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Characteristics of crystals precipitated in sintered apatite/wollastonite glass ceramics

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Abstract

In this paper, apatite/wollastonite (A/W) glass ceramics were obtained by sintering the A/W glass powder compact at 1200°C. XRD, TEM and EDX were used to identify the crystalline phase and determine the chemical composition. The results showed that, the precipitated crystals at 1200°C were wollastonite and whitlockite. The sintered A/W glass ceramics consisted of crystalline phases, while glass matrix was found on the grain boundary. Whitlockite crystal showed a hexagonal morphology, while wollastonite exhibited a column shape. The two crystals were non-stoichiometic, and certain amounts of Mg and Si were found in wollastonite and whitlockite. The existence of Si in whitlockite caused an increment in lattice volume while Mg did not change the lattice parameter of wollastonite due to different ion radius. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

In 1982, Kokubo et al. developed a material, an apatite/wollastonite containing glass ceramic (A/W glass ceramic), in the MgO–CaO–SiO_2–P_2O_5 system. [1] The glass ceramic can form a tight chemical bond with bone and produce a high mechanical strength [2–4]. Moreover, after heat treatment, fine crystals such as apatite, wollastonite and whitlockite will precipitate from the glass matrix [5,6]. The crystals can enhance the mechanical strength and even promote the bioactivity of the glass ceramic. Owing to such properties, A/W glass ceramic is used in clinic, either in powder form as bone filler or in bulk material for prosthetic applications [7,8]. The types of crystals formed in the glass matrix are determined by the heat treatment and glass composition. Slight changes in both of these cause different results. Optical microscopy (OM) and scanning electron microscopy (SEM) have been used to observe the crystal morphology, yet a detailed profile of these crystals has not been obtained.

In the present study, A/W glass ceramic was prepared by sintering glass powder compacts at 1200°C. X-ray diffractometer (XRD) analysis was used to identify the phase composition. Transmission electron microscopy (TEM) was used to observe the morphologies of precipitated crystals and energy disperse X-rays (EDX) were employed to analyze the chemical composition.

2. Experimental procedure

A batch of mixture of composition of SiO_2 34.2, MgO 4.6, CaO 44.9, P_2O_5 16.3 and CaF_2 0.5 in weight ratio was melted in an alumina crucible at 1450°C for 1 h. The raw materials used in the experiment are listed in Table 1. The melted glass was quenched in distilled water. After drying, the quenched glass was pulverized in an alumina ball mill for 72 h to achieve a grain size of −400 mesh. Chemical analyses werce made to check the composition. The obtained glass powder, mixed with

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distilled water in 10:1 weight ratio, was pressed into a disc 40 mm in diameter and 4 mm in thickness at a pressure of 0.5 MPa and then isostatically pressed at a pressure of 2 MPa. The glass powder compact was placed in a SiC furnace, and then heated up to 1200°C at a rate of 5°C min^{-1} for 2 h and then taken out of the furnace to cool in an ambient atmosphere.

Crystalline phases precipitated in the sintering process were identified using an X-ray diffractometer at 35 Kv and 25 mA. Scans were run from 10° to 80° 2θ at a speed of 2° min^{-1} and a step of 0.02° using Cu K_α X-rays of wavelength 1.5405 Å.

Observation of the morphologies of crystals generated in the sintered A/W glass ceramics were conducted employing TEM. Samples for TEM observation were machined into thin section of 3 mm in diameter and 30 μm in thickness, then ion-milled to a thickness of 100 nm. EDX was employed to analyze the chemical composition of the crystals observed in the sintered A/W glass ceramics. The crystal structures were determined by electron diffraction.

3. Results and discussion

3.1. Chemical composition

Chemical analysis of A/W glass powder is shown in Table 2. The composition for powder A is what we designer in the experiment, while the composition B is the results we got by chemical analysis. It is obvious that a certain amount of alumina was introduced to the glass powder due to manufacturing process. Omitting the alumina content, when we re-calculate the weight percentages of other oxides, they are close to what we expected, as composition C shown in Table 2.

