Synthesis of Tengerite Type Rare Earth Carbonates[1]

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(Received March 28, 1972)

Rare earth carbonates which give the same X-ray powder diffraction pattern as tengerite were prepared by heating aqueous solutions containing rare earth chlorides and ammonium trichloroacetate. Y, Er, Ho, and Gd gavee xactly the same X-ray powder pattern as tengerite, while Nd and Sm were similar to tengerite but with a few additional diffractions. X-ray powder data of the tengerite type rare earth carbonate were indexed and cell parameters of $a_0=9.20\pm0.02$ Å, $b_0=11.32\pm0.03$ Å, and $c_0=7.59\pm0.01$ Å for $Y_2(CO_3)_3\cdot nH_2O$ ($n=2$—3), with 4 moles of formula units per cell and orthorhombic symmetry were established. Linear correlations were demonstrated between refractive indices or cell parameters of the synthesized carbonates and their respective rare earth element atomic numbers.

The compositions and structures of rare earth carbonates have been the subject of numerous recent studies.[2] Some of the results reported in these studies are inconsistent. Most mineralogists consider the existence in nature of only three normal carbonates: lanthanite $La_2(CO_3)_3\cdot8H_2O$,[3] calkinsite $(La,Ce)_2(CO_3)_3\cdot4H_2O$,[4] and tengerite $Y_2(CO_3)_3\cdot nH_2O$ ($n=$ 2—3),[5] and several double carbonates such as burbankite $Na_2(Ca, Sr, Ba, Ce, La)_4(CO_3)_5$,[4] and sahamalite $(Ce, La, Nd)_2(Mg, Fe)(CO_3)_4$.[6]

Shinn and Eick[7] studied the structure of lanthanite and indicated that it contains 4 formula units in an orthorhombic unit cell of space group Pccn, with lattice parameters of $a_0=8.984\pm0.004$, $b_0=9.580\pm0.004$, and $c_0=17.00\pm0.01$ Å ($\rho_{obsd}=2.72\pm0.02$ g cm^{-3}; $\rho_{calcd}=2.732$ g cm^{-3}). Pecora and Kerr[4] examined calkinsite X-ray crystalographically and determined the following cell parameters; $a_0=9.57\pm0.02$, $b_0=12.65\pm0.08$, $c_0=8.94\pm0.02$ Å, space group $P2_122_1$ or D_2,[4] 4 formula units per cell. Among these rare earth carbonates, rather little has been known of the characteristics of tengerite, a very rare hydrous yttrium carbonate mineral, despite its early discovery at Ytterby, Sweden.

Regarding the composition of tengerite, Iimori[8] suggested the formula of a hydrous basic double carbonate of yttrium and calcium, $Y_3Ca(OH)_3(CO_3)_4\cdot3H_2O$(?) based on the analysis of the material from Suishoyama, Iisaka, Fukushima, Japan. On the other hand, the material from Baringer Hill, Texas, USA, was described as a hydrous double carbonate of yttrium and beryllium.[9]

To study the composition, a hydrated yttrium carbonate was synthesized by precipitation from a homogeneous aqueous solution containing yttrium chloride and ammonium trichloroacetate and digestion of the precipitate in the mother liquor for an extended period. The X-ray diffraction pattern of the precipitated carbonate agreed with that of tengerites from Suishoyama[10] and from Iveland, Norway (ASTM-16-698). The similarity between the sample from Suishoyama and the synthesized carbonate was also confirmed by DTA, TGA, and IR absorption data.[5] The analysis of the synthesized carbonate established the following molecular ratio; $Y_2O_3=1.00$: $CO_2=3.01$: $H_2O=2.35$ (average). This ratio is close to the normal carbonate of yttrium.

