SOLID SOLUTION IN THE WAGNERITE STRUCTURE*

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ABSTRACT

Complete substitution of Co^{++}, Ni^{++}, Cu^{++}, and Zn^{++} for Mg^{++} was made in the wagnerite structure. A complete solid solution series exists between the four derivatives and $Mg_2(PO_4)F$, producing linear changes in peak positions in the x-ray diffraction patterns. Co, Ni, and Cu are also completely soluble in "zinc wagnerite" and $Zn_3Mg(PO_4)_2F_2$, but in these cases non-linear changes in peak positions are observed. Ca^{++} was not soluble in Ni or Cu wagnerite, but 15 and 30 mole % Ca were soluble in $Mg_2(PO_4)F$ and $Co_2(PO_4)F$, respectively. Exploratory runs of Li^+, V^{5+}, and Cl^- solubilities showed that 0.6 mole of Li could be substituted in Mg, Co, and Ni wagnerites to give $Li_{0.6}M_{3.4}P_2O_8F_{1.4}\square_{0.6}$. Approximately 40 mole % V^{5+} could be substituted for P^{5+} in magnesium, cobalt, and nickel wagnerites. Complete substitution of Cl^- for F^- was possible in Cu and Zn wagnerites, but not in Mg, Co, and Ni analogues. The synthesis of the charge-coupled wagnerites $LiMg_3PSO_8F_2$ and $NaMg_3PSO_8F_2$ of Klement et al. (1941) was confirmed and the Co and Ni analogues were prepared.

INTRODUCTION

The primary purpose of this investigation was to study the crystal chemistry of wagnerite, particularly with respect to ions such as Co^{++}, Ni^{++}, and Cu^{++} which may produce crystals with unusual colours. However, special emphasis was placed on Zn^{++} due to its frequent replacement of Mg^{++} in various structures and some emphasis was placed on Li^{++}, Ca^{++}, V^{5+}, and Cl^-, all of which have a high probability of entering the wagnerite structure, at least in part. A limited number of trials with charge-coupled substitutions were made.

Previous studies

The history and properties of wagnerite have been reported by Palache *et al.* (1951). Wagnerite, $Mg_2(PO_4)F$, is monoclinic and occurs in limited quantities, commonly with Mg partly

replaced by Ca^{2+}, Fe^{2+}, and Mn^{2+}. CaO varies considerably; the high calcium material perhaps indicates an alteration toward apatite (Palache *et al.* 1951).

Strictly speaking, the name wagnerite applies only to the mineral $Mg_2(PO_4)F$, but this term has been applied to any substance with the general composition A_2XO_4Z. Compounds with the type formula A_2XO_4Z have been systematically studied in classifying phosphate, arsenate and vanadate minerals (Richmond 1940). Several papers have been published involving simple and charged-coupled substitutions into A, X, and Z sites (Mourelo 1915; Klement & Gembruck 1941; Klement & Haselbeck 1965; Gorbacheva 1959; Abramsen 1968).

The crystal structure of wagnerite was first determined by Coda *et al.* (1967). The most recent report on a new occurrence of wagnerite in Colorado (Sheridan *et al.* 1970) has again confirmed the monoclinic structure and space group $P2_1/a$. The lattice parameters of wagnerites as determined by several investigators are shown in Table 1.

A coordination number of five for magnesium is unusual, but similar results have been reported for melilite by Christie (1962) and for tarbuttite by Cocco *et al.* (1966).

The PDF x-ray pattern for wagnerite is one which was reported by Henriques (1957) for an iron-rich mineral from Hallsjoberget, Sweden.