Table 1
Raw material used for preparation of A/W glass ceramic powder[a]

Raw materials	SiO_2	$Mg(NO_3)_2{\cdot}6H_2O$	$CaCO_3$	$NH_4H_2PO_4$	CaF_2
Weight (g)	342	294.9	801.8	264	5

[a] Calculated according to 100g glass powder.

Table 2
Chemical composition of A/W powder obtained from ball milling process (wt.%)

Oxides	Comp. A (theoretically)	Comp. B experimentally	Comp. C (omitting Al_2O_3)
CaO	44.9	45.84	46.32
SiO_2	34.2	33.29	33.64
P_2O_5	16.3	15.63	15.79
MgO	4.6	4.21	4.25
CaF_2	0.5	–	–
Al_2O_3	–	1.03	–

3.2. Phase identification

Fig. 1a shows the XRD result of sintered A/W glass ceramics. The XRD pattern reveals a composite of glass and crystal phases. It can be seen from the flat baseline that, the content of glass phase is low. The sintered A/W glass ceramics mainly consists of crystal phases. Fig. 1b reveals the phase analysis result. The crystal phases precipitated in the sintered glass ceramics are identified as wollastonite (calcium silicate) and whitlockite (calcium phosphate) according to JCPDS card 9-169 and 29-372. Be contrast with the report of Kokubo et al. [5], apatite is not generated. The difference was caused by the different sintering process. It was reported in document [1] that, when heat-treated, the glass ceramic will precipitate apatite/wollastonite and wollastonite/whitlockite at 880 and 1100°C, respectively. The fact that Kokubo et al. obtained samples containing apatite by sintering A/W glass ceramic compacts at 1200°C with a rate of 1°C min^{-1} indicated that, apatite will probably generate when treated at a relatively slow rate. However, in our case, the compacts were sintered at a rate of 5°C min^{-1}, 5 times that of Kokubo. At such a rate, there is not enough time for apatite to precipitate from the compact.

3.3. TEM morphology and crystalline composition

TEM morphologies and related electron diffraction results are shown in Fig. 2. It can be seen from Fig. 2 that, the A/W glass ceramics sintered at 1200°C are dense and no pores exist in the micrograph. Moreover, consistent with the results of XRD analysis, the sintered A/W glass ceramics consisted mainly of crystal phases, the residual glass matrix locating on the grain boundary was hard to observe. Fig. 2a reveals the morphology for the precipitated whitlockite. Two hexagonal crystals (grain A and grain B) are clear in the micrograph. The electron diffraction pattern of grain A is shown in Fig. 2b. The pattern reveals a hexagonal structure and the crystal is identified as whitlockite. Fig. 2c shows precipitated crystals with column shape. Fig. 2d shows the electron diffraction pattern of grain C in the micrograph. The crystal is of triclinic structure and identified as wollastonite. Moreover, the glass matrix at the grain boundary is also observed. Fig. 2e shows a higher resolution image of glass matrix area in Fig. 2a. The electron diffraction pattern of area D is shown in Fig. 2f revealing the amorphous structure of the glass matrix.

EDX analyses of the phases in Fig. 2 are shown in Fig. 3. The chemical compositions of the oxides are listed in

Table 3. Although the data from EDX are not precise, however, it can be seen from the results that, all the crystals are found to be non-stoichiometic. The peak of Si in the EDX pattern for whitlockite (as shown in Fig. 3a) implies that a certain amount of Si enters the crystal structure. Also, Mg is found to enter the crystal structure of wollastonite. The residual glass matrix consists of Al_2O_3–SiO_2–P_2O_5 glass, suggesting that Al_2O_3 introduced by long time milling has no obvious effect on crystal formation.

