

SYNTHESIS OF NANO SODIUM-CALCIUM SILICATE (COMBEITE) BIOACTIVE CERAMICS IN GLASSY MATRIX

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Introduction

Rice husk (RH) is one of the by-products obtained during milling of rice. It is reported that approximately 0.23 tonnes of rice husk are formed from every tonne of rice produced (Jain *et al.*, 1996). The husk in turn contains between 15 and 20% of mineral matter the majority of which is amorphous silica (Groszek and Laughin, 2015).

After rice grain milling, rice husks remain as an agricultural waste material. Many people have tried to use this waste to produce useful materials such as silica, silicon carbide, silicon nitride or silicon for solar cells (Yalcin and Sevinc, 2001). Rice husk is one of the largest readily available but most unutilized biomass resources and has long been an ideal fuel for electricity generation (Kumar and Venugopal, 2013). Burning rice husk as fuel to generate energy, results in the waste product, rice husk ash (RHA). RHA is rich in silica (about 60%) and can be an economically viable raw material for production of silica gels and powders (Chakraverty and Kaleemullah, 1991; Kamath and Proctor, 1998). RHA has been evaluated and used as an adsorbent of minor vegetable oil components (Proctor *et al.*, 1995, Proctor and Palaniappan, 1990). Although various uses for rice husk and RHA have been suggested in literatures, Refractory brick manufacturing, lightweight building materials, and flame retardants are just a few of the industrial applications where rice husk has shown its potential (Obakin, 2020; Ajoke, 2021), their disposal or utilization remains a major concern. Soluble silicates produced from silica are widely used in glass, ceramics, cement as a major component, in pharmaceuticals, cosmetics and detergents industries as a bonding and adhesive agent. (Laxamana, 1982, Anon., 1997).

One of the most recent products of glass is the glass ceramics. Glass ceramics are fine-grained polycrystalline materials formed when glasses of suitable compositions are heat treated and thus undergo controlled crystallisation to the lower energy, crystalline state (McMillan, 1979; Hölland and Beall, 2002). The concern of the glass and glass ceramics industries is the availability of raw materials at an affordable price and the production of glass and glass ceramics by low energy consumption production processes. Numerous silicate based wastes, such as coal ash, slag from steel production, fly ash and filter dusts from waste incinerators, mud from metal hydrometallurgy, different types of sludge as well as glass cullet or mixtures of them have been considered for the production of glass ceramics (Rawlings *et al.*, 2009). As the demand for sustainable and renewable resources continues to grow, research on the industrial applications of rice husk in Nigeria has become an area of interest. Rice husk, which is a byproduct of rice milling, is rich in lignocellulose constituents and silica, making it a valuable biomass material (Ikpe *et al.*, 2019). Various studies have explored the potential uses of rice husk in different industries. It has been used as a raw material for making compounds such as silica silicon compounds and activated carbon. Additionally, rice husk has found applications as an industrial fuel, fertilizer substrate, pet food fiber, and substrate for silica silicon compounds (Elijah *et al.*, 2020; Osasona & Kanuhor, 2021). The industrial applications of rice

husk in Nigeria have been the subject of extensive research and experimentation. One such study focused on the use of rice husk as a filler in natural composites, with cashew nut shell resin as the matrix (Temitope *et al.*, 2015). The study aimed to investigate the mechanical properties of the resulting composites at different filler content. This research found that rice husk proved to be an effective filler, enhancing the mechanical properties of the composites. These findings open up new possibilities for utilizing rice husk in industries such as construction, automotive, and packaging (Temitope *et al.*, 2015).

The objective of this study is to synthesize Nano sodium-calcium silicate (combeite) ceramics in glassy matrix from rice husk ash. This work was carried out to mitigate the environmental effects of rice hush, and ash that lead to the release of methane gas, ash dust from burning activities, cost of producing glass and ceramics from analytical grade chemicals. Rice husk ash has a high content of silica, the cost of starting material for glass and ceramics synthesis by sol gel method and being readily available, with an estimated 3.4 million tons of rice produced yearly in Nigeria (Adesina, 2014), used as a substitute for the relatively expensive raw material employed in glass manufacturing without compromising the quality.

