

Substitutions of coloring ions and their effects on wagnerite pigments for ceramic glazes

Yong-Sun Chung and Keun Ho Auh

Ceramic Processing Research Center (CPRC), Hanyang University, Seoul 133-791, Korea

도자기 유약용 wagnerite의 합성 및 발색원소의 영향

정용선, 오근호

한양대학교, 세라믹공정연구센터, 서울, 133-791

Abstract In order to investigate the color variation and the solubility limit in wagnerites by metal ion substitution, wagnerite (A_2XO_3Z) was synthesized and then, substituted by coloring metal ions, especially Co^{2+} , Ni^{2+} and Cu^{2+} ions. When calcium was replaced with Mg, Co, Ni and Cu divalent ions, solid solutions were formed with a limited solubility. Single phase wagnerites were synthesized by the substitution of Ca with Mg and Co, and their colors were white and purple, respectively. Substitutions with Li^+ were succeeded in the specific composition and the substitution of vanadium for X^{5+} were attempted, resulting in the wagnerites of dark purple, dark gold and light yellow colors. The substitution of chlorine was, also, attempted for the fluorine site.

요 약 치환에 의한 wagnerite의 색상변화 및 고용체 형성한계를 살펴보기 위해 wagnerite (A_2XO_3Z)를 합성한 후 각 구성원소들을 치환하였다. Ca-wagnerite의 Ca 대신에 Mg, Co, Ni, Cu로 치환하여 용해도가 한정된 고용체를 얻었다. 이들 중 (Mg,Ca)-wagnerite와 (Co,Ca)-wagnerite의 경우에만 단일상의 wagnerite를 합성하였으며 이들의 색상은 각각 백색과 자주색이었다. 그 외의 조성 및 (Ni,Ca)-wagnerite와 (Cu,Ca)-wagnerite의 경우에는 여러상이 혼재해 있는 것으로 나타났다. A^{2+} 자리에 Li를 치환해 보았으며 또한 X^{5+} 대신 V을 치환하여 진한 자주 및 금색, 옅은 노란색의 wagnerite를 합성하였으며, Z^- 대신 Cl을 치환한 경우 단일상의 wagnerite를 얻지 못하였다.

1. Introduction

The mineral wagnerite is a very interesting compound because there are many possible substitutions which may form solid solutions and modify the optical properties of wagnerite. Currently the name wagnerite is applying to any substance of a composition A_2XO_4Z , where A, X and Z normally have +2, +5 and -1 charges, respectively whereas it was used to mean only the $Mg_2(PO_4)F$ compound. The morphological, optical, physical and chemical properties of wagnerite were studied by various workers and reported by Dana [1]. The mineral is monoclinic [2], occurs in limited quantities and it is very common to find that Ca^{2+} , Fe^{2+} and Mn^{2+} have substituted in part for Mg. The CaO percentage in different wagnerites varies considerably; the high calcium material perhaps indicates an alteration toward apatite [1].

Several kinds of minerals are related to wagnerite as follows. Strunz [3] proposed a new structure for cryphiolite ($MgCaPO_4F$), and claimed that it was similar to tilasite ($MgCaAsO_4F$) and durangite ($NaAlAsO_4F$). However, Richmond [4] did not agree with Strunz that cryphiolite was isomorphous with tilasite, durangite and sphene. He assumed that cryphiolite was a calcium-rich wagnerite. Deans et al. [5] examined a cryphiolite crystal from Naples. The x-ray evidence indicated that cryphiolite was related to neither tilasite nor isokite ($CaMgPO_4F$). Deans et al.

named a monoclinic mineral from northern Rhodesia as isokite and determined its lattice parameters and proved that isokite was homologous with the minerals tilasite, durangite and sphene. Banks et al. [6] confirmed that the spodiosite analogues, Ca_2CrO_4Cl and Ca_2PO_4Cl , were orthorhombic and Brixner et al. [7] reported the spoiosite analogues, Sr_2VO_4Cl and Sr_2VO_4Br , prepared single crystals and determined the lattice constants.

As mentioned above, wagnerite is known to be very stable up to its melting point and could be easily replaced with coloring metal elements. Therefore, it can be used as an important pigment for ceramic glazes or plastics. The primary purpose of this investigation is to study the limit of solubility and the color variation in wagnerite analogues by the substitutions, particularly with respect to ions such as Co^{++} , Ni^{++} and Cu^{++} , which may result in colorful wagnerites [8-10].

