ABSTRACT

In this research the solid state technique was used to synthesize five systems of glass-ceramic by combining Hydroxyapatite, Alumina and Silica in different molar percent. The X-ray diffraction analysis for all systems before and after sintering was present and discussed in this research, the morphology of these systems also investigated by scanning electron microscope (SEM), the composition of each system was analyzed by the energy dispersive x-ray diffraction (EDS). Exploitation of the Fourier Transform Infrared (FTIR) spectra to identify the chemical bonds as well as functional groups in the compound for all systems. The results present new phases such as Mullite (Al₆Si₂O₁₃) and Anorthite (CaAl₂Si₂O₈) that mean the components of these system was interacted very well. The in-vitro study also discussed by immersing the samples within the simulated body fluid (SBF). The XRD results proved the consistence of the apatite layer on the samples after immersion it in SBF.

Key words: Glass-ceramics, in-vitro, Hydroxyapatite, Alumina, Silica.

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1. INTRODUCTION

Since 1969, many investigators notified the different types of glasses and ceramics designed for bio applications as a group called "bioceramics". Bioceramics include glass, glass-ceramics, zirconia (ZrO₂), alumina (Al₂O₃), thin film coatings, Hydroxyapatite (HA) and bio-absorbable calcium phosphates. They have mainly been used for dental, skeletal and
orthopedic applications. This is on account of the chemical compatibility between the composition of certain ceramic materials and that of tissues such as bone and teeth [1-5]. Bioceramics are characterized by their nontoxicity, chemical constancy in biological mediums and biocompatibility. The purposes of bioceramics can be separated into bioinert, bioactive and bioresorbable, so this research combined this three types of bioceramics. Although traditional bioceramics exhibit brittleness and fatigue, their careful mechanical aspects can lead to many potential applications [6-10]. Some applications of functional bioceramics are dental encores, root canal cares, rebuilding the alveolar ridge, middle ear operation, spine surgery, facial and cranial bones, filling mastoid defects and to treat the defects of bone [11], substitute for hard tissue replacement, load-bearing implants, bone remodeling, as parts of devices installed in the body, skeletal and vertebral implants. Amongst the bioceramics other than glass ceramics of HA, HA has the property for usage in different forms (dense, coatings on metals, granules, putty) for biomedical applications depending on its inertness to foreign body reactions and its ability to frame new bonding with the bone and it has the properties of bioresorbable ceramics [11]. The important properties of α-alumina are chemical inertness and high hardness. Chemical and thermal constancy, relatively high strength, thermal and electrical insulation features joint with availability in abundance make aluminum oxide Al₂O₃, or alumina, attractive for bioengineering applications [12]. Abrasion resistance, strength and chemical inertness of aluminum oxides make it to be recognized as a ceramic for dental and bone implants [13]. Silica (SiO₂) is the most important and multilateral bioactive ceramic compound. It is widely existed in raw materials in the earth’s surface, and silica is a fundamental constituent of a wide range of ceramic products and glasses; its properties nominated it to be used in high-temperature and corrosive environments and as abrasives, refractory materials, fillers in paints, optical components and in bio-application materials [14].

2. MATERIALS AND METHODS

This article aims to preparing and studying different systems of glass ceramic from (HA, Al₂O₃ and SiO₂) as showing in table (1) in different molar percent, mixing the powders by the mechanical way using the balls miller and by using the handle mill. The second step was done by adding the deionized water to the mixing powder in a beaker then but on magnetic stirrer in 40 °C with 1000 r.p.m. for 4 hours, the solved was alkali (PH=9.4). In the next step, the beaker of solved was laid in ultra sonic (US) cleaner device for 4 hours to increase the homogeneity. The gel was filtered by using filtering paper for 96 hours and then the matter was dried in drying oven (Binder FED 53-UL Forced Convection Drying Oven) in 100 °C for 6 hours to remove the moisture. The dried mixture was mailed by using handle mill in two times to get very fine and mixed powder of system, contained homogenous particles of hydroxyapatite, alumina, and silica. The powder was put in American Crucible and then put in the kiln (Shin Sheng furnace, Korea) in 1100 °C for 4 hours to complete the reaction of the system contents, the mass of reactant powder was reduced because the moisture and the impurities were vanished. All five system present in table (1) will be prepare in the same way.

Table 1 The five systems prepared in different molar percent.