Materials and Method

The materials used for this work include (Rice Husk) sourced from Kujama (Chikun Local Government Kaduna State), Trioxonitrate(v)acid HNO_3 (Conc.), Sodium hydroxide (NaOH)(S), Calciumtrioxonitrate(iv)tetrahydrate $[\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ (aq) and Hydrochloric acid (HCl) (conc.).

Preparation of Silica from Rice Husk

Rice husk (RH) was collected from Kujama Rice Mill, Chikun Local Government, Kaduna State. The RH was separated from the remaining rice grain and unwanted materials washed with tap water several times till all the impurities that float on the water were completely removed. It was then dried at 110°C for 2 hours in an electric furnace (Gemco Son-Holland Type CFR 40/90/40, power 20KW, volt 4153 Ph, NR 91.442, frequency 50Hz). It was then combusted in a perforated metal container in the open air to burn out volatile materials before the residue ash at 700°C for 2h.

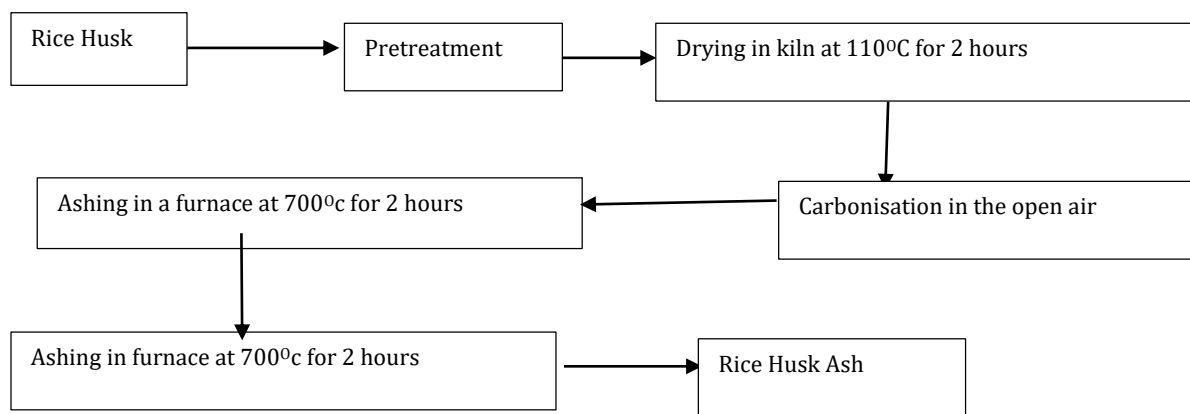


Fig.1 shows the flow chart for the preparation of the rice husk ash.

Characterisation of Rice Husk Ash

Chemical Analysis

Elemental content of RHA, were determined by X-ray fluorescence (EDXRF, Midi pal 4). The sample excited by X-rays emits a short wavelength radiation (fluorescence), characteristic of each alloying element. A parallel beam of the secondary radiation is directed by means of a collimator onto the analysing crystal; it is separated according to wavelengths and then reflected into a radiation

detector mounted on a high precision goniometer. The angular position of crystal and goniometer is a function of the wavelength and allows the identification of the element in the matrix.

Phase Analysis

RHA powder was analysed for crystalline phase contents by X-ray powder diffraction performed with a Pananalytical Diffractometer (Model: Empyrean). Powder sample was pack on a sample stage so that it could be irradiated by the X-ray. To detect the diffracted X-rays, an electronic detector was placed on the other side of the sample from the X-ray tube and rotated through different Bragg's angles. The goniometer kept track of the angle (θ), and the detector records the detected X-rays in units of counts/sec and sends this information to the computer. The operating parameters were:

- i. 40kV and 35mA with the Cu target, a step size of 0.02 (degree) with continuous scanning.
- ii. X-ray intensity (counts/sec) was plotted against the angle two-theta (2θ).
- iii. The angle (2θ) for each diffraction peak was then converted to d-spacing, using the Bragg equation. Both the XRF and XRD were carried out at the Nigerian Geological Survey Agency; National Geosciences Research Laboratory (NGRL), Kaduna.