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 (5mm in diameter and 10mm in length) and heated in a Hoskins furnace.

Phase analyses were made primarily using Ni-filtered $Cu K\alpha$ radiation in the 2

θ range $10^\circ - 65^\circ$ and for compounds containing Co^{+2} , Ni^{+2} or Cu^{+2} , Mn-filtered Fe $K\alpha$ radiation was employed in the 2θ range $20^\circ - 75^\circ$, at a scanning rate of 2/mim. For more accurate determination of d values, a scanning rate of $1/4^\circ$ 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 Bausch and Lomb petrographic microscope was used to examine impurities and to analyze the optical properties of wagnerites.

3. Results and discussion

3.1. Substitution of calcium in the A^{2+} site of wagnerites (a_2XO_4Z)

3.1.1. $\text{Mg}_4\text{P}_2\text{O}_8\text{F}_2$

As indicated in Table 1, Ca^{2+} was soluble in $\text{Mg}_4\text{P}_2\text{O}_8\text{F}_2$ to the extent of 15.5 mole percent at 930°C when heated in sealed platinum tubes. Using the presence of a secondary phase as an indicator, a very reliable limit of solubility was established. The wagnerite solid solutions underwent a large lattice contraction as shown in Fig. 1.

Two intermediate compounds appeared in this system at 25 mole percent of calcium ($\text{Mg}_3\text{CaP}_2\text{O}_8\text{F}_2$) and 50 mole percent of calcium ($\text{Mg}_2\text{Ca}_2\text{P}_2\text{O}_8\text{F}_2$). If $\text{Mg}_3\text{CaP}_2\text{O}_8\text{F}_2$ was held at 1000°C for 4 hours or for 24 hours, it decomposed to a distorted wagnerite. Reheating at 900°C for 24 hours

caused reversion to the compound $\text{Mg}_3\text{CaP}_2\text{O}_8\text{F}_2$. In contrast, the compound $\text{Mg}_2\text{Ca}_2\text{P}_2\text{O}_8\text{F}_2$ remained stable when heated at 1000°C for 4 hours and 24 hours, but it converted to wagnerite solid solution and $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ solid solution when heated at 1130°C for 4 hours. It is not known whether or not this reaction is reversible.

As mentioned before, there were various viewpoints on the minerals cryphiolite (MgCaPO_4F , proposed by Strunz [3]) and isokite (CaMgPO_4F , named by Deans et al. [5]). As far as cryphiolite is concerned, Deans et al. reported that it had the same molecular formula as isokite but that it was not structurally related to wagnerite, tilasite or isokite, and that it would be of interest to characterize this mineral structurally and mineralogically. As far as the data is concerned in the two papers, Dean's report is more clearly documented than Strunz's. CaMgPO_4F , therefore, would be regarded only as isokite in this investigation. Isokite has the same formula as the intermediate compound ($\text{Mg}_2\text{Ca}_2\text{P}_2\text{O}_8\text{F}_2$) obtained in this study. However, x-ray analysis showed that they do not have the same structure; therefore, the $\text{Mg}_2\text{Ca}_2\text{P}_2\text{O}_8\text{F}_2$ found in this study might be a high temperature form of isokite.

A compound, $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$, was prepared by heating a stoichiometric mixture of $\text{Ca}_3(\text{PO}_4)_2$ and CaF_2 in sealed platinum tubes at 930°C for 14 hours, at 1130°C for 4 hours and at 1130°C for 48 hours. Heating the mixture in air at 1130°C for

4 hours yielded CaO and the same compound which was obtained in sealed platinum tube experiments. Since Tiberg and Nordenskiöld investigated spodiosite, very little work has been done, and the temperature and pressure conditions under which it could be synthesized have not been defined. It cannot be obtained by heating batch materials in air. However, the chlor-analogue ($\text{Ca}_4\text{P}_2\text{O}_8\text{Cl}_2$) was prepared and studied by many investigators [6,7, 11].