<table>
<thead>
<tr>
<th>The system</th>
<th>Hydroxyapatite (HA) %</th>
<th>Alumina (Al₂O₃) %</th>
<th>Silica (SiO₂) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>9.5</td>
<td>48</td>
<td>42.5</td>
</tr>
<tr>
<td>3</td>
<td>10.5</td>
<td>66</td>
<td>23.5</td>
</tr>
<tr>
<td>4</td>
<td>16.5</td>
<td>42</td>
<td>41.5</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>65</td>
<td>26</td>
</tr>
</tbody>
</table>
Glass ceramic pellets were prepared by moistureless pressing a powder that was pan-granulated using Polypropylene Glycol (PGL) binder. From every system, five pellets were formed by pressing the powder in hardened steel die of a 10 mm diameter. The heat processing is one of the significant steps in the ceramic fabrication. Ceramic powder compacts be subjected to several important changes during heat treatment, this process was very necessary to completely prepare the glass ceramic system, the samples were sintered in 1250 °C for 3 hours with heating and cooling rate 7 degrees per minute. During sintering several ceramic structural changes occurs, such as densification and grain growth. Deionized water was used for mixing and makeup of all aqueous solutions throughout the study. The density of all pellets was studied from its mass and external dimensions, the bulk density of composites was determined by Archimedes’ method. The phase compositions of the composites were examined by X-ray diffraction (XRD; GNR, Instrument Analytical Group, Explorer, Italy) operated at 60 kV with a 60 mA Cu Kα radiation source. A morphology of systems will be investigated by SEM technique (Zeiss (LEO) 1450VP Scanning Electron Microscope), the SEM was coupled with an energy dispersive X-ray spectroscopy (EDS). To determine the elemental composition and the functional groups of all elements, some powder from every system investigation using the Fourier transform infrared spectroscopy (AVATAR 370 FT:IR Thermo Nocket).

3. RESULTS AND DISCUSSION:
The X-ray diffraction analysis in figure (1) refers that all systems' interaction at 1100 °C before sintering have the same behaviour and the same phases appear although the change in molar ratio. The peaks of Silica have the largest value of intensity although that the amount of Silica less than the amount of Alumina, the reason belong to the fact that the result of reaction produces the matter of less melting point steady on the composite, the silicon oxide has a very strong interaction with Alumina and the silicon oxide has the smallest melting point so its peaks appeared the largest. The effect of Hydroxyapatite appear in slight manner because it was added in small ratio in all systems.

![Figure 1](http://www.iaeme.com/IJCIET/index.asp)
The results after sintering present very high decrees in intensity relative to results before sintering. The systems present Mullite $\text{Al}_6\text{Si}_2\text{O}_{13}$ (Aluminum silicate) [15], and the Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Calcium Aluminum Silicate) [16, 17] as a result of the interaction of powders in 1250 °C. From the figures we noted that the peaks of Mullite and Anorthite was increased in intensity and the peaks of alumina and silica was decreased. By comparing the crystallite size before and after sintering that a clear decrease in it, which means the particles have a new form. In figure (2) the Anorthite phase was appear in systems (1) and (4), while the phase Mullite was appeared in figure (3) in systems (2), (3) and (5). The third system was sintered in 1400 °C for 4 hours and the result of XRD was present in figure (4), there were no effect of Hydroxyapatite that mean the systems must sintered in degree less than this temperature.

![Figure 2](image1.png)

**Figure 2** The X-ray diffraction analysis for (1) and (4) systems sintering at 1250 °C.

![Figure 3](image2.png)

**Figure 3** The X-ray diffraction analysis for (2), (3) and (4) systems sintering at 1250 °C.
Figure 4 The X-ray diffraction analysis for the third system (3) sintering at 1400.

Morphological and crystallographic information of the synthesized systems were studied by the Scanning Electron Microscopy (SEM). The Scanning electron microscopy images present in two magnification 100 and 2 µm as shown in figure (5), the particles of the first system (1) are convergent in size, and they are separated in homogeneous form and there were no very big agglomeration. There are some porous appear in the third (3) and forth (4) systems, these porous were helpful to interact the simulated body fluid with the system and to attached with the tissue. The particle consist of many grains, they were distributed uniformly and in clear manner.

The Energy dispersive x-ray spectroscopy results were present in figure (6) for all systems. Shows the average elemental composition of the powders that used in synthesized all systems. The following are the average percentage elemental composition of the raw materials as evaluated and include, for the first system (1) the elemental composition in weight percent: O (51.9%), Al (30%), Si (10%), P (3.24%) and Ca (4.38%). For the second system (2) the elemental composition in weight percent are: O (36%), Al (23.3%), Si (31.9%) and Ca (8.4%). For the third system (3) the elemental composition in weight percent: O (42.2%), Al (31%), Si (18%), P (1.51%) and Ca (6.54%). For the fourth system (4) the elemental composition in weight percent: O (47.8%), Al (22.3%), Si (18%), P (1.02%) and Ca (9.94%). And the elemental composition for the fifth system (5) was: O (41.05%), Al (34.74%), Si (17.22%) and Ca (6.99%).
Figure 5 The SEM images of five systems, every system in two ranges 100 and 2 µm.
Figure 6 The EDS images of the five systems.
The Fourier Transform Infrared (FTIR) spectra of the synthesized systems in the wavenumber range of 400-4000 cm\(^{-1}\) which identifies the chemical bonds as well as functional groups in the compound are present in figures (7) to (11) below show common bands assigned to various vibrations in the systems, respectively. The IR spectra of all specimens show broad bands in the high energy region that are probably water related bands [18-20].