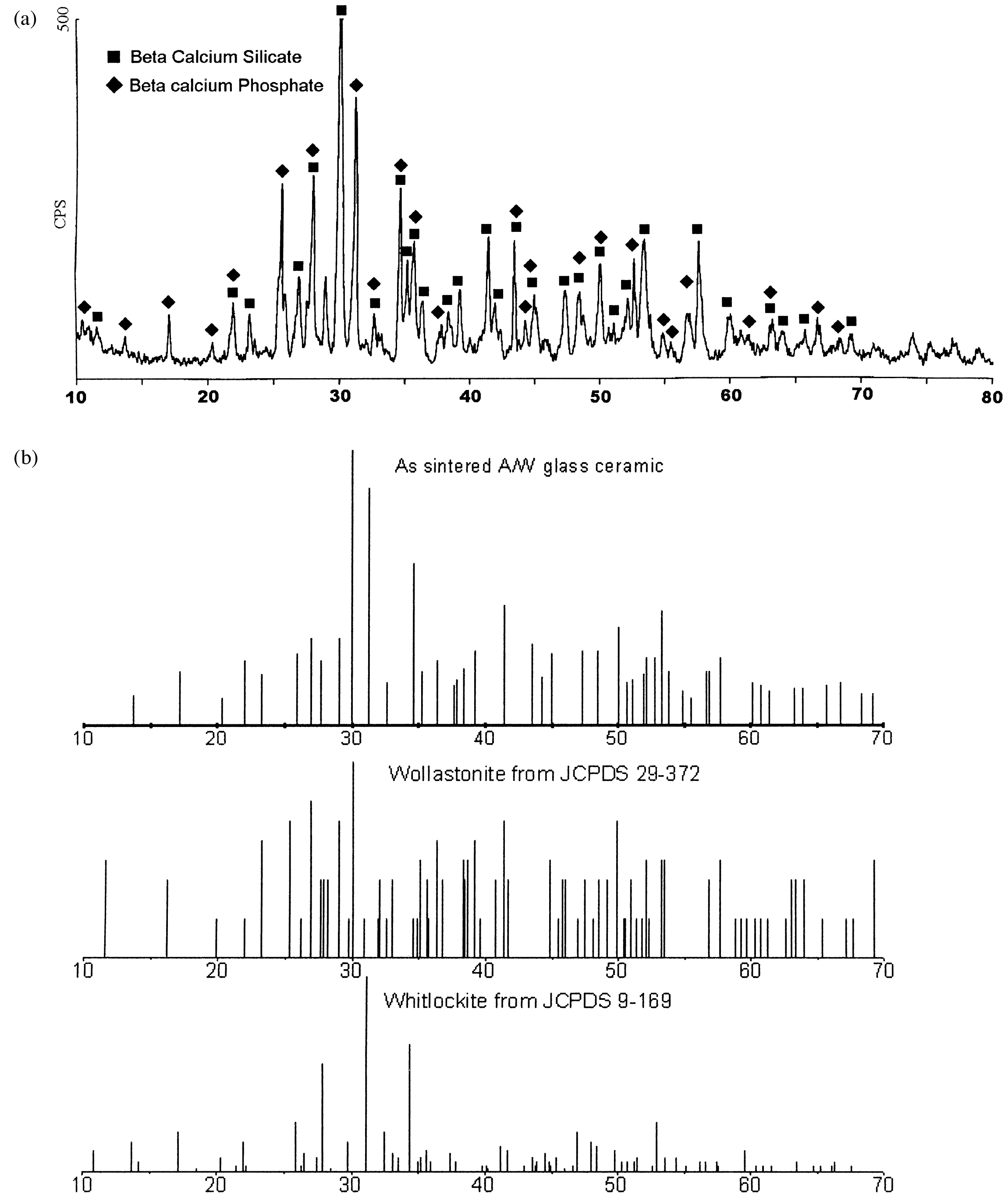
