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An examination of the effect of adding zirconia to bioactive glass-ceramic properties

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Abstract. Zirconia has been frequently used as a bone substitute based on its material properties and bioinert nature, which make it a suitable composite material for multiple bio applications. In this study, 45S5 bioactive glass ceramic (BGC) (45% SiO_2, 24.5% CaO, 24.5% Na_2O, 6% P_2O_5) was synthesised using a melt derivation process. The biocomposite for testing was prepared by mixing 1wt% of ZrO_2 with the prepared BGC. The sample of simple BGC was sintered at 900 °C, while the composite was sintered at 1170 °C. XRD diffraction testing confirmed the formation of $Na_2Ca_2Si_3O_8$ and $Na_2Ca_2Si_3O_9$ phases in the structure of pure the BGC sample, while the composite displayed the emergence of tetragonal and monoclinic ZrO_2 peaks in addition to bioglass ceramic peaks. SEM testing also showed distinct differences between the structures. The results suggest that adding ZrO_2 to the bioactive glass matrix improves its mechanical properties and increases density while decreasing the porosity value.

Keyword: bioactive glass ceramic, ZrO_2, XRD, SEM, density, porosity.

1. Introduction

Ceramics can be used for filling and rebuilding multiple non-healing bone defects and to encourage the healing of damaged or diseased parts of the muscular-skeletal system; these ae thus known as bio ceramics [1]. In the 1960s, Larry Hench first invented novel biomaterials to support full bone defects that would not rejected by people’s bodies; the first such material used with bone, discovered by Florida university, was called 45S5 bioactive glass [2]. The formulation for 45S5 bioactive glass was 45% SiO_2, 24.5% CaO, 24.5% Na_2O, 6% P_2O_5. However, the drawback of this material was its unsuitability for use in implants in load-bearing bones due to its weak mechanical characteristics. Bioglass mechanical drawbacks have often been managed by adding oxides such as magnesia, alumina, zirconia, or titania to the materials [3]. Zirconia was first utilised 20 years ago to resolve the issue of ceramic brittleness and the resultant potential failure of implants [4], as this offers an oxide ceramic with the best mechanical properties as a result of phase transformation toughening, which maximises its crack propagation strength [5]. This transformation toughening mechanism operating in the zirconia microstructure also offers additional interesting mechanical properties to zirconia-containing materials [6]. An attractive way of producing strong bioactive materials is to use composites of ZrO_2 and bioactive glass in Na_2O–CaO–SiO_2–P_2O_5 systems, allowing higher strength to be derived from the zirconia reinforcing phase while accessing the good compatibility and high bioactivity of the bioactive glass[7].

The aim of the current study was the synthesis of 45S5 bioactive glass ceramic using a melt derivation process to facilitate the preparation of bio ceramic matrix composites based on adding zirconia to the bioactive glass-ceramic. This allowed examination of the effect of adding zirconia on the mechanical and physical properties of the bioactive glass-ceramic.

2. Experimental procedure

2.1 Bioactive glass ceramic preparation

The 45S5 bioglass was prepared using 45 wt.% SiO_2, 24.5 wt.% CaO, 24.5 wt.% Na_2O and 6 wt.% P_2O_5. The materials were initially mixed in a planetary ball mill for four hours before being melted at 1,200 ˚C for 4 hours, with a rate of heating of 10 ˚C/min. The melting process was done using an alumina crucible and the melted material was then held in the furnace as it cooled. The produced material was then reheated again to 800 ˚C for 4 hours at a rate of 5 ˚C/min to complete the crystallisation process. The resulting bioactive glass ceramic was milled using a planetary ball mill for a further three to four hours.

