

Synthesis of Cerite

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Some compounds isostructural with cerite have been synthesized hydrothermally at temperatures from 500 to 720 °C. The compositional range for cerite, and its phase relation to the silicate apatites are established in terms of ionic radii of rare-earth and divalent ions. The proposed formula for cerite on the basis of isomorphism with whitlockite, $\text{Ca}_3(\text{PO}_4)_2$, is discussed. A solid-solution series between $\text{Ca}_9\text{P}_6\text{O}_{24}$ – $\text{Ca}_7\text{Mg}_2\text{P}_6\text{O}_{24}$ (whitlockite–Mg-whitlockite) has been established.

Key Words: Ca, Mg phosphate, hydrothermal synthesis, inorganic synthesis, mineral chemistry, rare-earth silicate, x-ray powder analysis.

1. Introduction

During a study of silicate apatites, a very wide compositional range for the cerite phase was found under hydrothermal conditions [1].¹ This range adjoins that for the rare-earth silicate apatites. Despite its early description, the rare-mineral cerite [2–7], from which the element cerium was discovered, has not yet been fully characterized, because of the complexity of its composition. In this paper, therefore, I report the conditions for its formation and its compositional range. Recently Keppler [8] reported an isostructural relation between cerite and whitlockite. I suspect that the maximum number of Mg ions in Mg-whitlockite may equal the number of divalent ions in cerite, consequently, the whitlockite–Mg-whitlockite solid-solution series was also investigated and the results are given here.

2. Results and Discussion

Cerite was synthesized from hydrosilicates which were precipitated in the ratio $\text{M}^{2+}:\text{M}^{3+}$ (i.e., rare earth): M^{4+} (i.e., Si) = 2:7:6. The precipitates were centrifuged, washed, dried, and in some experiments admixed with carbonates. The synthesis was completed by hydrothermal heating at 2 kbar and 550 to 680 °C. Whitlockite was synthesized from stoichiometric mixtures, prepared by the slow evaporation of alkaline solution containing calcium, magnesium nitrate and ammonium dihydrogen phosphate and heated in air at 1050 to 1120 °C. Experimental results are given in table 1 with the unit-cell dimensions calculated accord-

ing to the space group R3c [6]. X-ray powder diffraction data of Mg-La, Mg-Ho, and Co-La cerites and Mg-whitlockite, $\text{Mg}_2\text{Ca}_7\text{P}_6\text{O}_{24}$, were indexed and are given in tables 2 and 3.

TABLE 1. Results of the synthesis of cerite, whitlockite and Mg-whitlockite and the unit cell dimensions

Formula (tentative)	Temp °C	Pressure	Hour	a	c
$\text{Mg}_2\text{La}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	20	10.77	38.40
$\text{Mg}_2\text{Nd}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	700	2	20	10.64	37.63
$\text{Mg}_2\text{Sm}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	20	10.62	36.8
$\text{Mg}_2\text{Gd}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	20	10.49	36.64
$\text{Mg}_2\text{Dy}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	700	2	20	10.47	36.32
$\text{Mg}_2\text{Ho}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	680	2	48	10.44	35.92
$\text{Ni}_2\text{Ce}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	650	2	20	cerite ^a	
$\text{Ni}_2\text{Sm}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	20	10.58	36.74
$\text{Ni}_2\text{Ho}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	680	2	20	10.47	36.34
$\text{Co}_2\text{La}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	48	10.78	38.40
$\text{Co}_2\text{Ce}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	680	2	20	cerite ^a	
$\text{Co}_2\text{Sm}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	20	10.6	36.8
$\text{Co}_2\text{Dy}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	590	2	20	cerite & apatite	
$\text{Fe}_2\text{La}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	700	2	20	10.82	38.45
$\text{Fe}_2\text{Nd}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	20	cerite ^a	
$\text{Fe}_2\text{Sm}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	20	cerite ^a	
$\text{Fe}_2\text{Gd}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	680	2	48	cerite & other phase	
$\text{Mn}_2\text{La}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	680	2	20	10.88	38.5
$\text{Mn}_2\text{Ce}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	650	2	10	cerite ^a	
$\text{Mn}_2\text{Nd}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	20	cerite & apatite	
$\text{Mn}_2\text{Sm}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	20	cerite & apatite	
$\text{Mn}_2\text{Gd}_7\text{Si}_6$ ^b	550	2	20	apatite	
$\text{Mn}_2\text{Dy}_7\text{Si}_6$ ^b	550	2	20	apatite	
$\text{Mn}_2\text{Ho}_7\text{Si}_6$ ^b	550	2	20	apatite	
$\text{Mn}_{1.5}\text{Ca}_{3.5}\text{La}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$	550	2	20	cerite & apatite	
$\text{MnCaLa}_7\text{Si}_6$ ^b	550	2	20	apatite	
$\text{MnCaSm}_7\text{Si}_6$ ^b	550	2	20	apatite	
$\text{Mg}_2\text{Ca}_7\text{P}_6\text{O}_{24}$	1120	in air	20	10.31	37.25
$\text{Mg}_2\text{Ca}_8\text{P}_6\text{O}_{24}$	1120	in air	20	10.36	37.24
$\text{Ca}_9\text{P}_6\text{O}_{24}$	1120	in air	20	10.45	37.32
$\text{Co}_2\text{Ca}_7\text{P}_6\text{O}_{24}$	1050	in air	20	10.32	37.2
$\text{CoCa}_8\text{P}_6\text{O}_{24}$	1050	in air	20	10.34	37.2

