THE AMERICAN MINERALOGIST, VOL. 55, JULY-AUGUST, 1970

CRYSTAL CHEMISTRY AND COLOR IN APATITES CONTAINING COBALT, NICKEL, AND RARE-EARTH IONS[1]

D. A. GRISAFE[2] AND F. A. HUMMEL
Materials Science Department, the College of Earth and Mineral Sciences, The Pennsylvania State University, University Park, Pennsylvania 16802.

ABSTRACT

Simple substitutions of divalent cobalt and nickel and charge coupled substitutions of the alkali:RE^{3+}, $RE^{3+}:Si^{4+}$ and $RE^{3+}:O^{2-}$ (RE = La, Pr and Nd) types and defect varieties in the apatite structure have been explored. X-ray diffraction showed that the solubility limits of cobalt in the calcium fluor- and chlorapatite were 15 and 25 mole percent respectively but were less than 10 mole percent in the strontium analogues. The charge coupled substitutions produced apatites of a variety of stoichiometries. Lattice parameters were obtained for the defect silicate apatites $\square_2Pr_8(SiO_4)_6\square_2$, $\square Sr_3Pr_6(SiO_4)_6\square_2$, and $\square Pb_3Pr_6(SiO_4)_6\square_2$.

Cobalt, nickel, praseodymium and neodymium substitutions produce violet, pale yellow-green, light green and blue to blue-violet colored apatites respectively. Reflectance spectra for these apatites show that the positions of the absorption bands are not strongly affected by composition changes in the apatite. The cobalt and nickel spectra showed similarities to the spectra given by these ions in octahedral coordination.

INTRODUCTION

Virtually no information has been reported about the colors resulting from or modified by various ions which can be substituted into the apatite structure. In the present work, simple and charge coupled substitutions including cobalt, nickel, praseodymium and neodymium in the apatite structure and their resulting colors have been investigated.

LITERATURE

The complete substitution of strontium, barium, lead and cadmium in chlorapatite is well known. Niaki (1961) studied the phase relationships between the alkaline earth fluor-, chlor-, and bromapatites and determined their lattice parameters. For a given halide ion, the calcium-strontium and strontium-barium systems exhibited continuous solid solutions while the calcium-barium system contained a miscibility gap. Calcium-lead hydroxyapatite solid solutions were reported by Muller (1947). Lattice parameters of lead apatites were determined by Wondratschek (1963). Cadmium chlorapatite was reported by Ropp (1963) and Klement and Haselbeck (1965).

Limited substitutions of small divalent ions in calcium apatite have also been reported and are summarized in Table 1. It should be noted from Table 1 that the chlorapatite accepts more of a given transition metal ion than the fluorapatite. By contrast, Foertsch and

---

[1] Contribution No. 68-45 from the College of Earth and Mineral Sciences, The Pennsylvania State University, University Park, Pennsylvania 16802.

[2] Present address: Sylvania Electric Products, Inc., Chemical and Metallurgical Division, Towanda, Pennsylvania 18848.

TABLE 1. SOLUBILITY LIMITS OF DIVALENT METAL IONS IN APATITES OF THE $CA_{10-x}R_x(PO_4)_6Z_2$ TYPE 1

R	Z	x	Reference
Mg	F	1.0	Kreidler (1967)
Mn	Cl	10.0	Klement and Haselbeck (1963)
Co	Cl	3.0	Klement and Haselbeck (1963)
Ni	F	0.8	Kreidler (1967)
		1.0	Brasseur and Dallemagne (1949)
Ni	Cl	3.0	Klement and Haselbeck (1963)
Cu	Cl	4.0	Klement and Haselbeck (1963)
Zn	F	1.0	Brasseur and Dallemagne (1949)
Sn	F	5.0	Klement and Haselbeck (1963)
Sn	Cl	8.0	Klement and Haselbeck (1963)

Wondratschek (1965) reported that copper and zinc did not appear to replace lead in the chlorphosphate apatite.

The incorporation of rare earth ions into the apatite structure requires a charge coupled substitution Three logical choices are: (1) $R^+:RE^{3+}$ (such as $Na^+:La^{3+}$); (2) $RE^{3+}:X^{4+}$ (such as $La^{3+}:Si^{4+}$); and (3) $RE^{3+}:O^{2-}$. Lindberg and Ingram (1964) reported a natural apatite of the approximate stoichiometry $Ca_7RE_3(SiO_4)_3(PO_4)_3F_2$. Tromel and Eitel (1957) synthesized $Na_2Ce_8(SiO_4)_6F_2$ and $Ca_4Ce_6(SiO_4)_6F_2$ types while Sidorenko (1964) found a continuous solid solution existed between $Ca_{10}(PO_4)_6F_2$ and $Ca_4La_6(SiO_4)_6F_2$. The hydroxyl analogue of the latter apatite was reported by Cockbain and Gibbs (1967). Defect oxyapatites $La_{9.33}(SiO_4)_6O_2$ and $Sm_{9.33}(SiO_4)_6O_2$ were reported by Kuzmin and Belov (1965) while the closely related orthosilicates (halide sites vacant) of europium, samarium and neodymium, $RE_8(SiO_4)_6$, were synthesized by McCarthy *et al.* (1967). The neodymium compound was also reported by Miller and Rase (1964). Finally, $Sr_3La_6(SiO_4)_6$, $Sr_2La_8(SiO_4)_6O_2$ and similar apatites were investigated by Schwarz (1967) and Ito (1968). The lattice parameters for some of these apatites are listed in Table 6 in the results.

EXPERIMENTAL PROCEDURE

For apatites containing halides, orthophosphate compositions were used as intermediates in the reaction. Stoichiometric amounts of reagent grade metal carbonates or oxides and diammonium hydrogen phosphate and/or silicic acid were mortared in acetone. The dried sample was placed in a platinum or silica crucible, heated to 600°C to 650°C, remixed and reheated to temperatures which varied from 650°C to 1100°C. A stoichiometric amount of halide was added, and the mixture was heated from 300°C to 500°C up to the desired temperature. For reasons mentioned later, it was necessary to prepare the apatites containing cobalt in sealed platinum capsules. For apatites containing no halide, all of the apatite components were mixed, prefired, remixed and heated at temperatures up to 1350°C.

