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## The Effect of Sintering Temperatures on the Microstructure and Properties of B-TCP

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### ABSTRACT

The purpose of this study is to investigate in detail the effect of sintering temperatures on the microstructure, physical and mechanical properties of  $\beta$ -TCP. The physical and mechanical properties of  $\beta$ -TCP were intended to be developed as a biodegradable bone substitute.  $\beta$ -tricalcium phosphate ( $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ ) powder, synthesized by a wet precipitation method, was used to prepare powder compacts by uniaxial cold pressing into cylindrical pellet form. A pressure of 100 MPa was applied using a 12 millimeter diameter mould. The  $\beta$ -TCP pellets were then sintered in a conventional furnace with a heating rate of 10 ( $^\circ\text{C}/\text{min}$ ) and a soaking time of 120 minutes, at three different temperatures, viz 1200  $^\circ\text{C}$ , 1300  $^\circ\text{C}$ , and 1400  $^\circ\text{C}$ . The results indicated that the sintering temperature at 1300  $^\circ\text{C}$  showed the most optimum properties in terms of density, hardness and microstructural features.

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## INTRODUCTION

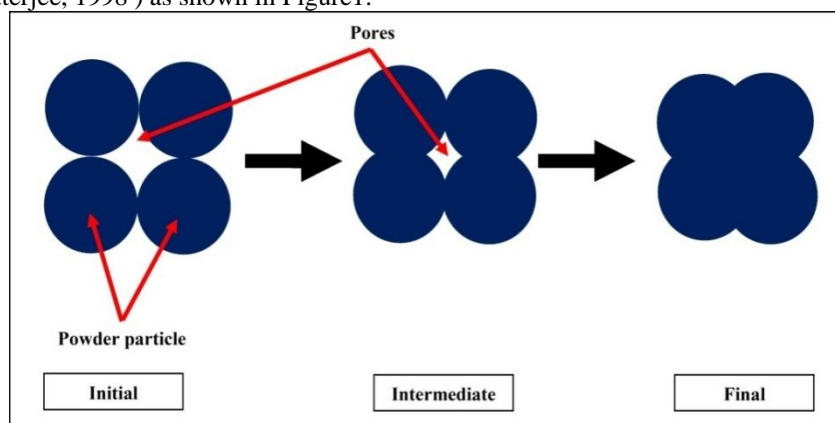
Biomaterial is a synthetic material, which is implanted to substitute living tissues for fulfilling normal functions of the body. Humans have realized that ceramics and their composites can be used to augment or replace various part of the body, particularly the bone. Therefore, ceramics used for such purpose are categorized as bioceramics (Park and Bronzino, 2003). Ceramic materials have been generally used in the medical field for more than 40 years to repair diseased or damaged hard tissue. The first generation of ceramics was first used in the 1970s; they are called bionert ceramics, made of alumina, and have been successfully implanted in humans. Meanwhile, increasing interest has been focussed on calcium phosphate materials due to their chemical composition being similar to that of the human bone. Calcium phosphate ceramics belong to the second generation of bioceramics. It has superior biological properties and began to be used in surgery from the 1980s (Champion, 2013). Ceramics used in fabricating implants can be classified as biodegradable or resorbable (non-inert), bioactive or surface reactive (semi-inert), and nonbiodegradable (relatively inert). The examples of ceramics used in biomedical applications include tricalcium phosphate [ $\text{Ca}_3(\text{PO}_4)_2$ ] which is a biodegradable ceramic, bioglass [ $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ ] and dense hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] which are bioactive ceramics, whilst alumina [ $\text{Al}_2\text{O}_3$ ], zirconia ( $\text{ZrO}_2$ ) and pyrolytic carbon are nonbiodegradable ceramics.

