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The Synthesis of Crystalline Hydrated Double Carbonates of Rare Earth Elements and Sodium

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Synopsis. Crystalline hydrated double carbonates of rare-earth elements and sodium were obtained by adding sodium carbonate solutions to rare-earth chloride solutions. The formula of the precipitates was determined to be $LnNa(CO_3)_2 \cdot 6H_2O$ (Ln=La, Ce, Nd, Sm, Gd, Dy, and Y). The products have similar X-ray powder diffraction patterns, which were indexed assuming a tetragonal symmetry. The cell parameters of the products were calculated, they decrease linearly with the decrease in the ionic radii of the rare-earth elements.

In preceding papers,[1] the preparation, formation temperature, optical properties, infrared spectra, and TG data of crystalline hydrated oxocarbonates and crystalline hydrated normal carbonates of rare-earth elements were reported. One of the articles[1] also included the formation of the crystalline hydrated double carbonates of rare-earth elements and sodium (rare-earth element: sodium=1: 1). As for the double carbonates with a 1: 1 composition, though, very little has been known so far. Tselik *et al.*[2] reported the formation of Y: Na=1: 1 double carbonate by mixing solutions of sodium carbonate and yttrium chloride. It is not clear, however, whether their product is of a crystalline or an amorphous phase.

In this study, the synthesis of crystalline double carbonates of rare-earth elements and sodium was attempted at various temperature in order to make clear the formation temperatures of double carbonates. Some other properties of the products were also studied.

Experimental

To solutions of 0.05 M rare-earth chlorides we added acetic acid-sodium acetate buffer solutions of pH 5; then we vigorously stirred in excessive amounts of solutions of sodium carbonates. The solutions containing the precipitates were stored in an air bath kept at the temperatures of 20, 30, 40, 50, 60, 70, and 80 °C, for four days. The changes in the crystallinity of the product during the aging were checked by X-ray powder diffractometry. In the dry air, the precipitates are not stable and slowly change into another phase; therefore, studies such as chemical analysis, X-ray powder diffractometry, thermal analysis, infrared spectrometry, and the measurement of the refractive index were carried out immediately after filtration.

Results

Chemical Analysis. The rare-earth elements used for the preparation of the double carbonates were La, Ce, Nd, Sm, Gd, Dy, Y, Er, Yb, and Sc. The products of La, Ce, Nd, Sm, Gd, Dy, and Y were obtained in crystalline form, while those of Er, Yb, and Sc were obtained in amorphous form. The results of the chemical analysis of Gd and Y compounds are shown in Table 1. On the basis of these results, the chemical formulas for the synthesized double carbonates were determined to be $LnNa(CO_3)_2$–$6H_2O$ (Ln=rare-earth elements).

TABLE 1. CHEMICAL ANALYSIS OF DOUBLE CARBONATES

Rare earth element	M_2O_3 :	CO_2 :	H_2O :	Na_2O
Gadolinium	1.00	1.97	6.05	0.98
Yttrium	1.00	1.97	5.95	1.00

The formation temperatures of the double carbonates by means of the present procedure are shown in Fig. 1. The La and Ce precipitates were found to be mixtures of double carbonates and lanthanite-type carbonates, $Ln_2(CO_3)_3 \cdot 8H_2O$, while the Nd, Sm, Gd, Dy, and Y compounds were double carbonates showing the same X-ray powder diffraction pattern.

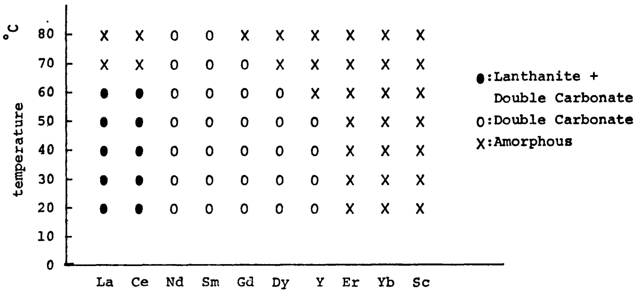

Fig. 1. Diagram showing the formation temperature of double carbonates.

X-Ray Data. The X-ray powder patterns were recorded on a Rigaku Denki Co., Ltd. The data of the synthesized crystalline, hydrated double carbonates of rare-earth elements and sodium are given in Table 2. The sample grains are too fine to be submitted to single crystal X-ray analysis. The indexing of the X-ray powder lines was done by the use of the indexing charts given by Bell *et zl.*[3] The probable indices for the powder data, assuming a tetragonal symmetry, are listed in Table 2. The assumed tetragonal symmetry is consistent with the optical properties. Based on these indexings, the unit-cell dimensions and unit-cell volumes were calculated. The results are also shown in Table 2. The relations between the unit-cell parameters and the ionic radii of rare-earth elements are shown in Fig. 2. Using the cell parameters and measured density (2.31 g/cm^3 at 20 °C) for the Y compound, the number of formula units per unit cell was calculated as eight. Since all the reflexions of *h*00 are observed in the X-ray powder patterns, the space group of the materials may be one

