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The Synthesis of Crystalline Rare Earth Carbonates

KOZO NAGASHIMA, Hisanobu WAKITA,* and Akihiko MOCHIZUKI
Department of Chemistry, Faculty of Science, Tokyo Kyoiku University, Bunkyo-ku, Tokyo 112

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The factors which influence the crystallization of rare earth carbonates were studied. Crystalline rare earth carbonates were precipitated at various temperatures from aqueous solutions by using sodium carbonate, sodium bicarbonate, trichloroacetic acid, and urea as precipitants. The crystal parameters, compositions, and factors concerning the formations of various carbonates, such as lanthanite-type $Ln_2(CO_3)_3 \cdot 8H_2O$(Ln=La, Ce), tengerite-type $Ln_2(CO_3)_3 \cdot nH_2O$(Ln=Nd, Sm, Gd, Dy, Ho, Er, and Y, n=2—3), monoxocarbonate-type $Ln_2O(CO_3)_2 \cdot nH_2O$($Ln$=La, Ce, Nd, and Sm, n=1—2) and a hydrated double carbonate of rare earth and sodium (rare earth= La, Ce, Nd, Sm, Gd, Dy, and Y) were determined by chemical analysis and X-ray powder diffractometry.

Rare earth carbonates of various compositions have been reported as a result of numerous syntheses and thermal analyses.[1-9] Many of the results reported and the accompanying discussions are, however, contradictory. The inconsistencies are due in part to preparatory difficulties and to a lack of structural data.

The carbonates of most metals are prepared by the following two common procedures: the precipitation of the compounds by alkali carbonates or bicarbonates from solutions containing the metal salt, and by passing carbon dioxide through an aqueous suspension of metal hydroxides. However, pure crystalline carbonates of the rare earth elements are difficult to prepare by these methods.

Crystalline rare earth carbonates are generally obtained by the hydrolysis of trichloroacetates of rare earth elements, but the precipitates of heavier lanthanoids prepared by other techniques usually appear amorphous when examined by X-ray powder diffractometry.[10]

Katsurai and Uda[11] prepared pure crystalline siderite, $FeCO_3$, by autoclaving a solution of ferrous ammonium sulfate in the presence of urea. The present authors have now successfully used this procedure in preparing the crystalline rare earth carbonates.

In general, the principal factors which influence the crystallization of scarcely-soluble compounds from aqueous solution are: (1) the nature of the precipitant, (2) the temperature and pressure, (3) the concentrations of the metal ion and the precipitant, and (4) the aging period. These factors have been repeated vaguely in almost all studies concerned with the synthesis of crystalline rare earth carbonates. To be considered in this investigation are the natures of the carbonates of lanthanum, cerium(III), neodymium, samarium, gadolinium, holmium, erbium, ytterbium(III), yttrium, and scandium, essentially even-atomic-numbered lanthanoids, as they are affected by the above conditions during the preparation.

Experimental and Results

Synthesis. *(1) Alkali Carbonate and Bicarbonate as Precipitant*: Similar results were obtained with sodium carbonate and sodium bicarbonate, but usually the bicarbonate gave a superior crystalline product. Crystalline carbonates of lanthanum, cerium(III), neody-

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[*] Present address. Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka 814.

[1] R. G. Charles. *J. Inorg. Nucl. Chem.*, **27**, 1498 (1965).

[2] E. L. Head and C. E. Holley, Jr., "Rare Earth Research II," Gordon and Breach, New York, N. Y. (1964), p. 51.

[3] E. L. Head and C. E. Holley, Jr., "Rare Earth Research IV," Gordon and Breach, New York, N. Y. (1965), p. 707.

[4] R. L. N. Sastry, S. R. Yoganarisimhan, P. N. Mehrota, and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, **28**, 1165 (1966).

[5] M. Clarus Strouth, Ph. D. Thesis, Michigan State University, 1962.

[6] G. Pannetier, J. Nataf, and A. Deireigne, *Bull. Soc. Chim. Fr.*, **5**, 318 (1965).

[7] S. D. Ross and J. Goldsmith, *Spectrochim. Acta*, **20**, 781 (1964).