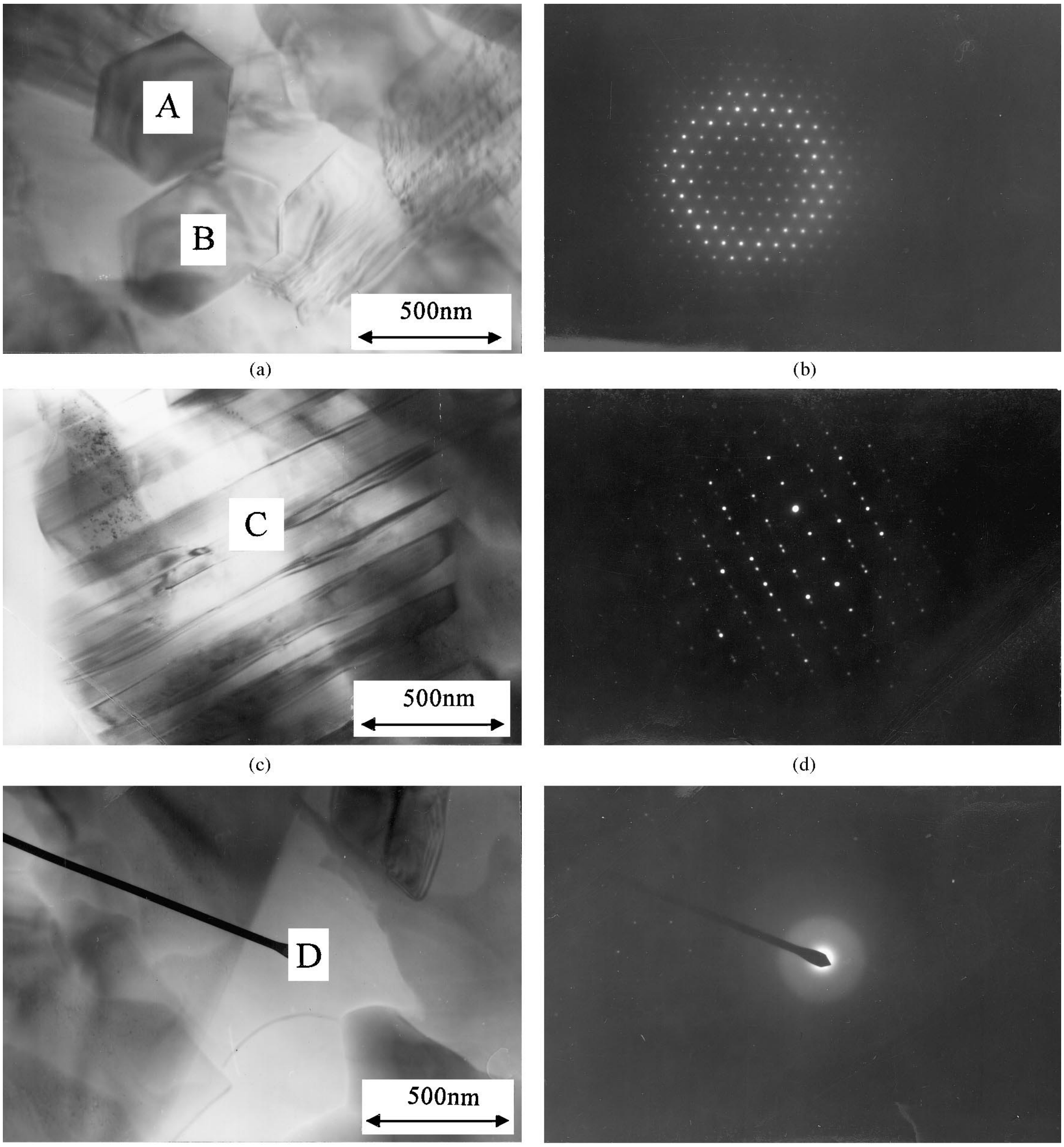


