The Synthesis of Hydrated Rare Earth Carbonate Single Crystals in Gels

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Hydrated rare earth carbonate single crystals were obtained in metasilicate gels. The formulas of the crystals were determined to be $(RE)_2(CO_3)_3 \cdot 8H_2O$ (RE=La, Pr) and $(RE)_2(CO_3)_3 \cdot 4.54H_2O$ (RE=Nd), and the crystal structures were determined to be of the lanthanit type.

Rare earth elements, having ionic radii larger than neodymium, were crystallized in lanthanite-type hydrated normal carbonates, $(RE)_2(CO_3)_3 \cdot 8H_2O$, whereas, rare earth elements with ionic radii smaller than neodymium were crystallized in tengerite-type hydrated normal carbonates, $(RE)_2(CO_3)_3 \cdot 2—3H_2O$.[1] The differences in the hydration numbers of, and in the ionic radii of rare earth elements in the lanthanite and tengerite type structures, seem to characterize differences in their structures and properties. Since these carbonates have been prepared as powders, accurate structural and chemico-physical data have not been obtained.[2] Shinn and Eick[3] obtained a single crystal of hydrated lanthanum carbonate, $La_2(CO_3)_3 \cdot 8H_2O$, by slow hydrolysis of lanthanum trichloroacetate. They determined the crystal structure of this crystal and found that it contains 4 formula units in an orthorhombic cell of space group Pccn with lattice parameters of $a=8.984\pm0.004$, $b=9.580\pm0.004$, and $c=17.00\pm0.01$ Å, and has a density, $\rho_{obsd}=2.72\pm0.02$ g cm^{-3}, which is very similar to the calculated value, $\rho_{calcd}=2.732$ g cm^{-3}.

Crystalline rare earth carbonates are generally obtained by the hydrolysis of trichloroacetates of rare earth elements, but they usually precipitate as a powder.[2] Henisch *et al.*[4] synthesized single crystals of various slightly soluble materials by means of a silica gel technique. Their results indicated that this technique could be adapted to the crystal growth of rare earth carbonates.

In this study, the crystal growth of hydrated normal rare earth carbonates by the gel method was attempted at various temperatures and with various ratios of rare earth ions and precipitant.

Experimental

Synthesis of the hydrated normal rare earth carbonates was carried out by the reaction between carbonates and rare earth salts in sodium metasilicate gels. Two methods have been examined for this purpose.[5] In the first the gel containing the carbonate was used. Aqueous mixtures of sodium metasilicate and various kinds of carbonates were prepared and the pH was adjusted. As carbonates, 0.008—0.2 M aqueous solutions of Na_2CO_3, $(NH_4)_2CO_3$, $NaHCO_3$, and NH_4HCO_3 were used. After the gel had set, rare earth salt solution was placed on top of the gel and allowed to diffuse. An aqueous solution of 0.008—0.2 M rare earth was prepared from $RECl_3$(RE= La, Ce, Nd, Sm, Gd, Dy, Ho, Yb, Sc). The gels were made from analytical grade $Na_2SiO_3 \cdot 9H_2O$. A 0.23 M Na_2SiO_3 aqueous solution, adjusted to a pH between 7 and 8 with dilute hydrochloric acid, was set in reaction tube and left overnight at room temperature. A simple test tube (25×200 mm) was used as the reaction tube. In the second method, each reagent, rare earth salt solution and carbonate solution, was diffused into the gel from each side of a U-tube (25×200 mm) or double tube. It appears that neither method has any significant advantage. Well-shaped crystals up to 2 mm in size were grown in 12 to 16 weeks. Well-shaped crystals were taken out of the tube and, after dissolving the gel with concentrated alkali solution, were washed with water, air-dried, and subjected to chemical, X-ray diffractometric, and thermal analyses.

Results and Discussion

In the test tube, milky precipitates appeared at the upper growth front and with time penetrated down into the gel. In the cases of lanthanum, praseodymium, and neodymium, well-shaped crystals separated from these milky precipitates after several weeks. Figure 1 shows a micrograph of a praseodymium carbonate crystal. The green, clear-cut crystals cleaved parallel to (001). In the cases of lanthanoids heavier than neodymium, well-shaped crystals did not appear even after several months. Sometimes, spherulites of the carbonates (RE=Nd) were obtained.

