (12, 13, 16). The above mentioned features for LaCO$_3$OH(II) are quite similar to those of A-LnCO$_3$OH. The structure of ancylite was reported by Dexpert et al. (10) and Negro et al. (17).

FIG. 3. X-ray diffraction patterns of two polymorphs. (a) LaCO$_3$OH(I), (b) LaCO$_3$OH(II).

The former group suggests that the CO_3^{2-} group in ancylite lies in parallel with $(LaOH)^{2+}$ planes, the oxygen atom of CO_3^{2-} being located between OH groups in two $(LnOH)^{2+}$ planes above and below. The characteristics of infrared spectrum are not in conflict with this structure. Therefore the infrared analysis strongly suggests that La CO$_3$OH(I) and (II) can be assigned to B- and A-type LaCO$_3$OH, respectively. Table I summarizes the observed frequencies according to the above notation for these two compounds and two polymorphs of Nd CO$_3$OH (13).

Figure 3 shows the X-ray powder diffraction patterns for the two polymorphs. The upper pattern was almost the same as reported earlier (5–7). This figure together with Fig. 2 clearly indicates that La CO$_3$OH(I) is the same as B-LaCO$_3$OH which has already been reported, although the preparation procedure is quite different; the pressure employed in this study was much lower than those reported. The X-ray pattern for a new modification, La CO$_3$OH(II), is different from the above. It was suggested from the infrared analysis that this modification may be A-LaCO$_3$OH, and thus we compared the pattern (Fig. 3b) with those of A-LnCO$_3$OH group (Ln = Pr, Nd, Sm, Eu, Gd, Tb, and Dy) reported by Sawyer et al. (11) who indexed the X-ray
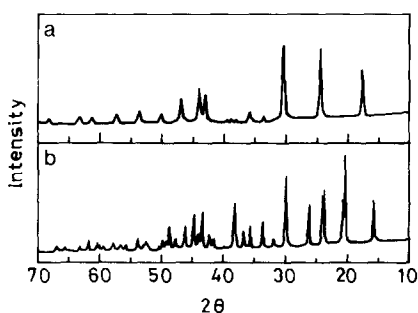
TABLE II

POWDER X-RAY DIFFRACTION DATA FOR
LaCO$_3$OH(II)^a

2θ (deg)	d_{exp} (Å)	I/I_1	d_{cal} (Å)	$h\,k\,l$
15.77	5.62	48	5.609	0 1 1
20.42	4.35	100	4.344	1 1 0
20.70	4.29	45	4.299	0 2 0
23.78	3.742	61	3.746	1 1 1
24.02	3.705	57	3.717	0 2 1
			3.701	0 0 2
26.25	3.395	46	3.399	0 1 2
29.95	2.983	81	2.990	1 2 1
			2.981	1 0 2
31.90	2.805	8	2.805	0 2 2
33.50	2.675	30	2.673	0 3 1
35.66	2.518	27	2.517	2 0 0
36.60	2.455	18	2.450	1 2 2
38.13	2.360	50	2.361	1 3 1
39.80	2.265	2	2.266	0 3 2
41.55	2.173	11	2.172	2 2 0
42.12	2.145	16	2.149	0 4 0
			2.145	1 1 3
43.40	2.085	40	2.084	2 2 1
43.90	2.062	15	2.064	0 4 1
44.80	2.023	38	2.023	2 1 2
46.12	1.968	23	1.969	1 2 3
47.68	1.907	10	1.910	1 4 1
48.76	1.868	26	1.870	0 3 3
49.32	1.848	8	1.850	0 0 4
49.70	1.834	9	1.832	2 3 1
50.40	1.811	3	1.809	0 1 4
52.20	1.752	7	1.753	1 3 3
52.64	1.739	10	1.744	1 4 2
			1.737	1 0 4
52.98	1.728	6	1.726	2 1 3
53.88	1.702	13	1.702	1 1 4
55.70	1.650	8	1.647	3 1 0
56.60	1.626	6	1.627	1 5 0
57.82	1.595	7	1.596	2 4 1
59.35	1.557	5	1.559	0 5 2
			1.555	0 3 4
59.90	1.544	6	1.543	1 4 3
60.44	1.532	9	1.529	3 2 1
			1.528	3 0 2
61.82	1.501	12	1.501	2 3 3

^{a} Orthorhombic: a = 5.033(3) Å, b = 8.598(5) Å, c = 7.401(3) Å.

powder patterns in terms of an orthorhombic unit cell. The present data showed a close resemblance to those for ancylite-type compounds; all of the patterns were indexable on orthorhombic symmetry. Refinement of the parameters yielded a = 5.033(3) Å, b = 8.598(5) Å, and c = 7.401(3) Å. The observed lattice spacings were in good accordance with the calculated values as shown in Table II. Sawyer et al. (11) found that the lattice parameters increased with the increase in the radius of Ln^{3+} ion, and established the following relationship between the cell volume and the radius (Å).

$$\text{Cell volume} = 81.85 + 223.58 \times r_{Ln^{3+}}. \tag{3}$$

In the case of an La compound the above equation predicts the cell volume of 319.1 Å^3, whereas the calculated value from the above parameters was 320.3 Å^3. The agreement is fairly good. As mentioned above Sawyer et al. (11) have reported seven homologs of A-LaCO$_3$OH. Tareen also prepared hydrothermally several A-LnCO$_3$OH for heavier rare earth elements (Gd–Yb), but for lighter elements (La, Ce, Pr, Nd, Sm, Eu, and Gd) B-LnCO$_3$OH have been found (18). The present study clearly indicates the existence of A-type polymorph for LaCO$_3$OH. Both the infrared spectrum and the X-ray diffraction patterns strongly support this identification.

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