Analysis calcium concentration of crab shells on variation of temperature and bioceramic material

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Abstract. Mangrove Crab (Scylla spp) has a large calcium content that can use as a material source of denture based bioceramic. In this study, we use some material to support a crab shell powder to produce ceramic-forming materials such as feldspar, quartz, and kaolin. The samples formed into variations composition and sintering time for 100°C and 900°C for 30 minutes. The calcium concentration of the sample determined by using X-Ray Fluoresence (XRF) and molecular bonds obtained from Fourier transform infrared (FTIR) characterization. From the results shows a good sample of further development with ratio composition of the samples are 1.33: 1.33: 0.67: 0.67 at 900°C obtained SiO$_2$ composition (66.84%), Al$_2$O$_3$ (19.44 %), Fe$_2$O$_3$ (0.63%), CaO (19.44%), K$_2$O (0.39%), while CaO has stronger of molecular bonding with each sample, both at sintering time for 100°C and 900°C temperature of sample. This data indicated that crab shell contains high calcium which is component that very effective to use as material of dentures based bioceramic.

1. Introduction
The development of ceramics made a new breakthrough especially in terms of bio ceramic development [1]. Applications of this bioceramics can be in the field of health, especially as orthopedics, dental implants and bone cement [1]. Other application such as Bio-Inert (alumina, zirconia), bioaktiv (Hidroksiapatit, glass bioaktif, dan glass tiles) [2]. Some previous research developed bio ceramic denture of various materials obtained from nature such as from egg shells and shells of blood clams. In this research we developed the manufacture of bio ceramic to be developed furthen using basic materials that are easy to obtain in nature and contain calcium carbonate (CaCO$_3$) abundantly. Crab shell content calcium carbonate 40% to 70% [3]. Crab shell is used in this research as the raw material because it is easy to find around. Crab shell content 85.85% of CaO and the sintering to 900°C obtained a pure hydroxiapatite (HAp) from a crab shell of 65.5% [4].

2. Experimental

2.1 Materials and tools
The materials that used in this research are natural materials such as Filedspar, Kaolin, Quartz, Mangrove Crab Shell (Scylla spp) which has been sieved by 250 mesh, Opaque Liquid, mold size 1x1 cm, Furnace labTech, XRF Thermo Scientfic, and FTIR.
2.2 Preparation of Bioceramic Samples
Mangrove crab shell (Scylla spp) has been crushed then sieved using a 250 mesh sieve, and mixed with Feldspar, Kaolin and Quartz. There are 4 variation composition and its sintering on temperature 100°C and 900°C for 30 minutes.

| Sample | Sintering | Composition (gr) | Feldspar | Quartz | Kaolin | Crab Shell |
|--------|-----------|------------------|----------|--------|--------|------------|
|        |           |                  | A1       | 0.45   | 1.77   | 133        | 0.45 |
| A2     | 900°C     |                  |          | 0.45   | 177    | 1.33       | 0.45 |
| B1     | 100°C     |                  | 0.66     | 1.33   | 1.33   | 0.66       |
| B2     | 900°C     |                  | 0.66     | 1.33   | 1.33   | 0.66       |
| C1     | 100°C     |                  | 0.5      | 1.77   | 1.33   | 0.5        |
| C2     | 900°C     |                  | 0.5      | 1.77   | 133    | 0.5        |
| D1     | 100°C     |                  | 1.33     | 1.33   | 0.67   | 0.67       |
| D2     | 900°C     |                  | 1.33     | 1.33   | 0.67   | 0.67       |

2.3 Sample Characterization
Characterization of each sample that has been sintering on temperature of 100°C and 900°C by X-Ray Flouresence (XRF) and the Fourier Transform Infrared (FTIR) which was conducted in Science Laboratory FMIPA Hasanuddin University.

3. Results and Discussion
3.1 Characterization of X-Ray Flouresence (XRF)
The X-Ray Flouresence spectrometer is used to analyze the chemical composition of bioceramic sample, both in the form oxide and element, see table 2.

| Sample | Element | Sample | Oxide |
|--------|---------|--------|-------|
|        | Si      | A1     | SiO₂  |
| A1     | 55.8    |        | 70.55 |
| A2     | 56      |        | 70.88 |
| C1     | 50.7    |        | 69.4  |
| C2     | 51.2    |        | 66.8  |
| D1     | 51.6    |        | 70.29 |
| D2     | 53.9    |        | 66.84 |

From the results obtained in table 1, there are different elements formed on the bioceramic samples of the crab shell mix (scylla spp) which is heated at a temperature of 100°C and 900°C. Increased the
sintering temperature will increase the concentration of Si. Sample A2 and B2 have the higher content of Si. This formed Si comes from quartz is derived from element Si-O forming of Silica dioxide [5] (SiO2) which is important as a ceramic body shaper [6]. Meanwhile, increased the temperature of sintering will decrease concentration of calcium in sample. The oxide data that formed by each sample is seen less than 30%. The sample C1 and D1 are sintered at 100°C, have a higher content of CaO, which is 29.87% and 28.85%. Compared with the sample C2 and D2 which content 25.62% and 19.44% of CaO. Concentration of Ca and CaO in each sample is reduced during sintering. The sample D2 has 19.44% of Al2O3, which is higher than standard (18.79% Al2O3).