Winter (1913) and Berak *et al.* (1965) studied the phase equilibria in the system $Mg_3(PO_4)_2$—MgF_2 and reported one intermediate compound, $Mg_4(PO_4)_2F_2$, which melted congruently. Winter claimed a melting point of 1253° and three polymorphic forms, and Berak *et al.* claimed a

TABLE 1. CELL DIMENSIONS OF NATURAL AND SYNTHETIC WAGNERITES

Natural	a	b	c	β
Gonyer (in Richmond 1940)	11.93Å	12.47Å	9.44Å	108°09'
Coda *et al.* (1967)*	9.644±.007	12.679±.008	11.957±.008	108°18'±9'
Kraus & Mussgnug (1935)	11.90	12.51	9.63	108°07'
Braitsch (1960)	11.91	12.69	9.66	108°20'
Sheridan *et al.* (1971)	11.929±.005	12.698±.008	9.633±.004	108°12'±3'
Synthetic (this study)				
Mg_2PO_4F	11.878	12.656	9.951	107.62°
Co_2PO_4F	11.918	12.675	9.638	107.82°
Ni_2PO_4F	12.036	12.641	9.688	108.06°
Cu_2PO_4F	12.019	12.941	9.853	106.94°
Zn_2PO_4F	11.944	12.672	9.594	107.89°

* a and c are interchanged

melting point of 1337° and four polymorphic forms.

EXPERIMENTAL PROCEDURE

Synthesis

Several investigators (Mourelo 1915; Gorbacheva 1959; Winter 1928; Berak & Tomczak 1965) claim to have prepared wagnerite in air. Two attempts were made by us to prepare the compound in air, but loss of fluorine and incomplete reaction led us to believe that such procedures were unreliable and that synthesis in sealed platinum tubes was necessary to assure phase-pure wagnerites of reliable stoichiometry.

In the first attempt, a stoichiometric mixture of $MgCO_3 \cdot Mg(OH)_2$, $(NH_4)_2HPO_4$ and MgF_2 was heated from room temperatures to 715° and held for 12 hours. X-ray analysis showed that $Mg_3(PO_4)_2$ and unknown phases were present, but no unreacted starting materials. After remixing in acetone, the product was heated in air at 1020° for 4 hours, giving wagnerite and unknown phases. After heating in air at 1130° for one-half hour, the product consisted of wagnerite and MgO.

A second attempt was made using $Mg_3(PO_4)_2$ and MgF_2 and heating to 1025° for one-half hour in air. X-ray analysis gave wagnerite and a trace of $Mg_3(PO_4)_2$. After 1100° for 3 hours, wagnerite and MgO were present. Repeated trials showed that about a 95% yield of wagnerite could be expected from this technique, but it was obvious from the two experiments that $Mg_3(PO_4)$ or MgO would appear and persist in samples heated at high temperatures in air and that some fluorine was lost.

The technique finally used to prepare all wagnerites and intermediate solid solutions was to make an orthophosphate intermediate and then react the intermediate with the required fluoride. This technique is particularly successful in the laboratory preparation of small samples of apatites (Kreidler & Hummel 1970) and wagnerites. If the ortho-compound intermediate was heated between 500-850° for 24 hours, usually a single phase ortho-compound was obtained, but complete reaction was not necessary for the successful synthesis of the final single-phase wagnerite.

Wagnerites were prepared by the use of 0.5 to 1.0 grams of ortho-compound and the required amount of fluoride, mixing at least three times for 20 minutes in acetone. The charge was placed in a platinum tube (0.5 cm diameter, 2.0 cm long) to one-half or two-thirds its length and welded in a D.C. arc. The encapsulated samples were heated for 1-15 hours between 550-1200° in a Globar furnace.

Phase identification

Phase analyses were made primarily with a Norelco wide-range diffractometer using Ni-filtered $CuK\alpha$ radiation in the 2θ range 10°-65°; for compounds containing Co^{++}, Ni^{++}, or Cu^{++}, Mn-filtered $FeK\alpha$ radiation was employed in the 2θ range 20°-75°, at a scanning rate of 2°/min. For more accurate determination of d values, a scanning rate of ¼° per minute and a silicon external standard were employed. The midpoint at the half height of the peak was taken as the true value of 2θ.

A petrographic microscope was used to examine the preparations for impurities and to determine the optical properties of wagnerites.

