

## Synthesis of wagnerite and its analogues for ceramic pigments (II)

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### 도자기 유약용 Wagnerite의 합성(II)

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**Abstract** In order to investigate the polymorphism of wagnerite, the single phase of  $Mg_2(PO_4)F$  was synthesized by heating the stoichiometric mixture of  $Mg_3(PO_4)_2$  and  $MgF_2$  in a sealed platinum tube at  $1040^\circ C$  for 3 hours. One reversible inversion was detected at  $1255^\circ C$  and the thermal decomposition was not observed until it reached the melting point. As a result, wagnerite is thermally stable enough to be used as pigments for glazes and plastics if substituted with divalent metal ions. The contractions of d-values in  $Zn_4P_2O_8F_2$  and  $Zn_3MgP_2O_8F_2$  phases were observed by the substitution with metal ions which resulted in intense purple, gold and green colors. Among the several attempts of charge-coupled substitution, only  $A^{1+}A_3^{2+}X^{5+}X^{6+}O_8F_2$  compositions were successful to synthesize the wagnerite phase.

**요 약** 합성원료로써  $Mg_3(PO_4)_2$ 와  $MgF_2$  분말을 혼합한 후 백금밀폐용기를 사용하여  $1040^\circ C$ 에서 단일상의 wagnerite( $Mg_2PO_4F$ )를 합성하였으며 이 결정상의 동질이상에 대하여 연구한 결과, 이미 발표된 연구 결과들과는 달리  $1255^\circ C$ 에서 단 한번의 가역적인 상전이가 관찰되었고,  $1340^\circ C$ 에서 용융될 때까지 열분해 현상은 나타나지 않았으며, 이로써 2가 금속이온의 치환에 의해 여러 종류의 고용체를 합성해 낼 경우, 유약 및 플라스틱의 색상발현을 위한 안료로 사용될 수 있는 것으로 밝혀졌다.  $Zn_4P_2O_8F_2$ 와  $Zn_3MgP_2O_8F_2$  wagnerite의 Zn 대신 2가 금속을 치환한 경우, 전반적으로 d값이 줄어들었으며 Co는 자주색, Ni은 금색, Cu는 녹색을 나타내었다. 또한 charge-coupled 치환을 시도한 결과,  $A^{1+}A_3^{2+}X^{5+}X^{6+}O_8F_2$ 의 경우만 wagnerite가 형성되었다.

## 1. Introduction

The history and properties of wagnerite ( $\text{Mg}_2(\text{PO}_4)\text{F}$ ) had been reported by Palache et al. [1]. Strictly speaking, the name wagnerite applies only to the compound  $\text{Mg}_2(\text{PO}_4)\text{F}$ . This term, however, has been widely used to any substance with the general composition  $\text{A}_2\text{XO}_4\text{Z}$ , where A, X and Z normally have +2, +5 and -1 charges, respectively. Therefore, there are several possible substitutions which may result in various solid solutions of wagnerites and present many different colors of wagnerites, depending on their substituting ions. Compounds with the type formula  $\text{A}_2\text{XO}_4\text{Z}$  had been systematically studied by Richmond in classifying phosphate, arsenate and vanadate minerals [2].

The crystal structure of wagnerite was first determined by Coda et al. [3] in 1967. They assumed that the chemical composition of the wagnerite was  $\text{Mg}_2(\text{PO}_4)\text{F}$  and that there were sixteen stoichiometric units ( $z=16$ ) in the unit cell, as previously reported [1,2]. The lattice parameters and the bond lengths of natural and synthetic wagnerites determined by several investigators were reported elsewhere [2-8]. Winter [9] and Berak et al. [10] studied the phase equilibria in the system  $\text{Mg}_3(\text{PO}_4)_2\text{-MgF}_2$  and reported one intermediate compound,  $\text{Mg}_4(\text{PO}_4)_2\text{F}_2$ , which melted congruently. Winter claimed a melting point of 1253°C and three polymorphic forms, and Berak et al. claimed a melting point of 1337°C and four polymor-

phic forms.

The main goals of this study were to investigate the crystal chemistry and the color variations of Zn-wagnerite by the additions of metal ions, particularly  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$  and  $\text{Cu}^{++}$  which may produce various wagnerite pigments for ceramic glazes and plastics [11-13].