Among the calcium phosphate compounds, hydroxyapatite (HA) has been extensively investigated, due to HA being the main inorganic compound of the human bone (Ryu, 2002). However, studies have shown that stoichiometric HA dissolves the slowest among the calcium phosphates (Shi, 2006). When HA ceramics are implanted, low biodegradability of HA limits the bone growth and affects the chemical bonding at the interface between the HA implant and the bone (Ryu, 2002). This drawback of dense HA is compared to tricalcium phosphate (TCP). The physical and mechanical properties of  $\beta$ -TCP has been developed as a biodegradable bone substitute which becomes important to serve the role as a support whilst it is designed to degrade gradually with time and be replaced by the natural host tissue. TCP is crystalline in three allotropic forms including  $\beta$ -TCP which is stable from room temperature up to 1125  $^\circ\text{C}$ ,  $\alpha$ -TCP which is stable from 1125  $^\circ\text{C}$  up to 1470  $^\circ\text{C}$  and  $\alpha'$ -TCP which is stable from 1470  $^\circ\text{C}$  up to the melting point (Perera, 2010).

A sintering technique is the process of heating the ceramic green body to very high temperatures but lower than the melting point of the ceramic for the elimination of porosity which leads to an increase in density of the

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ceramic material. Basically, sintering techniques can be divided into two types: liquid phase sintering and solid state sintering. Liquid phase sintering occurs when a liquid phase is present in the powder compact during sintering, whilst solid stage sintering occurs when the powder compact is densified wholly in the solid state at the sintering temperature. Sintering of powder compact occurs in three stages. The initial stage is characterized by a neck formation amongst the particles, the intermediate stage is characterized by the shrinkage of open porosity, and the final stage is the shrinkage of closed pores which occurs when grain boundary diffusion becomes dominant. All three stages can be accompanied by grain coarsening, but this is most obvious in the third stage (Chatterjee, 1998) as shown in Figure 1.



**Fig. 1:** Illustration of the stages in sintering of powder particles.

Within the three allotropic forms,  $\beta$ -TCP is preferred as a bioceramic because of its chemical stability, proper bioresorption rate and mechanical strength (Ryu, 2002). The mechanical properties of  $\beta$ -TCP in bulk are too low to be used in load-bearing clinical options (Perera, 2010). For  $\beta$ -TCP ceramic to be used as surgical implants, the mechanical strength of  $\beta$ -TCP must be as high as possible. Thus the objective in this study is to investigate in more detail the effect of sintering temperature on the microstructure of  $\beta$ -TCP, and the consequent effect on properties.

## MATERIALS AND METHODS

In this study, the raw material used was  $\beta$ -tricalcium phosphate ( $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ ) as synthesized by a wet precipitation method in the REKAGRAF Laboratory (USM). The physical and chemical properties of  $\beta$ -TCP is shown in Table 1.

**Table 1:** Physical and chemical properties of REKAGRAF  $\beta$ -TCP.

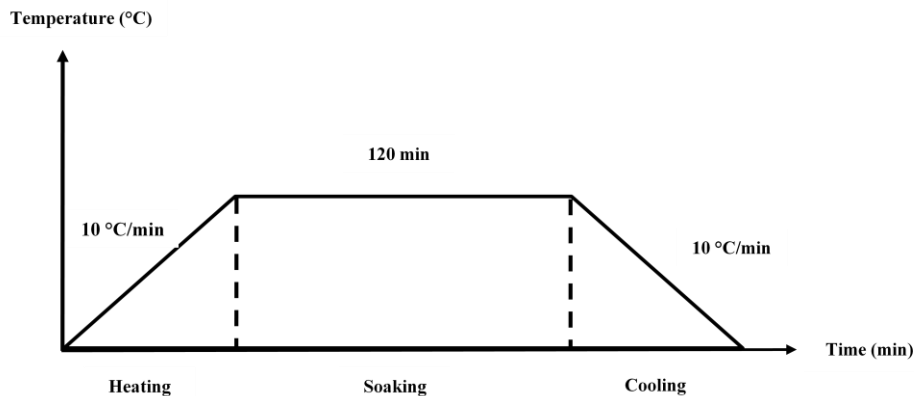
General properties	$\beta$ -tricalcium phosphate ( $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ )
Physical form	Solid powder
Colour	White
Odour	Odourless
Molecular weight	310.18 g/mol
Melting point	1670° C.
Solubility in water	Soluble

$\beta$ -TCP compacts were produced by uniaxial cold pressing into a cylindrical pellet form with an applied pressure of 100 MPa in a 12 millimeter diameter stainless steel die using a Specac manual hydraulic press machine. The pressure was held steadily for 2 minutes to ensure uniform pressure was applied to the pellets. The pressure was released slowly and the pellet was pushed out from the die. For aiding the ejection of the pellet and to remove the residual powders in the compaction die which could damage the die and the compacts being formed, chemically inert oil-based lubricant (WD-40) was used to reduce the friction.