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

[9] I. N. Tselik, V. Ya. Shvartsman, and V. D. Fedorenko, *Russ. J. Inorg. Chem.*, **13**, 53 (1968).

[10] H. Wakita and K. Nagashima, This Bulletin, **45**, 2476 (1972).

[11] T. Katsurai and M. Uda, *ibid.*, **43**, 3306 (1970).

Table 1. The influence of metal ion (Y^{3+}) concentration and aging period on the crystallization of rare earth carbonates[a)]

Temp. (°C)	50°C			70°C		
Concn of Y^{3+} (mol)	Aging period (day)			Aging period (day)		
	1	2	4	1	2	4
0.0002	No ppt	Large thin plate amor.	Large thin plate amor.	Large needle cryst.	Large needle cryst.	Large needle cryst.
0.0005	Thin plate amor.	Large thin plate amor.	Needle cryst.	Needle cryst.	Needle cryst.	Needle cryst.
0.0010	Thin plate amor.	Thin plate amor.	Needle cryst.	Needle cryst.	Needle cryst.	Needle cryst.
0.0020	Thin plate amor.	Needle cryst.	Needle cryst.	Small needle cryst.	Small needle cryst.	Small needle cryst.

a) All crystalline precipitates gave the tengerite type X-ray powder patterns.

mium, samarium, gadolinium, dysprosium, erbium, and ytterbium were produced by this method, whereas ytterbium and scandium gave only amorphous carbonates.

Procedure: To a constantly-stirred 10 ml portion of a 0.1M rare earth chloride solution contained in a beaker, we added a solution of twice the molar equivalent of sodium bicarbonate (or carbonate). The procedure was then repeated at various temperatures from 20 to 80°C. The total volume of the mixed solution was adjusted to 100 ml and was maintained at the desired temperature for one week. The precipitates were then filtered off, washed with water repeatedly, air-dried and subjected to microscopy, chemical analysis, X-ray powder diffractometry, and thermal analysis. The results for the precipitates obtained at higher temperatures agreed with those obtained by the other methods.

(2) Trichloroacetic Acid as the Precipitant: This is the most popular method for obtaining crystalline rare earth carbonates. Not only light lanthanoids, but also yttrium and heavy lanthanoids except for ytterbium, gave crystalline carbonates.[10)] Crystalline carbonates of the elements mentioned in (1) have been obtained in the temperature range from 40 to 120°C. Below 40°C, the rate of the hydrolysis of trichloroacetate was too slow for us to prepare sufficient amounts of carbonates.

Procedure: To a 10 ml portion of a 0.1M rare earth chloride solution contained in a beaker or flask, we added 5 ml of a 2.0 M trichloroacetic acid solution. The solution was adjusted with ammonia to pH 5—6, and the volume was adjusted to 100 ml. Beakers or flasks were placed in thermostatically-controlled baths at temperatures ranging from 40 to 120°C, at ten-degree intervals, for one week. For temperatures over 100°C, the flasks were equipped with reflux condensers, or sealed glass ampoules were used. The precipitates were then filtered off, washed with water, and air-dried.

(3) Urea as the Precipitant: A mixture of 10 ml of a 0.1M rare earth solution and 10 ml of a 0.2M urea solution was autoclaved for one week at various temperatures from 50 to 150°C. As has been mentioned by Head and Holley,[2)] the autoclaving of rare earth carbonates appears to produce good crystallization. The precipitates were filtered off, washed with water repeatedly, air-dried, and subjected to analysis.

In the case of yttrium, the formation reaction is expressed as:

$$3(NH_2)_2CO + 2YCl_3 + (6+n)H_2O \longrightarrow Y_2(CO_3)_3\cdot nH_2O + 6NH_4Cl.$$

(4) Factors Which Influence Crystallization: The following experiments were carried out for the purpose of studying the various factors which influence the crystallization of rare earth carbonates, such as the temperature, the concentration of metal ions and the aging period of the precipitates.