The analysis of these spectra revealed the weak broad band centered at around 3430 cm\(^{-1}\) for first system (1) and fifth system (5), and strong broad band centered at around 3427 cm\(^{-1}\) for second (2) and third (3) systems, and strong broad band centered at around 3448 cm\(^{-1}\) for fourth (4) system correspond to the overlapping of the O-H stretching bands of hydrogen-bonded water molecules (H-O-H...H) and SiO-H stretching of surface silanols hydrogen-bonded to molecular water (SiO-H...H2O) [21]. The weak absorption band and the medium intense absorption band corresponding to the adsorbed water (H-O-H) molecules deformation vibrations appear at 1625 cm\(^{-1}\) and 1630 cm\(^{-1}\) in all systems [22]. The very intense band at 1111 cm\(^{-1}\) for third system (3) and very intense band at 1106 cm\(^{-1}\) for (5) system assigned to the longitudinal optical (LO) modes of the Si-O-Si asymmetric stretching vibrations [23]. A strong peak centered at 1045 cm\(^{-1}\) transverse optical mode (TO \(\nu_{as}-Si-O-Si\)). The bonds at 1072 cm\(^{-1}\) corresponds to the symmetric (Al-O-Al) mode of boehmite. The weak shoulder band at around 693.24 cm\(^{-1}\) and 694 cm\(^{-1}\) appear in all systems is assigned to Si-OI stretching of the SiO\(_2\) [24, 25]. A sharp peak at 453 cm\(^{-1}\) corresponding to Si-O-Si band, a weak absorption at 945 cm\(^{-1}\) were belonged either to Si-O amorphous mode or due to silanol (Si-OH) stretching vibrations. And the bands at 884, 740, 621 and 479 cm\(^{-1}\) are attributed to the Al-O bands of boehmite. The sharp peak at 775-790 cm\(^{-1}\) corresponding to \(\Theta\)-alumina (Al\(_2\)O\(_3\)) phase. The peaks between 520 and 530 cm\(^{-1}\) belong to P-O band crystal. A peak at about 600 cm\(^{-1}\) corresponding to \(PO_4\)\(^{3-}\) and the sharp peak at 560 cm\(^{-1}\) belong to \(\alpha\)-Al\(_2\)O\(_3\) (corundum) [26]. The differences in spectra between all systems may attributed to the impurities present in substances or to different ratios of adding.

![Figure 7 The FTIR spectroscopy of the first system (1).](http://www.iaeme.com/IJCIET/index.asp)
Figure 8 The FTIR spectroscopy of the second system (2).

Figure 9 The FTIR spectroscopy of the third system (3).

Figure 10 The FTIR spectroscopy of the fourth system (4).
The bioactivity of the syntheses samples of glass ceramics systems was studied in-vitro by immersion the samples in the simulated body fluid (SBF). X-ray diffraction can illustrated the new phases that growth on the surfaces of the sample in comparing it with the results before immersion. In all systems present in figure (12) to figure (16) that clear the appearing of a new beaks of Hydroxyapatite, and increasing in the number of beaks of the Anorthite. These results improve that the small amount of Hydroxyapatite that was added in syntheses of systems will stimulation the samples to interact with the SBF.
Figure 13 The XRD for the second system (2) after immersion in the SBF.

Figure 14 The XRD for the third system (3) after immersion in the SBF.
Figure 15 The XRD for the fourth system (4) after immersion in the SBF.

Figure 16 The XRD for the fifth system (5) after immersion in the SBF.
4. CONCLUSIONS

By taking the conditions of syntheses for systems and the results of this study into account, the following conclusions can be abstracted in:

- Ceramics systems with a composition of (HA:Al₂O₃:SiO₂) were successfully synthesized by the solid state method.
- This method has the property to synthesized glass ceramic systems at a minimum temperature compared with the traditional melting route that requires high temperature.
- The results present new phases such as Mullite (Al₆Si₂O₁₃) and Anorthite (CaAl₂Si₂O₈) and there was no effect of adding Hydroxyapatite when sintering at 1400 °C that mean the systems contain Hydroxyapatite must sintering in temperature less than 1400 °C.
- Examination of apatite formation on the surface of a material in SBF is useful for predicting the in-vivo bone bioactivity of the material, not only qualitatively but also quantitatively. This method can be used for screening bone bioactive materials before animal testing and the number of animals used and the duration of animal experiments can be remarkably reduced by using this method, which can assist in the efficient development of new types of bioactive materials.
- In-vitro bioactivity study carried out in SBF solutions showed the formation of bone-like apatite layer on the (HA:Al₂O₃:SiO₂) ceramic systems.

REFERENCES

Structural Properties of HA:Al₂O₃:SiO₂ Glass Ceramics Systems for Bio Applications


