Journal of Korean Association of Crystal Growth
Vol. 7, No. 4 (1997) 640-647

Synthesis of wagnerite and its analogues for ceramic pigments (I)

Yong-Sun Chung and Keun Ho Auh
Ceramic Processing Research Center (CPRC), Hanyang University, Seoul 133-791, Korea

도자기 유약용 Wagnerite의 합성(I)

정용선, 오근호
한양대학교 세라믹공정연구센터, 서울, 133-791

Abstract Wagnerite(Mg_2PO_4F) was successfully synthesized in a sealed platinum tube and the complete substitutions of Co^{++}, Ni^{++}, Cu^{++} and Zn^{++} for Mg were made in the wagnerite structure. Wagnerite did not decompose until it reached its melting temperature. It was observed that wagnerite underwent only one inversion at 1255℃, prior to melting at 1340℃. The lattice parameters of wagnerites were linearly increased by the substitutions of Co^{++} and Zn^{++}, and decreased by the substitutions of Ni^{++} and Cu^{++}. The substitutions of wagnerite with Co^{++}, Ni^{++} and Cu^{++} resulted in purple, orange and green colors, respectively. The colors of pigments became more intense and suitable for coloring of glazes and plastics as the amount of metal ions increased.

요 약 백금밀폐용기를 사용하여 wagnerite(Mg_2PO_4F)를 합성하는데 성공하였으며, 유약용 안료로 사용하기에 적합한 발색을 위해 Co^{++}, Ni^{++}, Cu^{++} 등을 첨가하여 wagnerite의 Mg와 금속이온간의 전 성분구간에 걸쳐 고용체(solid solution)을 합성하였다. wagnerite는 용융점(1340℃)에 도달할 때까지 안정하여서 열분해되지 않았으며, 용융전에 오직 한 번의 가역적인 상전이가 1255℃에서 일어남을 관찰하였다. wagnerite의 격자상수는 금속이온의 첨가량에 비례하여 직선적으로 변화하였는데 Co^{++}와 Zn^{++} 첨가시는 증가하였으며, Ni^{++}과 Cu^{++}를 첨가한 경우에는 감소하였다. 또한 금속이온 첨가시, Co^{++}는 자주색, Ni^{++}는 노란색, Cu^{++}는 녹색을 발현시켰으며 이들의 색조는 첨가량이 증가할수록 밝고 진하여져서 유약 및 플라스틱을 착색하기에 적합한 색상을 나타내었다.

1. Introduction

The type mineral wagnerite, $Mg_2(PO_4)F$, was first found in quartz veins transversing clay slates at Hollgraben near Warfen and at Radelgraben near Bischofshofen in Salzburg [1] and named after F.M. von Wagner, a german mining engineer. Strictly speaking, the name wagnerite applies only to the compound $Mg_2(PO_4)F$, but this term has been applied to any substance with the general composition A_2XO_4Z, where A, X and Z normally have +2, +5 and −1 charges, respectively. Therefore, the mineral wagnerite is a very interesting compound because there are many possible substitutions which may be made into the structure. Compounds with the type formula A_2XO_4Z have been systematically studied in classifying phosphate, arsenate and vanadate minerals [2].

Figure 1 shows the connections among the eight nonequivalent Mg-atoms surrounded by the O- and F-atoms. Two types of magnesium atoms are found in Fig. 1; one is five-coordinated (=Mg_1, Mg_3, Mg_5, Mg_7) in trigonal bipyramids, and the other is six-coordinated (=Mg_2, Mg_4, Mg_6, Mg_8) in octahedra.

Each of the trigonal bipyramids shares one edge with a similar polyhedron, except the Mg_3 trigonal bipyramid, which shares one edge with a Mg_4 octahedron. Each of the octahedra shares three edges with as many octahedra, except the octahedron Mg_4 which shares one edge with Mg_3 trigonal bipyramid. The Mg_1 trigonal bipyramid as well as the Mg_2 octahedron share one edge with the centrosymmetric equivalent polyhedra. Each O-atom is shared by one tetrahedron and two Mg-polyhedra. Although it is not shown in Fig. 1, all the oxygens are coodinated by phosphorus. Each F-atom is at the common corner of three Mg-polyhedra [3].