Reaction products were identified by scanning the powdered sample on an X-ray diffractometer. For accurate X-ray data, −200 mesh powder was back-packed into a sample holder and scanned at one-quarter degree 2θ per minute, using a silicon disc as an external standard. When necessary, the analytical technique described by Cullity (1959) was used to index the X-ray pattern. Lattice parameters and standard deviations for selected silicate apatites were obtained from a least squares computer program.

Diffuse reflectance spectra were obtained from −200 mesh powder using a Beckman DK-2A Ratio Recording Spectrophotometer with a reflectance attachment and a tungsten lamp source. The instrument was calibrated with magnesium oxide. Absorption maxima wavelengths were considered accurate to ±5 nm.

RESULTS AND DISCUSSION

Cobalt. Cobalt possesses a divalent radius that is considerably less than one angstrom, too small to completely fill the divalent ion positions in the apatite structure. Partial replacements were attempted since this ion is well-known for its ability to produce color. Calcium and strontium fluor- and chlorapatites were prepared in dried air and served as X-ray standards.

No conclusions can be drawn regarding the solid solution of cobalt from apatite samples prepared in air. X-ray diffraction showed that samples fired between 850°C and 1250°C were mixtures of apatite, orthophosphate and cobalt oxides. Optical examinations detected an opaque phase in samples containing as little as two mole percent cobalt.

The stoichiometries of calcium-cobalt and strontium-cobalt fluor- and chlorphosphate apatites prepared in sealed platinum capsules are listed in Table 2. The detection of a second phase by X-ray diffraction showed that for calcium or strontium the cholorapatite accepted more cobalt than the fluorapatite.

The 410 and 004 lines in each sample were scanned on an X-ray diffractometer at 0.25 degree 2θ per minute, and the resulting 2θ values were used to calculate a and c lattice parameters to an accuracy of ±0.003 Å, respectively. The lattice parameters as a function of the cobalt concentration are tabulated in Table 3 and plotted in Figure 1. The contraction of the unit cell with increasing concentration of cobalt is very large along the c axis in both the fluor- and chlorapatite series. The fluorapatite structure undergoes a greater contraction relative to the chlorapatite structure along both axes. No change was observed in the a parameter of the chlorapatite series. Figure 1 shows that the solubility

TABLE 2. APATITE COMPOSITIONS USED FOR $Co2^+$ SOLUBILITY DETERMINATIONS AND FOR Co^{2+} AND Ni^{2+} SPECTRA

Composition	Heat Treatment and Container
$R_{10-x}Co_x(PO_4)_6F_2$, R = Ca or Sr $x = 0.45$, 0.9, 1.8 and 2.7 $R_{10-x}Co_x(PO_4)_6Cl_2$, R = Ca or Sr $x = 0.45$, 0.9, 1.8, 2.7, 3.6 and 4.5	975°C/8 hrs., Sealed Platinum Capsules
$R_{10-x}Ni_x(PO_4)_6F_2$, R = Ca, Sr, Ba and Pb $x = 0.2$, 0.5 and 1.0	800°C/4 hrs., Covered Crucibles

TABLE 3. LATTICE PARAMETERS IN CALCIUM-COBALT APATITES AS A FUNCTION OF THE COBALT CONCENTRATION

$Ca_{10-x}Co_x(PO_4)_6F_2$			$Ca_{10-x}Co_x(PO_4)_6Cl_2$		
x	a (Å)	c (Å)	x	a (Å)	c (Å)
0.00	9.373	6.870	0.00	9.645	6.758
0.45	9.365	6.862	0.45	9.643	6.755
0.90	9.358	6.849	0.90	9.644	6.754
1.80	9.347	6.839	1.80	9.643	6.751
2.70	9.347	6.833	2.70	9.643	6.748
			3.60	9.643	6.748
			4.50	9.644	6.749

limit of cobalt is around 15 and 25 mole percent in the fluor- and chlorapatite, respectively, and indicates that divalent cobalt behaves like nickel and magnesium, both of which have a greater solubility in calcium chlorphosphate apatite than in the fluorphosphate analogue.

The $Sr_{10-x}Co_x(PO_4)_6F_2$ and $Sr_{10-x}Co_x(PO_4)_6Cl_2$ solid solution series showed no changes in lattice parameters between 4.5 and 27 mole percent cobalt. Second phases were first detected by X-ray diffraction at 4.5 and 9.0 mole percent cobalt in the fluor- and chlorapatite series respectively. Hence, the solubility of cobalt is greater in calcium apatites than in strontium apatites.

All of the apatites containing cobalt were violet, a color usually suggesting a mixture of divalent cobalt in tetrahedral (blue) and octahedral or higher (pink) coordination. In all cases, the samples do not absorb extreme red and absorb little blue which accounts for their violet color. The spectra of calcium apatites containing low concentrations of cobalt (A and B, Figure 2) showed a very broad absorption band with two barely resolved maxima. By contrast, compositions containing a second phase by X-ray diffraction (C and D, Figure 2) yielded a somewhat different and better resolved spectra. The latter spectra are combinations of the absorption bands of apatite and the second phase. Similar results were observed for the strontium apatites containing cobalt. It is interesting to note that these spectra are similar to the spectra of divalent cobalt in certain alkali borate glasses reported by Weyl (1959).

The $Ca_{8.2}Co_{1.8}(PO_4)_6F_2$ and $Ca_{7.3}Co_{2.7}(PO_4)_6F_2$ compositions (curves C and D of Figure 2) contained second phases by X-ray diffraction and yielded spectra similar to divalent cobalt in octahedral coordination (McClure, 1959). These spectra are presumably superimposed spectra of divalent cobalt in at least two phases. Therefore, it would be erroneous to assume the absorption bands at 490 and 575 millimicrons correspond to the $^4T_1(F) \rightarrow {}^4T_1(P)$ and $^4T_1(F) \rightarrow {}^4A_2$ transitions respectively.