RESULTS AND DISCUSSION

Characterization of wagnerite

Wagnerite was prepared by heating a stoichiometric mixture of $Mg_3(PO_4)_2$ and MgF_2 in a sealed platinum tube at 850°/3 hrs., 930°/15 hrs. 1000°/4 hrs., 1040°/4 hrs., and 1100°/4 hrs. X-ray analysis showed that each heat treatment had produced phase-pure wagnerite with the pattern shown in Table 2. This pattern was used as a standard throughout this investigation, although it did not coincide exactly with the PDF pattern given by Henriques (1957) for natural wagnerite.

The claims of Winter (1931) and Berak & Tomazak (1965) for several inversions in wagnerite were not well-documented. Therefore, differential thermal analyses were run on well-crystallized material previously prepared in platinum tubes. Using a Tem-Pres unit, a sample of wagnerite and the alumina reference were each sealed in a one-eighth-inch diameter platinum tube, thus preventing fluorine volatilization from the wagnerite. Under these conditions, a small but distinct heat effect was noted at 1255°C during heating and cooling, and melting took place at 1340±5°C which is in excellent agreement with the 1337°C reported by Berek et al. (1965).

Runs on a du Pont apparatus were made in nitrogen and in each case, during heating and cooling, the inversion was obtained at 1255°C. All samples from the D.T.A. runs were examined by x-ray diffraction and found to be wagnerite. No decomposition had taken place in any of the runs.

As a further check on the polymorphism, a

TABLE 2. PARTIAL X-RAY POWDER DATA FOR SYNTHETIC WAGNERITES*

hkl	Mg$_2$PO$_4$F d_{calc}	d_{meas}	I/I_o	Co$_2$PO$_4$F d_{calc}	d_{meas}	I/I_o	Ni$_2$PO$_4$F d_{calc}	d_{meas}	I/I_o	Cu$_2$PO$_4$F d_{calc}	d_{meas}	I/I_o	Zn$_2$PO$_4$F d_{calc}	d_{meas}	I/I_o
021	5.212	5.199	11	5.245			5.161			5.277			5.246		
002	4.522			4.633			4.532	4.526	14	4.610	4.602	26	4.490		
121	4.450			4.461			4.408	4.345	12	4.498			4.474		
201	4.268			4.261			4.251	4.251	14	4.292			4.290	4.305	9
220	4.224	4.232	8	4.228	4.252	20	4.205	4.200	22	4.251	4.176	24	4.247	4.256	12
211	4.045	4.076	4	4.040			3.926	3.867	15	4.072	4.044	20	4.065		
031	3.838			3.857			3.800			3.890			3.859	3.857	12
$\bar{1}$31	3.785			3.809			3.791	3.786	18	3.833			3.807		
310	3.618			3.616			3.615	3.583	16	3.634	3.625	33	3.636		
221	3.541	3.533	7	3.540	3.559	54	3.514	3.506	65	3.571	3.594	42	3.558	3.560	62
230	3.388	3.439	16	3.394			3.368	3.409	14	3.544	3.506	62	3.403		
122	3.292	3.284	51	3.310	3.313	46	3.260	3.254	31	3.324	3.318	30	3.317	3.317	27
320	3.244	3.235	14	3.244			3.139	3.132	21	3.265			3.184	3.187	7
202	3.123	3.114	65	3.128	3.140	76	3.095	3.097	58	3.145	3.150	64	3.144	3.142	75
311	3.071			3.065			3.056			3.096	3.095	30	3.086	3.083	8
140	3.054			3.062			3.005	3.002	14	3.089			3.066		
401	2.972			2.985			2.983			2.981	2.964	44	2.993		
$\bar{1}$41	2.970	2.965	100	2.986	2.996	100	2.945	2.939	100	2.911	2.916	90	2.986	2.990	95
$\bar{4}$02	2.827	2.832	40	2.854	2.850	91	2.835	2.836	88	2.831	2.828	100	2.850	2.851	100
141	2.822			2.835			2.776	2.786	14	2.864			2.841		
330	2.816	2.802	21	2.818			2.803			2.840			2.829		
240	2.767			2.773			2.745	2.740	23	2.800			2.779		
$\bar{2}$41	2.764			2.785	2.784	26	2.746			2.797			2.780		
023	2.747	2.748	28	2.779	2.771	58	2.722	2.723	72	2.773	2.807	51	2.776	2.777	77

*Indexed with the cell dimensions given in Table 1. Complete patterns are in PDF set 24.

wagnerite solid solution containing a 15 mole % substitution of Co^{++} for Mg^{++} inverted at 1235°C in the Tem-Pres unit when in a sealed platinum tube.