Table 2. X-Ray powder data of double carbonates

Nd d(Å)	Nd I	Nd Probable hkl	Sm d(Å)	Sm I	Gd d(Å)	Gd I	Dy d(Å)	Dy I	Y d(Å)	Y I
13.31	100	100	13.17	100	13.08	100	13.02	100	12.98	100
6.61	80	200	6.56	80	6.53	80	6.47	70	6.44	70
4.37	80	300	4.35	100	4.33	90	4.31	50	4.30	50
3.28	20	302	3.26	20	3.24	5	3.22	5	3.21	5
2.62	60	500, 332	2.61	60	2.60	60	2.58	30	2.57	30
2.18	40	600, 252	2.17	20	2.16	30	2.15	10	2.15	20
1.87	10	353, 550	1.86	10	1.85	10	1.84	5	1.84	10
a=13.11Å c=9.93Å V=1706.7Å^3			a=13.05Å c=9.85Å V=1677.5Å^3		a=12.99Å c=9.77Å V=1648.6Å^3		a=12.93Å c=9.69Å V=1620.0Å^3		a=12.90Å c=9.65Å V=1605.8Å^3	

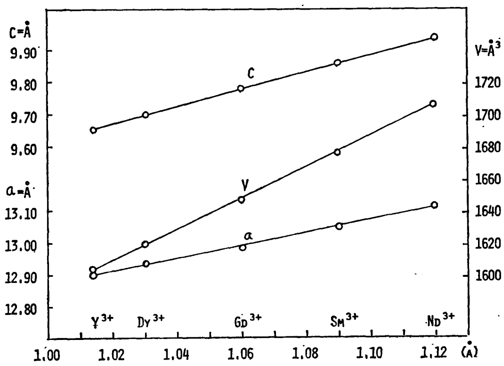

Fig. 2. Relationships between ionic radii of rare earth elements and unit cell parameters.

of P4 symmetries. These space groups have a four-fold axis in the unit cell, which is consistent with the fact that the materials have eight formula in a unit cell.

Refractive Indices. Under the microscope, the synthesized materials were very small rectangles and exhibited a straight extension. The refractive indices of the materials were determined by the immersion method. The immersion media were checked with an Abbe refractometer. The refractive indices of the Nd, Sm, Gd, and Dy compounds were found to have the same values of $\gamma=1.554$ and $\alpha=1.546$ within the limits of experimental error (± 0.001). The refractive indices of the Y compound are $\gamma=1.541$ and $\alpha=1.534$. The size of the crystals was so small that β and 2V could not be determined.

Infrared Absorption Spectra. The infrared absorption spectra were obtained by the KBr disk method. The absorption curve of the Nd compound is shown in Fig. 3 as an example. All the double carbonates of the rare-earth elements show spectra very similar as that in Fig. 3. The ν_1 band of CO_3^{2-} appears at 1070 cm^{-1} as a singlet absorption. On the other hand, the ν_2 and ν_3 band appears as doublet bands. The ν_2 band has peaks at 875 and 850 cm^{-1}, while ν_3 has its at 1530 and 1385 cm^{-1}. These splittings of ν_2 and ν_3 are rather common in rare-earth carbonates.[1] They may be due to the coupling between neighboring carbonate ions and/or to occupying two structurally different sites in the unit cell.

Thermal Analysis. The TG and DSC curves of Nd and Gd compounds are shown in Fig. 4. Based on the TG data, the process of the thermal decomposition of each sample may be considered to take place in one of the following ways.

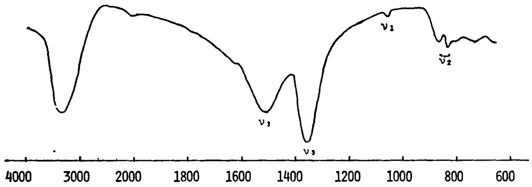

Fig. 3. Infrared absorption spectrum of double carbonate of neodymium and sodium.

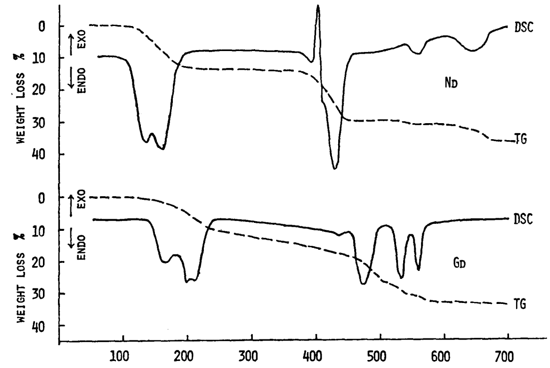

Fig. 4. TG and DSC curves of double carbonates.

$$(1)\quad NdNa(CO_3)_2\cdot 6H_2O \xrightarrow[120\sim 200^\circ C]{} NdNa(CO_3)_2\cdot 3H_2O \xrightarrow[370\sim 450^\circ C]{} NdNa(CO_3)_2 \xrightarrow[650^\circ C]{} NdNaO(CO_3)$$

$$(2)\quad GdNa(CO_3)_2\cdot 6H_2O \xrightarrow[70\sim 200^\circ C]{} GdNa(CO_3)_2\cdot 2H_2O \xrightarrow[370\sim 450^\circ C]{} GdNa(CO_3)_2\cdot H_2O \xrightarrow[400\sim 600^\circ C]{} GdNaO(CO_3)$$

The decomposition process of Sm carbonate is very similar to that of Nd carbonate, while the processes of Dy and Y carbonates are similar to that of Gd carbonate.

References

1) For instance, K. Nagashima, H. Wakita, and A. Mochizuki, This Bulletin, **46**, 152 (1972).

2) I. N. Tselik, G. F. Denieka, V. Ya. Shvartsman, and V. D. Fedorenko, *Russ. J. Inorg. Chem.*, **13**, 53 (1968).

3) J. C. Bell and A. E. Austin, "Battelle Indexing Charts for Diffraction Patterns of Tetragonal, Hexagonal and Orthorhombic Crystals," Battelle Memorial Institute, Columbus 1, Ohio, U.S.A.