Wagnerite is known to be very stable up to its melting point and 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 was to study the crystal chemistry and the color variation of wagnerite by the addition of metal ions, particularly with respect to ions such as Co^{++}, Ni^{++} and Cu^{++}, which may lead to crystals with unusual colors [4-6].

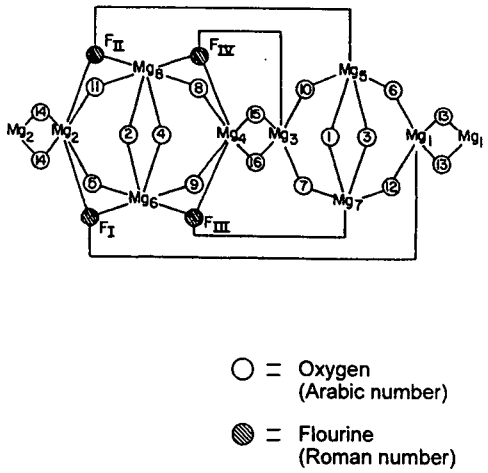

Fig. 1. Schematic diagram of the bonding structure among Mg-atoms (after Coda et al. [3]).

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.

Phase analyses were made primarily with a Norelco wide-range diffractometer using Ni-filtered Cu Kα radiation in the 2θ range 10°-65° and for compounds containing Co^{+2}, Ni^{+2} or Cu^{+2}, Mn-filtered Fe Kα radiation was employed in the 2θ range 20° −75°, at a scanning rate of 2°/mim. 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 2θ.

In order to study the thermal properties of wagnerites, 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 petrographic microscope was used to examine impurities and to analyze the optical properties of wagnerites.

3. Results and discussion

3.1. Synthesis of wagnerites

Synthesis of wagnerite is difficult due to fluorine volatilization at temperatures above 800℃, but several investigators [7-10] claimed to have prepared it in air. In this investigation several techniques for the synthesis were attempted as follows.

In the first attempt, a stoichiometric mixture of $MgCO_3 \cdot Mg(OH)_2$, $(NH_4)_2HPO_4$ and MgF_2 was heated 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. X-ray analysis indicated that wagnerite and unknown phases were present. After heating in air at 1130℃ for one-half hour, wagnerite and MgO were observed.

A second attempt was made using $Mg_3(PO_4)_2$ and MgF_2 and heating to 1025℃ for one-half hour in air. Wagnerites and a trace of $Mg_3(PO_4)_2$ were identified by X-ray analysis. When heated in air at 1100℃ for 3 hours, the product consisted of wagnerite and a trace of MgO. Using this technique, about a 95 percent yield of wagnerite could be obtained; however, it was not possible to obtain pure wagnerite. It was obvious from these two experiments that $Mg_3(PO_4)_2$ or MgO would be present and persist in samples heated at high temperatures in air and that the fluorine vaporized.

Finally, wagnerites were prepared by heating the stoichiometric mixtures of $Mg_3(PO_4)_2$ and MgF_2 in the sealed platinum tubes at 850℃ for 3 hours, 930℃ for 15

hours, 1000℃ for 4 hours, 1040℃ for 3 hours and 1100℃ for 4 hours. X-ray analyses showed that each heat treatment had produced phase pure wagnerites. The X-ray powder diffraction pattern for a wagnerite prepared at 1040℃ for 3 hours is listed in Table 1. This pattern was used as a standard throughout this investigateon, although it did not coincide exactly with the A.S.T.M pattern given for the mineral wagnerite by Henriques [11].