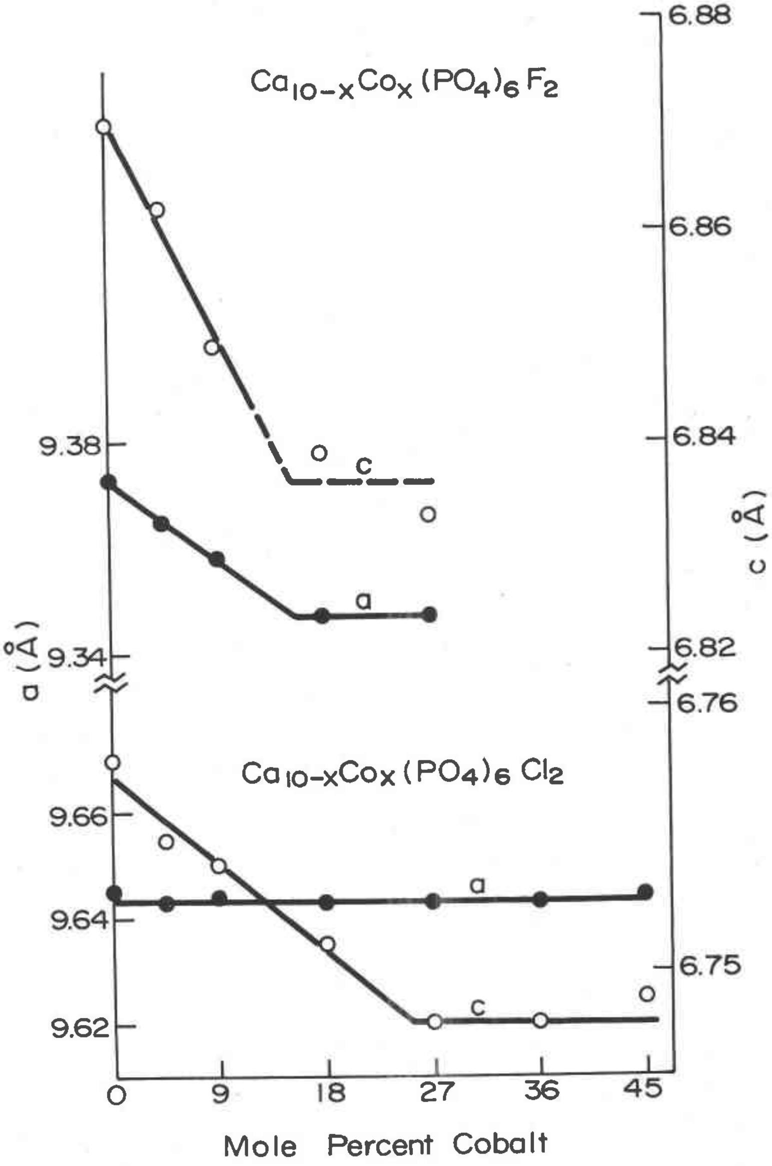

FIG. 1. Lattice parameters as a function of the cobalt concentration in the $Ca_{10-x}Co_x(PO_4)_6F_2$ and $Ca_{10-x}Co_x(PO_4)_6Cl_2$ series.

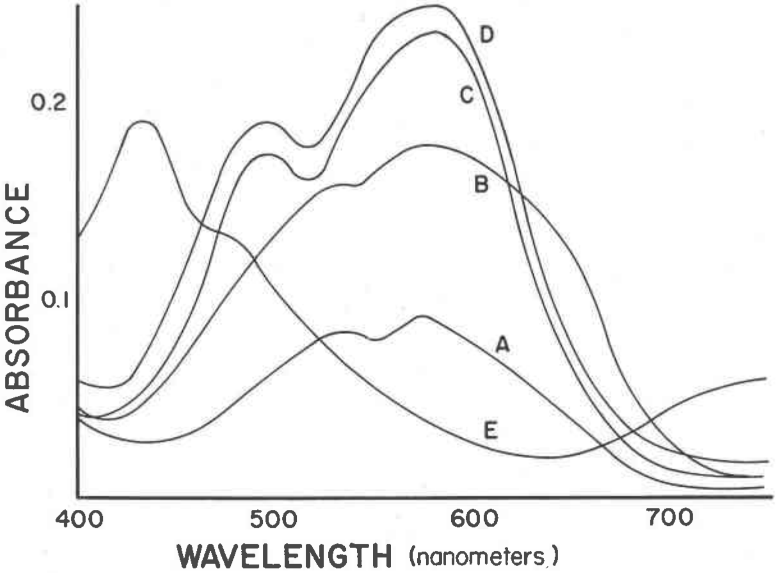

FIG. 2. Reflectance spectra of $Ca_{10-x}Co_x(PO_4)_6F_2$ apatites and $Ca_{9.1}Ni_{0.9}(PO_4)_6F_2$. A $= Ca_{9.55}Co_{0.45}(PO_4)_6F_2$, B $= Ca_{9.1}Co_{0.9}(PO_4)_6F_2$, C $= Ca_{8.2}Co_{1.8}(PO_4)_6F_2$, D $= Ca_{7.3}Co_{2.7}(PO_4)_6F_2$, E $= Ca_{9.1}Ni_{0.9}(PO_4)_6F_2$.

Nickel. The nearly identical ionic radii for divalent cobalt and nickel and the solubility limits for nickel given in Table 1 eliminate the need for a solubility study. When fired in air at 800°C, 1000°C, and 1250°C, apatite compositions containing two, five, and ten mole percent nickel were mixtures of apatite, orthophosphate, and nickel oxide. X-ray pure fluorapatites were formed by using a large excess of nickel fluoride in a covered crucible to generate a fluoride-rich atmosphere. A refractory platform separated the fluoride from the stoichiometric apatite compositions.