Experimental and Results

Preparation of the Tengerite Type Rare Earth Carbonates. Rare earth carbonates may be conveniently prepared by precipitation from homogeneous solution by hydrolysis of the trichloroacetates of rare earth elements.[11]

$$2M(C_2Cl_3O_2)_3 + (x+3)H_2O \rightarrow M_2(CO_3)_3\cdot xH_2O + 3CO_2 + 6CHCl_3$$

Rare earth carbonates thus obtained are usually coarse and easily filtered. However, the precipitates generally appear amorphous when examined by X-ray powder diffractometry. (This is probably the explanation for the many different results reported for the compositions of artificially prepared rare earth carbonates.) Crystalline precipitates of excellent quality were obtained by heating the solutions containing the precipitates for several days. As will be described in the following section, the crystalline yttrium carbonate prepared by this procedure has the tengerite structure.

The procedure applied throughout the study is as follows: Four g of trichloroacetic acid were added

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[1] Presented in part at the 23rd annual meeting of the chemical society of Japan, Tokyo, 1969.

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[2] R. G. Charles, *J. Inorg. Nucl. Chem.*, **27**, 1498 (1965); E. L. Head and C. E. Holley, Jr., "Rare Earth Research III," Gordon and Breach, New York, N.Y. (1964), p. 51; E. L. Head and C. E. Holley, Jr., "Rare Earth Research IV," Gordon and Breach, New York, N.Y. (1965), p. 707.

[3] A.S.T.M.; Alphabetical and Grouped Numerical Index of X-ray diffraction Data, 14—190.

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[5] K. Nagashima and H. Wakita, *Nippon Kagaku Zasshi*, **89**, 856 (1968).

[6] H.W. Jaffe, R. Meyrowitz, and H. T. Evans, Jr., *Am. Mineral.* **38**, 741 (1953).

[7] D. B. Shinn and H. A. Eick, *Inorg. Chem.*, **7**, 1340 (1968).

[8] T. Iimori, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **38**, 832 (1938).

[9] C. Palache, H. Berman, and C. Frondel, "Dana's System of Mineralogy," Vol. II, 7th ed., John Wiley & Sons, Inc., New York, N.Y. (1951), p. 275.

[10] A. Kato, "X-ray Powder Data for Radioactive Minerals," No. 11, Geological Survey of Japan, Tokyo, Japan, 1958, p. 127.

[11] M. L. Salutsky and L. L. Quill, *J. Amer. Chem. Soc.*, **72**, 3306 (1950).

to 250 ml of aqueous solution containing 6 mM yttrium chloride. The pH of the solution was adjusted between 4 and 5 with dilute ammonium hydroxide, then the solution was heated on a steam bath for two days.

Figure 1 shows a typical micrograph of yttrium carbonate prepared by this procedure.

Fig. 1. Hydrated yttrium carbonate.

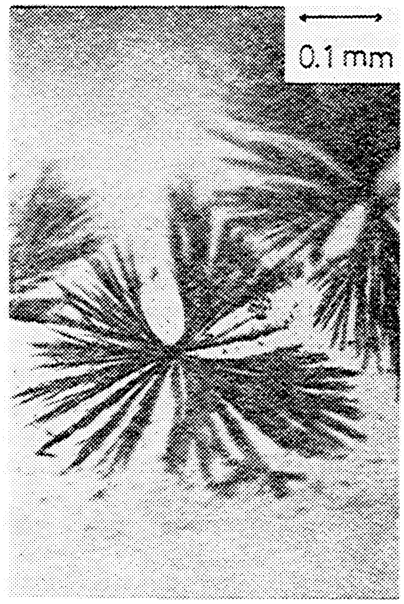

Fig. 2. Hydrated yttrium carbonate (prepared in a sealed tube).

Figure 2 is also a micrograph of yttrium carbonate prepared by maintaining the solution ($YCl_3+CCl_3COOH+NH_4OH$, pH=4—5) in a sealed glass ampoule for about one week at 70°C. Carbonates of the other rare earth elements were synthesized by applying the same procedure. Most of the specimens were in the form of radial aggregates of fine fibers as seen in Fig. 1. Carbonates samples other than yttrium exhibited admixed larger amorphous particles in addition to the crystalline particles.

X-Ray Powder Diffraction and Optical Properties.

The X-ray powder diffraction data for the synthesized yttrium carbonate are tabulated in Table 1, in which those for tengerite from Iveland, Norway (ASTM 16-698(1966)) are also represented for comparison.