Therefore, as far as the composition $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ is concerned in this study, it is a newly discovered phase, whose structure is unknown, but certainly different from that of the mineral spodiosite. However, it is very stable at 1200°C in a sealed platinum tube and can be obtained in a phase-pure form at room temperature. It

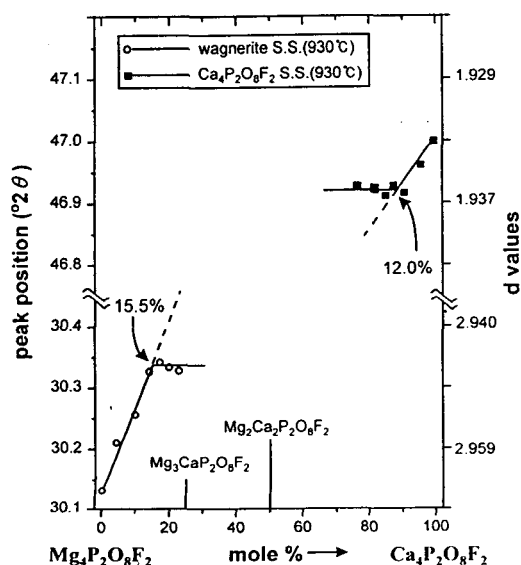


Fig. 1. Effect of Ca ion substitutions on the d-spacing values of Mg-wagnerites.

may be assumed that the composition $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ is a high temperature form of mineral spodiosite or a new compound. As shown in Figs. 1, 12 mole percent of magnesium was soluble in $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ at 930°C (sealed platinum tubes), causing a substantial expansion of the crystal lattice.

3.1.2. $\text{Co}_4\text{P}_2\text{O}_8\text{F}_2$

As shown in Fig. 2, approximately 30 mole percent of calcium was soluble in $\text{Co}_4\text{P}_2\text{O}_8\text{F}_2$, and about 10 mole percent of cobalt could be substituted for calcium in the new compound $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$. No intermediate compounds were found in this system. A mixture of $\text{Co}_4\text{P}_2\text{O}_8\text{F}_2$ and $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ crystalline solutions coexisted between 70 and 10 mole percent $\text{Co}_4\text{P}_2\text{O}_8\text{F}_2$. All compositions were prepared by heating a stoichiometric mixture of $(\text{Co,Ca})_3(\text{PO}_4)_2$

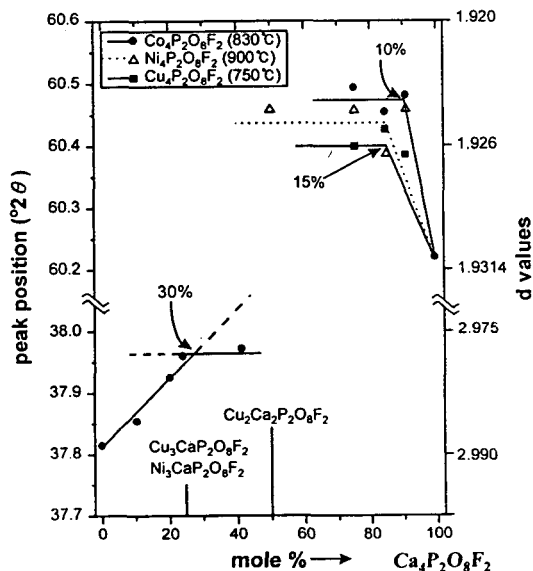


Fig. 2. Effect of Ca ion substitutions on the d-spacing values of (Co, Ni, Cu)-wagnerites.

and CoF_2 or CaF_2 at 830°C for 4 hours in sealed platinum tubes as shown in Table 1 and Table 2.

The presence of calcium in the cobalt wagnerite solid solutions contracted the lattice as expected, but the large contraction of the $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ solid solutions was completely unexpected and far different from the expansion obtained by the substitution of $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ with $\text{Mg}_4\text{P}_2\text{O}_8\text{F}_2$ (Fig. 1). The color changed from bright purple to light violet as the calcium content in $\text{Co}_4\text{P}_2\text{O}_8\text{F}_2$ increased.