The above apatites were pale yellow-green and yielded similar reflectance spectra. Curve E in Figure 2 shows the reflectance spectrum for $Ca_{9.1}Ni_{0.9}(PO_4)_6F_2$. A comparison to the spectra of divalent nickel given by McClure (1957), Low (1958), and Weyl (1959) shows that Curve E is similar to nickel in octahedral coordination. The weak very broad band between 700 and 750 nm can be attributed to the $^3T_1(F)$ and/or $^1E(D)$ transitions from the $^3A_2$ ground state. The poorly resolved band at 475 nm may correspond to the $^1T_2(D)$ transition or to a splitting of the $^3T_1(P)$. The strongest band at 430 nm corresponds to the $^3T_1(P)$ transition.

CHARGE COUPLED SUBSTITUTIONS INVOLVING RARE EARTH IONS

In the present study, alkali:RE^{3+}, RE^{3+}:Si^{4+} and RE^{3+}:O^{2-} charge coupled substitutions and defects were incorporated into the apatite structure. In general, the rare earths included lanthanum, praseodymium and neodymium. The apatite compositions and their heat treatments are summarized in Table 4.

Alkali:RE^{3+}. Table 4 shows that Na^+:RE^{3+} substitutions were more soluble than Li^+RE^{3+} substitutions in the apatite structure and that the former substitutions were favored by the smaller halide and tetrahedral ions and the highly polarizable lead ion. The latter ion presumably imparts flexibility to the structure which partially offsets the distortion produced by the Na^+:RE^{3+} substitution. X-ray diffraction showed that the Na^+:La^{3+} substitutions expanded the calcium apatites but contracted the strontium, barium, and lead analogues.

The first appearance of a second phase ($LaPO_4$) in the X-ray diffraction pattern of the $Na_3La_3Ba_4(PO_4)_6F_2$ composition (see Table 4), the numerous spurs on the greatly broadened X-ray diffraction peaks of the $Na_2La_2Ba_6(PO_4)_6F_2$ apatite and the inability to index these spurs as a second apatite indicate the spurs are due to distortion and not to a miscibility gap as observed by Niaki (1961) in the calcium-barium halophosphate apatites.

RE^{3+}:Si^{4+}. The RE^{3+}:Si^{4+} substitution was used to form alkaline earth and lead fluorsilicate apatites possessing $R_4RE_6(SiO_4)_6F_2$ and $\square RRE_8(SiO_4)_6F_2$ stoichiometries. These apatites were most easily synthesized by firing a stoichiometric mixture of RF_2 and $\square R_3RE_6(SiO_4)_6\square_2$ or $\square_2RE_8(SiO_4)_6\square_2$ (the latter two compounds are defect silicate apatites) respectively. Apatite formation was much faster by this method compared to heating mixtures of metal carbonate and/or fluoride, silicic acid and rare earth oxide (at the same temperature) since the fluoride easily filled empty sites in the silicate apatite structures.

RE^{3+}:O^{2-}. The RE^{3+}:O^{2-} substitution was used to form (Ca or Sr)$_8$ $RE_2(PO_4)_6O_2$ oxyapatites. It is logical to assume the oxide ions occupy the fluoride ion sites in view of their nearly identical sizes. These are true oxyapatites since the halide sites are completely filled and all mirror planes (and consequently the $P6_3/m$ space group) are preserved. By contrast, the lead oxyapatite $Pb_{10}(PO_4)_6O\square$, has only one-half of its sites filled thus eliminating some of the mirror planes and giving rise to a different space group.

TABLE 4. RESULTS OF ATTEMPTED APATITE COMPOSITIONS CONTAINING RARE EARTH IONS

Composition	Formation Temperature (°C)/Time (hrs)	Phases Identified
$Na^+:RE^{3+}$		
$Li_2La_2R_6(PO_4)_6F_2$: R = Ca, Sr, Ba	800/6 900/6	Apatite and large amount $LaPO_4$
$Li_2La_2Pb_6(PO_4)_6F_2$	850/3	Apatite and large amount $LaPO_4$
$Na_2RE_2Ca_6(PO_4)_6F_2$:		
RE = La, Pr, Nd	1000/8	Apatite
$Na_2RE_2Ca_6(PO_4)_6Cl_2$:		
RE = La, Pr, Nd	1000/8	Apatite and some $LaPO_4$
$Na_2La_2Sr_6(PO_4)_6F_2$	1000/8	Apatite
$Na_2La_2Sr_6(PO_4)_6Cl_2$	1000/8	Apatite and some $LaPO_4$
$Na_2La_2Ba_6(PO_4)_6Cl_2$	1000/8	Apatite (distorted?) + some $LaPO_4$
$Na_2RE_2Pb_6(PO_4)_6Z_2$:		
RE = La, Pr, Nd and Z = F, Cl	850/6	Apatite
$Na_2Nd_2Ba_6(VO_4)_6Z_2$: Z = F, Cl	1000/8	Little apatite, mostly orthovanadate
$NaLaBa_8(PO_4)_6F_2$	1000/8	Apatite
$Na_2La_2Ba_6(PO_4)_6F_2$	1000/8	Distorted apatite
$Na_3La_3Ba_4(PO_4)_6F_2$	1000/8	Distorted apatite + $LaPO_4$
$Na_4La_4Ba_2(PO_4)_6F_2$	1000/8	Little apatite, mostly $LaPO_4$
$Na_5La_5(PO_4)_6F_2$	1000/8	No apatite
$K_2La_2Ba_6(PO_4)_6Z_2$: Z = F, Cl	950/8	Apatite
$K_2La_2Ba_6(VO_4)_6Z_2$: Z = F, Cl	950/8	Apatite + second phase(s)
$La^{3+}:Si^{4+}$		
$R_8La_2(SiO_4)_2(PO_4)_4Z_2$:		Apatite (traces of second phase in chlorapatites)
R = Ca, Sr, Ba and Z = F, Cl	1000/18	
$Pb_8La_2(SiO_4)_2(PO_4)_4Z_2$: Z = F, Cl	875/12	Apatite
$R_4La_6(SiO_4)_6F_2$: R = Ca, Sr, Ba	1100/12	Apatite
$Pb_4La_6(SiO_4)_6F_2$	950/12	Apatite
$RE^{3+}:O^{2-}$		
$Ca_8RE_2(PO_4)_6O_2$: RE = La, Pr, Nd	1320/72	Apatite
$Sr_8RE_2(PO_4)_6O_2$: RE = La, Pr, Nd	1350/72	Apatite + traces second phase(s)
$Ba_8RE_2(PO_4)_6O_2$: RE = La, Pr, Nd	1350/48	No apatite
$Pb_8La_2(PO_4)_6O_2$	1000/10	Apatite (distorted?)
Defect Types		
$\square RLa_8(SiO_4)_6F_2$: R = Ca, Sr, Ba	1000/16	Apatite
$\square PbLa_8(SiO_4)_6F_2$	1000/10	Apatite
$\square_2RE_8(SiO_4)_6\square_2$:		
RE = La, Pr, Nd, Sm, Eu		Apatite
RE = Gd, Ho	1350/1400/72	No apatite
$\square R_3RE_6(SiO_4)_6\square_2$:		
R = Ca, Sr, Ba and		
RE = La, Pr, Nd	1350/1400/36	Apatite
$\square Pb_3RE_6(SiO_4)_6\square_2$:		
RE = La, Pr, Nd	1000/10	Apatite
$R_4Nd_6(SiO_4)_6O\square$: R = Ca, Sr, Ba	1350/20	Apatite + trace Nd_2O_3
$Pb_4Nd_6(SiO_4)_6O\square$	1000/16	Apatite
$\square R_5Nd_4(SiO_4)_4(PO_4)_2\square_2$:		
R = Ca, Sr	1350/16	Apatite
$\square Ba_5Nd_4(SiO_4)_4(PO_4)_2\square_2$	1350/16	Apatite + trace second phase
$\square Pb_5Nd_4(SiO_4)_4(PO_4)_2\square_2$	1000/12	Apatite
$\square_2ThRNd_6(SiO_4)_6\square_2$:		
R = Ca, Sr, Ba	1250/10, 1350/6	No Apatite
$\square_3Th_3Nd_4(SiO_4)_6\square_2$	1250/10, 1350/6	No Apatite