## 2. Experimental procedure

Pure chemical reagents were weighed to an accuracy of 0.1 milligram by an analytical balance and hand-mixed with acetone in glass mortars two or three times for 10 to 15 minute periods. The mixed powder was loaded in a platinum crucible (5 mm in diameter and 10 mm in length) and heated in a Hoskins furnace.

For the investigation of polymorphism in wagnerite, DTA runs were made using one manufactured by Tem Pres, Inc. for the specimen sealed in a platinum tube and the other by du Pont for the specimen in nitrogen atmosphere. A Bausch and Lomb petrographic microscope was used to examine impurities and to analyze the optical properties of wagnerites.

Phase analyses were made primarily using Ni-filtered  $\text{Cu K}\alpha$  radiation in the  $2\theta$  range 10°-65° and for compounds containing  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$  or  $\text{Cu}^{+2}$ , Mn-filtered  $\text{Fe K}\alpha$  radiation was employed in the  $2\theta$  range 20°-75°, at a scanning rate of 2°/min. For more accurate determination of  $d$  values, a scanning rate of 1/4° 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  $2\theta$ .

### 3. Results and discussion

#### 3.1. Polymorphism of wagnerite ( $Mg_2PO_4F$ )

Several investigators [9,10,14,15] claimed to have prepared wagnerite in air. Two attempts were made by us to prepare the compound in air, but the loss of fluorine and the 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 this investigation, wagnerites were synthesized by heating the stoichiometric mixtures of  $Mg_3(PO_4)_2$  and  $MgF_2$  in the sealed platinum tubes at  $1040^\circ\text{C}$  for 3 hours. X-ray analysis confirmed that the heat treatment had produced the single phase of wagnerite. The X-ray powder diffraction pattern for the Mg-wagnerite prepared at  $1040^\circ\text{C}$  for 3 hours is listed with the Zn-wagnerite in Table 1. These patterns were used as a standard throughout this investigation, although it did not coincide exactly with the A.S.T.M pattern given for the mineral wagnerite by Henriques [16].

As mentioned above, the reports of Winter [9] and Berak et al. [10] about several inversions in wagnerite were not

confirmed well. Therefore, DTA analyses were performed on the well-crystallized materials which were prepared in platinum tubes. The runs were made in two different methods; one in nitrogen atmosphere and the other in the sealed platinum tube (one-eight-inch diameter) in order to pre-

Table 1  
X-ray powder diffraction data for synthetic Mg and Zn-wagnerites

hkl	$Mg_2PO_4F$			$Zn_2PO_4F$		
	$d_{\text{calc}}$	$d_{\text{meas}}$	$I/I_0$	$d_{\text{calc}}$	$d_{\text{meas}}$	$I/I_0$
021	5.212	5.199	11	5.246		
002	4.522			4.490		
121	4.450			4.474		
201	4.268			4.290	4.305	9
220	4.224	4.232	8	4.247	4.256	12
211	4.045	4.076	4	4.065		
031	3.838			3.859	3.857	12
$\bar{1}31$	3.785			3.807		
310	3.618			3.636		
221	3.541	3.533	7	3.558	3.560	62
230	3.388	3.439	16	3.403		
122	3.292	3.284	51	3.317	3.317	27
320	3.244	3.235	14	3.184	3.187	7
202	3.123	3.114	65	3.144	3.142	75
311	3.071			3.086	3.083	8
140	3.054			3.066		
$\bar{4}01$	2.972			2.993		
$\bar{1}41$	2.970	2.965	100	2.986	2.990	95
$\bar{4}02$	2.827	2.832	40	2.850	2.851	100
141	2.822			2.841		
330	2.816	2.802	21	2.829		
240	2.767			2.779		
$\bar{2}41$	2.764			2.780		
023	2.747	2.748	28	2.776	2.777	77

vent the fluorine volatilization. A small heat peak was observed at 1255°C during heating and cooling in both cases, and melting took place at  $1340 \pm 5^\circ\text{C}$  which was in good agreement with the 1337°C reported by Berak [10]. No decomposition had taken place in any of the runs and the inversion was reversible, meaning that wagnerites can be used as pigments for ceramic glazes and plastics by the addition of metal elements such as  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Cu}^{++}$  etc. For the wagnerite solid solution substituted with 15 mole percent of  $\text{Co}^{++}$  for  $\text{Mg}^{++}$ , the inversion was observed at 1235°C. It was concluded that wagnerite underwent only one inversion at 1255°C and melts at 1340°C.