It was concluded that wagnerite undergoes only one inversion, at 1255°C, prior to melting at 1340°C.

FIG. 1. Variation of 2θ values as a function of composition for wagnerite solid solutions.

Cobalt substitution

Using (Mg$_{1-x}$Ni$_x$)$_3$(PO$_4$)$_2$, MgF$_2$, and NiF$_2$, samples containing 0.6, 1.2, 1.8, 2.4, 3.0, and 4.0 (Co$_4$P$_2$O$_8$F$_2$) moles of Co^{++} were heated at 850°/3 hrs. to produce a complete series of solid solutions, 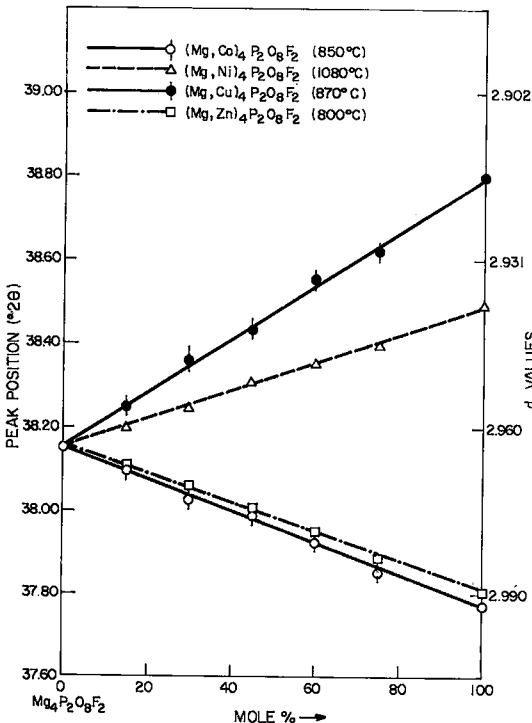yielding a variation in peak positions as shown in Figure 1. Heating at 900°/6 hrs. gave phase-pure solid solutions, but at 1000°/24 hrs., wagnerite and unidentified phases were present.

Attempts to prepare cobalt wagnerite or intermediate members of the solid solution series by heating a mixture of (Mg,Co)$_3$(PO$_4$)$_2$, CoF$_2$ and MgF$_2$, or 3MgCO$_3$·Mg(OH)$_2$,CoCO$_3$,(NH$_4$)$_2$·HPO$_4$, CoF$_2$, and MgF$_2$ at 715°/12 hrs., 1020°/4 hrs., or 1180°/½ hr. in air were unsuccessful.

Nickel substitution

Using (Mg$_{1-x}$Ni$_x$)$_3$(PO$_4$)$_2$, MgF$_2$, and NiF$_2$, samples containing 0.6, 1.2, 1.8, 2.4, 3.0, and 4.0 (Ni$_4$P$_2$O$_8$F$_2$) moles of Ni^{++} were heated at 1080°/3 hrs. to produce a complete series of solid solutions, yielding a variation in peak positions as shown in Figure 1. The compositions were stable if heated to 1200°/4 hrs., but higher temperatures or longer times produced wagnerite and secondary phases. Synthesis atttempts in air were not successful. The x-ray data for Ni$_4$P$_2$O$_8$F$_2$ are shown in Table 2.

Copper substitution

Using (Mg$_{1-x}$Cu$_x$)$_3$ (PO$_4$)$_2$, MgF$_2$, and CuF$_2$, samples containing (Cu$_4$P$_2$O$_8$F$_2$) moles of Cu^{++} were heated at 870°/1 hr. to produce a complete series of solid solutions, yielding a variation in peak positions as shown in Figure 1.