Preparation of Glass Gel Powder

Synthesis of Silica from Rice Husk Ash (RHA) RHA - 40g, $\text{NaOH}_{(s)}$ - 16.68g, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}_{(aq)}$ - 49.2g, HNO_3 (conc.) - 600 ml. Initially, 40g of RHA were taken and corresponding amount of $\text{NaOH}_{(s)}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}_{(aq)}$ were obtained. $\text{NaOH}_{(s)}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}_{(aq)}$ were dissolved in 200 ml and 10 ml of distilled water in different beaker which formed clear solutions. NaOH solution was warmed to temperature of 30°C , RHA was added into it in warm condition and volume was made 400 ml by adding water. The boiling was continued for 1 hr while volume was maintained up to 400 ml mark of beaker regularly at around time interval of 5 minutes. After 1 hour of boiling, RHA was dissolved in the solution of $\text{NaOH}_{(aq)}$, then the solution was filtered and 300 ml of sodium silicate solution ($\text{Na}_2\text{SiO}_3_{(aq)}$) was obtained according to Nayak, (2010) $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution was prepared by dissolving it in 10 ml of distilled water. Then 600 ml of HNO_3 (conc.) was added in $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ a solution was prepared, then titration of sodium silicate solution dropwise very slowly into the calcium trioxonitrate(iv)tetrahydrate and trioxonitrate (V) acid. Immediately, turbidity appeared in the solution. The titration was stopped and kept within 40 min gel was formed which has the solute glass phase and the liquid solvent phase. The gel formed was left for 3 days at room temperature for proper network formation. Then it was dried on a hotplate by evaporation to obtain xerogel powder. The synthesis of silica from RHA, preparation of solution, gel and drying to powder were carried out at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria.

Compaction

The powder was then compacted at 150 Psi forming the green body in (30×10×5) mm mould according to (Reed, 1989). The green glass powder after compaction was measuring (28×9×5) mm then, fired at 700°C in an electric furnace. The compaction was conducted at the Metallurgical Engineering Department Laboratory of Ahmadu Bello University, Zaria.

Sintering

The samples were heated in a closed electrical furnace (Gemco Son-Holland) to a temperature of 700°C for densification and sinter crystallisation of the glass compact this is as reported (Reed, 1989) that glass particle sinter at or below the transition temperature of the glass depending on the composition in this case Soda lime silicate glass. The sample was then allowed to cool to room temperature in the furnace before removal.

Microstructure and EDS Analysis

Microstructure of the Glass Ceramics specimen was analysed by a Scanning Electron Microscope (SEM, Model: Phenom prox manufactured by Phenom World, Eindhoven Ltd., Holland). Elemental analysis was carried out by Energy Dispersive X-ray spectroscopy analysis; (EDAX or EDS, Phenom Prox Instrument). In SEM, a hot tungsten filament electron gun under vacuum emits electrons which pass through a series of electromagnetic lenses. The sample is then bombarded with a fine beam of electrons having acceleration potentials range from 1-40 KV. A part of the beam is reflected as back scattered electrons (BSE) along with low energy secondary electron emission (SE), cathode luminescence, X-ray excitation and electron transmission also took place. Images formed from the (SE) beam were studied in the extrinsic mode of SEM. The emitted secondary electrons are detected and displayed on a scanning TV display. EDS technique was used to identify the elemental composition of the specimen. The EDS analysis system works as an integrated feature of an electron microscope.