The claims of Winter [9] and Berak et al. [10] for several inversions in wagnerite were not well-documented. Therefore, DTA runs were done on well-crystallized materials previously prepared in platinum

Table 1
X-ray powder diffraction data for synthetic wagnerites

hkl	Mg_2PO_4F			Co_2PO_4F			Ni_2PO_4F			Cu_2PO_4F			Zn_2PO_4F		
	d_{calc}	d_{meas}	I/I_0	d_{calc}	d_{meas}	I/I_0	d_{calc}	d_{meas}	I/I_0	d_{calc}	d_{meas}	I/I_0	d_{calc}	d_{meas}	I/I_0
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	3.328	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		
$\bar{4}01$	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			2.746	2.740	23	2.800			2.779		
$\bar{2}41$	2.764			2.785	2.784	26	2.745			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

tubes. The runs were made in two different types; one in the sealed platinum tube (one-eight-inch diameter) and the other in nitrogen atmosphere. First, the sample of wagnerite and the alumina reference were each sealed in a platinum tube, thus preventing the fluorine volatilization from the wagnerite. Under these conditions, a small but distinct heat effect was noticed at 1255℃ during heating and cooling, and melting took place at 1340±5℃ which was in excellent agreement with the 1337℃ reported by Berak [10]. Secondly, runs were also made in nitrogen and in each case, during heating and cooling, the inversion was observed at 1255℃. All samples from the DTA runs were examined by X-ray diffraction and found to be a wagnerite. No decomposition had taken places in any of the runs. Therefore, due to its thermal stability, wagnerites can be used as pigments for ceramic glazes and plastics by the addition of metal elements such as Co^{++}, Ni^{++}, Cu^{++} etc. As a further check on the polymorphism, a wagnerite crystalline solution containing a 15 mole percent substitution of Co^{++} for Mg^{++} inverted at 1235℃ in a sealed platinum tube. It was concluded that wagnerite underwent only one inversion, at 1255℃, prior to melting at 1340℃. The lattice parameters of natural [12] and synthetic wagnerites produced by this study were listed in Table 2.

3.2. Effect of metal ion substitution on the color of wagnerite

3.2.1. Cobalt substitution

As shown in Table 3, the complete series of crystal solution between $Mg_4P_2O_8F_2$ and $Co_4P_2O_8F_2$ can be prepared by heating at 850℃ for 3 hours in sealed platinum tubes, starting with $(Mg,Co)_3(PO_4)_2$ and MgF_2 or CoF_2. Wagnerite could be obtained by heating at 900℃ for 6 hours, but at 1000℃ for 24 hours wagnerite and unidentified phases were present.

The purple color of the crystal solution became more intense as the composition approached the pure cobalt wagnerite. Figure 2 shows the magnitude of the lattice expansion as Mg^{++} is substituted with Co^{++}. These X-ray powder diffraction data and the lattice parameters for $Co_4P_2O_8F_2$ are shown in Table 1 and Table 2, respectively, which were obtained with Fe Kα radiation.

Attempts to prepare a cobalt wagnerite or intermediate members of the crystal solution series by heating a mixture of $(Mg,Co)_3(PO_4)_2$ and MgF_2, or $MgCO_3\,Mg(OH)_2$, $CoCO_3$, $(NH_4)_2HPO_4$ and MgF_2, at 715℃ for 12 hours, 1020℃ for 4 hours and 1180℃ for one-half hour in air were unsuccessful. The reaction generally yielded $Co_3(PO_4)_2$, MgO, CoO and unknown phases.

3.2.2. Nickel substitution

As shown in Table 3, the series of solid solution between $Mg_4P_2O_8F_2$ and $Ni_4P_2O_8F_2$ can be prepared by heating a mixture of $(Mg,Ni)_3(PO_4)_2$ and MgF_2 or NiF_2 in sealed platinum tubes at 1080℃ for 3 hours. The solid solutions were stable if

heated to 1200℃ for 4 hours, but higher temperatures or longer times produced wagnerite and secondary phases. Synthesis of the solid solutions in air was not successful.