2.2 Bioglass-ceramic/ZrO_2 composite

The composite was prepared using the bioglass-ceramic powder as a matrix with ZrO_2-3Y, 99.95%, with a purity of 99.95% and a powder size of 20 nm as the reinforcement material. The powder mixture required for sintering was obtained by mechanically mixing the bioglass-ceramic powder with 1wt% of ZrO_2 nanoparticles. The powder was ground with ethanol using an alumina ball mill for 5 hours and the resulting slurry was dried in an oven at 80 °C for 48 h. The dried powder was then crushed and sieved to create a suitable powder for compacting.

2.3 Compacting bioglass-ceramic and bioglass-ceramic/ZrO_2 specimens

Both bioglass-ceramic and composite powders were mixed with 2%wt. polyvinyl alcohol (PVA) as a binding material. Uniaxial semi-dry pressing techniques were then used to form green ceramic specimens in stainless steel cylinder moulds of 10 mm diameter. Figure 1 shows the compacted specimens (a) before sintering and (b) after sintering with appropriate surface finishing (grinding and polishing). The pressure used was 150 MPa, and the solid specimens were bonded by sintering at temperatures of 900 °C with a heating rate of 7.5 °C/min for the pure specimens and 1,170 °C with a heating rate of 10 °C/min for the composite specimens; soaking time in each case was hours, and cooling down was done inside the furnace.

Figure1. Samples (a) before sintering, (b) after sintering with surface finishing (grinding and polishing).

3. Results and Discussion

3.1 Particle size analysis

The particle size distribution of bioglass ceramic powder was measured using a Bettersize2000 laser particle size analyser (Bettersize Instruments Ltd., China). This device was housed in the ceramic and building materials section of the Materials Engineering department at the University of Babylon.

Figure 2 shows the particle size distribution analysis result s for BGC powder. The distribution of the bioactive glass ceramic particles was in range 0.1 to 75µm, and the D10, D50, and D90 were 0.794, 3.288, and 4.760, respectively.

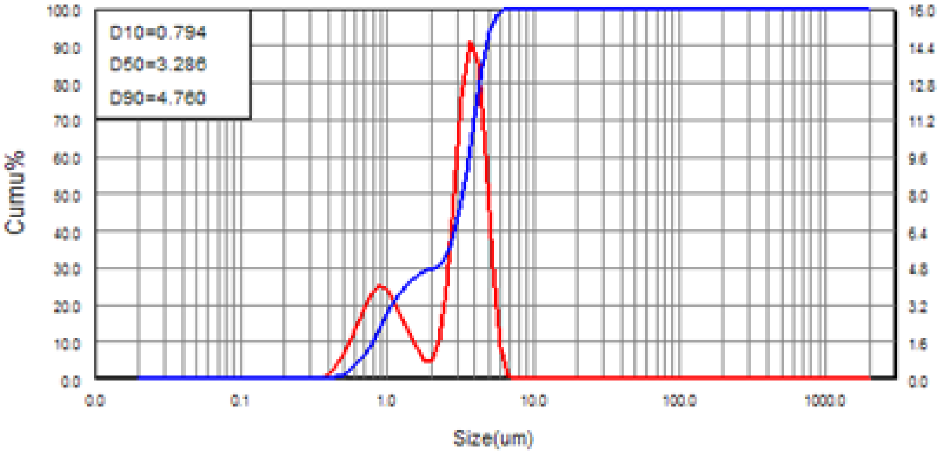


Figure 2. Particle size distribution of bioactive glass ceramic powder.

Particle size affects both mechanical and biological properties, as a small particle size leads to a higher surface area, which increases bioactivity. Moreover, control of the particle size leads to better control of the microstructure during sintering, and thus to greater control of the properties of the resulting bioglass-ceramic; this can be observed by physical, mechanical and biological properties testing.

3.2 XRD diffraction results

The phases of the prepared powders were obtained using XRD. Figure 3 represents the sodium calcium silicate (Na2Ca2Si3O9) scan for diffraction angles ranging from 20° to 80°, based on JCPDS, card NO. 22-1455; the $Na_2Ca_2Si_3O_8$ scan is also shown.