During SEM scanning, the specimen is bombarded with an electron beam. The bombarding electrons collide with the electrons of the specimen atoms, knocking some of them off, thus, transferring some of its energy by emitting an X-ray. By measuring the amounts of energy present in the X-rays being released by a specimen, the identity of the atom from which the X-ray is emitted can be established. The output EDS spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to an individual element. The concentration of the element in the specimen is indicated by the high intensity of the peak in a spectrum. The scanning Electron Microscopy was carried out at the Chemical Engineering Department of Ahmadu Bello University, Zaria.

Results and Discussion

The brown ash colour was prepared by burning rice husk at 700°C for 2 hours after pre-treatment, carbonisation and ash, this silica precursor was characterised by XRF analysis and XRDS analysis as shown in table 1 and figure 1.

Table 1: Showing Result of XRF of RHA

OXIDES OF ELEMENTS PRESENT	PERCENTAGE CONTENT
SiO ₂	79.98
P ₂ O ₅	1.80
SO ₃	0.26
Na ₂ O	0.42
K ₂ O	0.302
CaO	1.54
MgO	0.74
TiO ₂	0.11
V ₂ O ₅	0.01
Cr ₂ O ₃	0.014
MnO	0.17
Fe ₂ O	4.43
ZnO	9.85
CuO	0.017
BaO	0.05
EU ₂ O ₃	0.089

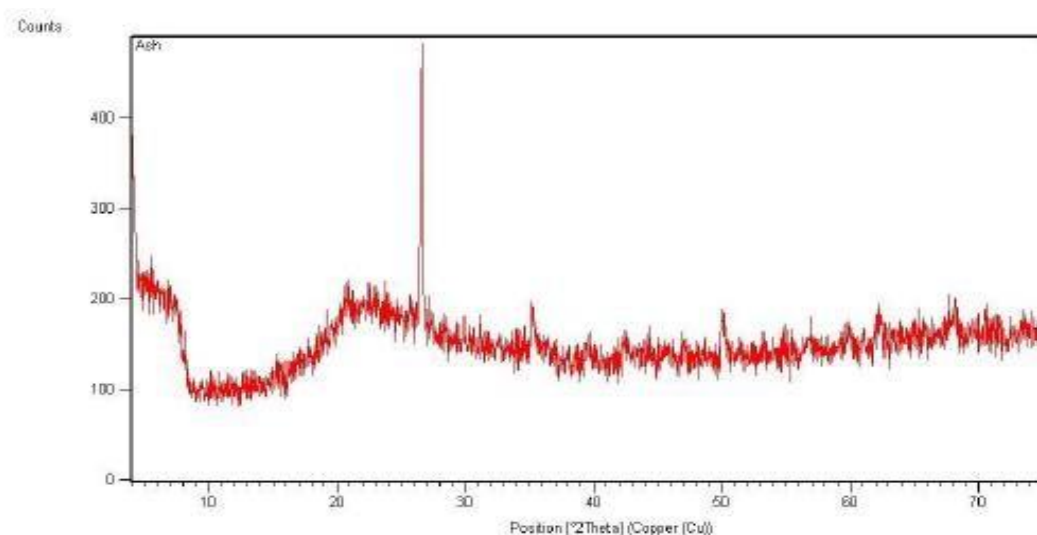


Figure 1: Result from XRD pattern of Rice Husk Ash, Source: Gideon, (2015)