The color changed from pale orange to orange as the amount of nickel was increased, and as shown in Fig. 2, a substantial contraction of the lattice occurred. X-ray data and the lattice parameters for

Table 2
Lattice parameters of natural and synthetic wagnerites

	a(Å)	b(Å)	c(Å)	β
Natural				
Sheridan et al.	11.929	12.698	9.633	108° 12′
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°

Table 3
Synthesis conditions and colors of Mg-wagnerite and associated solid solutions

Composition	Heat treatment (℃/hr)	Color	Composition	Heat treatment (℃/hr)	Color
$Mg_4P_2O_8F_2$	1100/4	white			
$Mg_{3.4}Co_{0.6}P_2O_8F_2$	850/3	light purple	$Mg_{3.4}Ni_{0.6}P_2O_8F_2$	1080/3	pale orange
$Mg_{2.8}Co_{1.2}P_2O_8F_2$	〃	〃	$Mg_{2.8}Ni_{1.2}P_2O_8F_2$	〃	〃
$Mg_{2.2}Co_{1.8}P_2O_8F_2$	〃	purple	$Mg_{2.2}Ni_{1.8}P_2O_8F_2$	〃	orange
$Mg_{1.6}Co_{2.4}P_2O_8F_2$	〃	〃	$Mg_{1.6}Ni_{2.4}P_2O_8F_2$	〃	〃
$Mg_{1.0}Co_{3.0}P_2O_8F_2$	〃	〃	$Mg_{1.0}Ni_{3.0}P_2O_8F_2$	〃	〃
$Co_{0.6}P_2O_8F_2$	〃	〃	$Ni_{0.6}P_2O_8F_2$	1100/4	〃
$Mg_{3.4}Cu_{0.6}P_2O_8F_2$	870/1	pale green	$Mg_{3.4}Zn_{0.6}P_2O_8F_2$	800/6	white
$Mg_{2.8}Cu_{1.2}P_2O_8F_2$	〃	light green	$Mg_{2.8}Zn_{1.2}P_2O_8F_2$	〃	〃
$Mg_{2.2}Cu_{1.8}P_2O_8F_2$	〃	〃	$Mg_{2.2}Zn_{1.8}P_2O_8F_2$	〃	〃
$Mg_{1.6}Cu_{2.4}P_2O_8F_2$	〃	〃	$Mg_{1.6}Zn_{2.4}P_2O_8F_2$	〃	〃
$Mg_{1.0}Cu_{3.0}P_2O_8F_2$	850/1.5	green	$Mg_{1.0}Zn_{3.0}P_2O_8F_2$	〃	〃
$Cu_{0.6}P_2O_8F_2$	810/4	〃	$Zn_{0.6}P_2O_8F_2$	850/3	〃

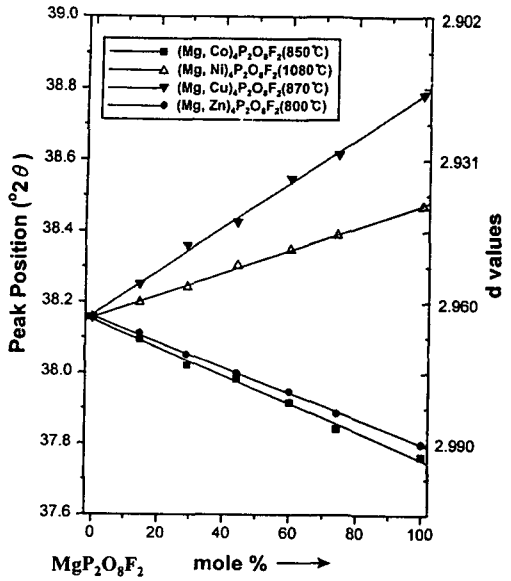

Fig. 2. Effect of metal ion substitutions on the d-spacing values of wagnerites.

$Ni_4P_2O_8F_2$ are listed in Table 1 and Table 2, respectively.

3.2.3. Copper substitution

Like cobalt and nickel, the complete solid solution series between $Mg_4P_2O_8F_2$ and $Cu_4P_2O_8F_2$ was prepared by heating a mixture of $(Mg,Cu)_3(PO_4)_2$ and MgF_2 or CuF_2 in sealed platinum tubes at 870℃ for 1 hour, as shown in Table 3. The series could be obtained by heating at 850℃ for 1.5 hours. However, at 1000℃ for 4 hours wagnerite and unknown phases were present.