Sintering was carried out by using a Lenton muffle furnace UAF15/5. The  $\beta$ -TCP pellets were sintered at a heating rate of 10 ( $^{\circ}\text{C}/\text{min}$ ), a soaking time of 120 minutes, and three different temperatures, viz 1200  $^{\circ}\text{C}$ , 1300  $^{\circ}\text{C}$ , and 1400  $^{\circ}\text{C}$ . Figure 2 illustrates the profile of the sintering process.

A field emission scanning electron microscope (FESEM, Supra 35 VP Zeiss) was used in this study to analyze the morphology of  $\beta$ -TCP fracture surface of the sintered pellets. In order to highlight the microstructure clearly, thermal etching was employed on  $\beta$ -TCP fracture surface by firing at a temperature 100  $^{\circ}\text{C}$  below the actual sintering temperature and soaked for 30 minutes. Linear shrinkage measurements performed in this study included the diameter and thickness of the sintered pellets which were measured before and after sintering. Dimension of the specimens were measured using a Mitutoyo digimatic calliper. Hardness test was performed on a micro scale. In this study, the micro hardness of sintered  $\beta$ -TCP pellets was measured using a

Future Tech Vickers Hardness Tester FV-7. The micro Vickers hardness test was conducted using 1 kilograms-force (kg-f) load, and a dwelling time of 8 seconds. In order to ensure a clear indentation mark on the specimen, very smooth surfaces of the pellets were obtained prior to this by polishing using an Imptech 30 V Grinder Polisher with 1.00  $\mu\text{m}$ , 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$  sized alumina powders. In addition, the bulk density and apparent porosity measurements were measured using the standard Archimedes method as specified in ASTM C 830-00.



**Fig.2:** Sintering profile of  $\beta$ - TCP pellets by conventional sintering.

## RESULTS AND DISCUSSION

### 1. Field Emission Scanning Electron Microscopy (FESEM):

The microstructure of the thermally etched fracture surface of the sintered specimens at temperatures of 1200 °C, 1300 °C, 1400 °C are shown in Figure 3.

In Figure 3, the fracture surfaces  $\beta$ -TCP sintered for 2 h at three temperatures (1200, 1300, 1400 °C) are shown. In all cases, thermal etching had successfully reveal the grain structure of the fractured surface. At 1200 °C, the grains, of about 1  $\mu\text{m}$  in size, are evident. However, the surface still exhibits a wavy fracture surface as well as the presence of some pores. At 1300 °C, the grains have grown in size (about 5 – 10  $\mu\text{m}$ ). However, the surface appears distinctly much flatter than the previous and there is virtually no pores present. At 1400 °C, the grains have growing size and the boundaries seem to be less distract. The surface appears to be glassy and there are pores observed within the grains (closed pores).

### 2. Linear shrinkage Measurement:

Linear shrinkage measurements performed in this study include the thickness and diameter of the pellets which were measured before and after sintering. The comparison between shrinkage in thickness and shrinkage in diameter is shown in Figure 4.

It can be observed that the linear shrinkage in thickness and diameter of the sintered specimens at 1300 °C is the highest. Both dimension increase in shrinkage from 1200 °C to 1300 °C. However, these dimension decrease in shrinkage as the temperature rose to 1400 °C. This can possibly be attributed to the occurrence of a slight bloating due to a liquid phase fraction as revealed by the smooth, glassy fracture surface (Fig. 3c). It is clear from the results that the shrinkage in diameter is highest than that in thickness at all temperatures. This can be attributed to the fact that the pellets had been pressed most in the vertical direction (thickness).

