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Characterization of crystalline phases of bone ash

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Abstract

Bone ash has been prepared from waste cattle bone choosing two different calcination temperatures (1050 ^{o}C and 1100 ^{o}C). The heat treatment was performed by conducting quenching and without quenching techniques. The prepared bone ash was characterized using XRF, XRD and FTIR techniques which revealed that the observed data were in excellent agreement with the standard values for hydroxyapatite (the prime raw material of bone china) and could be used as the raw material for bone china ceramic ware.

Keywords: Characterization, Bone ash, XRF, XRD, FTIR

Introduction

Bovine ash is the prime raw material for the fabrication of bone china, which is a very special and attractive porcelain ware throughout the world. The particular characteristics of bone china include whiteness, translucency, decoration quality, bright glaze and high strength. However, all these properties are strictly dependent on the quality of the raw materials used to fabricate bone china body. Traditionally bone china is produced using the raw materials bone ash, china clay and cornish stone [Gouvêa *et al.* 2009, Kara and Stevens 2002, Miyahara *et al.* 2007, Weyl 1941]. However, compositions of these raw materials may vary from one company to another but the constituents are within the approximate weight ratio of 2:1:1 respectively [Kara and Stevens 2002]. The minerals and oxides generally used in the manufacture of bone china are shown in Table I [Kara and Stevens 2002].

Table I : Weight % of minerals and oxides used in bone china

Raw material	Mineral	Oxides	Wt %
Bone ash	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	50
China clay	Kaolinite	Al_2O_3 $2SiO_2$ $2H_2O$	
	Feldspar	K_2O Al_2O_3 $6SiO_2$	25
Cornish stone	Quartz	SiO_2	
	Mica	$K_2O_3Al_2O_3$ $6SiO_2$ $2H_2O$	25

The traditional process of bone ash production is a combination of few steps which include: removal of meat, protein etc. using hot water, steam, solvents followed by drying and calcination at high temperature in order to remove organic constituents [Gouvêa *et al.* 2009]. The final product thus obtained is basically known as calcium hydroxyapatite (HA). However in addition to thermal decomposition, subcritical water process and alkaline hydrolysis are also used to extract HA from animal bone [Barakat *et al.* 2009, Ooi *et al.* 2007, Sobczak *et al.* 2009].

Although in Bangladesh the demand of bone china porcelain ware is extremely high compared to any other ceramic ware, but unfortunately the ceramic industries of this country are importing the raw materials to produce bone china porcelain ware. This import business costs a lot of foreign exchange which obviously affects the country's economy. However in the perspective of Bangladesh a developing country, this bone china porcelain ware industry can flourish significantly. Because huge amount of raw bones are abundant in our country which could be the potential source of raw materials for bone china porcelain ware. However to develop a cost-effective and optimized process for the fabrication of bone china, a number of factors e.g. temperature of heat treatment, time etc. need to be investigated properly, but unfortunately these are not well justified in the literature [Gouvêa *et al.* 2009]. From these points of views, in this paper an attempt has been taken to develop an effective protocol to prepare bone ash using waste cattle bone, which will also open up another way of material recycling technology for future waste management.

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Materials and Methods

The raw bones were collected from a local butcher shop and cleaned by removing spongy bones, bone marrow, any trace of meat and fat etc. It was then heat treated with steam at 100°C to get rid of any unwanted materials, blood content etc. This cleaning procedure followed by drying at 100 °C and the bones were crushed into small chips. These bone chips were treated at 1050 °C and 1100 °C temperatures using a 2 °C min^{-1} ramp and 30 min soaking time. The heat treatment was performed by conducting quenching and without quenching techniques. Complete burning of organic matters was ensured by providing air flux inside the furnace. The heat treated bone chips were transformed to fine powder through ball mill operation for 2 hrs and then subjected to various physical and chemical analyses.

Elemental analysis of the heat treated bone ash was performed by x-ray fluorescence spectroscopy (XRF) while the functional groups were identified by fourier transform infrared spectrometer (FTIR). The experimental spectra were recorded by using KBr disks (sample-to-KBr ratio = 1:100) and the samples were scanned in the wave number range of 4000 cm^{-1} - 400 cm^{-1}. The spectrometer had a resolution of 4 cm^{-1}. Phase analysis of the bone ash samples was carried out by x-ray diffractometer (XRD). The intensity data were collected in 0.02° steps following the scanning range of $2\theta = 20^{o}$ - 80° using CuKα ($\lambda = 1.54178^{o}$A) radiation. The phases were compared with the standard JCPDS files.

Result and Discussion

As a preliminary step of physical characterization the density of the calcined bone ash powder was calculated. The observed values as summarized in Table II show that only the density of bone ash powder calcined at 1100 °C without quenching condition is in good agreement with the standard density value of hydroxyapatite (3.145 g/cm^3) [Bahrololoom *et al.* 2009]. Hence this bone ash sample was further subjected to XRF, XRD, FTIR and SEM analyses.