^a Cell dimensions not measured.

^b Cation ratio in starting gel.

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE 2. X-ray powder diffraction data for synthetic cerites and magnesium whitlockite (Cu K α , Ni filter)

Space group R3c, Hexagonal

Formula	Mg ₂ La ₇ Si ₆ O ₂₃ (OH) ₃		Mg ₂ Ho ₇ Si ₆ O ₂₃ (OH) ₃		Co ₂ La ₇ Si ₆ O ₂₃ (OH) ₃	
	550 °C 2 kbar a = 10.77Å c = 38.40Å		550 °C 2 kbar a = 10.44Å c = 35.92Å		550 °C 2 kbar a = 10.78Å c = 38.40Å	
Conditions						
<i>hkl</i>	<i>d</i> obs.	<i>I/I</i> ₀	<i>d</i> obs.	<i>I/I</i> ₀	<i>d</i> obs.	<i>I/I</i> ₀
012	8.378	3	8.110	10	8.445	3
104	6.661	3	6.393	5		
006	6.421	5				
110	5.376	20	5.217	20	5.440	15
202	4.532	25	4.379	30	4.535	30
018	4.273	30	4.026	60	4.275	20
116	4.137	5				
024						
10,10	3.545	25	3.351	90	3.561	15
122	3.466	60			3.479	40
208	3.348	10	3.193	60	3.353	10
214	3.304	30			3.316	40
00,12	3.222	5	3.129	5		
300	3.112	25	3.019	50	3.116	40
02,10	2.964	100	2.813	100	2.968	100
128	2.859	20	2.728	30	2.848	20
300	2.801	25	2.693	50	2.801	20
220	2.691	50	2.608	60	2.698	70
21,10	2.600	20	2.478	30	2.606	15
312	2.547	3				
134	2.497	5	2.417	5		
20,14	2.367	3	2.224	5	2.366	5
042	2.327	5				
318	2.268	3	2.18	25	2.327	5
30,12	2.231	20	2.126	30	2.223	20
13,10	2.138	10	2.058	20	2.144	8
02,16		5			2.140	10
048	2.095	10	2.021	15	2.099	15
324		10				
410	2.063	10				
232	2.018	3				
40,10						
21,16	1.989	15	1.914	10	1.995	10
238	1.953	40	1.888	15	1.958	40
416	1.943	15	1.870	15	1.944	10
01,20,3114	1.884	10	1.797	20	1.871	3
	1.865	10				
502	1.857	10			1.860	10
054	1.831	10	1.771	10	1.836	10
	1.812	3				
330	1.794	5	1.737	10	1.799	5
20,20	1.776	20	1.668	20	1.779	20
30,18,13,16	1.761	15	1.657			
508	1.737	3				