3.1.3. $\text{Ni}_4\text{P}_2\text{O}_8\text{F}_2$

No solubility of calcium in $\text{Ni}_4\text{P}_2\text{O}_8\text{F}_2$ was found, but approximately 15 mole percent of nickel could be substituted for calcium in $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ at 900°C in sealed platinum tubes as shown in Table 2. One intermediate compound occurred at 25 mole percent of calcium ($\text{Ni}_3\text{CaP}_2\text{O}_8\text{F}_2$) when heated at 900°C for 4 hours in a sealed platinum tube. The x-ray analysis indicated that it was structurally similar to $\text{Ni}_3(\text{PO}_4)_2$ (prepared by heating a stoichiometric mixture of NiCO_3 and $(\text{NH}_4)_2\text{HPO}_4$ at $1140^\circ\text{C}/15$ hours in air), but it had certain of its own characteristic peaks. No starting materials or known phosphate compounds were present, and there was no coincidence with $\text{Mg}_3\text{CaP}_2\text{O}_8\text{F}_2$, $\text{Mg}_2\text{Ca}_2\text{P}_2\text{O}_8\text{F}_2$ or the mineral isokite.

When heat treated at 1000°C for 4 hours, $\text{Ni}_3\text{CaP}_2\text{O}_8\text{F}_2$ decomposed to $\text{Ni}_4\text{P}_2\text{O}_8\text{F}_2$ and $\text{Ni}_3\text{CaP}_2\text{O}_8\text{F}_2$. Between 100 and 75 mole percent of nickel, a mixture of Ni_4P_2

O_8F_2 and $\text{Ni}_3\text{CaP}_2\text{O}_8\text{F}_2$ coexisted, and between 75 and 15 mole percent a mixture of $\text{Ni}_3\text{CaP}_2\text{O}_8\text{F}_2$ and $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ coexisted at 900°C in sealed platinum tubes. Nickel contracted the lattice of $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ as shown in Fig. 2. A bright yellow color was characteristic of the intermediate compound ($\text{Ni}_3\text{CaP}_2\text{O}_8\text{F}_2$).

3.1.4. $\text{Cu}_4\text{P}_2\text{O}_8\text{F}_2$

No calcium was soluble in $\text{Cu}_4\text{P}_2\text{O}_8\text{F}_2$, whereas about up to 15 mole percent copper could enter $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ at 750°C in sealed platinum tubes as shown in Table 2. Two intermediate compounds were observed; the $\text{Cu}_3\text{CaP}_2\text{O}_8\text{F}_2$ compound of green color at 25 mole percent and the $\text{Cu}_2\text{Ca}_2\text{P}_2\text{O}_8\text{F}_2$ compound of greenish blue color at 50 mole percent of calcium at 750°C . As indicated in Table 2, the two intermediate compounds were stable at 750°C for either 4 or 48 hours. Both compounds formed the solid solutions of green or blue color with either side of the stoichiometric composition. The $\text{Ca}_4\text{P}_2\text{O}_8\text{F}_2$ lattice was less contracted by Cu^{2+} , relative to the cobalt and nickel crystalline solutions.

3.2. Substitution of lithium in the A^{2+} site of wagnerites ($A_2\text{XO}_4\text{Z}$)

3.2.1. $\text{Mg}_4\text{P}_2\text{O}_8\text{F}_2$

If lithium is substituted directly for magnesium in such a way as to preserve electrostatic neutrality, more than four cations would be available for the A^{2+}

site, and any solid solubility would require that lithium occupied an interstitial position, a very unlikely event. Therefore, Li_3PO_4 might be expected to form, as shown in Table 2. The wagnerite and Li_3PO_4 of white colors were in fact obtained, and it is not possible to make this type of substitution.

If lithium is substituted for magnesium so as to preserve a total of four atoms on the A site, halide vacancies would be required to preserve a charge balance. It must be assumed that no vacancies could be created in the network forming (O_8) oxygen sites.

If as many as two atoms of lithium could be substituted on the magnesium

site, this would produce the completely halide vacant wagnerite, $\text{Li}_2\text{Mg}_2\text{P}_2\text{O}_8\Box_2$. If half the halide sites were vacant, the formula would be $\text{LiMg}_3\text{P}_2\text{O}_8\text{F}\Box$. Actually, it was found that only 0.6 mole of Li^+ could be soluble giving a white compound of $\text{Li}_{0.6}\text{Mg}_{4.4}\text{P}_2\text{O}_8\text{F}_{1.4}\Box_{0.6}$ (Table 1).