### 3.2. Effects of metal ion substitutions for the zinc site of $\text{Zn}_4\text{P}_2\text{O}_8\text{F}_2$ and $\text{Zn}_3\text{MgP}_2\text{O}_8\text{F}_2$

#### 3.2.1. Cobalt substitution

The phases of  $\text{Zn}_4\text{P}_2\text{O}_8\text{F}_2$  and  $\text{Zn}_3\text{MgP}_2\text{O}_8\text{F}_2$  were prepared by heating a stoichiometric mixture of  $(\text{Mg,Zn})_3(\text{PO}_4)_2$  and  $\text{MgF}_2$  or  $\text{ZnF}_2$  at 850°C for 3 hours and 800°C for 6 hours in sealed platinum tubes, respectively. Heating at 1100°C for 1 hour produced  $\text{Zn}_3(\text{PO}_4)_2$  as a major phase. Synthesis of the solid solution in air was not successful.

As shown in Table 2, the complete solid solutions between  $\text{Zn}_4\text{P}_2\text{O}_8\text{F}_2$  and  $\text{Co}_4\text{P}_2\text{O}_8\text{F}_2$  and between  $\text{Zn}_3\text{MgP}_2\text{O}_8\text{F}_2$  and  $\text{Co}_3\text{MgP}_2\text{O}_8\text{F}_2$  can be prepared in the sealed platinum tubes. In the system  $\text{Zn}_4\text{P}_2\text{O}_8\text{F}_2$  and  $\text{Co}_4\text{P}_2\text{O}_8\text{F}_2$ , a stoichiometric mixture of  $(\text{Zn,Co})_3$

$(\text{PO}_4)_2$  and  $\text{CoF}_2$  was heat-treated at 820°C for one and half hours. Also, these wagnerite solid solutions could be produced by various heat treatments, such as 850°C for one hour or 750°C for three hours. Solid solutions between  $\text{Zn}_3\text{MgP}_2\text{O}_8\text{F}_2$  and  $\text{Co}_3\text{MgP}_2\text{O}_8\text{F}_2$  were prepared by heating a mixture of  $(\text{Zn,Co})_3(\text{PO}_4)_2$  and  $\text{MgF}_2$  at 900°C for 2 hours when the compositions were near the zinc-rich end. As the concentration of cobalt increased, the temperature should be decreased to 800°C in order to avoid a secondary phase.

As shown in Fig. 1 and Fig. 2, the value of  $2\theta$  went through an unusual maximum in each series. Careful X-ray analysis indicated that only the wagnerite phase was present and that no starting materials or secondary phases were present. The compositions which showed the maximum lattice contraction in Fig. 1 and Fig. 2 gave X-ray peak intensities which were considerably different from the end members, indicating substantial distortions of the wagnerite structure.

Both crystal solution series produced a purple color which became more intense as the concentration of cobalt increased. The effect of cobalt substitution on the colors of Zn-wagnerite was strong, compared with the (Zn,Mg)-wagnerite at the same concentration of cobalt.

#### 3.2.2. Nickel substitution

As indicated in Table 2, the complete crystal solutions between  $\text{Zn}_4\text{P}_2\text{O}_8\text{F}_2$  and  $\text{Ni}_4\text{P}_2\text{O}_8\text{F}_2$  and between  $\text{Zn}_3\text{MgP}_2\text{O}_8\text{F}_2$  and  $\text{Ni}_3$

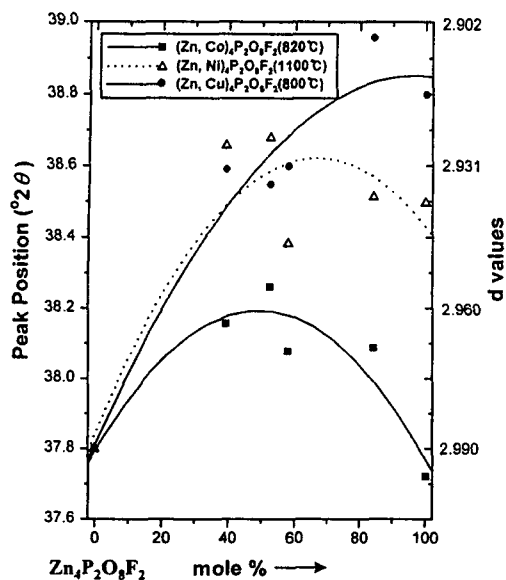


Fig. 1. Effect of metal ion substitutions on the d-spacing values of Zn-wagnerites.