TABLE 5. X-RAY POWDER DATA FOR DEFECT SILICATE APATITES CONTAINING PRASEODYMIUM

	$\square_2Pr_8(SiO_4)_6\square_2$		$\square Sr_3Pr_6(SiO_4)_6\square_2$		$\square Pb_3Pr_6(SiO_4)_6\square_2$	
hkl	d(Å)	I	d(Å)	I	d(Å)	I
110	4.800	4	4.790	5	4.820	6
200	4.161	33	4.156	28	4.181	33
111	3.974	27	3.981	23	4.001	33
002	3.534	16	3.567	13	3.576	12
102	3.255	38	3.277	38	3.286	42
210	3.145	38	3.145	47	3.159	39
211	2.873	100	2.872	100	2.888	100
112	2.847	46			2.872	75
300	2.774	34	2.771	32	2.786	32
202	2.692	4	2.706	5	2.717	2
310	2.309	8	2.305	7	2.320	2
103	—	—	—	—	2.298	2
221	2.277	5	—	—	2.287	4
302	—	—	2.189	5	2.199	6
113	2.116	12	2.131	9	2.138	12
400	2.079	5	—	—	2.091	4
222	1.986	26	1.991	28	2.000	24
312	1.932	14	1.936	18	1.946	16
320	1.909	6	1.907	8	—	—
213	1.885	29	1.897	27	1.903	24
321	1.842	16	1.844	15	1.852	16
410	1.815	22	1.814	18	1.824	14
402	1.792	25	1.796	22	1.804	20
004	1.767	11	1.784	10	1.788	10
	Remainder of Reflections weak ($I < 10$)					
313	—		1.649		—	
204	1.628		1.640		1.644	
412	—		1.618		—	
420	—		1.572		1.579	
331	1.562		1.562		1.570	
214	1.540		1.552		1.556	
502	1.506		1.508		1.514	
510	1.491		—		—	
304	1.485		1.501		1.504	
323	1.483		1.489		1.494	
511	1.462		1.461		1.468	
332	1.459		—		1.467	
404	1.346		1.355		1.360	
333	1.3245		—		1.3346	
423	—		1.3139		—	
521	1.3093		1.3092		1.3152	
215	—		1.3005		1.3037	
602	1.2902		1.2920		—	
432	—		—		1.2838	
414	1.2667		1.2730		1.2771	
513	—		—		1.2706	
522	1.2475		1.2482		1.2540	
504	1.2117		—		—	
440	1.2011		1.2009		1.2075	
424	—		1.1794		1.1849	
006	1.1752		—		—	
701	1.1718		—		—	
523	—		1.1632		1.1684	
116	1.1447		1.1554		1.1581	
206	—		1.1439		1.1478	
442	1.1362		—		—	
702	1.1269		1.1280		1.1336	
613	1.1173		1.1200		1.1252	
216	1.1025		—		—	
335	1.0600		—		—	
226	1.0579		1.0665		1.0696	
614	1.0307		—		—	
406	1.0250		1.0336		1.0365	
542	1.0201		1.0212		—	
632	1.0053		1.0055		1.0112	
802	0.9979		0.9986		1.0040	
444	0.9935		0.9966		1.0008	
	plus 5 lines to 0.8926		plus 5 lines to 0.8930		plus 9 lines to 0.8494	

TABLE 6. LATTICE PARAMETERS OF HALIDE VACANT, RARE EARTH SILICATE APATITES
LATTICE PARAMETERS (Å)[a]

Apatite	a_0	c_0	References
$\square_{0.67}La_{9.33}(SiO_4)_6\square_2$	9.55	7.14	Kuzmin and Belov (1965)
$\square_{0.67}Sm_{9.33}(SiO_4)_6\square_2$	9.33	6.85	Kuzmin and Belov (1965)
$\square_2Sm_8(SiO_4)_6\square_2$	9.497(3)	6.949(2)	McCarthy *et al.* (1967)
$\square_2Pr_8(SiO_4)_6\square_2$	9.613(2)	7.068(2)	Present Study
$\square Sr_3La_6(SiO_4)_6\square_2$	9.710	7.244	Schwarz (1967)
$\square Sr_3Pr_6(SiO_4)_6\square_2$	9.611(2)	7.144(2)	Present Study
$\square Pb_3Pr_6(SiO_4)_6\square_2$	9.662(1)	7.162(1)	Present Study

[a] Numbers in parentheses are errors in the last figure.