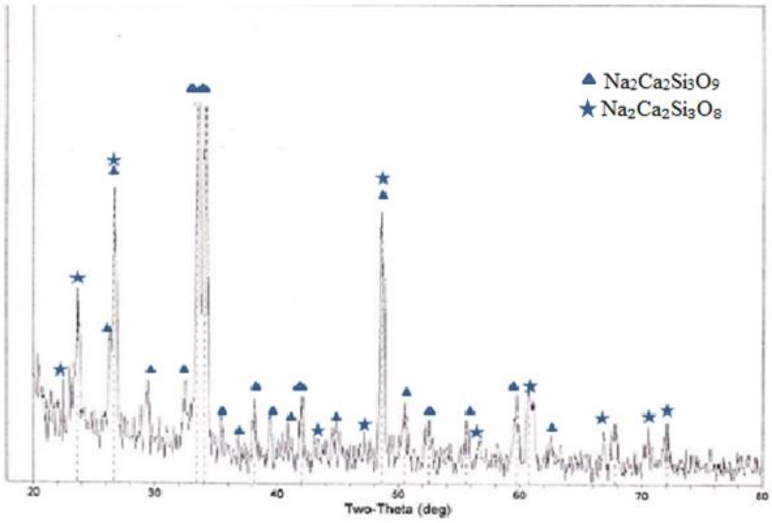
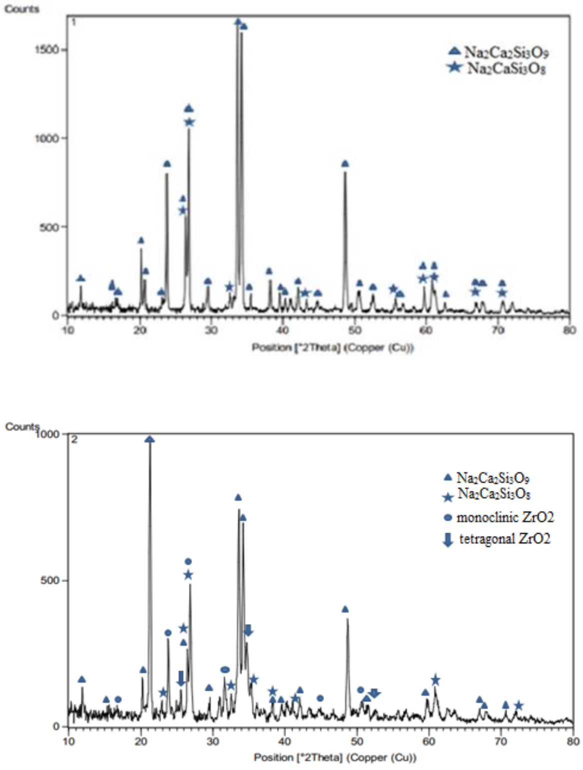


Figure 3: XRD patterns for bioactive glass ceramic powder.

Figure 4 a and b illustrate the XRD patterns of BGC sintered at **900** ˚C and the composite samples. Two types of sodium calcium silicate phases appear ($Na_2Ca_2Si_3O_9$), in agreement with JCPDS, card NO.12-0671, alongside the $Na_2Ca_2Si_3O_8$ phase common to $Na_2Ca_2Si_3O_9$ scanned at diffraction angles ranging from 10º to 60º. The peaks show agreement with the results from several other researchers [8][9][10]. Figure 4 b highlights the presence of peaks corresponding to the ZrO_2 crystals, in agreement with JCPDS, card NO.41-0017, as well as the BGC crystals.



a)

b)

Figure 4. XRD Pattern for a) BGC sintered at 900 ˚C and b) composite sample.

3.3 SEM results

The microstructure of the pure bioactive glass ceramic and composite materials (BGC with 1% wt. of zirconia) was visualised using a scanning electron microscope. The images show a dark region, representing the BGC matrix, with the reinforcement of zirconia showing as bright grains, as in Figure 5. The composite material image shows no agglomeration of zirconia in the matrix of the BGC, however [11-14].