$\text{MgP}_2\text{O}_8\text{F}_2$  were formed in sealed platinum tubes. Solid solutions between  $\text{Zn}_4\text{P}_2\text{O}_8\text{F}_2$  and  $\text{Ni}_4\text{P}_2\text{O}_8\text{F}_2$  were prepared by heating a mixture of  $(\text{Zn,Ni})_3(\text{PO}_4)_2$  and  $\text{NiF}_2$  at  $1100^\circ\text{C}$  for 1.5 hours. The mixtures were rather stable when fired at higher and lower temperatures than the optimum. The gold color of the crystal solutions became more intense as the composition approached the pure nickel wagnerite. As shown in Fig. 1, a maximum occurred in the  $2\theta$  versus composition curve, similar to that found for the cobalt series.

In the system  $\text{Zn}_3\text{MgP}_2\text{O}_8\text{F}_2$ - $\text{Ni}_3\text{MgP}_2\text{O}_8\text{F}_2$ , a mixture of  $(\text{Zn,Ni})_3(\text{PO}_4)_2$  and  $\text{MgF}_2$  was generally heat treated at  $1000^\circ\text{C}$  for 2 hours, but the heating temperature was lowered to  $800^\circ\text{C}$  as the amount of the nickel increased. The crystal solutions were very sensitive to heat treatment; at

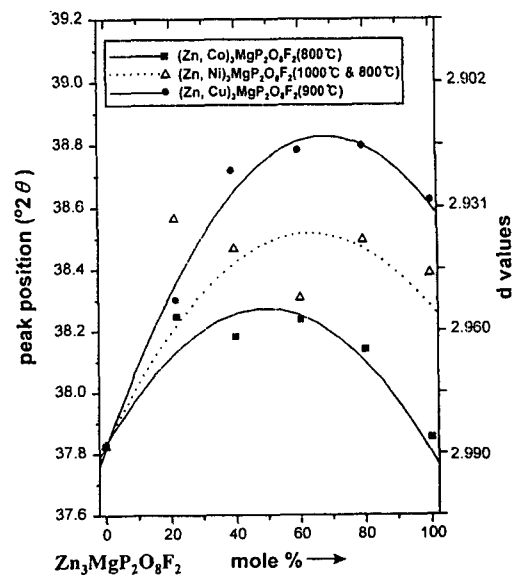


Fig. 2. Effect of metal ion substitutions on the d-spacing values of (Zn,Mg)-wagnerites.

lower temperatures than the optimum, starting materials were observed, and at higher temperatures than the optimum, a secondary phase was present. As shown in Fig. 2, a maximum in the  $2\theta$  versus composition curve was obtained similar to the cobalt series. Yellow colors were obtained in this solid solution system, compared with the gold color of  $(\text{Zn,Ni})_4\text{P}_2\text{O}_8\text{F}_2$  solid solutions.

### 3.2.3. Copper substitution

Like cobalt and nickel substitutions, a complete crystal solutions between  $\text{Zn}_4\text{P}_2\text{O}_8\text{F}_2$  and  $\text{Cu}_4\text{P}_2\text{O}_8\text{F}_2$  and between  $\text{Zn}_3\text{MgP}_2\text{O}_8\text{F}_2$  and  $\text{Cu}_3\text{MgP}_2\text{O}_8\text{F}_2$  could be formed in sealed platinum tubes; but due to the great sensitivity to all heat treatments, a trace of unidentified phase was present in

Table 2  
Synthesis conditions and colors of Zn-wagnerite and associated solid solutions

