



Structural and mechanical characteristics of whitlockite ceramics fabricated via a mineralization-assisted cold sintering process

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ABSTRACT

We demonstrate, for the first time, the low-temperature densification of whitlockite (WH), which thermally decomposes at approximately 700 °C, using a cold sintering process (CSP) with simulated body fluid (SBF). Under uniaxial pressure of 800 MPa at 180 °C, WH was densified to 96.4% without undergoing thermal decomposition and exhibited a dense and fine microstructure. In addition, the cold-sintered WH exhibited a Vickers hardness of 2.69 ± 0.06 GPa, a fracture toughness of 0.77 ± 0.01 MPa·m^{1/2}, and a Young's modulus of 67.7 ± 1.4 GPa. These values are comparable to or even higher than those of WH conventionally sintered at 600 °C or 1000 °C, representing the first report on the mechanical properties of WH ceramics in a single phase. These results establish CSP with SBF as an efficient low-temperature processing route for fabricating highly dense thermally unstable bioactive ceramics with great potential for biomedical applications.

1. Introduction

Whitlockite (WH) is a naturally occurring calcium phosphate mineral found in rocks and biological tissues [1]. In biological tissues, WH has recently been represented by the composition $\text{Ca}_{18}\text{Mg}_2(\text{HPO}_4)_2(\text{PO}_4)_{12}$ [2–4]. Its crystal structure closely resembles that of β -tricalcium phosphate (β -TCP; $\text{Ca}_3(\text{PO}_4)_2$), which is currently used in clinical applications, and both possess a common structural feature known as column B. The primary difference lies in column A: β -TCP consists solely of Ca^{2+} ions and phosphate groups, whereas WH additionally contains Mg^{2+} ions and hydrogen phosphate (HPO_4^{2-}) [5–7]. In 2014, the synthesis of single-phase WH was first reported [6], and in 2023, Kizalaite *et al.* demonstrated a simplified hydrothermal synthesis method for WH [8]. Since the synthesis methods of single-phase WH were reported, its biochemical properties have been evaluated in various forms, including powders [9,10], polymer composites [11–13], and pellets [6,9,13,14]. WH is particularly promising for application as a bone substitute due to its excellent biocompatibility and osteoconductivity. For bone substitute materials, a design tailored to bulk shapes and mechanical properties suited to patients and surgical sites is

critically important, and fundamental material-specific property data are essential for achieving these [15]. However, WH exhibits thermal instability owing to the presence of HPO_4^{2-} groups in its crystal structure, leading to its decomposition into magnesium-substituted β -TCP and α - or β -calcium pyrophosphate (CPP; $\text{Ca}_2\text{P}_2\text{O}_7$) at approximately 600–700 °C [6,8]. Thus, this thermal instability makes it difficult to fabricate bulk WH using conventional high-temperature sintering processes, which are conducted at temperatures above 1000 °C. This significantly restricts processing options and material design with respect to mechanical suitability. Consequently, no studies have reported on controlling the density of bulk WH with a single-phase composition, particularly on the densification of sintered bulk bodies. As a result, its fundamental properties, including physical and mechanical properties, are still unknown. Hence, establishing a non-conventional sintering method to densify and shape WH bulk materials while maintaining their single-phase nature without inducing thermal decomposition represents a critical and urgent challenge.

The cold sintering process (CSP), one of the representative low-temperature sintering techniques, was first reported in 2016 [16]. CSP is a hydrothermal-like low-energy sintering technique inspired by the

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natural formation of rocks, shells, and pearls under ambient conditions [16]. By introducing water or mildly acidic/basic solutions and applying pressures (50–500 MPa) at temperatures below 300 °C, CSP can achieve densification through mechanisms including particle rearrangement, dissolution-reprecipitation, and crystal growth [16,17]. Densification via CSP has been extensively demonstrated for moderately soluble inorganic materials, including oxides, bromides, chlorides, fluorides, and carbonates [18]. However, challenges remain for materials with low solubility, such as WH [1]. Recently, Gubarevich *et al.* reported the densification of WH via CSP [19]. Under conditions of 100 MPa using ultrapure water, they achieved densification of WH with newberyite as a secondary phase to a relative density of approximately 75%. These results highlight the inherent limitations of conventional CSP, which uses ultrapure water for the densification of materials with low solubility and reactivity. For such materials, tuning the ionic composition of the transient solution has been shown to promote and control dissolution-reprecipitation reactions [17,18,20,21–23]. For example, in the case of low-solubility materials such as MgO, densification could be enhanced by using a solution containing the same ionic component as the raw material [20]. In addition, using a supersaturated solution with respect to BaTiO₃ for densification can overcome heterogeneous solubility, resulting in successful densification [21].

In this context, there are previous reports on the use of simulated body fluid (SBF), a solution with an ionic composition similar to that of human plasma, as a transient solution in CSP. This approach, referred to as the low-temperature mineralization sintering process (LMSP) and proposed by Seo *et al.* [24–28], was shown to enhance crystal formation and growth by inducing biomineralization-like reactions on the surfaces of bioactive inorganic materials, in addition to the common CSP densification mechanisms. For instance, bioactive glass nanoparticles were densified using CSP with SBF, where low-crystallinity apatite was formed, filling the vacant areas between the glass nanoparticles with a high relative density of 92% [26]. Moreover, using the same process, transparent hydroxyapatite (HAp) was achieved with a relative density exceeding 98% and a visible-light transmittance of over 80% at temperatures below 200 °C [27]. Nevertheless, densification by CSP using SBF has thus far been confined to materials with high solubility that readily interact with SBF and form apatite, such as bioactive glasses and low-crystalline HAp. To date, no studies have applied this approach to other calcium phosphate ceramics with moderate apatite-forming capabilities, such as WH [6,13]. Consequently, it remains unclear whether SBF-assisted densification can be extended to bioactive inorganic materials that lack high solubility or strong apatite-forming ability.

In this study, we demonstrated the fabrication of dense single-phase WH bulk ceramics using CSP with SBF and clarified the densification behavior and mechanical properties of the sintered WH. For this purpose, WH nanoparticles were mixed with the SBF solution to enhance densification during the CSP. The CSP conditions, such as temperature, pressure, and sintering time, were controlled to achieve optimal densification conditions based on the relative density. Additionally, to investigate the effects of SBF, WH nanoparticles were densified using CSP with ultrapure water under the optimized conditions. Furthermore, the efficiency of the low-temperature densification method used in this study was compared with that of conventional high-temperature sintering. The correlations among the crystal structures, microstructural properties, and mechanical properties were also discussed. To the best of our knowledge, this is the first study to report the densification of single phase WH without thermal decomposition and to comprehensively elucidate its mechanical properties.

