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Study of *in vitro* bioactivity and mechanical properties of diopside nano-bioceramic synthesized by a facile method using eggshell as raw material

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ABSTRACT

In this study, diopside bioceramic was synthesized using a mechanical milling process and subsequent heat treatment. The simplicity of experiments and also the high energy available in ball milling lead to rapid synthesis of the products in comparison with other synthesis methods. Magnesium oxide (MgO), silicon dioxide (SiO_2) and eggshell (as the calcium source) powders were weighted in stoichiometric conditions and milled to initial activation of the surface of the powder's mixture. Then a sintering process was conducted to complete formation of diopside nanopowder and also evaluates its thermal stability. The mechanisms occurred during the synthesis of this bioceramic were carefully investigated. X-Ray diffraction analysis (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetry (TG), differential thermal analysis (DTA), and inductive coupled plasma atomic emission spectroscopy (ICP-AES) were used for gathering and analyzing data. The ability and rate of apatite formation on the sample surface were evaluated by Simulated Body Fluid (SBF) test, a method that is well recognized to characterize the in vitro bioactivity of ceramic materials. According to the results obtained, the diopside samples had a significant potential to form apatite layer on their surface during soaking in the SBF solution. Besides, the bonding strength of this bioceramic was about 350 ± 7 MPa which was almost more than three times of that reported for hydroxyapatite. An excellent fracture toughness of 4 ± 0.3 MPa $m^{0.5}$ was also obtained for this ceramic which was higher than that of previously reported works.

1. Introduction

Diopside ($CaMgSi_2O_6$) as a magnesium-silicate source is a member of the solid solution series of the pyroxene group with chemical formula $CaMgSi_2O_6$. Applications in the field of phosphors, biomaterials, coatings, nuclear and solid oxide fuel cells have recently made diopside as a remarkable material [1].

According to the previous studies, the presence of magnesium ions in the crystal lattice can prevent early decomposition of the calcium/phosphate phases and lead to a low degradation of diopside in Simulated Body Fluid (SBF). It was shown also that the bond energy of Mg—O is higher than that of Ca—O one, which leads to greater stability of crystal system and prevents the rapid degradation of diopside [2]. Previous reports also showed that diopside has remarkable mechanical properties making it capable for load bearing applications [3]. Whereas, the commercially available calcium phosphate bioceramic implants have no good mechanical properties and therefore cannot be nominated for stress and load-bearing applications [4].

Various methods have already been used for the synthesis of nanocrystalline diopside powders including solid state [5], sol gel [6–8] method, coprecipitation process [9] and hydrothermal method [10], which are time and energy consuming, and have limitation when applied to bulk synthesis.

In comparison with microparticle ceramics, nanostructure and nanocrystalline ceramics have improved properties such as high contact area, high diffusion rates, reduced sintering time or temperature, and high mechanical properties. To illustrate, nanocrystalline hydroxyapatite improves osteoblast cells adhesion, differentiation, proliferation, osteointegration and Ca containing minerals deposition on its surface better than microcrystalline hydroxyapatite [11]. In comparison to sol-gel based methods, high energy ball milling (HEBM) is a simple, novel, powerful and economical method for synthesizing nanomaterials. [12,13].

In this study, diopside bioceramic was synthesized using a mechanical milling process and subsequent heat treatment. The simplicity of experiments and also the high energy available in ball

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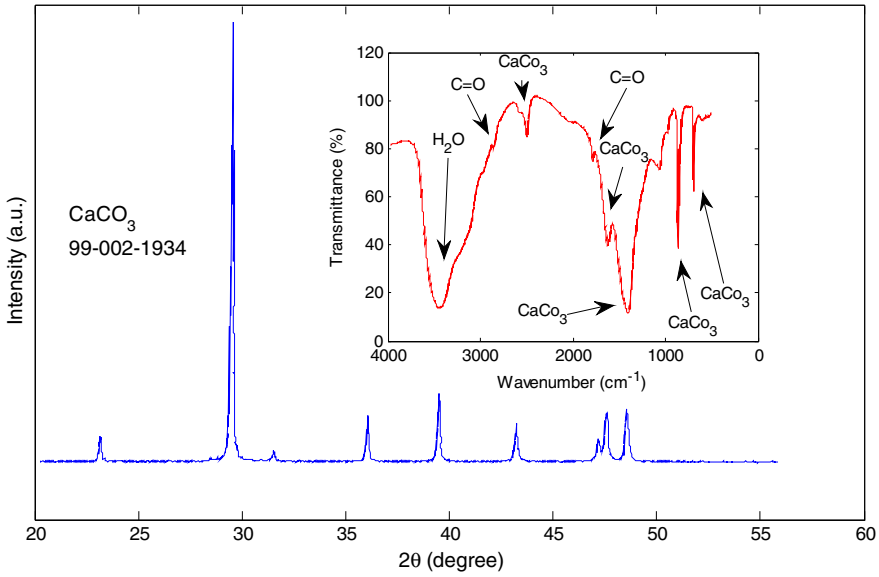

Fig. 1. XRD patterns and FTIR analysis of the produced eggshell powder.

milling lead to rapid synthesis of the products in comparison with other synthesis methods. Moreover, the use of egg shells as the calcium source will help to reduce costs.