Composition	Heat treatment (°C/hr)	Color	Composition	Heat treatment (°C/hr)	Color
Zn <sub>3.0</sub> Co <sub>1.0</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	820/1.5	light purple			
Zn <sub>2.4</sub> Co <sub>1.6</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	purple	Zn <sub>2.4</sub> Co <sub>0.6</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	900/2	light purple
Zn <sub>1.8</sub> Co <sub>2.2</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	"	Zn <sub>1.8</sub> Co <sub>1.2</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	purple
Zn <sub>1.2</sub> Co <sub>2.8</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	"	Zn <sub>1.2</sub> Co <sub>1.8</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	800/3	dark purple
Zn <sub>0.6</sub> Co <sub>3.4</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	"	Zn <sub>0.6</sub> Co <sub>2.4</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	purple
Zn <sub>3.0</sub> Ni <sub>1.0</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	1100/1.5	light gold			
Zn <sub>2.4</sub> Ni <sub>1.6</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	gold	Zn <sub>2.4</sub> Ni <sub>0.6</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	1000/2	light orange
Zn <sub>1.8</sub> Ni <sub>2.2</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	"	Zn <sub>1.8</sub> Ni <sub>1.2</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	orange
Zn <sub>1.2</sub> Ni <sub>2.8</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	"	Zn <sub>1.2</sub> Ni <sub>1.8</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	800/3	yellow
Zn <sub>0.6</sub> Ni <sub>3.4</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	"	Zn <sub>0.6</sub> Ni <sub>2.4</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	"
Zn <sub>3.0</sub> Cu <sub>1.0</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	800/1	light green			
Zn <sub>2.4</sub> Cu <sub>1.6</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	grey	Zn <sub>2.4</sub> Cu <sub>0.6</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	900/2	whitish green
Zn <sub>1.8</sub> Cu <sub>2.2</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	820/1.5	dark green	Zn <sub>1.8</sub> Cu <sub>1.2</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	grey
Zn <sub>1.2</sub> Cu <sub>2.8</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	green	Zn <sub>1.2</sub> Cu <sub>1.8</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	greyish green
Zn <sub>0.6</sub> Cu <sub>3.4</sub> P <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	"	Zn <sub>0.6</sub> Cu <sub>2.4</sub> MgP <sub>2</sub> O <sub>8</sub> F <sub>2</sub>	"	light green

several compositions at the optimum temperatures listed in Table 2. No optimum temperature was found which could insure the formation of a completely phase pure wagnerite.

As shown in Fig. 1, a very large lattice contraction occurred as Cu<sup>++</sup> was substituted for Zn<sup>++</sup>, similar to the contraction for the Mg<sub>4</sub>P<sub>2</sub>O<sub>8</sub>F<sub>2</sub>-Cu<sub>4</sub>P<sub>2</sub>O<sub>8</sub>F<sub>2</sub> series [8]. In the case of Zn<sub>3</sub>MgP<sub>2</sub>O<sub>8</sub>F<sub>2</sub>-Cu<sub>3</sub>MgP<sub>2</sub>O<sub>8</sub>F<sub>2</sub> series, a maximum occurs in the 2θ versus composition curve, parallel to the case for Co<sup>++</sup> and Ni<sup>++</sup>, as shown in Fig. 2.

In both systems, the color changed from pale green to green as the concentration

of Cu<sup>++</sup> increased. Generally, the green colors of Zn-wagnerites were more intense in the Zn<sub>4</sub>P<sub>2</sub>O<sub>8</sub>F<sub>2</sub>-Cu<sub>4</sub>P<sub>2</sub>O<sub>8</sub>F<sub>2</sub> solid solutions than in the Zn<sub>3</sub>MgP<sub>2</sub>O<sub>8</sub>F<sub>2</sub>-Cu<sub>3</sub>MgP<sub>2</sub>O<sub>8</sub>F<sub>2</sub> solid solutions.

### 3.3. Charge-coupled substitutions of wagnerite

The formula of wagnerite structure can be written as A<sub>2</sub>XO<sub>4</sub>Z (or A<sub>4</sub>X<sub>2</sub>O<sub>8</sub>Z<sub>2</sub>). Therefore, many charge-coupled substitutions could be attempted, such as A<sup>1+</sup>A<sup>3+</sup>, X<sup>4+</sup>X<sup>6+</sup>, A<sup>1+</sup>A<sub>3</sub><sup>2+</sup> with X<sup>5+</sup>X<sup>6+</sup> and A<sup>2+</sup>A<sup>4+</sup> with X<sup>4+</sup> and Z<sup>2-</sup>. A few of these were

tried as follows.

### 3.3.1. $A^{1+}A^{3+}PO_4F$ substitution

For the synthesis of  $LiAlPO_4F$  phase, a mixture of  $AlPO_4$  and  $LiF$  was heated at  $700^\circ C$  for 2 hours in sealed platinum tubes, resulting in the mineral amblygonite.  $(Li,Na)AlPO_4(F,OH)$  is known as mineral amblygonite. Heating the mixture at  $1000^\circ C$  for 2 hours yielded an unknown phase.