2. Materials and methods

2.1. Synthesis of WH powders

WH powders were synthesized via the hydrothermal method using calcium hydrogen phosphate dihydrate (CaHPO₄·2 H₂O, 99.1%,

Eurochemicals, Vilnius, Lithuania) and magnesium acetate tetrahydrate (Mg(CH₃COO)₂·4 H₂O, ≥ 98%, Carl Roth®, Karlsruhe, Germany) as starting materials [8]. Certain amounts of CaHPO₄·2 H₂O and Mg (CH₃COO)₂·4 H₂O were dissolved in a mixture of 250 mL of deionized water and 32.5 mL of 1 mol/L phosphoric acid (H₃PO₄, 75%, Carl Roth®, Karlsruhe, Germany) in a 500 cm³ Teflon-liner. Total metal ion concentration and a Ca-to-Mg molar ratio were 0.06 mol/L of 9:1, respectively. The solution was stirred magnetically at room temperature until complete dissolution of the precursors. Subsequently, concentrated ammonia solution (NH₄OH, 25%, Chempur®, Karlsruhe, Germany) was added under continuous stirring until the pH reached 6.47, resulting in the immediate formation of white precipitates. The Teflon-liner was locked in a stainless-steel autoclave and heated at 160 °C for 2.0 h in the oven. After cooling to room temperature, the obtained product was vacuum-filtered, washed with deionized water, and dried at 50 °C overnight.

2.2. Densification of WH powders

To investigate the effect of CSP using SBF, the obtained WH powders were mixed with a 25 wt% SBF solution prepared according to Kokubo's method [29] using a mortar and pestle. The resulting mixture was then placed into a cylindrical mold with a diameter of 12 mm and heated under uniaxial pressure. To optimize the densification conditions, different sintering temperatures (150–190 °C), uniaxial pressures (300–800 MPa), and sintering times (0.5–6.0 h) were investigated. After sintering, the mold was cooled to room temperature, and the applied pressure was gradually released to prevent cracking. The obtained WH ceramics were dried overnight in an oven at 60 °C. For comparison, the WH powders, mixed with 25 wt% ultrapure water, were densified under the optimized conditions. The cold-sintered samples obtained under the optimized conditions using SBF were denoted SBF-(t) and those using ultrapure water were denoted Water-(t), where (t) represents the sintering time. In addition, another WH bulk samples were prepared using the conventional high-temperature sintering method (CS). Initially, the WH powders were uniaxially molded at 100 MPa, followed by cold isostatic pressing at 200 MPa for 1.0 min to prepare a green body. The obtained pellets were sintered at 600 °C or 1000 °C for 2.0 h. The obtained conventionally sintered samples were denoted CS-600 °C and CS-1000 °C based on their sintering temperatures.

2.3. Characterization

The phase structures of the raw WH powders were analyzed by X-ray diffraction (XRD, D8 Advance, Bruker AXS GmbH, Karlsruhe, Germany) using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at 40 kV and 40 mA. An internal standard silicon powder (Si, 99.999%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) was mixed with the raw WH powder at a ratio of 10 wt%, and the volume fractions of the crystalline phases were calculated by fitting full-spectrum XRD through Rietveld refinement using the TOPAS software (TOPAS V5, Bruker AXS GmbH, Karlsruhe, Germany). The chemical structures of the raw WH powders were examined using Fourier-transform infrared spectroscopy (FT-IR, FT/IR-6600, JASCO, Tokyo, Japan). Morphological observations of the WH powders were conducted using a field-emission scanning electron microscope (FE-SEM, SU9000, Hitachi High-Tech Corp., Tokyo, Japan) operated at an accelerating voltage of 20 kV. The average particle size ($n = 200$) was measured from the FE-SEM images using the image analysis software ImageJ. The thermal decomposition temperature of the WH powder was determined using thermogravimetric analysis (TGA, TG-DTA8122, RIGAKU Corp., Tokyo, Japan). The measurement was performed in a dry air flow from room temperature to 1200 °C at a heating rate of 10 °C/min. The true density of the synthesized WH powder was determined using a helium gas pycnometer (AccuPyc® II 1345, Micromeritics, GA, USA). The densities of the green bodies before heating were measured using a geometric method with a digital

micrometer (MDC-25MJ, Mitutoyo Corp., Kanagawa, Japan). The densities of the sintered WH were measured using Archimedes' method with absolute ethanol (EtOH, 99.5%, FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) as the liquid medium. The relative densities were calculated as the ratio of the measured density to the true density of the raw WH powders. The microstructures of the fractured surfaces of the sintered WH were observed by FE-SEM at 20 kV after coating all samples with osmium using an osmium plasma coater (OPC-60A, SPI Supplies, PA, USA). The structural changes were further investigated using XRD. Chemical transformations in the sintered WH were examined by FT-IR and, ^1H and ^{31}P solid-state nuclear magnetic resonance (MAS NMR, AVANCE III 600 WB, Bruker BioSpin GmbH, Rheinstetten, Germany). The ^1H and ^{31}P MAS NMR measurements were conducted with reference to previously reported conditions [30]. To characterize the crystalline phase morphology of the WH sample with the highest relative density, high-resolution transmission electron microscopy (HR-TEM, JEM-ARM200F, JEOL Ltd., Tokyo, Japan) was employed. Vickers hardness test was performed on the polished sample surfaces using a Vickers hardness tester (FV-310e, Future-tech Corp., Kanagawa, Japan) under a 9.8 N load with a holding time of 15 s. The fracture toughness (K_{IC}) was measured under the same conditions as the Vickers hardness test and calculated using the indentation fracture method based on the crack lengths [31].

$$K_{IC} = 0.0089 \left(\frac{E}{H_V} \right)^{\frac{2}{5}} \left(\frac{P}{a l^2} \right) \quad (1)$$

E is the Young's modulus, H_V is the Vickers hardness, P is the applied load during the Vickers hardness test, a is half of the indentation diagonal, and l is the crack length from the vertices of the indentation to the crack tip. The Vickers hardness and fracture toughness values were averaged from five indentations per sample. Young's modulus was determined using the ultrasonic pulse-echo method, measuring ultrasonic velocities with a digital storage oscilloscope (DSOX3052T, Keysight, Tokyo, Japan) and an ultrasonic pulser/receiver (Model 5072, PANAMETRICS, MA, USA). The Vickers indentation morphologies of the sintered WH were also observed using FE-SEM at 30 kV after coating all samples with osmium using an osmium plasma coater.

3. Results and discussion

3.1. Characterization of the synthesized WH powders

The crystal structure of the raw powder was analyzed by XRD analysis (Fig. 1(a)). The XRD pattern of the powder exhibited low-crystallinity WH (PDF no. 00-070-2064), and no peaks attributable to other crystalline phases were detected. A broad increase in the baseline was observed in the range of $2\theta = 20\text{--}40^\circ$, suggesting the presence of an amorphous phase. The Rietveld refinement results indicated that the amorphous phase accounted for 4.89 wt% of the raw powder (Fig. S1). Since WH and β -TCP exhibit very similar XRD patterns, FT-IR was employed to confirm the presence of HPO_4^{2-} groups. As shown in Fig. 1(b), the FT-IR spectrum of the raw powder showed characteristic peaks of HPO_4^{2-} , with a weak peak at 891 cm^{-1} and a sharp peak at 918 cm^{-1} , both of which indicate the presence of WH phase [32,33]. The strongest