Defect Apatites. Combinations of charge coupled substitutions including defects were used to synthesize rare earth silicate apatites containing no halide ions (see Table 4). The $\square_2RE_8(SiO_4)_6\square_2$ types contain more vacancies on the calcium site, as well as in the unit cell, than other types of apatites reported in the literature. Failure to form the gadolinium and holmium analogues fixed the lower size limit of the rare earth ion for these apatites between europium and gadolinium in agreement with McCarthy *et al.* (1967).

The $Pb_4Nd_6(SiO_4)_6O\square$ apatite (formed in dry air) is probably isostructural to the oxypyromorphite $Pb_{10}(PO_4)_6O\square$. The analogous alkaline earth compositions contained small amounts of Nd_2O_3 by X-ray diffraction so they are likely close to the $\square_{0.67}R_4Nd_{5.33}(SiO_4)_6\square_2$ apatite composition similar to the $\square_{0.67}Sr_4La_{5.33}(SiO_4)_6\square_2$ reported by Schwarz (1967) or a solid solution between $\square_{0.67}R_4Nd_{5.33}(SiO_4)_6\square_2$ and $R_4Nd_6(SiO_4)_6O\square$.

The spacings for neodymium silicate reported by Miller and Rase (1964) can be partially indexed by analogy to the samarium silicate data of McCarthy *et al.* (1967). The latter authors realized these $2RE_2O_3 \cdot 3SiO_2$ compounds possessed the $P6_3/m$ space group but not that they were apatite structures (personal communication). The spacings, visual intensities and Miller indices for the previously unreported $\square_2Pr_8(SiO_4)_6\square_2$, $\square Sr_3Pr_6(SiO_4)_6\square_2$ and $\square Pb_3Pr_6(SiO_4)_6\square_2$ apatites are presented in Table 5 while their lattice parameters are included in Table 6. A comparison of the praseodymium or neodymium silicate data of this study to that of Miller and Rase's neodymium silicate showed the latter authors had not reported several reflections (including the strong 112 line). The rare earth silicate apatite structure contracts along both the a and c directions with decreasing size of the rare earth ion as might be expected from the well-known lanthanide contraction.

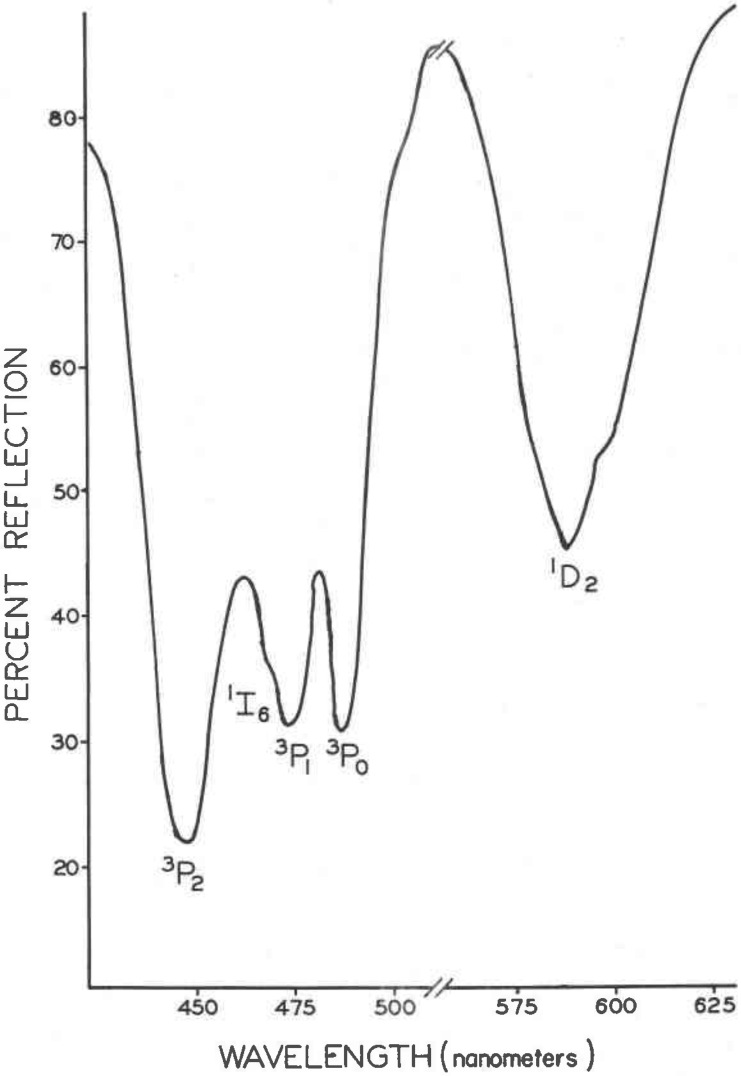

FIG. 3. Reflectance spectrum for $\square_2Pr_8(SiO_4)_6\square_2$.