3.2.2. $\text{Co}_4\text{P}_2\text{O}_8\text{F}_2$ and $\text{Ni}_4\text{P}_2\text{O}_8\text{F}_2$

About 0.6 mole of lithium could be substituted for Co-wagnerite, as shown in Table 1. The color of this compound was purple. Attempts to prepare the excess atom substitution were not successful. Also, approximately 0.6 mole of lithium was substituted in $\text{Ni}_4\text{P}_2\text{O}_8\text{F}_2$ and presented the yellow color, as shown in Table 1.

Table 1

Synthesis conditions and colors of wagnerites and associated solid solutions

Composition	Heat treatment (°C/hr)	Color	Composition	Heat treatment (°C/hr)	Color
$\text{Mg}_{3.8}\text{Ca}_{0.2}\text{P}_2\text{O}_8\text{F}_2$	930/15	white			
$\text{Mg}_{3.6}\text{Ca}_{0.4}\text{P}_2\text{O}_8\text{F}_2$	"	"	$\text{Co}_{3.6}\text{Ca}_{0.4}\text{P}_2\text{O}_8\text{F}_2$	830/4	purple
$\text{Mg}_{3.5}\text{Ca}_{0.5}\text{P}_2\text{O}_8\text{F}_2$	"	"	$\text{Co}_{3.4}\text{Ca}_{0.6}\text{P}_2\text{O}_8\text{F}_2$	"	"
$\text{Mg}_{3.4}\text{Ca}_{0.6}\text{P}_2\text{O}_8\text{F}_2$	"	"	$\text{Co}_{3.2}\text{Ca}_{0.8}\text{P}_2\text{O}_8\text{F}_2$	"	"
$\text{Mg}_{3.3}\text{Ca}_{0.7}\text{P}_2\text{O}_8\text{F}_2$	"	"	$\text{Co}_{3.0}\text{Ca}_{1.0}\text{P}_2\text{O}_8\text{F}_2$	"	"
$\text{Mg}_{3.0}\text{Ca}_{1.0}\text{P}_2\text{O}_8\text{F}_2$	1000/4	"	$\text{Co}_{2.0}\text{Ca}_{2.0}\text{P}_2\text{O}_8\text{F}_2$	"	"
$\text{Li}_{0.6}\text{Mg}_{3.4}\text{P}_2\text{O}_8\text{F}_{1.4}\Box_{0.6}$	930/4	white			
$\text{Li}_{0.6}\text{Co}_{3.4}\text{P}_2\text{O}_8\text{F}_{1.4}\Box_{0.6}$	620/3	purple			
$\text{Li}_{0.6}\text{Ni}_{3.4}\text{P}_2\text{O}_8\text{F}_{1.4}\Box_{0.6}$	620/3	yellow			
$\text{Mg}_4\text{P}_{1.6}\text{V}_{0.4}\text{O}_8\text{F}_2$	1050/4	white	$\text{Co}_4\text{P}_{1.6}\text{V}_{0.4}\text{O}_8\text{F}_2$	700/12	dark purple
$\text{Mg}_4\text{P}_{1.2}\text{V}_{0.8}\text{O}_8\text{F}_2$	"	"	$\text{Co}_4\text{P}_{1.2}\text{V}_{0.8}\text{O}_8\text{F}_2$	"	"
$\text{Ni}_4\text{P}_{1.6}\text{V}_{0.4}\text{O}_8\text{F}_2$	700/12	dark gold	$\text{Zn}_4\text{P}_{1.6}\text{V}_{0.4}\text{O}_8\text{F}_2$	700/12	light yellow
$\text{Ni}_3\text{MgP}_{1.6}\text{V}_{0.4}\text{O}_8\text{F}_2$	1050/4	"	$\text{Zn}_3\text{MgP}_{1.6}\text{V}_{0.4}\text{O}_8\text{F}_2$	800/6	"
$\text{Ni}_3\text{MgP}_{1.2}\text{V}_{0.8}\text{O}_8\text{F}_2$	"	"	$\text{Zn}_3\text{MgP}_{1.2}\text{V}_{0.8}\text{O}_8\text{F}_2$	"	"

3.3. Substitution of vanadium in the X^{5+} site of wagnerites (A_2XO_4Z)

3.3.1. $Mg_4P_2O_8F_2$

As shown in Table 1, about 40 mole percent of V^{5+} can be substituted for P^{5+} in $Mg_4P_2O_8F_2$, resulting in white compounds. The sample was prepared by heating a stoichiometric mixture of $Mg_3(P, V)_2O_8$ and MgF_2 at 1050°C for 4 hours in a sealed platinum tube. An attempt was made to prepare a completely substituted vanadium wagnerite, but $Mg_3(VO_4)_2$ and an unidentified phase were formed.