Heating at 850°/1.5 hrs. produced pure phases, but at 1000°/4 hrs. wagnerite and unknown phases were present. The bright green colour became more intense as the amount of copper was increased, but as the samples were heated at higher temperatures or longer times than the optimum, the colour changed to light brownish gray, indicating reduction of Cu^{++} to Cu^{+}. X-ray diffraction data for $Cu_4P_2O_8F_2$ are shown in Table 2.

Zinc substitution

Using $(Mg_{1-x}Zn_x)_3(PO_4)_2$, MgF_2, and ZnF_2, samples containing 0.6, 1.2, 1.8, 2.4, 3.0, and 4.0 ($Zn_4P_2O_8F_2$) moles of Zn^{++} were heated at 800°/6 hrs. to produce a complete series of solid solutions, yielding a variation of peak positions as shown in Figure 1. The zinc substitutions contract the structure in a manner almost identical with cobalt, whereas Ni^{++} and Cu^{++} expand the structure. X-ray diffraction data for $Zn_4P_2O_8F_2$ are shown in Table 2.

Heating at 1100°/1 hr. in sealed tubes produced $Mg_3(PO_4)_2$ and $Zn_3(PO_4)_2$ as major phases and synthesis in air was not successful.

Substitution in the zinc site of $Zn_4P_2O_8F_2$ and $Zn_3MgP_2O_8F_2$

Using $(Zn_{1-x}Co_x)_3PO_4$, $(Zn_{1-x}Ni_x)_3(PO_4)_2$, $Zn_{1-x}Cu_x)_3(PO_4)_2$, MgF_2, ZnF_2, CoF_2, NiF_2, and CuF_2, molar substitutions of Co^{++}, Ni^{++}, and Cu^{++} were made in $Zn_4P_2O_8F_2$ and $Zn_3MgP_2O_8F_2$ at levels of 1.0, 1.6, 2.2, 2.8, 3.4, and 0.6, 1.2, 1.8, and 2.4, respectively. Heat treatments were at 820°/1.5 hrs., 1100°/1.5 hrs., and 820°/1.5 hrs. for Co^{++}, Ni^{++}, and Cu^{++} in $Zn_4P_2O_8F_2$ and at 800 - 900°/2-3 hrs., 800-1000°/2-3 hrs. and 900°/2 hrs. for Co^{++}, Ni^{++}, and Cu^{++} in $Zn_3MgP_2O_8F_2$, respectively. These solid solutions were much more sensitive to temperature and time of heat treatment than those previously described and careful choice of both variables had to be made in order to avoid the presence of unreacted starting materials at low temperatures or secondary phases at temperatures higher than the optimum. The variations of 2θ values as a function of composition are shown in Figures 2 and 3. The maxima and non-linearity in the curves indicate that some interesting packing effects are in operation as the transition metal ions substitute for Zn^{++}. The expanding effect of Cu^{++} is still evident, but much modified from the linear behavior shown in Figure 1. The compositions which showed maximum deviation from linearity in Figures 2 and 3 gave x-ray peak intensities which were con-
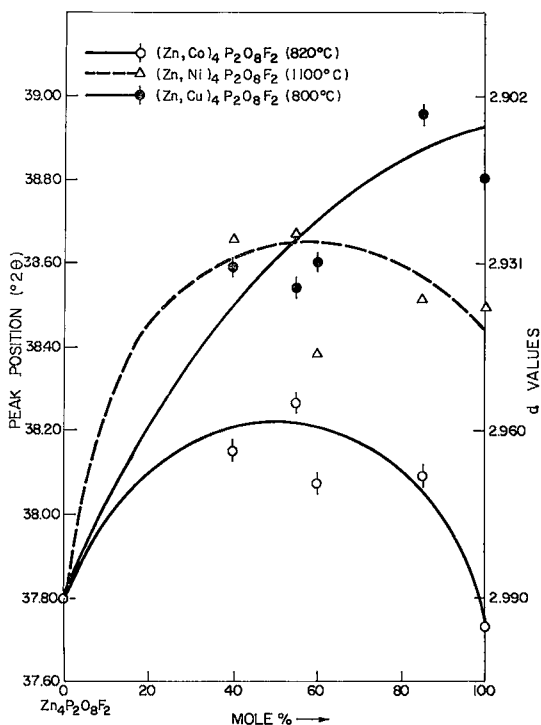