The X-ray powder data of the synthesized sample are virtually identical with those of natural tengerite.

Table 1. X-Ray powder data and their indices for natural tengerite and synthesized hydrated yttrium carbonate

I		II				
d_{obs} Å	I/I_0	d_{obs} Å	I/I_0	$Q(1/d^2)_{obs}$	Probable hkl	$Q(1/d^2)_{calc}$
7.54	60	7.589	90	0.017	001	0.017
5.60	60	5.673	70	0.031	020	0.031
4.57	70	4.604	100	0.047	200	0.047
3.86	100	3.890	70	0.066	201	0.065
3.77	20	3.782	30	0.070	030	0.070
3.55	60	3.573	50	0.078	220	0.079
		3.046	5	0.108	300	0.106
2.95	70	2.967	40	0.114	310	0.114
		2.919	8	0.117	230	0.118
2.68	20	2.696	15	0.136	320	0.138
2.59	10	2.598	10	0.148	222	0.148
2.53	50	2.537	30	0.155	321	0.155
		2.520	10	0.158	003	0.156
		2.406	10	0.173	240	0.172
		2.372	10	0.178	330	0.177
		2.334	5	0.184	312	0.184
2.29	30	2.295	10	0.190	241	0.190

I: Iveland, Norway (ASTM). Fe/Mn rad.=1.9373 Å.

II: Synthesized hydrated yttrium carbonate, Cu/Ni rad.=1.5418 Å.

Under the microscope the synthesized sample shows a straight extinction and positive axial character. The refractive indices of the synthesized yttrium carbonate are

$\gamma=1.624\pm0.002$, $\alpha=1.612\pm0.001$ and $\gamma-\alpha=0.012\pm0.003$

Those of natural tengerite from Suishoyama, Japan measured by Kato[10] are

$\gamma=1.642$, $\alpha=1.622$, and $\gamma-\alpha=0.020$

The small difference between the two materials may be due to the compositional difference. The other optical properties could not be measured accurately, because the synthesized sample is too finely grained. The above data lead the assignment of tetragonal or orthorhombic (or hexagonal) symmetry to the carbonate.

The indexing to the X-ray powder data for tengerite was accomplished through the application of Battelle indexing charts,[12] since a literature survey, did not reveal an index to the X-ray powder data for tengerite.

In Table 1 the probable indices are given, and good agreement is shown between the observed and calculated Q values when an orthorhombic cell with $a_0=9.20\pm0.02$, $b_0=11.32\pm0.03$, $c_0=7.59\pm0.01$ Å was assumed. Applying these cell parameters and measured density (3.3—3.1 g cm^{-3}), the number of the formula units in a cell was calculated as 4. The results of electron diffraction studies were used to determine the crystal system and cell parameters.

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[12] 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.

Chemical Analysis of Rare Earth Carbonates. The results of the chemical analyses of air dried carbonates are given in Table 2. Table 2 also shows that the molar ratios, $R_2O_3 : CO_2$ (: H_2O) are not whole numbers except in the case of yttrium carbonate which corresponds to $Y_2(CO_3)_3{\cdot}nH_2O$ (n=2—3, a part of H_2O may be zeolitic). This apparent anomaly may be attributed to the admixed amorphous particles and to the instability of the carbonates. Concerning the instability of rare earth carbonates, Shinn and Eick[7] mentioned two bonding positions of carbonate ions in the lanthanite structure, one coordinates as a unidentate ligand and one as a bidentate ligand. Water molecules behave similarly; one coordinates to a metal ion and one does not, therefore some of the carbonate ions and water molecules may be expected to be rather easily lost from the structure.

TABLE 2. CHEMICAL ANALYSES OF SYNTHESIZED RARE EARTH CARBONATE

	M_2O_3	:	CO_2 (molar ratio)	:	H_2O
$Y_2(CO_3)_3{\cdot}nH_2O$	1.00	:	3.01	:	2.35
Yb-[a)]	1.00	:	2.05	:	3.87
Er-[b)]	1.00	:	3.01	:	2.25
Ho-	1.00	:	2.43	:	4.58
Dy-	1.00	:	2.84	:	2.79
Gd-	1.00	:	2.92	:	2.58
Sm-	1.00	:	2.87	:	2.34
Nd-	1.00	:	2.79	:	2.29
La-	1.00	:	2.97	:	8.04

a) Amorphous by X-ray examination.
b) Prepared in a sealed tube.