3.3.2. $Co_4P_2O_8F_2$

About 40 mole percent of P^{5+} could be substituted by V^{5+} by heating a mixture of $Co_3(P, V)_2O_8$ and CoF_2 at 700°C for 12 hours and the compounds of dark purple color were obtained, as shown in Table 1. Attempts to prepare an all-vanadium wagnerite in black color were unsuccessful, as were attempts to prepare other solid solutions by heating a mixture of $Co_3(P, V)_2O_8$ and MgF_2 at 600°C for 4 hours, as shown in Table 2.

3.3.3. $Ni_4P_2O_8F_2$

Heating a mixture of $Ni_3(P, V)_2O_8$ and NiF_2 or a mixture of $Ni_3(P, V)_2O_8$ and MgF_2 yielded wagnerite solid solutions containing up to 40 mole percent vanadium, when heat treated at 700°C for 12 hours and at 1050°C for 4 hours, respectively.

These solid solutions produced a dark gold color, as shown in Table 1. Attempts

to prepare an all-vanadium wagnerite were unsuccessful, as were attempts to prepare other solid solutions, as shown in Table 2.

3.3.4. $Cu_4P_2O_8F_2$ and $Zn_4P_2O_8F_2$

All attempts to prepare $Cu_3MgV_2O_8F_2$ and $Cu_4V_2O_8F_2$ were unsuccessful, as shown in Table 2. For the case of $Zn_4P_2O_8F_2$, about 40 mole percent of P^{5+} could be substituted by V^{5+} by heat treating a mixture of $Zn_3(P, V)_2O_8$ and ZnF_2 or MgF_2 at 700°C for 12 hours and at 800°C for 6 hours, respectively. The compounds of light yellow color were obtained, as shown in Table 1. Attempts to make a complete vanadium substitution and other solid solutions with $Zn_4P_2O_8F_2$ were not successful, as indicated in Table 2.

3.4. Substitution of chloride in the Z^- site of wagnerites (A_2XO_4Z)

Attempts to prepare $Mg_4P_2O_8Cl_2$ by heating a stoichiometric mixture of $Mg_3(PO_4)_2$ and $MgCl_2$ in sealed platinum tubes and in air at various temperatures were not successful, resulting in the white compound mixed with several phases, as shown in Table 3. Other attempts using excess NH_4Cl with the stoichiometric mixture, also, were not successful. Klement et al. [12] claimed that a $Mg_4P_2O_8Cl_2$ wagnerite could be made, but this could not be substantiated in this work. A partial substitution of chlorine for fluorine may be possible, of course.