Factors Which Influence Crystal Growth. The following experiments were carried out in order to investigate the various factors which influence the growth behavior of neodymium carbonate: the temperature, the concentration of rare earth (in this case of neodymium) and carbonate ions, and the growth period of the crystals. In Fig. 2-a, r, the penetration depth[7,8] of the crystal-growth front is plotted against the square root of the diffusion time. It is observed in Fig. 2-a that r increases linearly with the increase of the square root of t until the diffusion time reaches 49 h. Over 49 h the slope

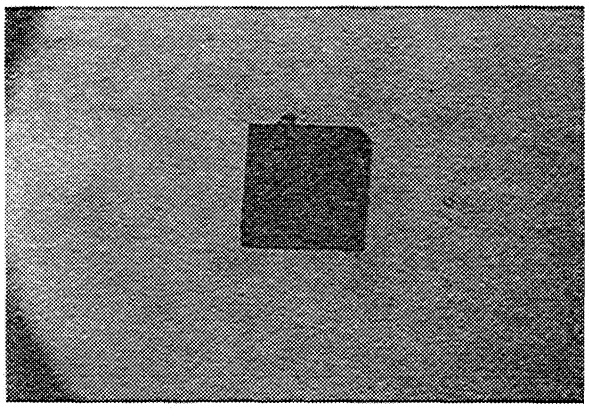

Fig. 1. Micrograph of praseodymium carbonate. Edge lengths of this plane: 2.5 mm.

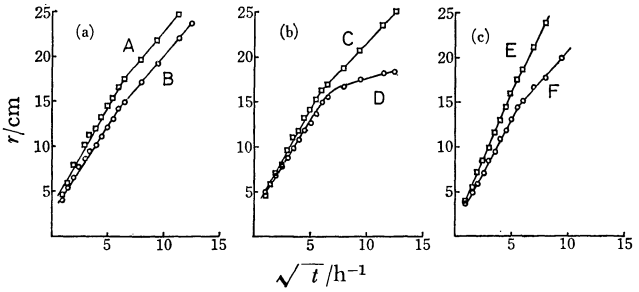

Fig. 2. Penetration rates of neodymium ions in gels.

	Concentration of neodymium	System's temepratures	Molar ratios of Na_2SiO_3: $(NH_4)_2CO_3$
	mol/l	°C	
A	0.1	35	3 : 1
B	0.1	25	3 : 1
C	0.1	30	3 : 1
D	0.1	30	2 : 1
E	0.2	25	3 : 1
F	0.1	25	3 : 1

Added volumes of neodymium ion are 0.5 ml. The pH of the gels is 7.4.

changed with time. During the period in which the linear relationship is maintained, the penetration rates obey a first order kinetic relationship. Beyond 49 h, because masses of the precipitate interfere with the diffusion of neodymium ions, this linear relationship breaks down. In Figs. 2-a, 2-b, and 2-c, the penetration rates were plotted against changes in temperature, concentration of the precipitant, and concentration of neodymium salt, respectively. As for sparingly soluble salts such as the rare earth carbonates, the penetration rates are primarily criteria of the diffusion rates. In the synthesis of single crystals of slightly soluble salts, it is important to have a controlled supply of the reactant; that is, the diffusion rates are to be controlled. Well-shaped and large crystals were produced under the following conditions: the temperature was at 25 °C, Na_2SiO_3: $(NH_4)_2CO_3$ was 3: 1 and the concentration of neodymium ion was 0.2 M.

TABLE 1. CHEMICAL ANALYSIS OF SYNTHESIZED RARE EARTH CARBONATES
(Quantities are molar ratios.)

RE	RE_2O_3 :	CO_2 :	H_2O
La	1.00	3.00	8.04
Pr	1.00	2.99	7.90
Nd	1.00	2.99	4.54
Sm	1.00	2.85	2.85
Gd	1.00	2.76	2.59

Chemical Analysis. Carbon, hydrogen, and rare earth elements of the crystals obtained were analysed using elemental analytical techniques. The carbonates obtained from this method are liable to be contaminated by sodium and silicon because sodium metasilicate gel were used. However, no sodium and silicon were detected from these carbonates by either flame analysis or EPMA. The results of the chemical analyses of air-dried carbonates are given in Table 1; the molar ratios of the first two correspond to $RE_2(CO_3)_3 \cdot 8H_2O$ (RE= La, Pr), the next to $RE_2(CO_3)_3 \cdot 4.54H_2O$ (RE=Nd), and last two to $RE_2(CO_3)_3 \cdot 2—3H_2O$ (RE=Sm, Gd), respectively. The absence of OH^- ions was demonstrated by infrared spectroscopy. Molar ratios are not whole numbers, this anomaly was described in a previous paper.[1] Carbonates of holmium, ytterbium, and scandium could not be analysed, because they were very fine powdered samples and they could not be separated from the gels. Cerium carbonate was not analysed because it was amorphous and contaminated.