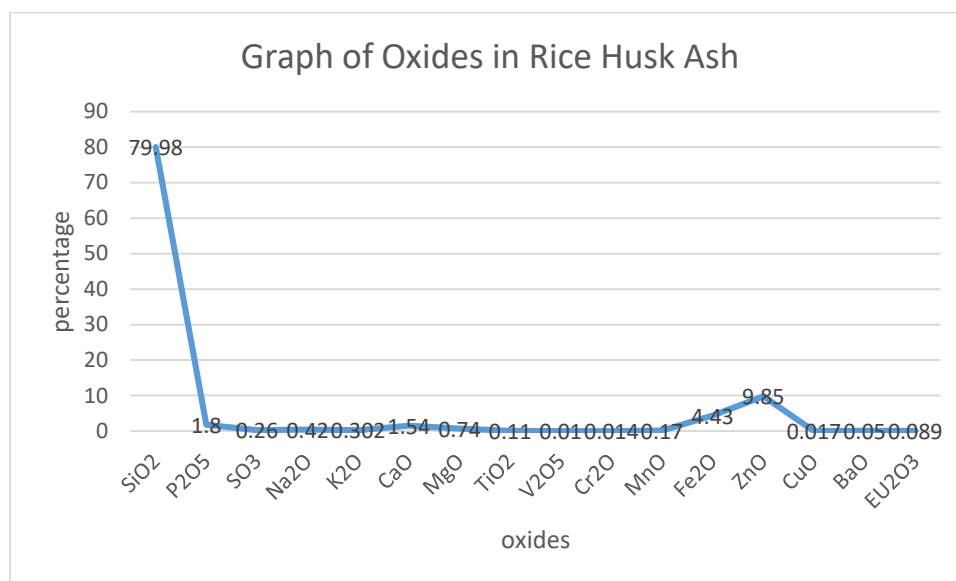


Fig. 2 Graph showing percentage of oxides, Source: Gideon, (2015)

The chemical analysis XRF of the RHA contains 79.98% SiO₂ and the rest 20.02% in which 1.80% P₂O₅, 0.42% Na₂O, 1.54% CaO, 0.05% BaO, 0.11% TiO₂ which are major and minor glass formers. In Figure 1 that shows the X-ray diffraction patterns of RHA, a broad peak zone centred near 2θ=22° signifying the amorphous nature of silica-based materials. A sharp crystalline peak in raw husks at 2θ=26.86° was due to the presence of impurities sand particles as the peak was identified to match with quartz or due to the transformation of the silica to any of its crystalline phase tridymite or cristobalite.

Nano Synthesis of Sodium-Calcium Silicate (Combeite)

RHA mixed with NaOH_(s) solution giving a solution of sodium silicate. The solution of sodium silicate was titre against calcium trioxonitrate (iv)tetrahydrate and trioxonitrate (v) acid, turbidity appeared and then gel within 40 min. The gel was left for three days to age; white shinny speck powder was obtained (xerogel) from the process of drying. Then, compacted into the green bodies using mould and sintered to glass ceramics, grey colour piece and whitish colouration after cooling.

Phase Analysis of Glass Ceramics

Figure 3 shows XRD patterns of 700°C sintered glass powder compact, shows the presence of sodium calcium silicate phase (Na₄Ca₄Si₆O₁₈) combeite at 2θ = 33.5-34.1 being the highest peaks a bioactive ceramics glass family as reported by Warji (2010).