Experiment: 2-, 5-, 10-, and 20-ml portions of 0.1M rare earth chloride solutions were placed in beakers, and 1-, 2.5-, 5-, and 10-ml portions of a 2.0M trichloroacetic acid solution were added respectively. Then the pH values of mixed solutions were adjusted to 5—6 with ammonia and the volumes were adjusted to 100 ml. The beakers were placed in a thermostatically-controlled bath maintained in the temperature range of 50 to 70°C. After several days, the precipitates were filtered off, washed with water, air-dried, and subjected to microscopy and X-ray powder diffractometry. The results for the experiment using yttrium are summarized in Table 1.[12)] It can be seen that longer aging periods and lower concentrations of the metal ion produce larger crystals. It was also revealed that varying the concentration of metal ion does not change the structure of rare earth carbonates within the concentration range of the present work. In all cases, the tengerite structure was obtained.

Chemical Analyses and X-Ray Powder Diffractometry. Chemical analyses were carried out on the rare earth

Table 2. Chemical analysis of synthesized rare earth carbonates (quantities are molar ratios)

	M_2O_3 :	CO_2 :	H_2O
Monoxocarbonate type (La compound)	1.00	2.14	1.41
Lanthanite type (La compound)	1.00	2.97	8.04
Tengerite type (Y compound)	1.00	3.01	2.35
Yb compound[a)]	1.00	2.05	3.87
Sc compound[b)]	1.00	0.00	3.00

a) X-Ray amorphous. b) Hydroxide.

[12)] La, Ce, -and Nd gave good crystalline precipitates under the conditions of Table 1.

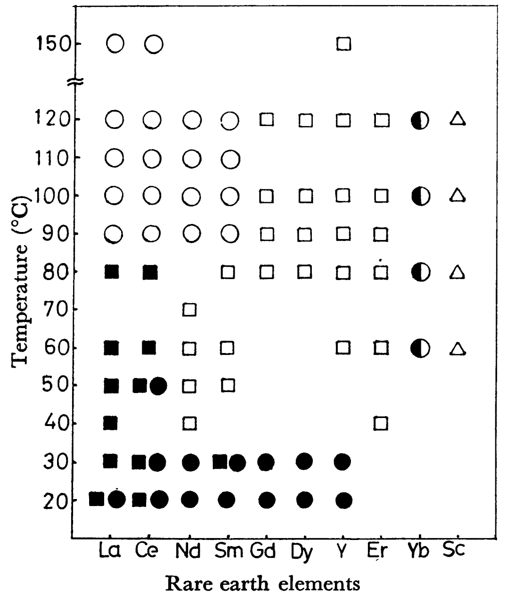

Fig. 1. Diagram showing the phases, formation temperature, and rare earth elements.
○: monoxocarbonate type, ●: double carbonate, ◐: amorphous, □: tengerite type, ■: lanthanite type, △: hydroxide

carbonates prepared by the prescribed methods. The carbonates were classified into five types according to their compositions. It was found that the compositions were affected by the temperature, but were not dependent on the method of preparation. The results of the chemical analyses of typical samples are shown in Table 2. The types of rare earth carbonates obtained at various temperatures are illustrated in Fig. 1. Rare earth elements on a horizontal axis are shown according to their ionic radii. The X-ray powder diffractions of the synthesized samples were recorded on a Rigaku Denki Geigerflex Diffractometer, applying Ni-filtered Cu*K*α radiation and employing metallic silicon as the internal standard.

By chemical and X-ray analyses, the natures of the following carbonates were determined.

(A) Monoxocarbonate Type (shown by open circles in Fig. 1). Experimental formula: $Ln_2O_3\cdot2CO_2\cdot nH_2O(n=1-2)$——Table 2. Carbonates of lanthanum, cerium(III), neodymium, and samarium prepared at 90°C and higher are of this type. The X-ray powder data for the lanthanum compound of this type are given in the third column of Table 3. So far as we can discover in the literature surveyed, this is the first report on the X-ray powder data for rare earth monoxocarbonate. Though a possibility still exists that the compound is a hydroxocarbonate, this type of carbonate was classified as monoxocarbonate $Ln_2O(CO_3)_2\cdot nH_2O$ $(n=1-2)$ through thermal analysis and a study of its infrared spectrum.