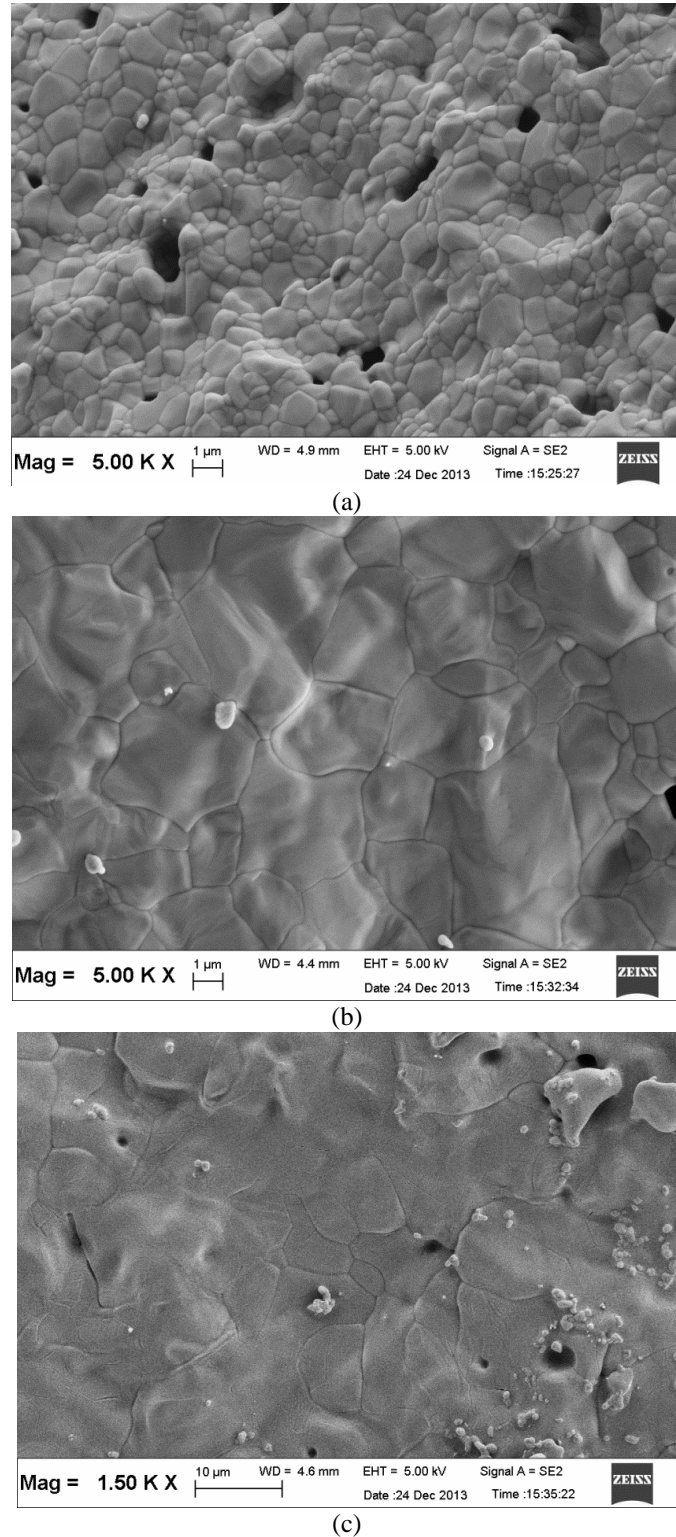
### 3. Density and porosity measurement:

The bulk density and apparent porosity measurements were performed using the standard Archimedes method as specified in ASTM C 830-00. The results of porosity and density are shown in Figure 5.