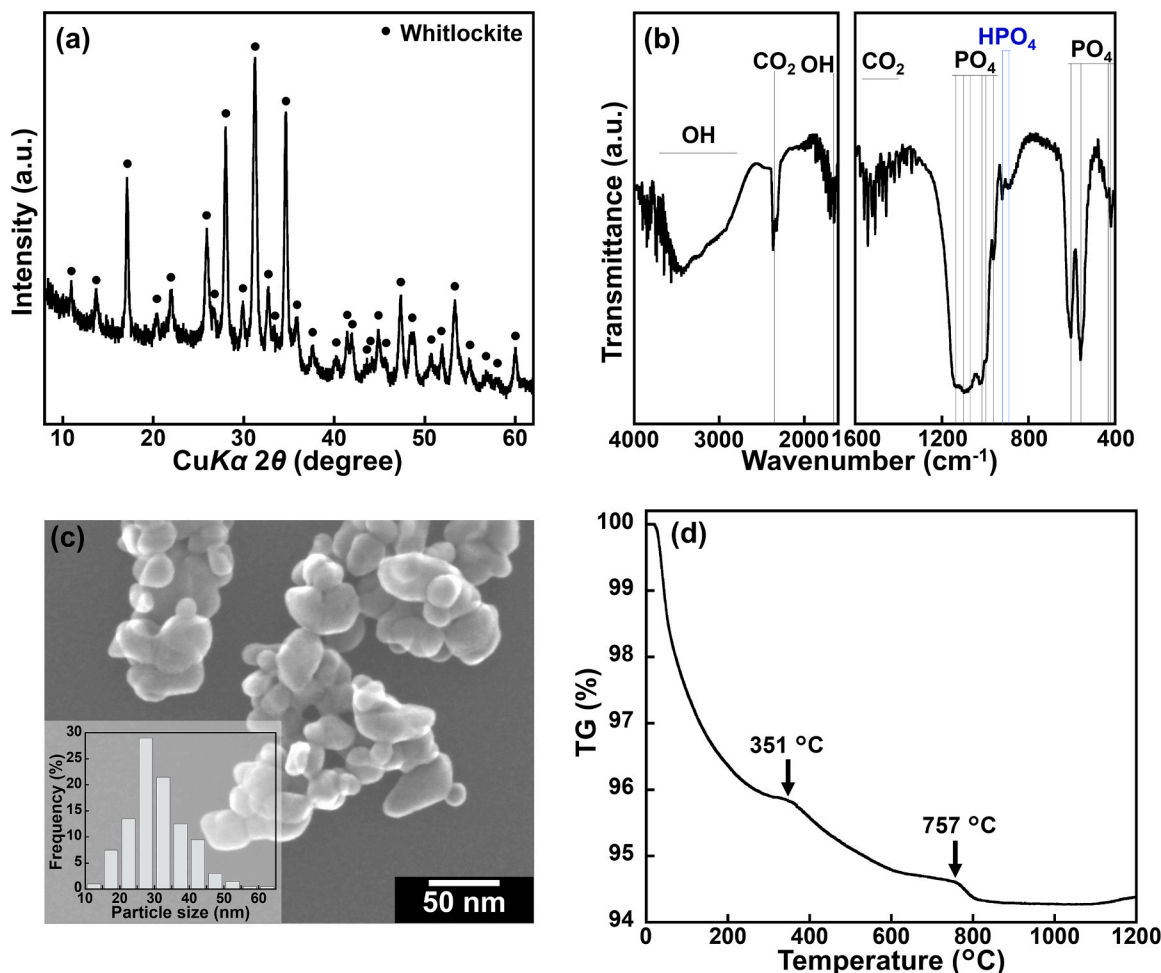


Fig. 1. (a) XRD pattern, (b) FT-IR spectrum, (c) FE-SEM image and particle size distribution, and (d) TGA curve of the raw powder.

absorption band in the range of $415\text{--}1150\text{ cm}^{-1}$ corresponds to the vibration modes of the phosphate groups. The absorption bands at approximately $1200\text{--}950\text{ cm}^{-1}$ are assigned to PO_4^{3-} stretching vibrations (ν_3 and ν_1), while the bands at $640\text{--}500\text{ cm}^{-1}$ and 430 cm^{-1} correspond to PO_4^{3-} bending vibrations (ν_4 and ν_2), respectively [32–35]. Furthermore, the peaks related to OH vibrations indicated that the raw WH powder contained trapped water originating from the hydrothermal synthesis [36,37]. The XRD and FT-IR results indicated that the synthesized powder consisted of WH in a single phase.

The FE-SEM image (Fig. 1(c)) showed that the synthesized WH powder consists of elliptical nanoparticles. The average diameter of the primary particles measured by randomly selecting 200 particles from the FE-SEM image was $31 \pm 8\text{ nm}$. The true density of the raw WH particles, measured using a pycnometer, was $2.84 \pm 0.02\text{ g/cm}^3$. The measured density was lower than the reported density of 3.03 g/cm^3 [1], which is attributed to the low crystallinity of the raw powder, as well as the presence of hydrothermal synthesis-derived trapped water and minor amounts of amorphous phases, as indicated by the experimental results.

The thermal behavior of raw WH powder was analyzed using TGA. The TGA curve (Fig. 1(d)) was consistent with previous studies reporting weight loss of WH as temperature increased [8]. The initial weight loss is attributed to the evaporation of adsorbed water. The weight loss observed in the range of $351\text{--}1000\text{ }^\circ\text{C}$ was 1.6%, which is greater than the amount of water released calculated theoretically based on the composition of WH (0.84%). Considering that amorphous calcium phosphate contains 6–19% structural water released above $120\text{ }^\circ\text{C}$ [38], this weight loss is likely due to the release of structural water from the trace amorphous components estimated by Rietveld analysis, as well as

the decomposition of WH. For WH, the weight loss observed above $351\text{ }^\circ\text{C}$ indicates the partial decomposition of HPO_4^{2-} , while the rapid weight loss between $757\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ suggests that most of HPO_4^{2-} in the WH structure decomposed into $\text{P}_2\text{O}_7^{4-}$, transforming into a mixture of the β -TCP and CPP phases [6,8,39]. These results confirm that obtaining sintered WH ceramics as a single phase using conventional high-temperature sintering processes is highly limited, highlighting the necessity of a low-temperature sintering process for fabricating dense bulk WH with a single phase.