TABLE 7. ABSORPTION MAXIMA (NM) OF TRANSITIONS OCCURRING IN APATITES CONTAINING PRASEODYMIUM IN THE VISIBLE REGION

Composition	Transitions Occurring from $^3H_4$ Ground State to: $^3P_2$	$^3P_1$ ($^1I_6$)	$^3P_0$	$^1D_2$
$\square_2Pr_8(SiO_4)_6\square_2$	448	473	487	588
$Na_2Pr_2Ca_6(PO_4)_6F_2$	447	472	485	586
$Na_2Pr_2Pb_6(PO_4)_6F_2$	447	472	486	590
Pr_2O_3 (White, 1967)	449	474	485	589

Color. All of the apatites containing praseodymium and neodymium were light green and light blue-violet respectively. Regardless of the stoichiometry of the apatites, their reflectance spectra were similar to the reflectance spectra of the praseodymium and neodymium oxide respectively.

Figure 3 shows the reflectance spectrum of trivalent praseodymium in the defect apatite $\square_2Pr_8(SiO_4)_5\square_2$. The transitions giving rise to the absorption bands were easily identified by analogy to those reported by Dieke *et al.* (1961) and White (1967). Table 7 compares the position (in nm) of the maxima of the absorption bands of trivalent praseodymium in three apatites. These data show that the presence of large amounts of defects in the apatite structure do not change the positions of the praseodymium absorption bands from the bands in the apatites whose sites are completely filled. All of the apatites show spectra similar to the spectrum of Pr_2O_3 reported by White (1967).

The reflectance spectrum for trivalent neodymium is considerably more complicated than the above spectrum of praseodymium. The neodymium spectra published by Dieke *et al.* (1961) and White (1967) allowed the identification of several of the absorption bands that occurred

TABLE 8. ABSORPTION MAXIMA (NM) IN THE VISIBLE REGION OF SOME TRANSITIONS[a] OCCURRING IN NEODYMIUM WHEN INCORPORATED IN APATITE LATTICES

Composition	Transitions Occurring from $^4I_{9/2}$ Ground State to: $^2P_{3/2}$	$^2D_{5/2}$	$^2P_{1/2}$	$^2G_{9/2}$	$^2G_{7/2}$		($^{2,4}G_{7/2,5/2}$)	$^2H_{11/2}$		$^4F_{9/2}$
$\square_2Nd_8(SiO_4)_6\square_2$	386	423	434	527	575		585	628		686
$Na_2Nd_2Ca_6(PO_4)_6F_2$	not resolved		432	526		581		627		684
$Na_2Nd_2Pb_6(PO_4)_6F_2$	not resolved		432	526		581		629		687
$\square Ca_3Nd_6(SiO_4)_6\square_2$	385	423	434	526	575		584	628		686
$\square Sr_3Nd_6(SiO_4)_6\square_2$	384	422	431	524	574		584	627		685
$\square Ba_3Nd_6(SiO_4)_6\square_2$	385	423	433	525	575		584	628		686
$\square Pb_3Nd_6(SiO_4)_6\square_2$	385	423	432	525	574		584	628		686
									635	
Nd_2O_3 (White, 1967)	390	427	435	528		583		628		687
									645	

[a] Where splitting occurred, only the wavelength of the strongest absorbing line was usually reported.

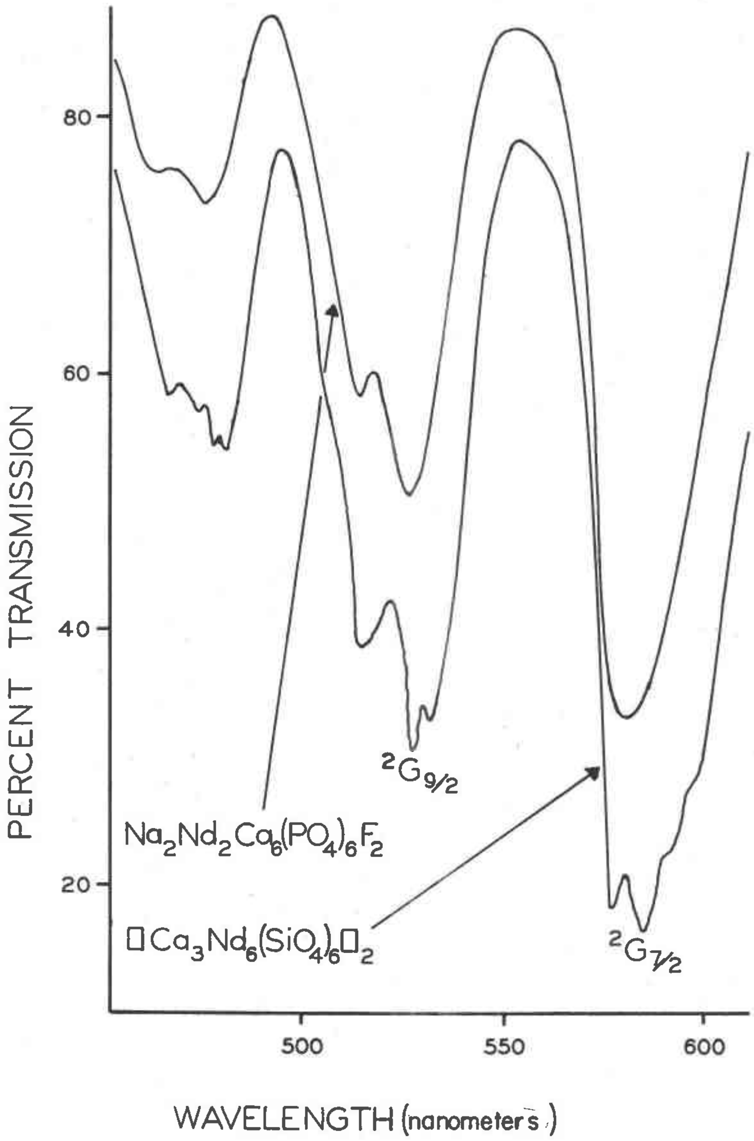

Fig. 4. Reflectance spectra of the $Na_2Nd_2Ca_6(PO_4)_6F_2$ and $\square Ca_3Nd_6(SiO_4)_6\square_2$ apatites.

in the reflectance spectra of apatites containing neodymium. All of the bands found in these apatite spectra were observed in the Nd_2O_3 spectrum reported by White (1967). Table 8 lists several of the absorption bands found in these apatite spectra. Like praseodymium, the composition and stoichiometry of the apatite did not alter the wavelength at which the absorption maxima occurred. The latter values were identical (within instrumental error) to those published by White (1967) for Nd_2O_3.