From 8 samples of bioceramic material, good sample to be developed is D2 sample with content SiO2 (66.84%), Al2O3 (19.44%), Fe2O3 (0.63%), CaO (19.44%), K2O (0.39%) although CaO is still below the standard 61.60%.

3.2 Characterization of Fourier Transform Infrared (FTIR)
The result of characterization of FTIR Test by comparing 4 samples at temperature difference 100°C and 900°C can be seen in the picture below:

![Figure 1](image1.png)
**Figure 1.** Sample Bioceramic A1 dan A2

![Figure 2](image2.png)
**Figure 2.** Sample Bioceramic B1 dan B2

![Figure 3](image3.png)
**Figure 3.** Sample Bioceramic C1 dan C2

![Figure 4](image4.png)
**Figure 4.** Sample Bioceramic D1 dan D2

From the four samples obtained OH group appears very sharp on the wave number 3600 cm⁻¹, namely in figure 1 at 3695.61 cm⁻¹ and 3641.60 cm⁻¹, figure 2 pada 3695.61 cm⁻¹, 3620.39 cm⁻¹ and 3641.60 cm⁻¹,
figure 3 3695.61 cm$^{-1}$ and 3641.60 cm$^{-1}$; figure 4 3695.61 cm$^{-1}$ and 3643.53 cm$^{-1}$. The sharp peak at the wave number represents the typical OH peak of Ca(OH). CO groups in all four samples have wave numbers 1400s is a typical peak of CO$_3^{2-}$. Numbers in waves 900-700 also still the CO category but the typical peak at that point CaCO$_3$. The CaO group is the typical peak of asymmetric vibrations PO$_4^{3-}$.

The existence of such clusters is possible crab shells containing phosphate groups. The phosphate group is the group that has the sharpest peak of the wave number since the main group HAp is a phosphate group. On the four FTIR samples can be seen that at temperature 100$^\circ$C more visible pick compared to sintering temperature 900$^\circ$C with a higher pickup, in the sense that there are still many impurity factors at temperature 100$^\circ$C and better sample on sintering 900$^\circ$C, the peak wavelength of the four samples can be seen in table 3.

**Tabel 3. Bioceramic wave numbers of mangrove Crab Shells**

| Wave Numbers (Cm$^{-1}$) | A1 100$^\circ$C | A2 900$^\circ$C | B1 100$^\circ$C | B2 900$^\circ$C | C1 100$^\circ$C | C2 900$^\circ$C | D1 100$^\circ$C | D2 900$^\circ$C |
|--------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| OH                       | 3695.61        | 3641.60        | 3695.61        | 3620.39        | 3641.60        | 3695.61        | 3695.61        | 3643.53        |
| CO$_3^{2-}$              | 1481.33        | 1423.47        | 1460.11        | 1529.55        | 1477.47        | 1425.40        | 1465.90        | 1421.54        |
|                          | 1429.25        | 790.81         | 1431.18        | 1462.04        | 792.74         | 788.89         | 1427.32        | 788.89         |
|                          | 912.33         | 912.33         | 1425.40        | 1425.40        | 914.26         |                |                |                |
|                          | 794.67         | 792.74         | 790.81         |                |                |                |                |                |
| PO$_4^{3-}$              | 1111.00        | 1085.92        | 1109.07        | 1085.92        | 1085.92        | 1085.92        | 1105.21        | 1087.85        |
|                          | 1083.99        | 462.92         | 1085.92        | 462.92         | 1033.85        | 462.92         | 1089.78        | 462.92         |
|                          | 1033.85        | 1033.85        | 1008.77        | 1033.85        |                |                |                |                |
|                          | 1008.84        | 1006.84        | 538.14         |                |                |                | 1008.77        |                |
|                          | 538.14         | 538.14         | 466.77         |                |                |                | 540.07         |                |
|                          | 468.70         | 468.70         |                |                |                |                |                |                |

4. Conclusion

It can be concluded that a good composition of bioceramic material is in sample D2 with content SiO$_2$ (66.84%), Al$_2$O$_3$ (19.44%), Fe$_2$O$_3$ (0.63%), CaO (19.44%), K$_2$O (0.39%) although CaO is still below the standard i.e 61.60%. Concentration CaO need to be incresed to get a better sample.

5. References

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