3.2. Densification and microstructure of WH sintered via CSP using SBF

The densification parameters, such as sintering temperature, uniaxial pressure, and sintering time, were optimized based on the relative density of WH sintered via CSP using SBF. As shown in Fig. 2(a), during optimization of each densification parameter, the other densification conditions were kept constant. Under a pressure of 300 MPa and a sintering time of 1.0 h, the relative density increased slightly with increasing sintering temperature, attaining 82.1% at $170\text{ }^\circ\text{C}$ before exhibiting plateau behavior and reaching the highest value of 82.2% at $180\text{ }^\circ\text{C}$. However, surface cracks in the sintered WH were observed after CSP at $190\text{ }^\circ\text{C}$ due to thermal contraction [40,41]. Therefore, $180\text{ }^\circ\text{C}$ was selected as the optimal sintering temperature. In terms of pressure, under a temperature of $180\text{ }^\circ\text{C}$ and a sintering time of 1.0 h, the relative density increased with increasing pressure, reaching 93.7% at 800 MPa (Fig. 2(b)). This significant increase in density with applied pressure can be attributed to particle rearrangement through particle sliding and plastic deformation, as well as the enhanced solubility due to pressure solution creep [17]. Finally, the sintering time was adjusted under the

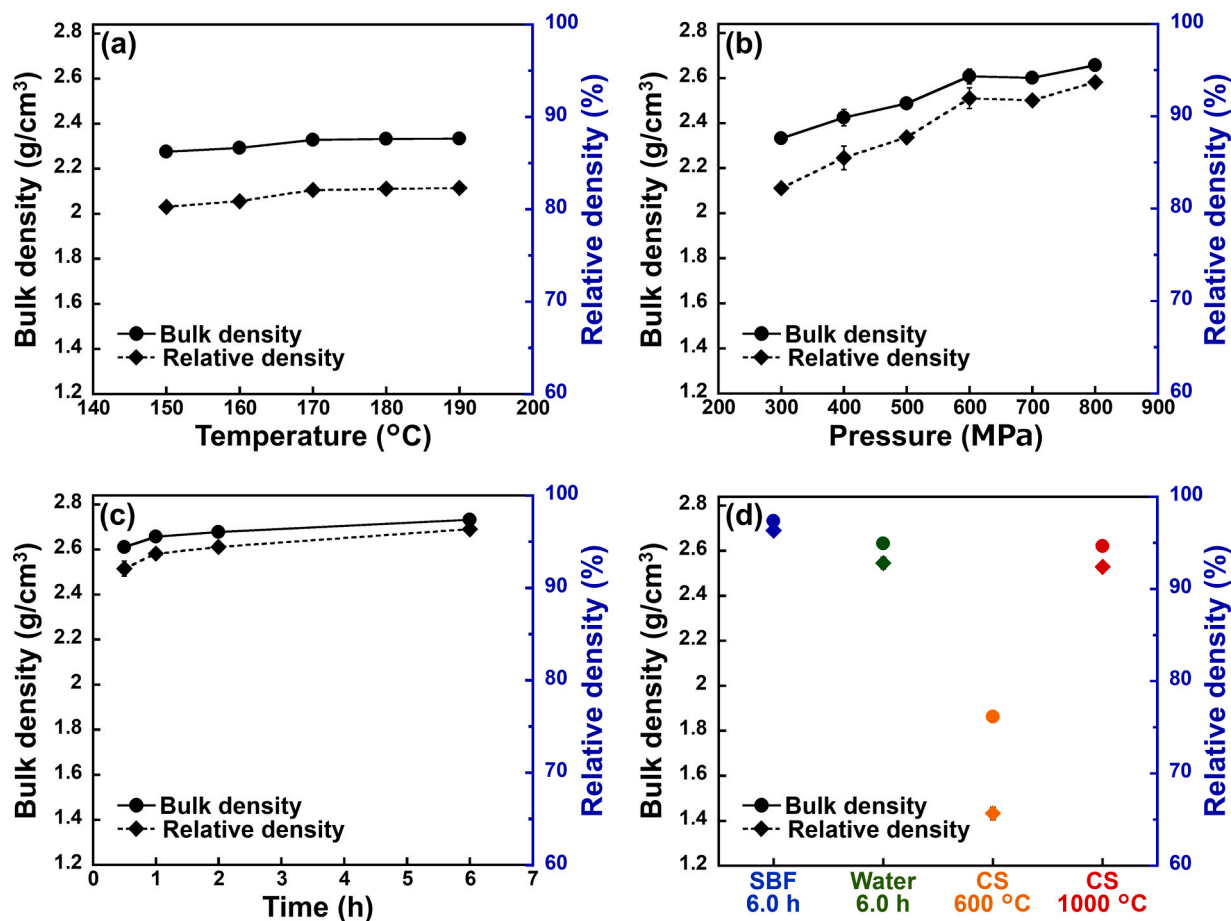


Fig. 2. Bulk density and relative densities of WH sintered using CSP with SBF against (a) temperatures (300 MPa, 1.0 h), (b) pressures (180 °C, 1.0 h), (c) times (180 °C, 800 MPa). (d) Comparison of bulk density and relative densities for SBF-6.0 h, Water-6.0 h, CS-600 °C, and CS-1000 °C.

optimized conditions of 180 °C and 800 MPa (Fig. 2(c)). The relative densities obtained at sintering times of 0.5 h, 1.0 h, 2.0 h, and 6.0 h were 92.1%, 93.7%, 94.4%, and 96.4%, respectively, indicating that the relative density increased gradually with longer sintering time. Thus, by optimizing the densification conditions (180 °C, 800 MPa, 6.0 h), highly dense WH with a maximum relative density of 96.4% was successfully achieved at the low temperature of 180 °C via CSP using SBF.

For comparison with CSP using SBF, WH was cold-sintered under the optimized conditions using ultrapure water. The relative densities of the green bodies formed at 800 MPa with SBF and water were 69.3% and 69.1%, respectively, which were nearly equivalent. However, after heating and pressing, the relative density of Water-6.0 h increased to 92.8%, which was 3.6% lower than that of SBF-6.0 h and comparable to those of SBF-0.5 h and SBF-1.0 h (Fig. 2(d)). The enhanced densification observed when SBF was used in prolonged CSP, compared with ultrapure water, is attributed to the presence of ions in the solution, which more effectively promotes a biomineralization-like precipitation process [24,26]. Additionally, CS was applied to densify WH at sintering temperatures of 600 °C and 1000 °C for 2.0 h. In the case of CS, WH sintered

at 600 °C exhibited the lowest relative density of 65.7% owing to an insufficient sintering temperature. However, the relative density increased to 92.4% at 1000 °C, which was comparable to that of Water-6.0 h. Thus, CSP with SBF exhibited greater densification efficiency than CSP with water and even CS at 1000 °C.

To further investigate and compare densification behaviors of sintered WH samples, the fracture surfaces of SBF-6.0 h, Water-6.0 h, CS-600 °C, and CS-1000 °C were observed using FE-SEM (Fig. 3). Although no significant differences were observed between SBF-6.0 h and Water-6.0 h in Fig. 3(a)–(d), SBF-6.0 h formed a denser structure with particles more clearly interconnected, showing minimal gaps at the fracture surface. These microstructures consist of compressed particles retaining the original fine particle size (Fig. 1(c)). On the other hand, CS samples exhibited different fracture surface features compared with SBF-6.0 h and Water-6.0 h (Fig. 3(e)–(h)). As shown in Fig. 3(e) and (f), CS-600 °C exhibited obvious neck formation and partial grain growth which was typical sintering behavior. Furthermore, as shown in Fig. 3(g) and (h), CS-1000 °C showed further grain growth, and as indicated by the arrows in Fig. 3(h), in contrast to the other samples, both