For the synthesis of  $NaAlPO_4F$ , a mixture of  $AlPO_4$  and  $NaF$  was heated at  $700^\circ C$  for 2 hours in a sealed tube. As a result, a phase with the structure of the mineral sphene ( $CaTiSiO_5$ ) was produced. At  $1000^\circ C$  for 2 hours, an unidentified phase was produced. Baur [17] reported that amblygonite and sphene have analogous structures, but in this investigation the X-ray patterns for the two synthetic mineral preparations mentioned above

Table 3

Synthesis conditions that the single phase of wagnerite was not formed by charge-coupled substitutions

Composition	Heat treatment ( $^\circ C/hr$ )	Color	Major phase
$LiAlPO_4F$	700/2	white	amblygonite
"	1000/2	white	unknown
$NaAlPO_4F$	700/2	white	sphene
"	1000/2	white	unknown
$LiCrPO_4F$	700/2	green	unknown
$NaCrPO_4F$	700/2	green	unknown
$LiMg_3PSO_8F_2$	1000/2	white	wagnerite & unknown
$NaMg_3PSO_8F_2$	1000/2	white	unknown
$CaTi(SiO_4)O$	1250/4	white	sphene
"	1400/4	white	melt
$MgTi(SiO_4)O$	1400/4	white	$MgTi_2O_5$ & unknown
$CoTi(SiO_4)O$	1250/4	dark green	unknown
$NiTi(SiO_4)O$	"	yellow	unknown
$CaTi(GeO_4)O$	"	white	tilasite
$MgTi(GeO_4)O$	"	white	unknown
$CoTi(GeO_4)O$	1150/4	light purple	unknown
$NiTi(GeO_4)O$	1250/4	light green	unknown
$Mg_4SiSO_8F_2$	1150/2	white	olivine
$Mg_4GeSO_8F_2$	"	white	olivine

were different.

In order to obtain  $\text{LiCrPO}_4\text{F}$  and  $\text{NaCrPO}_4\text{F}$  phases, a mixture of  $\text{CrPO}_4\text{F}$  and  $\text{LiF}$  or  $\text{NaF}$  was heated in sealed platinum tubes at  $700^\circ\text{C}$  for 2 hours and produced unknown phases, as shown in Table 3.

### 3.3.2. $A^{1+}A_3^{2+}X^{5+}X^{6+}O_8F_2$ substitution

Klement et al. [18] claimed that both  $\text{LiMg}_3\text{PSO}_8\text{F}_2$  and  $\text{NaMg}_3\text{PSO}_8\text{F}_2$  compounds had the wagnerite structure. Heating a mixture of  $\text{MgSO}_4$ ,  $\text{MgF}_2$  and  $\text{LiMgPO}_4$  or  $\text{NaMgPO}_4$  at  $900^\circ\text{C}$  for 2 hours yielded wagnerite, confirming the work of Klement et al. [18]. If  $\text{LiMg}_3\text{PSO}_8\text{F}_2$  were heated at  $1000^\circ\text{C}$  for 2 hours, wagnerite and a trace of unknown were present, whereas  $\text{NaMg}_3\text{PSO}_8\text{F}_2$  converted to an unidentified phase.

$\text{LiCo}_3\text{PSO}_8\text{F}_2$  heated at  $900^\circ\text{C}$  for 2 hours formed wagnerite, as did  $\text{NaCo}_3\text{PSO}_8\text{F}_2$  when heated to  $700^\circ\text{C}$  for 2 hours. Both  $\text{LiCo}_3\text{PSO}_8\text{F}_2$  and  $\text{NaCo}_3\text{PSO}_8\text{F}_2$  compounds produced a purple color. Both  $\text{LiNi}_3\text{PSO}_8\text{F}_2$  and  $\text{NaNi}_3\text{PSO}_8\text{F}_2$  compositions could be obtained as wagnerite, yielding an orange color, as shown in Table 4.