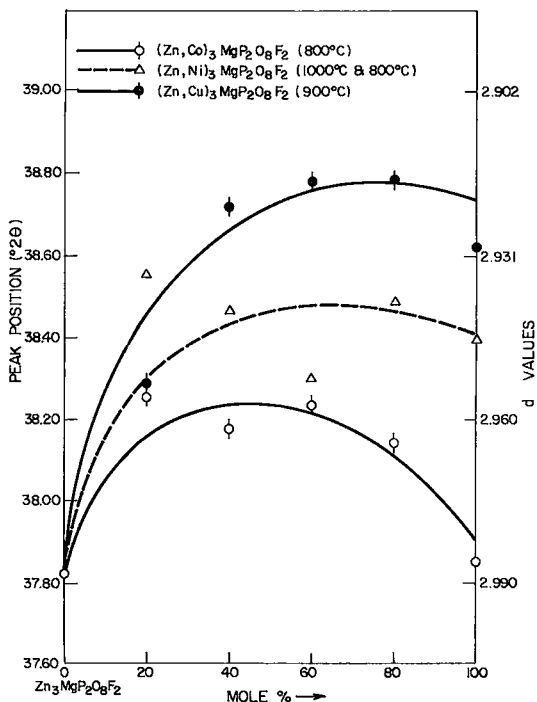FIG. 2. Variation of 2θ values as a function of composition for $Zn_4P_2O_8F_2$ solid solutions.

FIG. 3. Variation of 2θ values as a function of composition for $Zn_3MgP_2O_8F_2$ solid solutions.

siderably different from the end members, indicating substantial distortion of the structure.

Calcium substitution

Ca^{++} was found to be soluble in $Mg_4P_2O_8F_2$ and $Co_4P_2O_8F_2$ but not in $Ni_4P_2O_8F_2$ and $Cu_4P_2O_8F_2$. Using the presence of a secondary phase as an indicator, the limits of solubility shown in Figure 4 were established. Large expansions of the structure were observed. Heat treatments were at 930°/15 hrs. and 830°/4 hrs. in the Mg and Co series, respectively.

The work on synthesis and luminescence of wagnerites by Gorbacheva (1959) is suspect because all heat treatments were made in air at temperatures where it was likely that orthophosphates would be formed.

Subsequent studies of the Mn^{++}-activated luminescence of the so-called wagnerites of Gorbacheva by B. Bacik (1970) have shown his original work to be unreliable. His claim for the preparation of $Ca_4P_2O_8F_2$ as a wagnerite is especially doubtful, since this is the composition ascribed to the mineral spodio-

site. He gave no evidence to substantiate his claim. The temperature and pressure conditions under which fluorine spodiosite can be synthesized apparently have not yet been determined, but the chlorine analogue, ($Ca_4P_2O_8$-Cl_2), has been prepared by heating in air by many investigators.

Lithium substitution

If lithium is substituted for magnesium so as to preserve a total of four atoms in the A site, halide vacancies would be required to preserve a charge balance. If as many as two atoms of lithium could be substituted in the magnesium site, this would produce the completely halide-vacant wagnerite, $Li_2Mg_2P_2O_8\square_2$, similar to the well-known completely halide-vacant lead apatites. If half the halide sites were vacant, the formula would be $LiMg_3P_2$-$O_8F\square$. It was found that only 0.6 mole of Li^+ was soluble in Mg^{++}, Co^{++}, and Ni^{++} wagnerites, giving the general formula, $Li^+_{0.6}Mg_{3.4}$-$P_2O_8F_{1.4}\square_{0.6}$. Heat treatments were at 930°/4 hrs., 620°/3 hrs., and 620°/3 hrs. for Mg^{++}, Co^{++}, and Ni^{++}, respectively.

Vanadium and chlorine substitutions

About 40 mole % V^{5+} can replace P^{5+} in $Mg_4P_2O_8F_2$, $Co_4P_2O_8F_2$, $Ni_4P_2O_8F_2$, and Zn_4-$P_2O_8F_2$, using heat treatments of 1050°/4 hrs. for $Mg_4P_2O_8F_2$ and 700°/12 hrs. for the other three compositions.