Table II: Physical properties of bone ash

Temperature	1050 °C		1100 °C	
	Quenching	Without Quenching	quenching	Without quenching
% of loss on ignition	3.18	3.33	3.95	4.04
Density g/cc	0.24	2.60	0.27	3.24

The chemical composition of this bone ash sample as investigated by XRF is shown in Table III. Clearly the principal chemical constituents are within the expected range as observed previously [Gouvêa *et al.* 2009, Bahrololoom *et al.* 2009, Haberko *et al.* 2006]. The slight discrepancy of these observed values could be due to the different type of bone used. The bones were purchased from the local market and hence the exact information about the breed and age of the cattle are unknown. Although these information acts as the influential parameters in regulating the composition of HA in the calcified tissues. However, the negligible presence of iron content (0.01%) ensures the application of this raw material to achieve optimal visual properties of bone china. Because iron affects the whiteness of bone china as a colouring impurity.

Table III: Chemical analysis of bone ash sample treated at 1100 °C

Parameters	Amount present in %
SiO_2	2.40
Al_2O_3	2.34
Fe_2O_3	0.14
CaO	53.00
SO_3	0.30
MgO	1.52
Na_2O	1.08
K_2O	0.15
ZrO_2	0.00
BaO	0.14
P_2O_5	38.19

The result of FTIR analysis is tabulated in Table IV. It is observed from the FTIR data that the observed bands are in well matched position representing the phosphate group as found in previous investigation [Zaki *et al.* 2006, Tas 2000, Xu *et al.* 2001] where the author also observed the presence

Table IV: FTIR of calcined (1100 °C) bone ash sample (without quenching)

Observed band position (cm^{-1})	Corresponding assignments	References to match the observed band positions
462.9	PO_4^{3-} (v_2)	Tas 2000, Xu *et al.* 2001,
567.0	PO_4^{3-} (v_4)	Haberko *et al.* 2006,
603.7	PO_4^{3-} (v_4)	Joschek *et al.* 2000
947.0	PO_4^{3-} (v_3)	
979.8	PO_4^{3-} (v_3)	
1458.1	CO_3^{2-}	

of phosphate group in v_3 and v_4 mode at 1150 - 963 cm^{-1} and 655 - 548 cm^{-1} respectively. A small peak at band position 1458.1 cm^{-1} could be due to the CO_3^{2-} group. Since the presence of CO_3^{2-} group is a common impurity effect in both synthetic and natural hydroxyapatite [Haberko *et al.* 2006, Joschek *et al.* 2000].

A typical XRD diffraction of bone ash sample is presented in Figure 1. The diffractogram ensures the presence of hydroxyapatite (HA) having hexagonal structure (space group $P6_3/m$) as the dominant phase with the characteristic 2θ positions at 31.88296° (2 1 1), 32.1828° (1 1 2) and 32.9927° (3 0 0). On the other hand β -TCP is also indexed as mixed phase (JCPDS File # 09-0169) having rhombohedral structure (space group R3c) [Ahmed *et. al* 2008]. Particularly the diffraction peaks at 2θ positions 29.8314 (3 0 0), 31.2638 (0 2 10) and 34.5834 (2 2 0) plane confirmed the presence of β-TCP along with the HA. This observation is quite satisfactory because at 1000° C-1100° C sintering temperature, HA usually forms crystallized β-TCP according to the following equation.

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2 + CaO + H_2O \text{ ---------- (1)}$$

The lattice parameters for both phases were calculated considering the Bragg reflections at (0 0 2), (3 0 0) planes and (0 2 10), (3 0 0) planes for HA and β -TCP respectively. The volume of the hexagonal unit cell for HA and the rhombohedral unit cell for β -TCP were calculated using Equations 2 and 3 [Ahmed *et. al* 2008] respectively.

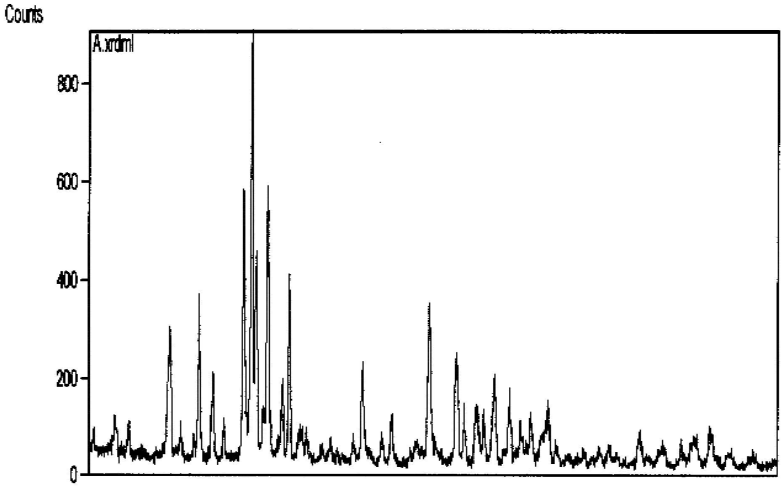

Fig. 1: XRD of calcined (1100 °C) bone ash sample (without quenching)