B) Lanthanite Type (shown by solid squares in Fig. 1). Lanthanum and cerium(III) ions, the largest two of the lanthanoid ions, form this type of carbonate in the temperature range from 20 to 80°C. This type of carbonate has the composition of $Ln_2(CO_3)_3\cdot8H_2O$ (Table 2) and gives an X-ray-powder-diffraction pattern (Table 3) identical with that of lanthanite,[8] a very rare, hydrated, rare earth carbonate mineral.

(C) Tengerite Type (shown by open squares in Fig. 1). Neodymium (40—70°C), samarium (30—80°C), gadolinium, dysprosium, yttrium, and erbium form this type of carbonate, with the formula of $Ln_2(CO_3)_3\cdot nH_2O(n=2-3)$[10] (Table 2). Because of the experimental difficulty, the central area of Fig. 1 remains incomplete at present. It may be said, however, that the formation of the tengerite-type carbonate is characteristic of the heavier lanthanoids, excluding ytterbium. The X-ray diffraction data listed in Table

TABLE 3. X-RAY POWDER DATA FOR SYNTHESIZED RARE EARTH CARBONATES

Lanthanite type (La)			Tengerite type (Y)			Monoxocarbonate type (La)		Double carbonate (Gd)	
d (Å)	*I*	*hkl*	*d* (Å)	*I*	Probable *hkl*	*d* (Å)	*I*	*d* (Å)	*I*
8.61	100	002	7.589	90	001	5.65	60	13.23	100
4.79	15	020	5.673	70	020	5.00	20	6.56	45
4.50	10	200	4.604	100	200	4.37	60	4.35	35
4.27	50	113 004	3.890	70	201	4.32	50	3.254	1
4.18	15	022	3.782	30	030	3.74	100	2.602	12
3.98	10	202	3.573	50	220	3.42	90	2.167	7
3.89	10	014	3.046	5	300	2.986	70	1.856	1
3.85	10	104	2.967	40	310	2.812	15		
3.58	5	114	2.919	8	230	2.672	50		
3.29	15	213 220	2.696	15	320	2.457	20		
3.19	10	221 024	2.598	10	222	2.368	60		
3.07	20	204 222	2.537	30	321	2.146	20		
3.02	10	115				2.090	20		

a_0=9.00Å (calculated from 200)
b_0=9.58Å (calculated from 020)
c_0=17.22Å (calculated from 002)

a_0=9.21Å
b_0=11.35Å
c_0=7.59Å

3 coincide well with those of natural tengerite.[10] In the table, the indices and cell edges as well as the d values and intensities for the lanthanite-type lanthanum carbonate and those for the tengerite-type yttrium carbonate are listed.

(D) Double Carbonate (shown by the solid circle in Fig. 1). The double carbonate was obtained when sodium carbonate was used as the precipitant at lower temperatures. Lanthanum (20°C), cerium(III) (20—50°C), neodymium, samarium, gadolinium, dysprosium, and yttrium (20—30°C) form this double carbonate. In the cases of lanthanum and cerium(III), either the lanthanite type or the double carbonate forms, depending on minor variations in the preparation process. The composition of this double carbonate may be expressed as a hydrated double carbonate of rare earth and sodium. Further study is necessary, however, to determine the compositions of the compounds. The X-ray powder data for the double carbonate of gadolinium are listed in the last column of Table 3.

Table 4. X-Ray powder data for synthesized monoxocarbonates

La		Ce		Nd		Sm	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
5.65	60	5.63	65	5.54	35	5.51	30
5.00	20						
4.37	60	4.34	100	4.29	80	4.26	75
4.32	50	4.30	75	4.25	100	4.24	70
3.74	100	3.72	95	3.68	80	3.66	70
3.42	90	3.39	80	3.33	40	3.30	100
2.986	70	2.974	80	2.953	30	2.937	20
2.955	25			2.932	40	2.894	60
2.812	15						
2.676	50	2.670	70	2.641	70	2.629	50
2.457	20	2.441	20	2.410	15	2.390	20
2.377	60			2.329	60	2.318	50
2.368	40			2.321	40	2.295	60
2.146	20	2.144	30	2.124	40	2.120	20
2.090	20	2.078	40	2.056	20	2.045	30
2.066	35	2.059	30	2.039	40	2.031	30
2.029	20	2.016	30	1.989	15	1.972	20
1.974	25	1.958	30	1.932	20	1.915	20
1.886	35						
1.873	60	1.869	40	1.835	35	1.822	35
1.855	15	1.833	15	1.806	15	1.789	20
1.745	10	1.738	20	1.717	15	1.703	15
1.706	15	1.690	20	1.664	10	1.648	10