2. Materials and methods

The eggshells were collected, micro powdered and heat treated at 120 °C for 2 h in order to eliminate their wastes. XRD patterns and FTIR analysis of the produced eggshell powder are shown in Fig. 1 which is in accordance with $CaCO_3$ powder. Regarding the reaction 1, MgO (Merck, 99%, 1–3 μm), SiO_2 (Merck, 99%, 10–30 μm) and eggshell ($CaCO_3$) powders (50 μm) were weighed and then milled in a planetary mill with a ball to powder weight ratio of 10 for 6 h. X'pert software based Scherrer formula predicted a nanoscale size in the range of 20 to 40 nm for the grains in this case.

$$CaCO_3\ (\text{egg shell powder}) + MgO + 2SiO_2 \rightarrow CaMgSi_2O_6\ (\text{diopside}) + CO_2 \quad (1)$$

Table 1 shows some of the experimental parameters and also weight of the raw materials used in this study.

The resultant powders were then pressed at 410 lb/in^2 in a cylindrical form with a size of 10 mm × 2 mm (diameter × thickness) and transferred to the furnace for sintering process at a rate of 5° per minute up to 1200 °C in order to complete the synthesis of diopside bioceramic. The holding time at 1200 °C was there hours. A part of the 6 h milled powders (without pressing) was also sintered with a rate of 5° per minute up to 1200 °C with a holding time of 3 h, for more accurate evaluation of thermal stability.

Table 1
Some of the experimental parameters and also weight of the raw materials used in this study.

Type of mill	Planetary ball mill (PM 400 – RETSCH)
Vial speed	400 rpm
Ball to powder weigh ratio	10:1
Amount of process control agent	1 wt%
Maximum sintering temperature	1200
Holding time at 1200 °C	3 h
Total weight of powder	10 g
$CaCO_3$ (eggshell) weight	3.84 g
MgO (Merck, 99%, 1–3 μm) weight	1.54 g
SiO_2 (Merck, 99%, 1–3 μm) weight	4.61 g

The crystallite size and crystalline phase of the obtained nanopowders were determined by X-ray powder diffraction (XRD) using Bruker AXS Germany, with the CuKα amount of 1.5405 Å at 30 kV and 15 mA, following a scanning rate of 51/min. Fourier transform infrared spectroscopy (FTIR, Bomen MB 100) was used for determination of functional groups. The surface morphology of the samples was examined by scanning electron microscopy (SEM, JSM/JEOL-6360). Simultaneously the elemental compositions of the samples are analyzed using Energy Dispersive Spectroscopy (EDS). The experiment is carried out at an accelerating voltage 20 kV and probe current 1 mA with counting rate 9755 cps and energy range 0–20 keV. The shape and size of prepared diopside samples were visualized by means of transmission electron microscopy (TEM, Hyundai, 100 keV). Thermogravimetry (TG), and differential thermal analysis (DTA) measurements were performed with a simultaneous thermal analyzer (SDTQ-600/Thermo Star of TA). The compression tests were performed on cylindrical samples using a Hounsfield H50KS universal testing machine at a crosshead speed of 0.5 mm/min. The mean values of porosities of the diopside samples were measured according to Archimedes method. The porosity (P) was calculated according to the following formula:

$$P = (W_2 - W_1)/(W_2 - W_3) \times 100\% \quad (2)$$

where W_1 is the weight of the sample in air, W_2 is the weight of the sample with water, and W_3 is the weight of the sample suspended in water.

SBF solution (for in vitro bioactivity testes) is prepared in laboratory with the ionic concentration nearly similar to human blood plasma, according to Kokubo method [14]. Table 2 shows the concentration of the SBF ingredients. The concentrations of Mg and P ions in Simulated Body Fluid (SBF) after soaking were tested using inductive coupled plasma atomic emission spectroscopy (ICP-AES; Zaies 110394c).

3. Results and discussions

Fig. 2 shows the thermal analyses of the raw materials powders milled for 6 h. The first endothermic peak starts at around 550 °C