Cerite was not found in previous studies of rare-earth oxides-silica systems. Divalent ions play an essential role in the formation of cerite. The compositional range of cerites and a part of that of apatites in terms of ionic radii of the divalent ions and the rare-earth ions has been determined and is given in figure 1. It appears likely that the divalent and rare-earth ion sites are ordered, and that no appreciable partial replacement of rare-earth sites by divalent ions takes place. Unit-cell dimensions of the cerite change only when the size of either the divalent or the rare-earth ion is changed, but not when the ratio of the amounts of two given cations in the source material is changed. A calcium end member of cerite phase does not exist under the present conditions, although the chemical analyses of natural cerite usually show several percent of calcium. The Mn analogs are converted to Mn-apatite at temperatures above 650 °C under 2 kbar H₂O pressure. The tentative boundary for cerite apatite conversion at 550 °C under 2 kbar is drawn in figure 1. The reverse

reaction has not been observed, possibly because the reaction is too slow; but it may be that the equilibrium phase field for apatite is larger than indicated.

All the analogs of cerite were converted into apatite or apatite plus other phases after dehydration in air at temperatures above 900 °C. It was quite unexpected that the smaller rare-earth ions such as Dy or Ho also form cerite, because cerites found in nature contain exclusively large size rare-earth ions such as: La, Ce, Pr, Nd, and Sm.

Magnesium replacement in whitlockite was limited at the composition, Ca₇Mg₂P₆O₂₄. Starting material containing more Mg than corresponds to this end member gave an inferior whitlockite x-ray powder pattern without change in the unit-cell dimensions. With further increase of Mg in the charge, a second phase Ca₃Mg₃(PO₄)₄ appears. The whitlockite solid-solution series is demonstrated in figure 2. Unit-cell dimensions vary as a function of Mg content.

Only a partial solid-solution series exists between cerite and whitlockite despite their close isomorphism

TABLE 3. X-ray powder diffraction data for synthetic Mg-whitlockite $\text{Ca}_7\text{Mg}_2\text{P}_6\text{O}_{24}$. (Cu $K\alpha$, Ni filter; 1150 °C in air)

Space group R3c, Hexagonal.

$a = 10.31 \text{ \AA}$		$c = 37.23 \text{ \AA}$	
hkl	$d \text{ obs. \AA}$	hkl	$d \text{ calc. \AA}$
012	8.05	20	8.04
104	6.43	33	6.44
110	5.15	50	5.15
202	4.333	20	4.337
018	4.130	20	4.126
024	4.019	20	4.023
10,10	3.437	45	3.437
211	3.358	15	3.357
122	3.316	20	3.304
208	3.227	20	3.219
214	3.160	75	3.159
300	2.972	30	2.973
02,10	2.857	100	2.859
128	2.730	30	2.731
306	2.685	20	2.683
11,12	2.660	15	2.659
220	2.577	70	2.575
01,14	2.525	15	2.551
223	2.525	15	2.521
21,10	2.503	25	2.500
226	2.384	10	2.378
12,11	2.347	15	2.349
315	2.347	15	2.349
10,16	2.250	10	2.252
11,15	2.239	10	2.240
404	2.169	20	2.169
30,12	2.148	20	2.147
21,14	2.093	10	2.089
321	2.039	10	2.043
232	2.039	10	2.034
324	2.013	15	1.999
048	2.013	15	2.012
22,12	2.003	10	1.982
11,18	1.916	30	1.920
40,10	1.916	30	1.913
238	1.879	20	1.873
416	1.839	20	1.857
01,20: 31,14	1.824	20	1.823
32,10	1.795	10	1.794
502	1.762	10	1.776
054	1.753	10	1.752
20,20	1.719	30	1.719
30,18	1.700	15	1.724