X-Ray Diffraction Analyses. The X-ray powder diffraction data of these carbonates are shown in Table

TABLE 2. X-RAY POWDER DATA FOR SYNTHESIZED RARE EARTH CARBONATES

La		Pr		Nd			Sm		Gd	
d/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*hkl*	*d*/Å	*I*	*d*/Å	*I*
8.61	100	8.47	100	8.59	100	002	7.70	100	7.65	60
4.79	15	4.71	10	4.75	10	020	5.74	20	5.69	15
4.50	10	4.45	10	4.48	10	200	3.95	70	3.92	100
4.27	50	4.23	30	4.25	40	113 004	3.86	75	3.82	60
4.18	15	4.12	10	4.13	10	022	3.09	5		
3.98	10	3.93	10	3.95	10	202	3.02	5		
3.89	10	3.85	15	3.88	10	014	2.76	5		
3.85	10	3.82	15	3.83	10	104	2.57	40	2.55	35
3.58	5	3.55	5			114	2.41	5		
3.29	15	3.24	15	3.24	15	213 220	2.25	5		
3.19	10	3.15	10	3.16	5	221 024	2.07	30	2.06	50
3.07	20	3.06	10	3.07	10	204 222	1.97	10	1.96	15
3.02	10	3.02	15	3.02	15	115			1.81	10
a= 9.00 Å		a= 8.90 Å		a= 8.96 Å (calculated from 200)						
b= 9.58 Å		b= 9.42 Å		b= 9.50 Å (calculated from 020)						
c=17.22 Å		c=16.94 Å		c=17.18 Å (calculated from 002)						

2. This table indicates that the X-ray powder data of lanthanum, praseodymium, and neodymium are almost identical to that of lanthanite, while the data for samarium and gadolinium are almost identical to that of tengerite. A single crystal of the neodymium carbonate was employed in taking Weisenberg and precession photographs in order to determine the cell parameters and the space group. Systematic absence occured for $h00$, $0k0$, and $00l$ when h, k, or $l=2n+1$, for $0kl$ and $h0l$ when $l=2n+1$ and for $hk0$ when $h+k=2n+1$. Therefore, Pccn is a possible space group. The lattice parameters obtained from powder diffractometric data are: $a=8.97$ (calculated from 200), $b=9.49$ (calculated from 020), and $c=17.18$ (calculated from 002) Å. The density (2.76 g cm^{-3}) calculated for four formula units was in agreement with the density obtained by the heavy liquid method (2.75 g cm^{-3}). The crystalline carbonate of cerium was not obtained by this method. Perhaps cerium(III) in the starting solution had been oxidized in cerium(IV) during the diffusion. No report of a carbonate of cerium(IV) was found in the literature surveyed. Because the carbonates were not separated from the gels, no X-ray powder diffraction peaks of the carbonates of holmium, ytterbium, and scandium were obtained. This is the first report of samarium and gadolinium carbonates crystallizing with the tengerite type structure at such low temperatures (≈25 °C) and that neodymium carbonate crystallizes with a lanthanite type structure.

Thermal Analyses. The thermal analysis of the carbonates of lanthanite type was carried out with a heating rate of 10 °C/min in air. The results of the thermogravimetric analysis, TGA, and differential scanning calorimetry, DSC, of the carbonates of lanthanum and neodymium are shown in Fig. 3. The decomposition processes of neodymium and lanthanum carbonate were similar. On the TGA curve for the neodymium carbonate, there is initially a loss of water, which corresponds to the formation of anhydrous carbonate. This step is also prominent for the lanthanum compound. The DSC curve in Fig. 3 shows that the endothermic effects in the 100—200 °C range corresponds to the formation of the anhydrous carbonate. The continuous raising of the temperature leads to the formation of some intermediate phases, shown in the following schemes:

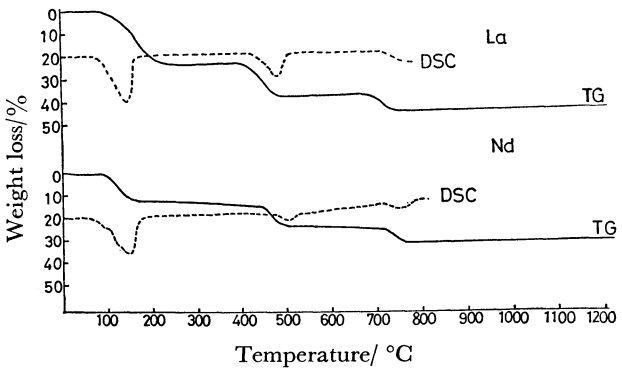

Fig. 3. Thermal analyses of lanthanum and neodymium carbonates.

$$Nd_2(CO_3)_3\cdot 8H_2O \xrightarrow{ca.\ 150\,^\circ C} Nd_2(CO_3)_3 \xrightarrow{ca.\ 450\,^\circ C}$$
$$Nd_2O(CO_3)_2 \xrightarrow{ca.\ 750\,^\circ C} Nd_2O_3 \quad (1)$$

$$La_2(CO_3)_3\cdot 8H_2O \xrightarrow{ca.\ 150\,^\circ C} La_2(CO_3)_3 \xrightarrow{ca.\ 450\,^\circ C}$$
$$La_2O_2(CO_3) \xrightarrow{ca.\ 700\,^\circ C} La_2O_3 \quad (2)$$

The intermediate phases appearing at *ca.* 450 °C were different with each carbonate sample, despite the fact that the initial compositions of these compounds were identical. The results of the thermal analysis of samarium and gadolinium carbonates obtained were similar to that of tengerite.[6]

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