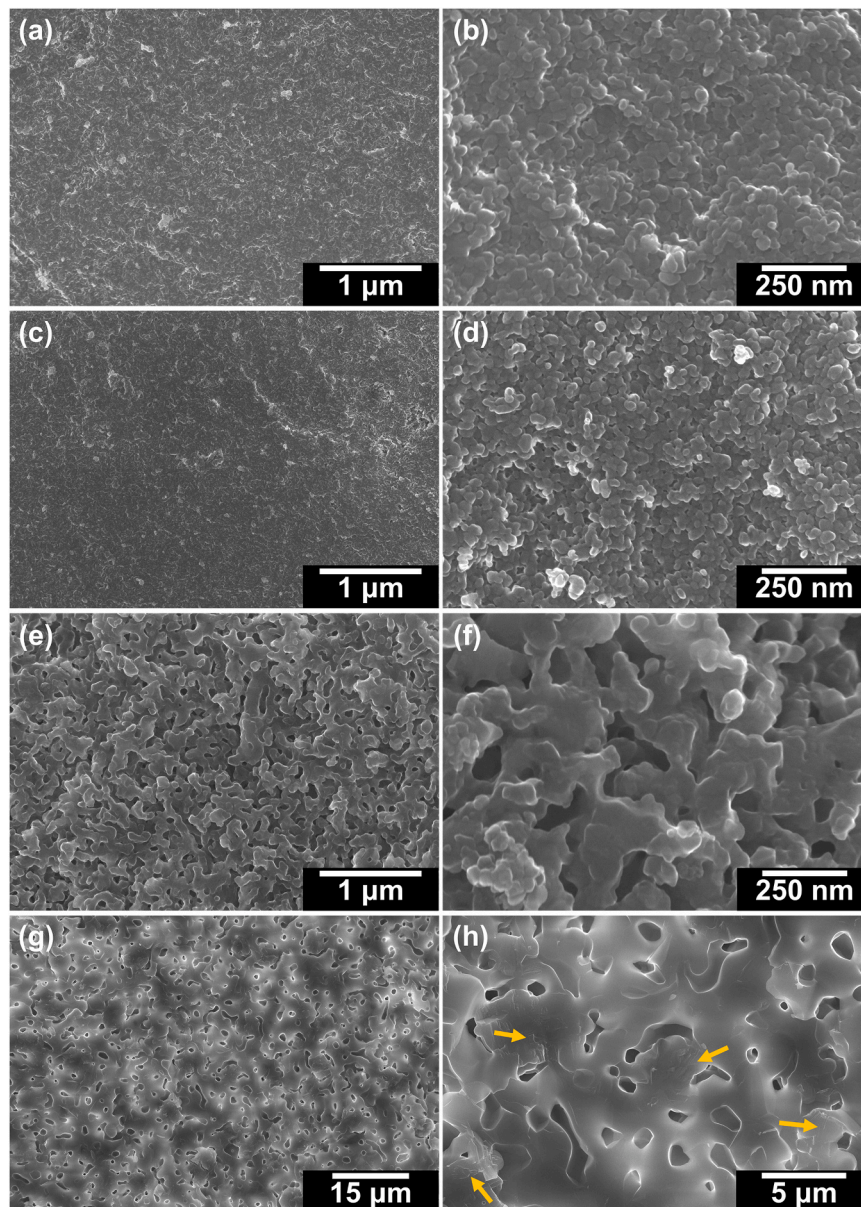


Fig. 3. Fracture surfaces of (a, b) SBF-6.0 h, (c, d) Water-6.0 h, (e, f) CS-600 °C, and (g, h) CS-1000 °C.

intergranular fractures and transgranular fractures were observed on the fracture surface. These differences in microstructural evolution between CSP and CS are attributed to their respective mass transfer mechanisms, namely dissolution-reprecipitation in CSP and thermally activated diffusion in CS.

The grain boundary structure of SBF-6.0 h, which was the most densified WH at 180 °C, was further investigated using HR-TEM. As shown in Fig. 4(a), grains with triple junctions were observed without visible pores or defects at the grain boundaries. Based on the lattice fringe spacings observed in Fig. 4(b), the crystalline phases and crystallographic planes at each grain were identified and attributed to the WH. Moreover, lattice fringes identical to those within the grains were observed at the grain boundaries, indicating that WH maintained a single-phase structure even after the CSP process. A more detailed analysis of the phase structure of the sintered WH samples is presented in the subsequent section. These results confirm that highly dense WH can be successfully fabricated at a remarkably low temperature of 180 °C via CSP with SBF.

3.3. Comparison of crystal structure between CSP and CS samples

To identify the crystalline phase after sintering, XRD, FT-IR as well as ^1H and ^{31}P MAS NMR were conducted for the raw powder, SBF-6.0 h, Water-6.0 h, CS-600 °C, and CS-1000 °C. As shown in Fig. 5(a), the XRD patterns of SBF-6.0 h and Water-6.0 h were similar to that of the raw powder. In addition, in the patterns of CS-600 °C, only diffraction peaks corresponding to WH were observed, which slightly increased in crystallinity. In contrast, CS-1000 °C exhibited some peaks derived from magnesium-substituted β -TCP ($(\text{Ca}, \text{Mg})_3(\text{PO}_4)_2$, PDF no. 00-013-0404) and β -CPP ($\text{Ca}_2\text{P}_2\text{O}_7$, PDF no. 00-009-0346), indicating that thermal decomposition of WH had occurred. These results are consistent with the thermal decomposition behavior of the WH powders as determined by TGA analysis (Fig. 1(d)).

The FT-IR spectra of the raw powder and the sintered WH samples are shown in Fig. 5(b). The raw powder, SBF-6.0 h and Water-6.0 h exhibited only peaks corresponding to WH, and characteristic HPO_4^{2-} peaks at 918 cm^{-1} and 891 cm^{-1} of the WH structure were confirmed in their spectra [32,33]. Although CS-600 °C exhibited peaks attributed to WH, with a clear HPO_4^{2-} peak at 918 cm^{-1} , the shoulder peak at 891 cm^{-1} of HPO_4^{2-} disappeared, and a slight β -CPP-related phosphate peak emerged at 725 cm^{-1} [42], suggesting partial thermal decomposition of WH. In CS-1000 °C, distinct β -CPP-related phosphate peaks were observed at 725 cm^{-1} and 490 cm^{-1} [42], while the HPO_4^{2-} peaks at 918 cm^{-1} and 891 cm^{-1} disappeared, indicating that WH had decomposed. Additionally, the OH-related peaks decreased due to the desorption of adsorbed water and hydroxyl groups from the low crystallinity structure as the sintering temperature increased.