Proton magnetic resonance of the synthesized hydrated lanthanum carbonate (lanthanite type) and hydrated yttrium carbonate (tengerite type) were run at room temperature using a broad-line NMR spectrometer. A spectrum composed of a broad and a sharp absorption indicating two bonding positions for water molecules, was obtained for the lanthanum compound, while a signal with one sharp absorption was obtained for the yttrium compound.

X-Ray Powder Diffraction of Some Rare Earth Carbonates. By the procedure described in the prior section, hydrated carbonates were obtained from lanthanum, neodymium, samarium, gadolinium, dysprosium, holmium, erbium and ytterbium. The X-ray powder diffraction patterns and the powder data of these carbonates are shown in Fig. 3 and Table 3 respectively. Figure 3 indicates the X-ray powder patterns of gadolinium, dysprosium, and holmium carbonates are almost identical with that of yttrium carbonate. The increase in d values with increasing ionic radii of the metals is well recognized (Table 3).

As for neodymium and samarium compounds, although several additional diffractions, for example at 5.529(Nd) and 5.481Å(Sm), were observed, the arrangements and intensities of most of the diffractions are almost the same as those of yttrium carbonate. The lanthanum compound given an X-ray powder pattern quite different from that of yttrium carbonate and similar to that of lanthanite.[3] The pattern and powder data for ytterbium and scandium compounds are not listed in the figure and table, because only an amorphous phase for ytterbium and a hydroxide for scandium were obtained by the present procedure. These results may indicate the fact that La^{3+} is too large and Yb^{3+} and Sc^{3+} are too small for the tengerite structure.

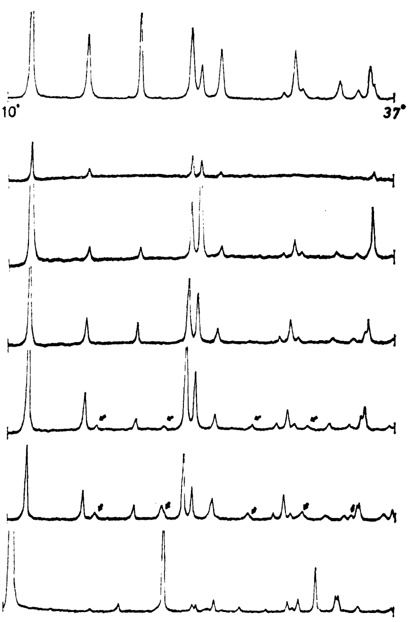

Fig. 3. X-ray powder diffraction patterns of hydrated rare earth carbonates.
Arrows indicate peaks not observed in the diffractions of tengerite

In Table 3, in addition to the powder data, cell parameters a_0, b_0, c_0 and refractive indices γ and α of

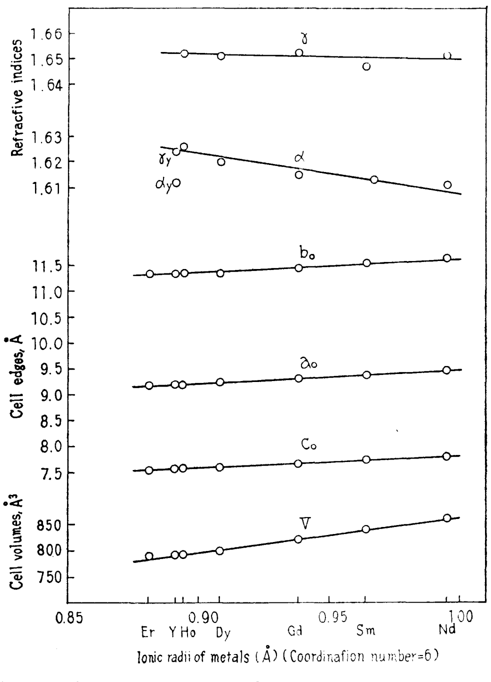

Fig. 4. Lattice parameters, refractive indices *vs.* ionic radii of rare earth metals.