With ytterbium, a crystalline carbonate was not formed by these procedures within the given temperature range; only an amorphous basic carbonate was obtained. Scandium, however, formed a crystalline hydroxide upon the hydrolysis of trichloroacetate or urea. The X-ray data of the respective monoxocarbonates (La, Ce, Nd, Sm) are listed in Table 4. In the table, it can clearly be seen that d values of carbonates of this type increase linearly with an increase in the ionic radii of rare earth elements.

Thermal Analysis of Monoxocarbonates. The thermal decomposition study of the monoxocarbonates was performed with a Choryo Keiki Thermobalance modified to record the thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential thermogravimetric analysis (DTG) curves simultaneously. The measurements were made in air at a heating rate of 5.4°C/min, using approximately 100 mg samples. The results of the TGA, DTA, and DTG analyses of lanthanum and neodymium monoxocarbonates are shown in Figs. 2 and 3. The decomposition processes of cerium and samarium monoxocarbonate were similar to that of neodymium. On the TGA curve for the lanthanum compound, there is initially a loss of water, leading to the plateau, which corresponds to the step of the anhydrous monoxocarbonate. The stability of this compound in one of the bases for assuming the formula of the initial compound to be hydrated monoxocarbonate. This plateau is prominent for the lanthanum compound. On the TGA curve for the neodymium compound, the temperature rise leads to dehydration and decarbonatation at the same time. The difference observed in the TGA curves was also observed in the DTA curves. The DTA curve in Fig. 2 shows that the exothermic effects in the 250—400°C range corresponds to the formation of the anhydrous monoxocarbonate. The continuous raising of the temperature leads to the formation of some intermediate phases, shown in the following processes, (1) and (2):

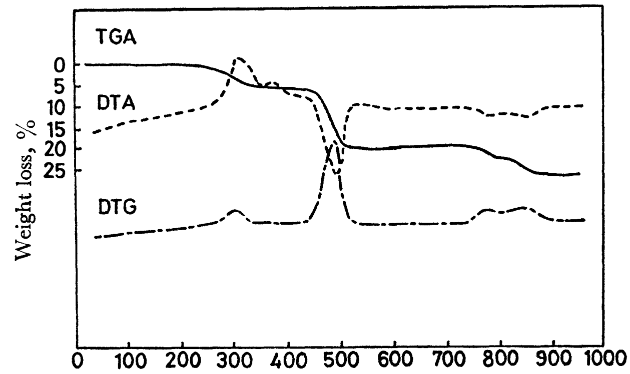

Fig. 2. TGA, DTA, and DTG curves of $La_2O(CO_3)_2 \cdot 1.4H_2O$

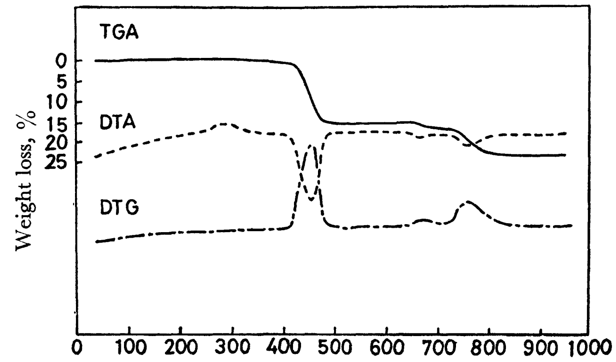

Fig. 3. TGA, DTA, and DTG curves of $Nd_2O(CO_3)_2 \cdot 1.5H_2O$

$$La_2O(CO_3)_2 \cdot 1.4H_2O \xrightarrow{ca.\ 300^\circ C} La_2O(CO_3)_2 \xrightarrow{ca.\ 530^\circ C} La_2O_3 \cdot 0.8CO_2 \xrightarrow{ca.\ 800^\circ C} La_2O_3 \cdot 0.4CO_2 \xrightarrow{ca.\ 900^\circ C} La_2O_3 \quad (1)$$

$$Nd_2O(CO_3)_2\cdot 1.5H_2O \xrightarrow{ca.\ 500^\circ C} Nd_2O_3\cdot 0.9CO_2 \xrightarrow{ca.\ 700^\circ C} Nd_2O_3\cdot 0.7CO_2 \xrightarrow{ca.\ 800^\circ C} Nd_2O_3 \qquad (2)$$