### 3.3.3. $A^{2+}A^{4+}X^{4+}O_4Z^{2-}$ substitution

No substitutions in a synthetic compound have been reported, but the formula  $\text{CaTiSiO}_4\text{O}$  is known as the mineral sphene.  $\text{CaTiSiO}_4\text{O}$  heated at  $1250^\circ\text{C}$  for 4 hours gave a phase whose X-ray pattern was similar to the mineral sphene, and  $\text{CaTiGeO}_4\text{O}$  heated at  $1250^\circ\text{C}$  for 4 hours

yielded a phase analogous to the mineral tilasite.

In cases of  $\text{MgTiSiO}_4\text{O}$  and  $\text{MgTiGeO}_4\text{O}$  phase syntheses,  $\text{MgTiSiO}_4\text{O}$  heated at  $1400^\circ\text{C}$  for 4 hours yielded what were probably  $\text{MgSiO}_3$  and  $\text{MgTi}_2\text{O}_5$  phases, and  $\text{MgTiGeO}_4\text{O}$  gave a phase similar to amlygonite structure, as shown in Table 3.

Heating  $\text{CoTiSiO}_4\text{O}$  and  $\text{CoTiGeO}_4\text{O}$  at  $1250^\circ\text{C}$  and  $1150^\circ\text{C}$  for 4 hours, respectively, yielded unidentified phases. Also, heating  $\text{NiTiSiO}_4\text{O}$  and  $\text{NiTiGeO}_4\text{O}$  at  $1250^\circ\text{C}$  for 4 hours yielded unidentified phases.

### 3.3.4. $Mg_4X^{4+}X^{6+}O_8F_2$ substitution

Klement et al. [18] attempted to prepare  $\text{Mg}_4\text{SiSO}_8\text{F}_2$ , but it was not successful. Present attempts to prepare  $\text{Mg}_4\text{SiSO}_8\text{F}_2$  and  $\text{Mg}_4\text{GeSO}_8\text{F}_2$  by heating a mixture of  $\text{MgSO}_4$ ,  $\text{MgF}_2$  and  $\text{Mg}_2\text{SiO}_4$  or  $\text{Mg}_2\text{GeO}_4$  at  $1150^\circ\text{C}$  for 2 hours in sealed platinum tubes were again not successful, as shown in Table 3.

Table 4

Synthesis conditions and colors of wagnerites produced by charge-coupled substitutions

Composition	Heat treatment ( $^\circ\text{C}/\text{hr}$ )	Color
$\text{LiMg}_3\text{PSO}_8\text{F}_2$	900/2	white
$\text{NaMg}_3\text{PSO}_8\text{F}_2$	900/2	white
$\text{LiCo}_3\text{PSO}_8\text{F}_2$	900/2	purple
$\text{NaCo}_3\text{PSO}_8\text{F}_2$	700/2	purple
$\text{LiNi}_3\text{PSO}_8\text{F}_2$	900/2	orange
$\text{NaNi}_3\text{PSO}_8\text{F}_2$	900/2	greyish orange



#### 4. Conclusions

One reversible inversion of wagnerite was observed at 1255°C, contrary to the claims of Winter and Berak et al., and the melting point was observed at 1340°C. The thermal decomposition of wagnerite did not occur until it melted.

The substitutions of divalent metal ions ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ ) for the zinc site of  $\text{Zn}_4\text{P}_2\text{O}_8\text{F}_2$  and  $\text{Zn}_3\text{MgP}_2\text{O}_8\text{F}_2$  solid solution resulted in the contractions of d-spacing and presented purple, gold and green colors, respectively, and became intense as the concentrations of metal ions increased.

For the charge-coupled substitutions,  $\text{A}^{1+}\text{A}^{3+}\text{PO}_4\text{F}$ ,  $\text{A}^{1+}\text{A}_3^{2+}\text{X}^{5+}\text{X}^{6+}\text{O}_8\text{F}_2$ ,  $\text{A}^{2+}\text{A}^{4+}\text{X}^{4+}\text{O}$ ,  $\text{Z}^{2-}$  and  $\text{Mg}_4\text{X}^{4+}\text{X}^{6+}\text{O}_8\text{F}_2$  substitutions were attempted but only  $\text{A}^{1+}\text{A}_3^{2+}\text{X}^{5+}\text{X}^{6+}\text{O}_8\text{F}_2$  substitution was successful to synthesize the wagnerite. The colors of wagnerites produced by this substitution were purple, orange and white. The other attempts resulted in the phase other than wagnerite, as a major phase.

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