Fig. 1. XRD pattern and phase identification of as received A/W glass ceramics; (a) XRD pattern of A/W glass ceramic sintered at 1200°C. The pattern revealed a composite of glass and crystalline phases. The precipitated phase were wollastonite and whitlockite. (b) Identification of crystalline phase. The columns represent peaks and related intensities for A/W glass ceramics, whitlockite and wollastonite, respectively.

Calculation of the lattice parameters for whitlockite and wollastonite were carried out using XRD peak intensities. A computer program was employed to carry out the procedure. The results are listed in Table 4. When compared to standard parameters from JCPDS card and parameters calculated from the experiments, certain changes are evident. The existence of Si in whitlockite causes an increment in length of *c* axis and thus increases the cell volume. However, Mg causes no change in wollastonite structure. The effect can be explained by the differences of roles of ions played in the structure. The data for the ions given by Pauling are listed in Table 5. In wollastonite structure, each Calcium ion is symmetrically surrounded by six oxygen ions and they form a regular octahedron. Although the radius of magnesium ion is much smaller than that of calcium ion, magnesium ion have the same charge and close electronegativitiy to the latter. When entering the



(a) (b)

(c) (d)

(e) (f)

Fig. 2. TEM morphologies and related electron diffraction patterns of precipitated whitlockite and wollastonite: (a) TEM morphologies of whitlockite; (b) electron diffraction pattern of whitlockite; (c) TEM morphology of wollastonite; (d) electron diffraction pattern for wollastonite; (e) TEM morphology of glass matrix; (f) electron diffraction pattern for glass matrix.

wollastonite structure, magnesium ion will replace the position of calcium ion and form a substitutional solid solution. Since the ion radius of magnesium is smaller than that of calcium, the replacement of magnesium ion for calcium ion has no obvious effect on the crystal parameter. However, things are different for whitlockite. Both silicon and phosphorus are located in the center of tetrahedron formed by four oxygen ions.