TABLE 3. X-RAY POWDER DATA, CELL PARAMETERS$^{a)}$ AND REFRACTIVE INDICES FOR SYNTHESIZED RARE EARTH CARBONATES

$Y_2(CO_3)_3 \cdot H_2O$			Er-	Ho-	Dy-	Gd-	Sm-	Nd-	La-
d (Å)	I/I_0	probable *hkl*	*d* (Å)	*d* (Å)	*d* (Å)	*d* (Å)	*d* (Å)	*d* (Å)	*d* (Å)
7.589	90	001	7.563	7.589	7.609	7.681	7.755	7.823	8.588
5.673	70	020	5.673	5.673	5.684	5.731	5.780	5.825	6.800
							5.481$^{b)}$	5.529$^{b)}$	5.627
4.604	100	200	4.601		4.618	4.659	4.695	4.738	5.001
							4.254$^{b)}$	4.295$^{b)}$	4.066
3.890	70	201	3.887	3.893	3.897	3.933	3.965	4.001	3.890
3.782	30	030	3.778	3.784	3.789	3.824	3.858	3.897	3.850
3.573	50	220	3.576	3.579	3.580	3.616	3.645	3.678	3.651
							3.295$^{b)}$	3.334$^{b)}$	3.403
3.046	5	300	3.045		3.045	3.079	3.104	3.131	3.184
2.967	40	310	2.965		2.975	3.000	3.026	3.050	3.021
2.919	8	230	2.915		2.930	2.952	2.979	3.006	2.988
							2.889$^{b)}$	2.929$^{b)}$	2.988
2.696	15	320	2.699		2.714	2.734	2.759	2.780	
2.598	10	222	2.595		2.607	2.626	2.648	2.675	
								2.637$^{b)}$	
2.537	30	321	2.517			2.564	2.585	2.607	
$Y_2(CO_3)_3 \cdot nH_2O$			Er-	Ho-	Dy-	Gd-	Sm-	Nd-	La-
$a_0=9.20\pm0.02$ Å			9.20	9.21	9.24	9.32	9.39	9.48	
$b_0=11.32\pm0.03$ Å			11.35	11.35	11.37	11.46	11.56	11.65	
$c_0=7.59\pm0.01$ Å			7.56	7.59	7.61	7.68	7.76	7.82	
$\gamma=1.624$				1.652	1.651	1.652	1.647	1.651	
$\alpha=1.612$				1.626	1.620	1.615	1.613	1.611	

a) Except for yttrium compound, calculated from 001, 020, and 200.
b) Additional diffractions. In calculation of a_0, b_0, c_0, these diffractions were neglected.

the compounds are listed. The values of a_0, b_0, and c_0 for samarium and neodymium compounds were calculated by applying the indices of tengerite to most of the diffractions and neglecting the weak diffractions to which indices of tengerite could be given.

Relations between Lattice Parameters and Refractive Indices of Rare Earth Carbonates and the Ionic Radii of Rare Earth Elements. In Fig. 4, cell parameters a_0, b_0, and c_0 and refractive indices γ and α, of the synthesized carbonates are plotted *versus* ionic radii of rare earth metals.[13] It is observed in Fig. 4 that cell parameters a_0, b_0, and c_0 and unit cell volumes of tengerite type rare earth carbonates increase linearly with increasing ionic radii of the metals, while refractive indices, (which closely follow the densities) decrease with increasing ionic radii of the metals.

The authors wish to express their thanks to Dr. Y. Kuroda and Dr. S. Shimoda, Geological and Mineralogical Institute, Tokyo Kyoiku University, Dr. A. Kato, National Science Museum, Dr. K. Harada, Exploration Department, Sumitomo Metal Mining Co., and to Mr. K. Furuhashi of this department for their generous helps.

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[13] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, (1969), B25, 925.