Some interaction of the rare earth ion with the apatite structure occurs. Since there should be no direct rare earth—rare earth interactions, it is safe to assume that differences in the ligand arrangement around the rare earth ion cause these interactions.

As shown in Figure 4, not as much splitting of the absorption bands of the rare earth ions occurs in apatites containing completely filled sites, *e.g.* $Na_2Nd_2Ca_6(PO_4)_6F_2$ compared to those containing defects, *e.g.* $\square Ca_3Nd_6(SiO_4)_6\square_2$. It is assumed that the rare earth ion is always distributed on both the Ca_I and Ca_{II} sites. In particular, the halide site occupation may be very important. The splitting of various bands is appreciable in apatites containing empty halide sites and this defect site is in the nearest coordination sphere of the Ca_{II} site in the apatite structure. By contrast, cation defects are partially shielded from the rare earth ions occupying Ca_I sites by oxygens.

In conclusion, the color and the positions of the absorption maxima for a given rare earth ion are not affected by the composition (including defects) of the host apatite.

BIBLIOGRAPHY

BRASSEUR, HENRI, AND MARCEL J. DALLEMAGNE (1949) Synthèse de l'Apatites. *Bull. Soc. Chim. Fr.* **1949,** D135–137.

COCKBAIN, A. G., AND G. V. SMITH (1967) Alkaline earth-rare earth silicate apatites. *Mineral. Soc. London, Notice* **148.**

CULLITY, B. D. (1959) *Elements of X-ray Diffraction.* Addison-Wesley Publishing Co., Iuc., Reading, Massachusetts, 514 p.

DIEKE, G. H., H. M. CROSSWHITE, AND B. DUNN (1961) Emission spectra of the doubly and triply ionized rare earths. *J. Opt. Soc. Amer.* **51,** 820–827.

FÖRTSCH, E., AND HANS WONDRATSCHEK (1965) Zur Kristallachemie der Minerale der Pyromorphit-Gruppe. *Naturwissenschaften,* **52,** 182.

ITO, JUN (1968) Silicate apatites and oxyapatites. *Amer. Mineral.* **53,** 890–907.

KLEMENT, ROBERT, AND HELMUT HASELBECK (1963) Über Phosphate und Arsenate des zweiwertigen Zinns. *Chem. Ber.* **96,** 1022–1026.

KLEMENT, ROBERT, AND HELMUT HASELBECK (1965) Apatite und Wagnerite zweiwertiger Metalle. *Z. Anorg. Allg. Chem.* **336,** 113–128.

KREIDLER, ERIC R. (1967) *Stoichiometry and Crystal Chemistry of Apatite.* Ph.D. Dissertation in Ceramic Science, The Pennsylvania State University.

KUZMIN, E. A., AND N. V. BELOV (1965) Crystalline structure of simple silicates, lanthanum and samarium. *Dokl. Akad. Nauk SSSR,* **165,** 88–90.

LINDBERG, MARIE L., AND B. INGRAM (1964) Rare-earth silication apatite from the Adirondack Mountains, New York. *U. S. Geol. Surv. Prof. Pap.* **501*B***, B64–65.

LOW, W. (1958) Paramagnetic and optical spectra of divalent nickel in cubic crystalline fields. *Phys. Rev.* **109**, 247–255.

MCCARTHY, G., W. B. WHITE, AND R. ROY (1967) Preparation of $Sm_4(SiO_4)_3$. *J. Inorg. Nucl. Chem.* **29**, 253–254.

MCCLURE, D. S. (1957) The distribution of transition metal cations in spinels. *J. Phys. Chem. Solids* **3**, 311–317.

——— (1959) *Electronic Spectra of Molecules and Ions in Crystals.* Academic Press Inc., New York, New York, 175 p.

MILLER, R. O., AND D. E. RASE (1964) Phase equilibrium in the system Nd_2O_3–SiO_2. *J. Amer. Ceram. Soc.* **47**, 653–654.

MULLER, MARCEL (1947) The precipitation and X-ray examination of the $Ca_{10}(PO_4)$. $(OH)_2$-$Pb_{10}(PO_4)_6(OH)_2$ solid solutions. *Helv. Chim. Acta*, **30**, 2069–2080.

NIAKI, ALI-NAGHI AKHAVAN (1961) Etude des substitutions dans les apatites. *Ann. Chim.* (Paris) **6**, 51–79.

ROPP, R. C. (1963) A study of cadmium chlorphosphate phosphor. *J. Electrochem. Soc.* **110**, 113–117.

SCHWARZ, H. (1967) Vergindungen mit Aptitstruktur. I. Ungewohnliche Silicatapatite. *Inorg. Nucl. Chem. Lett.* **3**, 231–236.

SIDORENKO, G. A. (1964) Crystallochemistry of silicates having an apatite type structure. *Rentgenogr. Mineral'n. Syr'ya, Vses. Nauchin.-Issled. Inst. Mineral'n. Syr'ya, Akad. Nauk SSSR* **4**, 39–61.

TROMEL, GERHARD, AND WILHELM EITEL (1958) Synthesis of silicate apatites of the britholite-abukumalite group. *Z. Kristallogr.* **109**, 231–239.

WEYL, WOLDEMAR A. (1959) *Coloured Glasses.* Dawson's of Pall Mall, London, England, 541 p.

WHITE, WILLIAM B. (1967) Diffuse-reflectance spectra of rare earth oxides. *Appl. Spectrosc.* **21**, 167–171.

WONDRATSCHEK, HANS (1963) Untersuchungen zur Kristallchemie der Blei-Apatite (Pyromorphite). *Neues Jahrb. Mineral. Abh.* **99**, 113–160.

Manuscript received, October 1, 1969; accepted for publication, March 12, 1970.