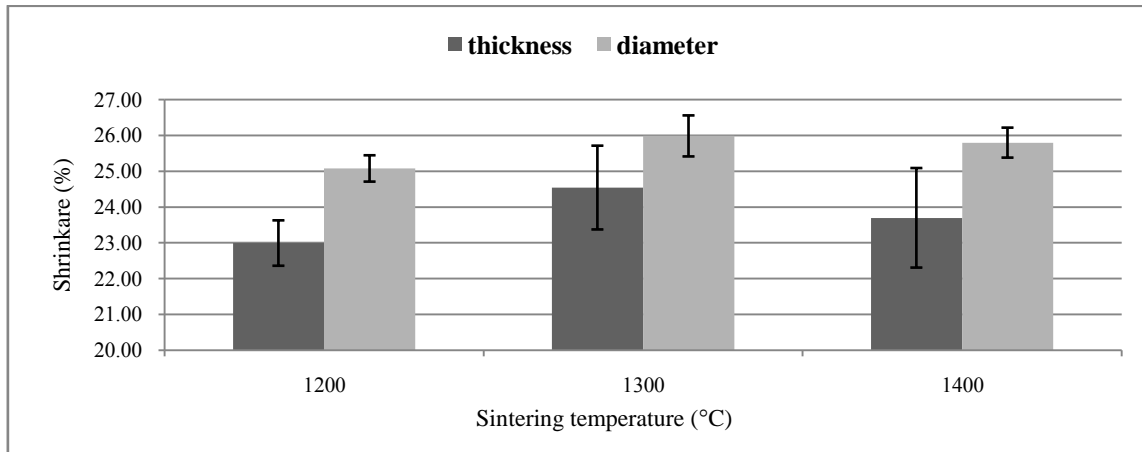
The bulk density and apparent porosity of the sintered specimens were determined as a function of temperature using the Archimedes's Principle. Figure 5(a) represents the apparent porosity of the sintered specimens at three sintering temperatures and the percentage values are 2.27 %, 1.19 %, and 1.13 % at 1200 °C, 1300 °C and 1400 °C, respectively. Figure 5(b) represents the bulk density of the sintered specimens and the results are 2.94 ( $\text{g}/\text{cm}^3$ ), 2.99( $\text{g}/\text{cm}^3$ ), and 2.95( $\text{g}/\text{cm}^3$ ), respectively. It was observed that the apparent porosity of sintered specimens at 1300 °C is slightly higher than that at 1400 °C. This can be explained by the presence of more closed pores at 1400 °C. On the other hand, the density of sintered specimens at 1300 °C is the highest value when compared with rest of the sintering temperatures. This can be explained by the microstructural features observed which confirms that the specimens sintered at 1300 °C has the most compact structure.

#### 4. Hardness test:

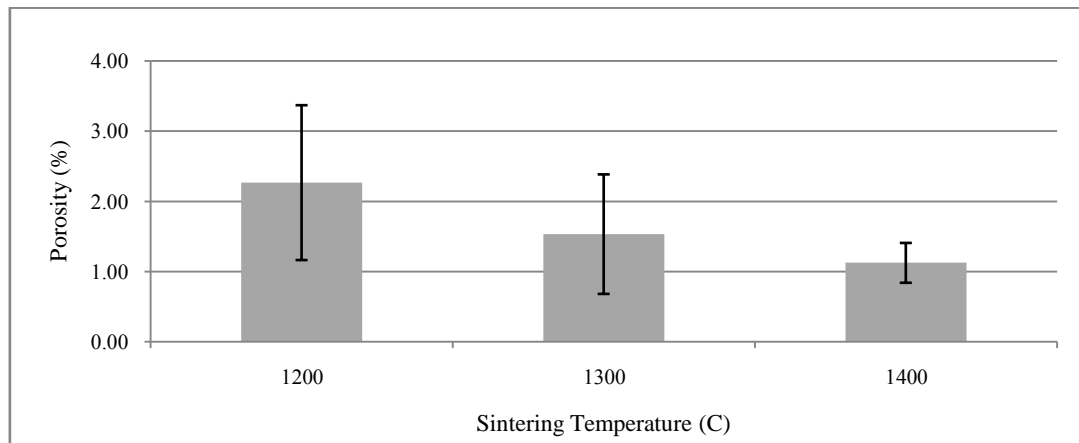
Micro Vickers Hardness test was conducted to investigate the effect of sintering temperature on the mechanical of the specimens. The hardness of sintered pellets at are 4.05 GPs, 4.62 GPa and 3.79 GPa at the sintering temperatures of 1200 °C, 1300 °C, and 1400 °C, respectively. The hardness values observed correlate well with the density and porosity values. It can be seen that the sintering temperature at 1300 °C shows the highest hardness among the three sintering temperatures.