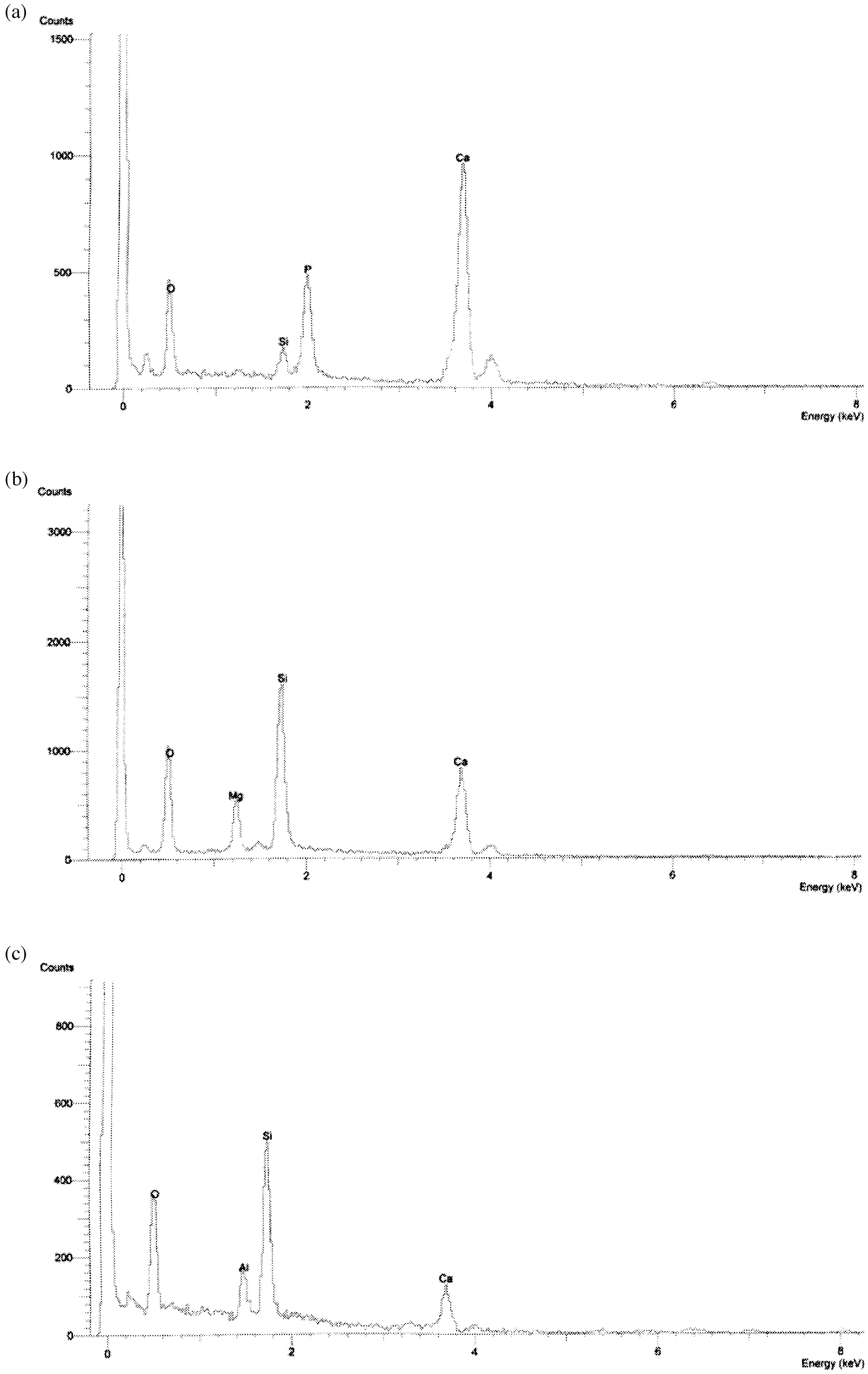


Fig. 3. EDX analysis of chemical composition for whitlockite, wollastonite and glass matrix: (a) spectrum of whitlockite; (b) spectrum of wollastonite; (c) spectrum of glass matrix.

Table 3
Chemical composition of crystals precipitated in sintered A/W glass ceramics

Phase	Oxides weight percentage (wt%)				
	CaO	MgO	SiO_2	P_2O_5	Al_2O_3
Whitlockite	37.20	–	8.10	54.70	–
Wollastonite	24.82	14.43	60.47	–	–
Glass matrix	27.26	–	63.48	–	9.36

Table 4
Lattice parameters for whitlockite and wollastonite

Source	Lattice parameters (Å)						Volume (Å^3)
	a	*b*	*c*	α	β	γ	
Standard JCPDS 9-169	10.429	10.429	37.38	90	90	120	–
Standard JCPDS 29-372	7.894	7.371	7.037	90.02	95.32	102.93	–
Calculated from 9-169	10.43	10.43	37.4	90	90	120	3522.9
Calculated from 29-372	7.90	7.36	7.03	89.97	95.29	102.98	397.16
Calculated from XRD pattern for whitlockite	10.45	10.45	39.0	90	90	120	3689.9
Calculated from XRD pattern for wollastonite	7.89	7.35	7.04	90.11	95.43	102.90	396.55

Table 5
Data of the ions

Data	Ions			
	Magnesium	calcium	silicon	phosphorus
Radius	0.65 (Å)	0.99 (Å)	0.41 (Å)	0.34 (Å)
Coordinator number	6	6	4	4
Coordinator polyhedron	MgO_6 octahedron	CaO_6 octahedron	SiO_4 tetrahedron	PO_4 tetrahedron
Electronegativity	1.2	1.0	1.8	2.1

However, the ion radius of silicon is greater than that of phosphorus, when silicon ion replaces phosphorus ion, it will cause distortion of the crystal structure, and lead to the increment of crystal parameter.

4. Conclusion

From the experiment, conclusions can be drawn as following:

1. Sintering of A/W glass ceramics at 1200°C obtained a dense material. Whitlockite and wollastonite were identified as the main crystal phase in the material with a glass matrix found on the boundaries. Apatite was not formed due to the sintering process.
2. The precipitated crystals showed different morphologies. Hexagonal crystals of whitlockite and column ones of wollastonite were found.
3. The precipitated crystals are non-stoichiometic, with Si in whitlockite and Mg in wollastonite. The existence of Si in whitlockite increases the lattice volume while Mg in wollastonite did not influence the lattice parameters. Al_2O_3 introduced by milling remained in the glass matrix and had no effect on the crystal phases.

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