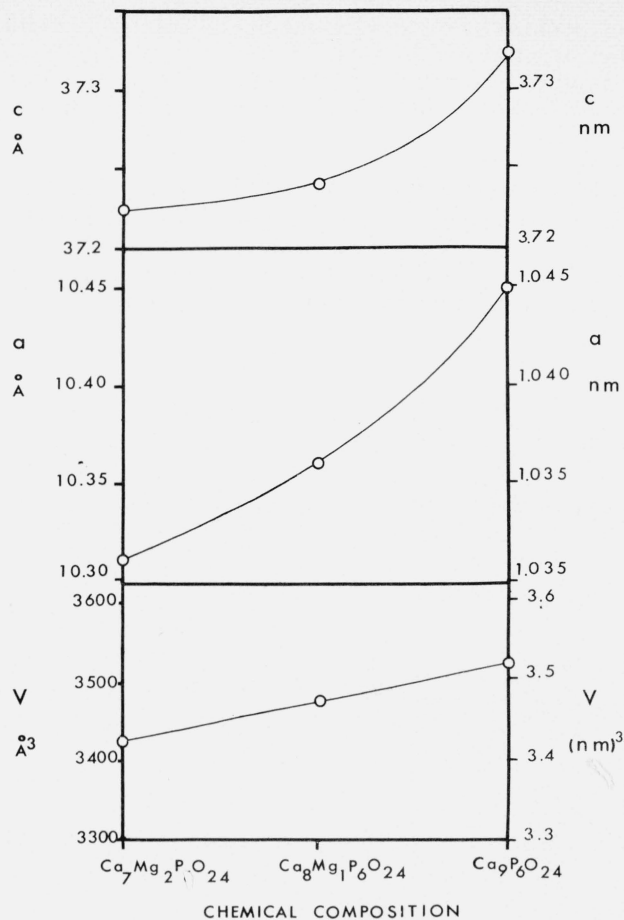


FIGURE 2. Whitlockite and Mg-whitlockite solid-solution series. Open circles = cerite, closed circles = apatite, crosses = mixed unidentified phases.

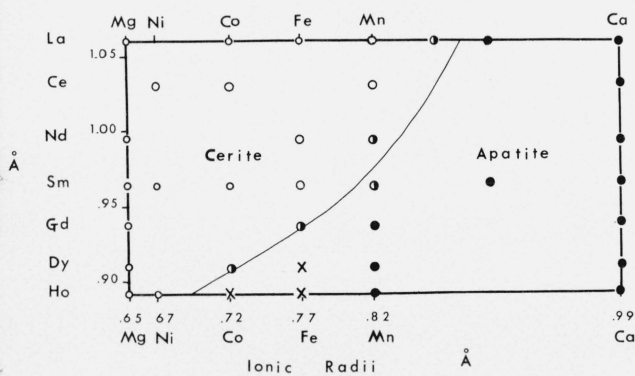


FIGURE 1. Compositional stability range of cerites.

Abscissa is the ionic radii for divalent cations given by Wells (1962) [9], ordinate is rare-earth radii given by Templeton and Dauben (1954) [10].

and close structural relationship. Large fields of stability for phospho-silico-apatites and monazites are present between the two compounds under the conditions used in the present experiments. Limited solid solution may extend from one toward the other. The

probable limits of solid solution may be around $\text{CaMg}_2\text{Ln}_6\text{Si}_5\text{PO}_{23}(\text{OH})_3$ for cerite, and $\text{Ca}_8\text{LnP}_5\text{SiO}_{24}$ for whitlockite, but there is evidence to indicate that the solid-solution limit is a function of the size of rare-earth ion.

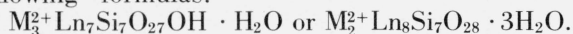
Infrared absorption spectroscopic analysis by R. Wilkins at Harvard University, showed abundant hydroxyl ion (up to several percent) in the synthetic Mg-La cerite possibly in two crystallographic sites (3690 cm^{-1} strong infrared line and 3660 cm^{-1} medium line). Synthetic Ca and Ca-Mg whitlockite, however were shown to be anhydrous as originally expected.

Europium and terbium activation of Mg-Gd analogs of cerite show typical red and yellow visible emission under a mercury fluorescent lamp, but their luminescent intensities are much lower than those displayed by the silicate apatites [1].

From the results here presented, the formula $\text{Mg}_2^+\text{Ln}_7\text{Si}_6\text{O}_{23}(\text{OH})_3$ seems in best agreement with the chemical analysis, infrared analysis, and synthesis of cerites. This formula is essentially the same as that given by Gay [6] and is isomorphous with Mg whitlockite except for two additional hydroxyl ions. However, calcium and magnesium ions in cerite do

not seem to be distributed randomly within rare-earth sites as suggested by Gay.

In the absence to date of a complete x-ray structure determination on cerite, the experimental results could be given an alternative interpretation by the following formulas:



They correspond to that suggested by Keppler [8] for whitlockite. The latter formula was also that given by Glass et al. [7], from their extensive study on natural cerite from Mountain Pass, California.

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3. References

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