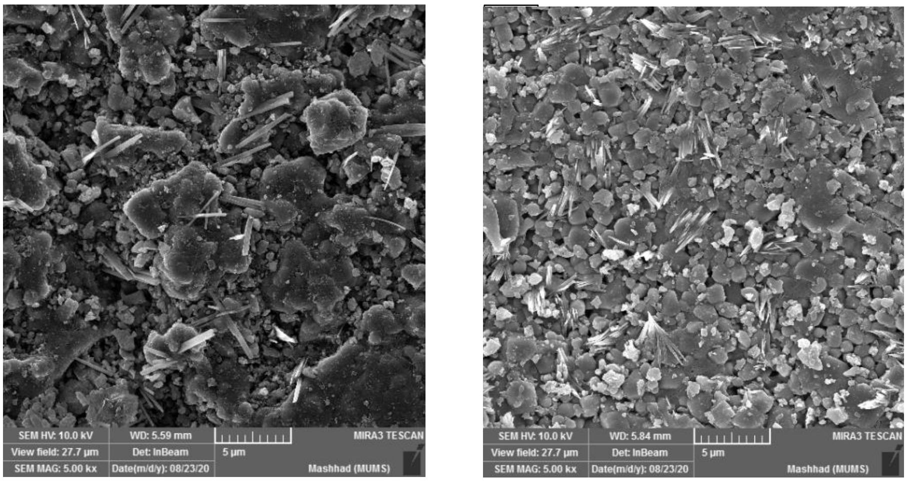


Figure5. SEM images of a) pure sample and b) composite sample.

3.4 Mechanical properties

Compression strength was determined using an electronic universal testing machine (Ceramic Department, Engineering materials, University of Babylon). The cylindrical specimens were prepared with dimensions D=13 mm, H=26 mm, and testing was done according to ASTM standard C-1424.

Vickers hardness was determined using disc specimens of 13 mm diameter and 5 mm height. The test was done according to ASTM standard C1327-90, using a digital micro Vickers hardness tester (TH-717) at 1 kg with a dwell time of 15 second.

The results of compression strength and Vickers hardness tests for the pure and composite samples showed increases when the ZrO_2 was added, with compression strengths of 15.3 MPa and 44.47 MPa and hardness results of 110 HV and 471 HV for pure and composite samples, respectively as shown in table 1. The mechanical properties' values were higher for the composites than for the pure BGC, with increases in values of about 2 to 3 times higher due to the phase transformation property which accrues with sintering at 1,170 ˚C [5] .

Table 1. Compressive strength and Vickers hardness of BGC and composite materials.

Samples	Compression Strength (MPa)	Vickers Hardness, HV
BGC sintered at 900 ˚C	15.3	110
Composite	44.47	471

3.5 Physical properties

The apparent porosity and bulk density were calculated by employing the Archimedes method according to ASTM C373-88.

The bulk density of the bioglass-ceramic samples was 2.4 gm/cm^3; this was increased to 2.49 gm/cm^3 with the addition of ZrO_2. This increase in density is due to the fact that ZrO_2 is a heavy element (ZrO_2 = 5.68 gm/cm^3) as shown in table 2 [11].

With regard to apparent porosity, the results showed that the apparent porosity was 14. % for bioglass-ceramic samples, and 13.3% for composites, which means that the ZrO_2 addition increases density and decreases porosity.

Table2. Physical properties of the BGC and composite material.

Samples	Density (gm/cm^3)	Porosity (%)
BGC sintered at 900 ˚C	2.41	14.6
Composite	2.49	13.3

4. Conclusions

- Synthesis of 45S5 bioactive glass ceramic using a melt derivation process is feasible.
- The compression strength and Vickers hardness of the composite were twice or three times higher than those of the glass ceramic matrix material.
- The addition of ZrO_2 to bioglass-ceramic increases density while decreasing porosity.

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