The ^1H MAS NMR spectra of the raw powder and the sintered WH samples are shown in Fig. 5(c). In the spectra of the raw powder, SBF-6.0 h, Water-6.0 h, and CS-600 °C, the HPO_4^{2-} -related peak characteristic of the WH was observed at 9.8 ppm [8]. On the other hand, this peak was scarcely observed in the spectrum of CS-1000 °C, indicating that the WH structure almost no exists in CS-1000 °C due to thermal decomposition. Subsequently, ^{31}P MAS NMR analysis was performed to probe the local structure of the phosphate groups and to identify potential trace amounts of secondary calcium phosphate phases (Fig. 5(d)). The spectra of the raw powder, SBF-6.0 h and Water-6.0 h exhibited similar chemical shifts. These spectra exhibited three peaks at 2.1, 1.1, and -0.5 ppm, corresponding to the different states of $\text{P}(2)$, $\text{HP}(1)\text{O}_4^{2-}$, and $\text{P}(3)$ within the WH structure, respectively [7,8]. In contrast, the spectrum of CS-600 °C showed sharper peaks, indicating increased crystallinity, while that of CS-1000 °C exhibited a shape characteristic of β -TCP [43]. Furthermore, a weak signal in the range from -4 to -14 ppm (Fig. 5(e)), attributed to β -CPP [43], was observed not only in CS-1000 °C but also in CS-600 °C. This indicates that only the CS samples were thermally decomposed during sintering.

Based on the XRD, FT-IR, and NMR analyses, SBF-6.0 h and Water-6.0 h were considered to be single-phase WH. In particular, SBF-derived ions assisted WH densification without significantly affecting the WH structure. This is likely attributable to the extremely small number of ions introduced from the added SBF (0.15 g) (Table S1). Based on previous studies [24,25], these ions are expected to be preferentially distributed at the grain boundaries through interfacial reactions, although their direct detection is difficult because of their trace amounts. The NMR results showed no significant structural differences between the starting WH powder and SBF-6.0 h, whereas TEM observations revealed well-defined lattice fringes extending to the grain boundaries. These results suggest that SBF-derived ions may be present mainly at the grain boundaries and assist densification without significantly altering the WH structure. Overall, these findings highlight the effectiveness of CSP in enabling the densification of thermally unstable materials without causing thermal decomposition.

3.4. Comparison of mechanical properties between CSP and CS samples

To evaluate the mechanical properties of SBF-6.0 h, Water-6.0 h, CS-600 °C, and CS-1000 °C, their Vickers hardness, fracture toughness, and Young's modulus were measured. The obtained values were plotted for each sample (Fig. 6).

As shown in Fig. 6(a), the Vickers hardness of SBF-6.0 h, Water-6.0 h, CS-600 °C, and CS-1000 °C showed 2.69 ± 0.06 GPa, 2.41 ± 0.10 GPa, 0.87 ± 0.01 GPa, and 2.17 ± 0.06 GPa, respectively, exhibiting trends similar to those of the relative densities (Fig. 2(d)). Notably, the CSP samples sintered at a low temperature of 180 °C,

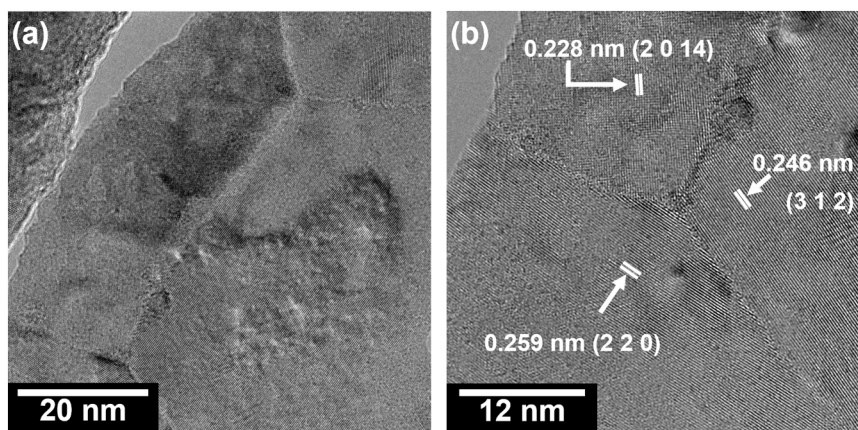


Fig. 4. HR-TEM images of SBF-6.0 h from (a) low magnification to (b) high magnification.

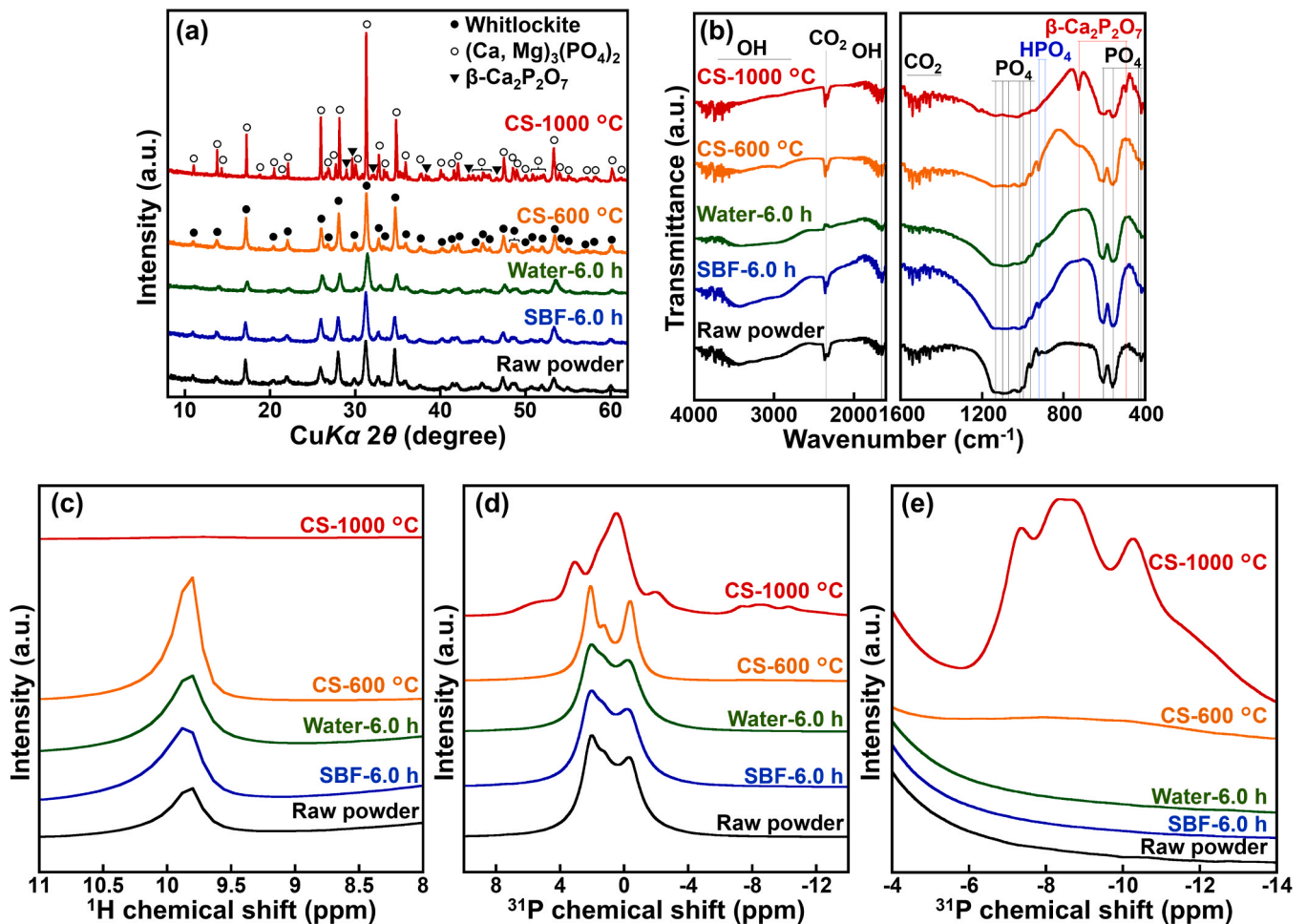


Fig. 5. (a) XRD patterns, (b) FT-IR spectra, (c) ^1H MAS NMR spectra, (d) ^{31}P MAS NMR spectra, and (e) ^{31}P MAS NMR spectra in the range of -4 to -14 ppm of the raw powder, SBF-6.0 h, Water-6.0 h, CS-600 °C, and CS-1000 °C.