Klement & Haselbeck (1965) reported the synthesis of $Mg_4P_2O_8Cl_2$ and $Co_4P_2O_8Cl_2$, but all attempts to duplicate these results by heating in sealed tubes or air failed. The use of an excess of NH_4Cl in the starting mixture was also unsuccessful. Poorly-crystallized $Cu_4P_2O_8$-Cl_2 and $Zn_4P_2O_8Cl_2$ were prepared by heating in air at 300° and 180° for two hours. Traces of unknown phases were present in both preparations and the zinc compound melted at 300°. It is possible, of course, that partial substitution of Cl^- for F^- could be made in most of the wagnerites so far mentioned, but this was beyond the scope of the present work.

Charge-coupled substitutions

Klement et al. (1941) had claimed the preparation of $LiMg_3PSO_8F_2$ and $NaMg_3PSO_8F_2$ as wagnerites and this was confirmed in the present work by heat treating $MgSO_4$, MgF_2 and $LiMgPO_4$ or $NaMgPO_4$ at 900°/2 hrs. At 1000° /2 hrs., the compounds begin to convert to other phases. The analogues $LiCo_3PSO_8F_2$, $NaCo_3$-PSO_8F_2, $LiNi_3PSO_8F_2$ and $NaNi_3PSO_8F_2$ were
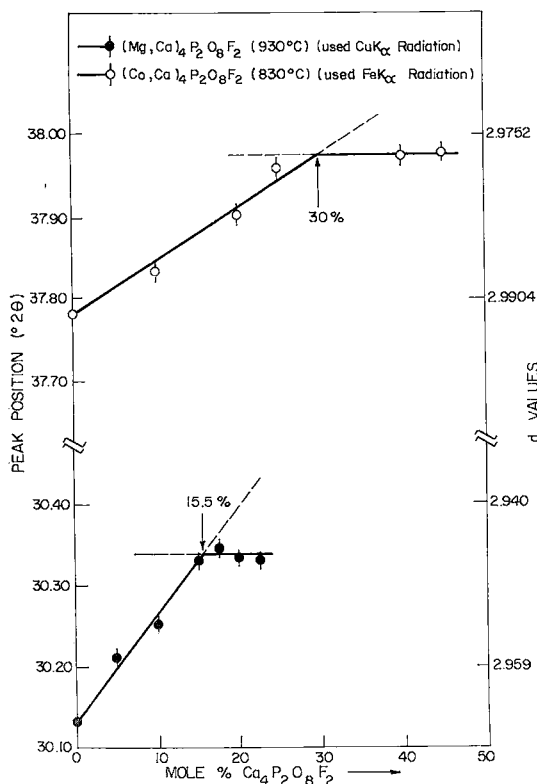
FIG. 4. Solubility of Ca in $Mg_4P_2O_8F_2$ and $Co_4P_2O_8$-F_2.

prepared by heating at 900°/2 hrs., 700°/2 hrs., 900°/2 hrs., and 900°/2 hrs., respectively. The sodium-nickel compound was poorly crystallized, but phase-pure.

SUMMARY

Conditions for the synthesis of phase-pure wagnerite have been established. Wagnerite undergoes only one reversible polymorphic inversion at 1255°, contrary to the several inversions reported previously. Analogous Co^{++}, Ni^{++}, Cu^{++}, and Zn^{++} wagnerites form complete series of solid solutions with magnesium wagnerite, and Co^{++}, Ni^{++} and Cu^{++} form complete solid solution series with zinc wagnerite. Exploratory work on the substitution of Ca^{++}, Li^+, V^{5+} and Cl^- in the new wagnerites showed that partial substitution was possible for Ca^{++}, Li^+ and V^{5+} in some of the preparations, but highly specific behavior was evident. Complete substitution of Cl^- for F^- was possible only under carefully controlled conditions in copper and zinc wagnerites. New charge-coupled cobalt and nickel wagnerites were prepared.

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