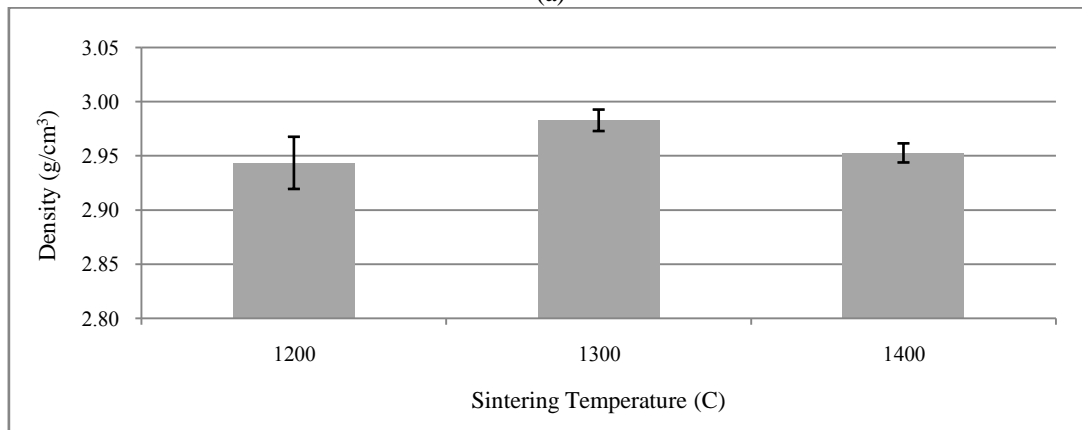
**Fig. 3:** FESEM micrographs of thermally etched fracture surface of  $\beta$ - TCP pellets (heating rate : 10 °C/min; soaking time: 2 hours) sintered (a) 1200 °C, (b) 1300 °C and (c) 1400 °C.



**Fig. 4:** Comparison between shrinkage in diameter and thickness of sintered specimens at three difference temperatures.

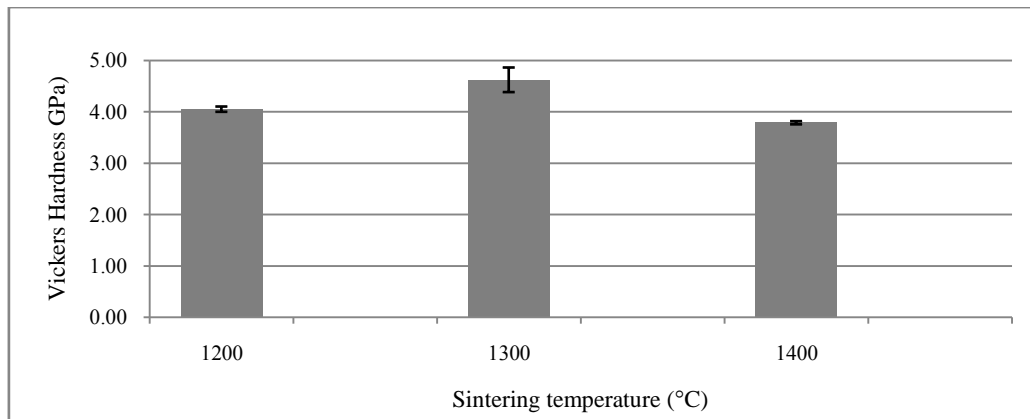


(a)



(b)

**Fig. 5:** Apparent porosity (%) and (b) Bulk density (g/cm<sup>3</sup>) of specimens samples at three different sintering temperatures.



**Fig. 6:** Hardness values of sintered specimens at three different sintering temperatures.

### **Conclusion:**

Based on the results of this study, FESEM micrographs of thermally etched fracture surface at 1300 °C can be observed to exhibit the least porosity when compared to the other temperatures. From the linear shrinkage measurement results, it can be observed that the linear shrinkage in thickness and diameter of the sintered specimens at temperature 1300 °C is the highest. The density measurement result at 1300 °C similarly shows the highest value except for porosity due to the presence of more closed pores at 1400 °C. Results from the hardness tests show that the specimens sintered at 1300 °C have the highest hardness values. Overall it can be concluded from this study that the sintering temperature of 1300 °C exhibits the optimum properties of  $\beta$ -TCP in terms of density, hardness and microstructural features.

### **ACKNOWLEDGEMENT**

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