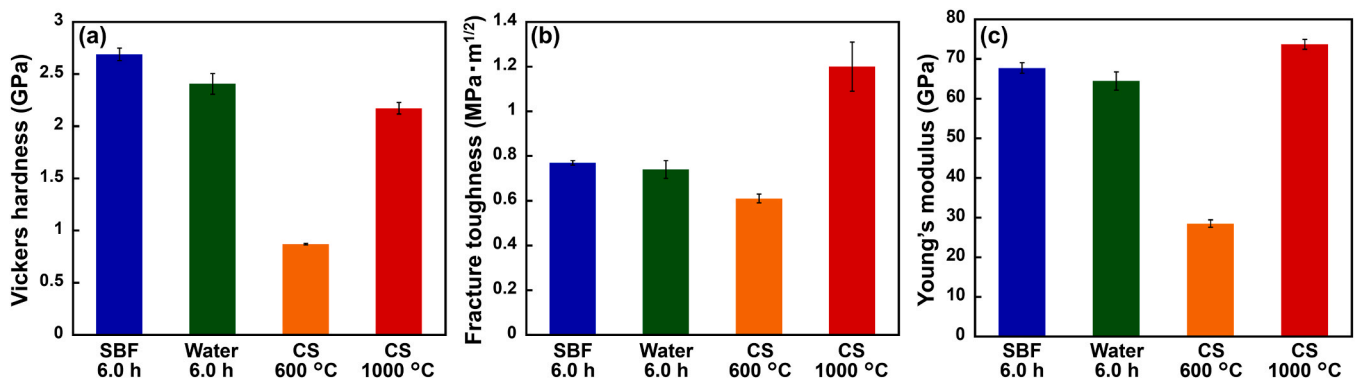


Fig. 6. (a) Vickers hardness (b) fracture toughness, and (c) Young's modulus of SBF-6.0 h, Water-6.0 h, CS-600 °C, and CS-1000 °C.

exhibited higher hardness than CS-1000 °C. These results are attributed to the highly dense microstructure of the CSP samples, which consist of nanoparticles with interfacial bonding [44]. On the other hand, the trend in fracture toughness against the relative densities differs from that observed for Vickers hardness. As shown in Fig. 6(b), CS-1000 °C exhibited highest values, $1.20 \pm 0.11 MPa \cdot m^{1/2}$. Additionally, SBF-6.0 h, Water-6.0 h, and CS-600 °C showed $0.77 \pm 0.01 MPa \cdot m^{1/2}$, $0.74 \pm 0.04 MPa \cdot m^{1/2}$, and $0.61 \pm 0.02 MPa \cdot m^{1/2}$, respectively, following the same order as their relative densities, whereas the gap between the CSP samples and CS-600 °C was less pronounced. These

results are consistent with previous research indicating that CSP samples exhibit lower fracture toughness than CS samples at equivalent densities [45]. This is attributed to crack propagation with low energy due to the countless crystalline grain boundaries composed of fine particles and the shorter crack deflection paths along them [45]. As shown in Figs. 2(d) and 6(c), the Young's modulus also exhibited a correlation with relative density for SBF-6.0 h ($67.7 \pm 1.4 GPa$), Water-6.0 h ($64.5 \pm 2.3 GPa$), and CS-600 °C ($28.5 \pm 1.0 GPa$). On the other hand, the highest value was obtained from CS-1000 °C, showing $73.7 \pm 1.3 GPa$. Although CS-1000 °C had a lower relative density than the CSP samples, it

exhibited higher Young's modulus due to its coarse grain size [46]. The above trends in the different mechanical properties of the CSP and CS samples are attributed to the microstructure, which depends on the densification mechanism.

To clarify the different correlations between the Vickers hardness and fracture toughness in SBF-6.0 h and CS-1000 °C, their indentations and associated cracks formed after the Vickers hardness test were observed using FE-SEM. As shown in Fig. 7(a) and (c), SBF-6.0 h exhibited a smaller indentation size and longer crack lengths compared to CS-1000 °C. This indicates that SBF-6.0 h possesses higher hardness but lower fracture toughness than CS-1000 °C based on Eq. (1). Additionally, the crack lengths observed in the four directions in Fig. 7(a) are noticeably different, which may be attributed to residual stress. Since the CSP samples were fabricated under a high uniaxial pressure of 800 MPa, significant residual stress has likely remained in the bulk, promoting crack growth along specific stress directions and consequently reducing fracture toughness. In Fig. 7(b), the nanoparticle morphology was clearly observed along the crack propagating straight, indicating that the fracture mode of SBF-6.0 h is intergranular. In contrast, no distinct grain morphology was observed in CS-1000 °C (Fig. 7(d)), and the fracture surface in Fig. 3(h) exhibited both intergranular and transgranular fracture. These crack propagation behaviors suggest that, in addition to the influence of short deflection paths due to the fine grain structures of CSP, the interparticle bonding formed via the dissolution-precipitation reaction in CSP is weaker than the necking formed through thermal diffusion in CS.

Subsequently, the cross-sections of Vickers indentations were observed using FE-SEM, as shown in Fig. 8. In SBF-6.0 h (Fig. 8(a), (b)), the cracks induced by the Vickers indentation extended not only along the surface but also deep into the interior of the sintered WH. In addition, cracks around the indentation propagated laterally along the material surface within the bulk, indicating the low toughness of the material [47]. In contrast, the fracture surface of CS-1000 °C (Fig. 8(c), (d)) exhibited no visible cracks inside the bulk, suggesting superior toughness resistance. Thus, the CSP and CS samples exhibited distinct fracture behaviors governed by differences in the microstructure, interparticle bonding, and crystalline phase arising from their fundamentally different densification mechanisms.