Infrared Spectroscopy. Herzberg[13] gave the frequencies for the four modes of the free carbonate ion: ν_1, 1063 cm^{-1}; ν_2, 879 cm^{-1}; ν_3, 1415 cm^{-1}; and ν_4, 680 cm^{-1}, when the ν_3 and ν_4 modes degenerate. The ν_1 symmetrical streching mode is infrared-inactive for the free ion, but it may become active in the crystalline stage. Its presence and the splitting of degenerate modes indicate the presence of a dipole within the carbonate group. The D_{3h} symmetry of the free carbonate ion is thus lowered either to C_{2v} or to C_s symmetry. The splitting of the non-degenerate bands is generally an indication of nonequivalent carbonate groups in a given structure.[14]

The infrared spectra of the rare earth carbonates obtained in this work are shown in Fig. 4. The multiple splittings of all modes for the crystalline rare earth carbonates (lanthanite-type, tengerite-type, monoxocarbonate-type, and double carbonate) must be caused by several types of carbonate ions situated at crystallographically non-equivalent site.

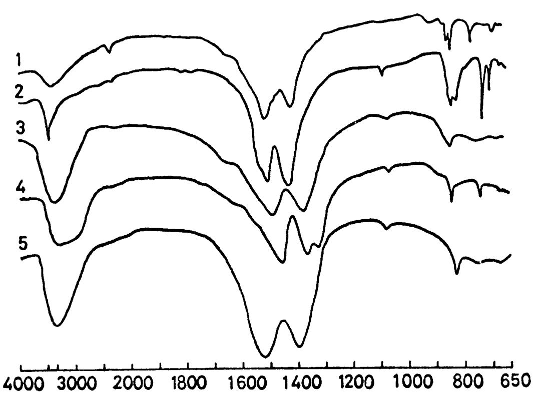

Fig. 4. Infrared absorption spectra of rare earth carbonates (in KBr disk).
1: tengerite type (Y), 2: monoxocarbonate type (Sm), 3: double carbonate (Sm), 4: lanthanite type (La), 5: amorphous carbonate (Yb).

The minerals —shortite, huntite, and parisite— which contain two nonequivalent CO_3^{2-} groups show similar spectra, with the splittings of all modes.[15]

Conclusion

It was found in this study that crystalline rare earth carbonates may be classified into several phases according to the ionic radii of rare earth elements and the preparation temperatures, and that the concentrations of the rare earth ion and the aging periods affect mainly the crystallization.

The preparation and the structure of lanthanite-type rare earth carbonates were previously studied by Shinn and Eick,[8] and the preparation and cell parameters of tengerite-type rare earth carbonates were described by Wakita and Nagashima.[10] The present investigation was clarified the formation temperature range for lanthanite-type and tengerite-type carbonates and the elements which form those carbonates.

The formation of rare earth monoxocarbonates through the decomposition of hydrated rare earth carbonates or oxalates has been reported by many investigators. The formation of crystalline substances in those cases is doubtful, however, because of the procedures used, and none of the investigators have referred to the formation of monoxocarbonate from an aqueous solution.

A rare earth double carbonate is indicated by the results of X-ray powder analyses, chemical analyses, infrared spectrometry, and thermal analyses. This appears to be the first time that such a rare-earth double-carbonate compound has been reported; further investigation of this class of rare earth carbonates is desirable.

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[13] G. Herzberg, "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co. Inc., New York, N. Y. (1945), p. 179.

[14] R. P. Turcotte, J. O. Sawyer, and L. Eyring, *Inorg. Chem.*, **8**, 238 (1969).

[15] H. H. Adler and P. F. Kerr, *Am. Mineral.*, **48**, 839 (1963).