Table 2

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

Composition	Heat treatment (°C/hr)	Color	Phases
Ca substitution			
$Mg_{3.2}Ca_{0.8}P_2O_8F_2 \sim Mg_{2.4}Ca_{1.6}P_2O_8F_2$	930/15	white	$Mg_3CaP_2O_8F_2$, $Mg_2Ca_2P_2O_8F_2$, wagnerite
$MgCa_3P_2O_8F_2 \sim Mg_{0.6}Ca_{3.4}P_2O_8F_2$	930/15	white	$Mg_2Ca_2P_2O_8F_2$, $Ca_4P_2O_8F_2$
$Co_{2.0}Ca_{2.0}P_2O_8F_2 \sim Co_{0.4}Ca_{3.6}P_2O_8F_2$	830/4	purple or violet	$Ca_4P_2O_8F_2$, wagnerite
$Ni_{3.6}Ca_{0.4}P_2O_8F_2 \sim Ni_{0.4}Ca_{3.6}P_2O_8F_2$	1000/4	orange or yellow	$Ni_3CaP_2O_8F_2$, $Ca_4P_2O_8F_2$, wagnerite
$Cu_{3.6}Ca_{0.4}P_2O_8F_2 \sim Cu_{0.4}Ca_{3.6}P_2O_8F_2$	750/4	green	$Cu_3CaP_2O_8F_2$, $Ca_4P_2O_8F_2$, $Cu_2Ca_2P_2O_8F_2$, wagnerite
Li substitution			
$Mg_{3.4}Li_{1.2}P_2O_8F_2 \sim MgLi_6P_2O_8F_2$	950/4 700/24	white	wagnerite, $Li_3(PO_4)$, $Mg_3(PO_4)_2$
$Co_{2.4}Li_{1.2}MgP_2O_8F_2 \sim Co_{0.6}Li_{4.8}MgP_2O_8F_2$	630/4	purple	wagnerite, $Li_3(PO_4)$
$Ni_{1.6}Li_{2.4}MgP_2O_8F_2 \sim Ni_{0.6}Li_{4.8}MgP_2O_8F_2$	950/4	yellow	$Ni_3(PO_4)_2$
V substitution			
$Mg_4P_{0.8}V_{1.2}O_8F_2 \sim Mg_4P_{0.4}V_{1.6}O_8F_2$	1050/4	white	wagnerite, unknown
$Co_3MgP_{1.6}V_{0.4}O_8F_2 \sim Co_3MgP_{0.4}V_{1.6}O_8F_2$	600/4	black	$Co_3(VO_4)_2$, unknown
$Co_3MgV_2O_8F_2$	700~900/12~4	black	$Co_3(VO_4)_2$, unknown
$Ni_3MgP_{0.8}V_{1.2}O_8F_2 \sim Ni_3MgP_{0.4}V_{1.6}O_8F_2$	1050/4	yellow	wagnerite, unknown
$Cu_3MgV_2O_8F_2 \sim Cu_4V_2O_8F_2$	700~900/4~12	black	unknown
$Zn_3MgP_{0.8}V_{1.2}O_8F_2 \sim Zn_3MgP_{0.4}V_{1.6}O_8F_2$	800/6	light yellow	wagnerite, $Zn_3(VO_4)_2$

As listed in Table 3, attempts to synthesize $Co_4P_2O_8Cl_2$, $Ni_4P_2O_8Cl_2$, $Cu_4P_2O_8Cl_2$ and $Zn_4P_2O_8Cl_2$ wagnerites were made, but failed to form the single phase of wagnerite, in spite of the claim of success by Klement et al. [12]. Generally an unknown phase was formed with the wagnerite and the colors of compounds were not bright and intense.

4. Conclusions

Ca-wagnerite was synthesized by heating a stoichiometric mixture of $Ca_3(PO_4)_2$ and CaF_2 in a sealed platinum tube at 1130°C for 4 hours. The limited solubilities between Ca-wagnerite and Mg-wagnerite were observed; 12 mole percent of Mg and 15.5 mole percent of Ca were soluble

Table 3
Synthesis conditions that the single phase of wagnerite was not formed by the Cl-substitutions

Composi- tion	Heat treatment (°C)	Color	Phases
Mg ₄ P ₂ O ₈ Cl ₂	300~1130	white	wagnerite Mg ₃ (PO ₄) ₂ unknown
Co ₄ P ₂ O ₈ Cl ₂	300~1000	dirty purple	unknown
Ni ₄ P ₂ O ₈ Cl ₂	300~1000	dirty yellow	unknown
Cu ₄ P ₂ O ₈ Cl ₂	300~1000	light green	wagnerite unknown
Zn ₄ P ₂ O ₈ Cl ₂	180~300	greyish white	wagnerite unknown

in either wagnerite, resulting in white color. The limited amount of cobalt, nickel and copper were solved in Ca-wagnerite whereas no calcium was soluble in Ni₄P₂O₈F₂ and Cu₄P₂O₈F₂.

By the limited substitutions of calcium, Mg-wagnerite of white color and Co-wagnerite of purple color were obtained at 930°C for 15 hours and 830°C for 4 hours, respectively. Also, wagnerites of same color were synthesized by the lithium substitution of 0.6 mole.

By the vanadium substitutions, Co-wagnerite showed dark purple color and Ni-wagnerite dark gold color whereas the color of Zn-wagnerite became light yellow. Generally, the attempts to synthesize wagnerite by the substitution of chlorine

for fluorine were not successful and resulted in mixed-phase compounds.

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