Because there have been no reports on the mechanical properties of single-phase WH, the results obtained in this study were also compared with previously reported mechanical properties of β -TCP, which has a

crystal structure similar to that of WH. Tricoteaux *et al.* [48] reported that β -TCP ceramics fabricated by pressureless sintering at 1040 °C exhibited a relative density of 89%, a Vickers hardness of 2.54 ± 0.17 GPa, and a fracture toughness of 1.47 ± 0.13 MPa·m^{1/2}. These values are close to those of CS-1000 °C, indicating a similar correlation between the Vickers hardness and fracture toughness compared with SBF-6.0 h, which exhibited higher hardness and lower toughness. On the other hand, Babaie *et al.* [49] reported that magnesium-substituted TCP fabricated by microwave sintering at 1150 °C, which contained a minor secondary phase with relatively restrained grain growth, exhibited an intergranular fracture mode with a Vickers hardness of 2 GPa or less and a fracture toughness of 0.682 MPa·m^{1/2}. In comparison, SBF-6.0 h exhibited even higher density and mechanical properties at a sintering temperature approximately 1000 °C lower (180 °C). Thus, although slight differences in mechanical properties may arise depending on the sintering process, the mechanical properties of WH ceramics fabricated by CSP can be regarded as reasonable values. These results demonstrate that CSP is a highly efficient densification method that, owing to its low sintering temperature, can also prevent the thermal decomposition of WH. Accordingly, this technique enabled, for the first time, a comprehensive evaluation of the mechanical properties of a single-phase WH.

4. Conclusions

We successfully fabricated dense WH ceramics in a single phase for the first time using CSP with SBF solution and clarified their mechanical properties. The highest relative density of 96.4% was achieved under optimized CSP conditions at 180 °C and 800 MPa for 6.0 h using a 25 wt % SBF solution (SBF-6.0 h). In comparison with CSP with ultrapure water, the use of SBF solution allowed for approximately 3.6% higher relative density, suggesting that ions in SBF contribute to improved densification. In addition, the relative density of SBF-6.0 h was even higher than those of WH conventionally sintered at 600 and 1000 °C. The cold-sintered WH was solely composed of single-phase WH, whereas conventionally sintered WH underwent thermal decomposition to β -TCP and β -CPP during the sintering process, representing that CSP can effectively densify thermally unstable materials. The mechanical properties of single-phase WH could be evaluated with the cold-sintered WH samples. SBF-6.0 h exhibited a Vickers hardness of 2.69 ± 0.06 GPa, fracture toughness of 0.77 ± 0.01 MPa·m^{1/2}, and Young's modulus of 67.7 ± 1.4 GPa, all of which exceeded those of CS-600 °C. However, CS-

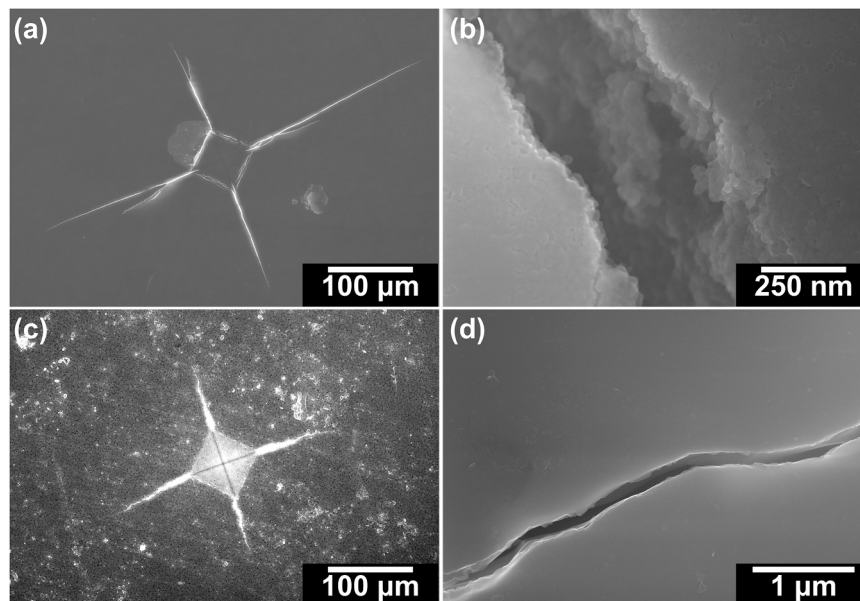


Fig. 7. FE-SEM images of Vickers indentation cracking morphologies in (a, b) SBF-6.0 h and (c, d) CS-1000 °C.

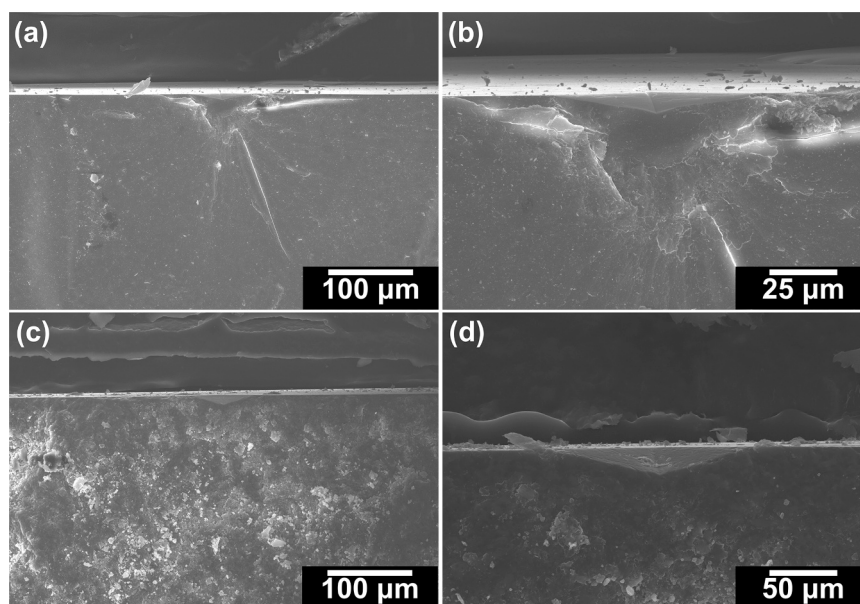


Fig. 8. Cross-sectional surfaces of Vickers indentation cracking morphologies in (a, b) SBF-6.0 h and (c, d) CS-1000 °C.

1000 °C showed higher fracture toughness and Young's modulus ($1.20 \pm 0.11 \text{ MPa}\cdot\text{m}^{1/2}$, $73.7 \pm 1.3 \text{ GPa}$). These differences are attributed to microstructure and grain boundary strength arising from distinct densification mechanisms of CSP and CS, and further elucidate the characteristic fracture modes of CSP, distinguishing them from those of CS. These results highlight that mineralization-assisted CSP using solutions containing various ions, such as SBF, is an efficient low-temperature processing route for fabricating highly dense thermally unstable bioactive ceramics. The fundamental properties of WH and the low-temperature processing route for high-density WH, as demonstrated in this study, are expected to provide a basis for future research on functional ceramics, including biomedical applications.

CRediT authorship contribution statement

Tohru Sekino: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Tomoyo Goto:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Yeongjun Seo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Shiori Nawa:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Yoshifumi Kondo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Aivaras Kareiva:** Writing – review & editing, Supervision, Methodology. **Aleksej Zarkov:** Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Data curation, Conceptualization. **Agne Kizalaite:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Jonas Stadulis:** Writing – review & editing, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jeurceramsoc.2026.118824](https://doi.org/10.1016/j.jeurceramsoc.2026.118824).

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