$$V = 2.589a^2c \text{ ---------- (2)}$$

and $$V = 0.866a^2c \text{ ---------- (3)}$$

The crystallite sizes of HA and β-TCP were determined from Scherrer's relationship D = 79.5/ Δ cos θ, where D = crystal size (°A), Δ = FWHM in degree. The crystallo

Table V: Crystallographic parameters of the bone ash sample

Sample	Phase and symmetry	Lattice constants (°A)		Unit cell volume, V (°A)	Crystallite sizes, nm
		$a = b$	c		
Bone ash	HA				
	Hexagonal	9.41	6.88	1577.25	42.0
	β -TCP	10.37	37.12	3457.11	84.6
	Rhombohedral				
JCPDS File # 09-0432	HA Hexagonal	9.42	6.88	1580.84	
JCPDS File # 09-0169	β-TCP Rhombohedral	10.43	37.38	3520.91	

graphic parameters of the bone ash sample were compared with the standard JCPDS files and summarized in Table V. The data shown in Table V indicates that although the crystallographic parameters for HA matches with the standard value but in case of β-TCP the values slightly differs from the standard values which could be due to formation of β-TCP in poor crystalline form.

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References

Ahmed S and Ahsan M (2008). Synthesis of Ca-hydroxyapatite bioceramic from egg shell and its characterization, *Bangladesh J. Sci. Ind. Res.* **43**(4): 497 - 508.

Ahmed S and Ahsan M (2008). Structural characterization of Ca-phosphate bio-ceramics from egg shell, *Proceeding of the Bangladesh Chemical Congress,* 160-166.

Bahrololoom ME, Javidi M, Javadpour. S and Ma J (2009). Characterization of natural hydroxyapatite extracted from bovine cortical bone ash, *J. Ceram. Proc. Res.,* **10**(2): 129 - 138.

Barakat NAM, Khil MS, Omran AM, Sheikh FA and Kim HY (2009). Extraction of pure natural hydroxyapatite from the bovine bones biowaste by three different methods, *J. Materials Processing Technology*, **209**(7): 3408 - 3415.

Gouvêa D, Alatrista GAV, Brito SLM, Castro RHR and Kahn H (2009). Surface modification of bovine bone ash prepared by milling and acid washing process, *Ceramics International*, **35:** 3043 - 3049.

Haberko K, Bucko MM, Brzezińska-Miecznik. J, Haberko M, Mozgawa W, Panz T, Pyda A and Zarębski J, (2006). Natural hydroxyapatite - its behaviour during heat treatment, *J. Euro. Ceram. Soc.,* **26**(4-5): 537-542.

Joschek S, Nies B, Krotz R and Gopferich A (2000). Chemical and physicochemical characterization of porous hydroxyapatite ceramics made of natural bone, *Biomaterials,* **21:** 1645 - 1658.

Kara A and Stevens R (2002). Characteruzation of biscuit fired bone china body microstructure. Part I: XRD and SEM of crystalline phases, *J. Euro. Ceram. Soc.,* **22:** 731-736.

Miyahara RY, Gouvêa D and Toffoli SM (2007). Preparation and characterization of bovine bone ash for the fabrication of bone china. *Cerâmica,* **53**(327): 234-239.

Ooi CY, Hamadi M and Ramesh S. (2007). Properties of hydroxyapatite produced by annealing of bovine bone, *Ceramics International,* **33:** 1171 - 1177.

Sobczak A, Kowalski Z and Wzorek Z (2009). Preparation of hydroxyapatite from animal bone, *Acta of Bioengineering and Biomechanics,* **11**(4): 23-28.

Tas, AC (2000). Synthesis of biomimetic Ca-hydroxyapatite powders at 37°C in synthetic body fluids, *Biomaterials,* **21** 1429.

Weyl WA (1941). Phosphates in ceramic ware: II, Role of phosphorus in bone china, *Journal of the American Ceramic Society,* **24:** 245-247.

Xu, G, Aksay, IA and Groves JT (2001). Continuous Crystalline Carbonate Apatite Thin Films. A Biomimetic Approach, *J. Am. Chem. Soc.,* **123** 2196.

Zaki. MI, Knozinger H, Tesche B and Mekhemer GA H (2006). Influence of phosphonation and phosphonation on surface acid-base and morphological properties of CaO as investigated by in situ FTIR spectroscopy and electron microscopy, *J. Colloid Inter. Sci.,* **303**(1): 9 - 17.

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