The bright green color became more intense as the amount of copper was increased. When the copper wagnerites were heat treated at higher temperatures or longer times than the optimum, the color changed from green to light brownish grey, indicating reduction of Cu^{++} to Cu^{+}. Attempts to prepare the solid solutions series in air were not successful.

As shown in Fig. 2, the magnitude of the lattice contraction was greatest as Mg^{++} was substituted by Cu^{++}. X-ray powder data and the lattice parameters for $Cu_4P_2O_8F_2$ are listed in Table 1 and Table 2, respectively.

3.2.4. Zinc substitution

As shown in Table 3, a complete solid solution series between $Mg_4P_2O_8F_2$ and $Zn_4P_2O_8F_2$ was prepared by heating a stoichiometric mixture of $(Mg,Zn)_3(PO_4)_2$ and MgF_2 or ZnF_2 at 800℃ for 6 hours in sealed platinum tubes. Heating at 1100℃ for 1 hour produced $Mg_3(PO_4)_2$ and $Zn_3(PO_4)_2$ as major phases. Synthesis of the solid solution in air was not successful.

Figure 2 shows that zinc substitutions expand the lattice in a manner almost identical to cobalt substitutions. X-ray diffraction data and the lattice parameters for $Zn_4P_2O_8F_2$ using Cu Kα radiation are listed in Table 1 and Table 2, respectively.

4. Conclusions

Phase-pure wagnerites were synthesized by heating a stoichiometric mixture of $Mg_3(PO_4)_2$ and MgF_2 at 1040℃ for 3 hours. Generally, it was necessary to use a sealed platinum tube for the synthesis of wagnerites. Contrary to the several inver-

sions reported by other investigators, only one reversible inversion was observed at 1255℃.

The complete series of solid solution between Mg-wagnerite and divalent metal ions(Co^{++}, Ni^{++}, Cu^{++} and Zn^{++}) were obtained by heating at the temperature between 850℃ and 1100℃, depending on their compositions. The substitution of cobalt resulted in the increase of lattice parameters and the intense purple color. The substitution of nickel decreased the lattice parameters and the orange color became more intense as the amount of nickel was increased. The lattice parameters of wagnerite were contracted by the substitution of copper and the green color became brighter and more intense. The substitution of zinc expanded the lattice parameters of wagnerite. However, the color of wagnerite was not affected by the zinc substitution. As a result, the substitutions of metal ions (Co^{++}, Ni^{++}, and Cu^{++}) were effective on the synthesis of wagnerite pigments for glazes and plastics.

Acknowledgement

The authors would like to thank to the YoungDo Research Institute for their partial support during the course of this work.

References

[1] J.N. Fuchs, J. Chemie U. Phys. 33 (1821) 269.

[2] W.E. Richmond, Am. Min. 25 (1940) 441.

[3] A. Coda, G. Giuseppetti and C. Tadini, Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis. Mat. Natur. 43 (1967) 212.

[4] K.K. Kvyatkovskaya, A.G. Zazhigin and E.S. Kosorukova, Steklo Keram. 4 (1987) 21.

[5] T.D. Wise, S.H. Murdock and R.A. Eppler, Ceram. Eng. Sci. Proc. 12 (1991) 275.

[6] S. Djambazov and R. Nikolov, World Cong. Ceram. Tile Qual. (1994) 136.

[7] J.R. Mourelo, Rev. Gen. Sci. 26 (1940) 394.

[8] N.A. Gorbacheva, Izvest. Akad. Nauk SSSR, 23 (1959) Ser. Fiz. 1310.

[9] H. Winter, Leipzing (1913) [International Critical Tables 4 (1928) 62].

[10] J. Berak and I. Tomczak, Roczniki Chem. 39 (1965) 519.

[11] A. Henriques, Arkiv. Mineral Geol. 2 (1957) 149.

[12] D.M. Sheridan, S.P. Marsh, M.E. Mrose and R.B. Taylor, Can. Mineral. 10 (1971) 919.