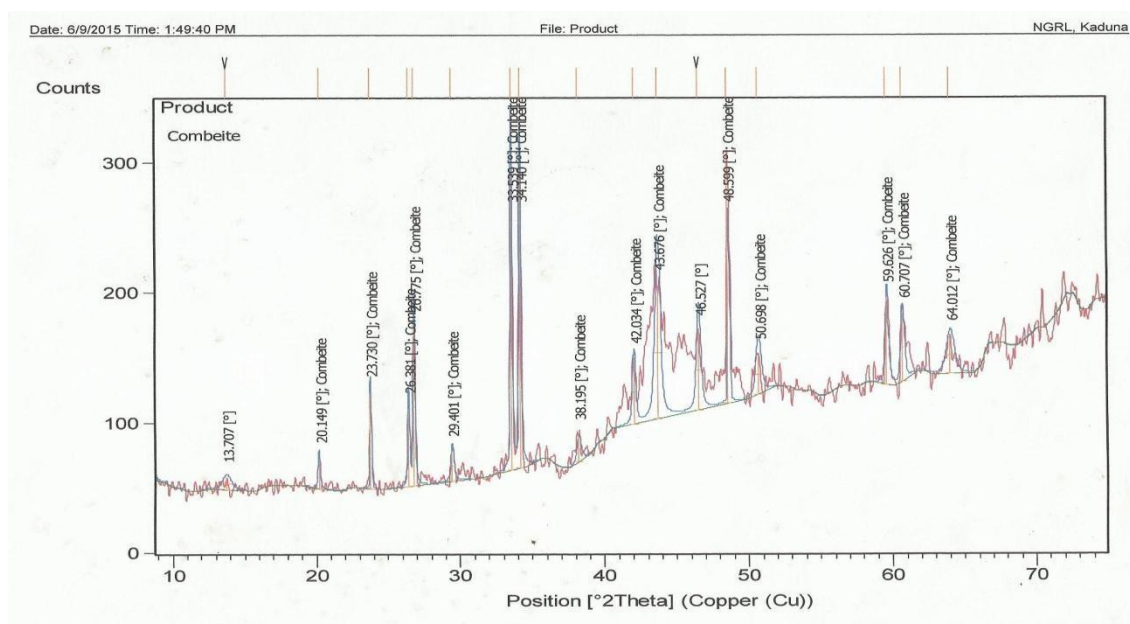


Figure 3: XRD Pattern of Sintered Glass Powder Forming the Product, Source: Gideon, (2015)

Scanning Electron Microscopy of Glass Ceramics

Figure 3 shows a circular morphology of glass ceramics is due to the precipitation of ceramics in glassy matrix. So, the grains and clusters shown by this surface are attributed to the formation of phosphate phases. Similar changes in apatite morphologies have been reported for nano (sol-gel) derived glasses and glass ceramics (Nayak, 2010). The glass ceramics specimen with a circular structured morphology with EDS elemental spectra showing Si, Ca, P and Na in plate I.

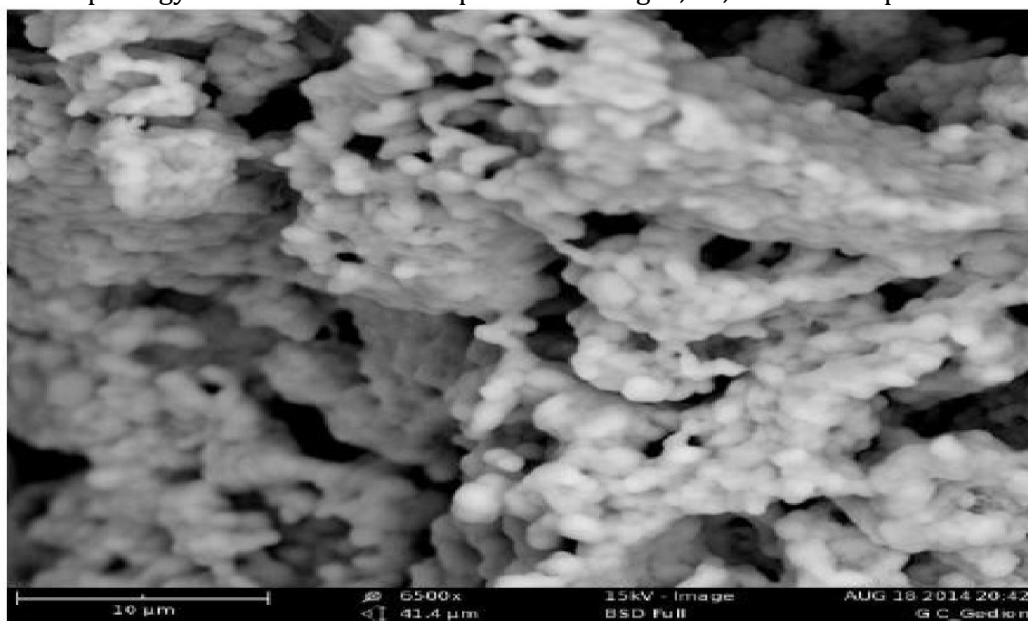


Plate I: SEM of the Sintered Glass Product Magnified at 6500×, Source: Gideon, (2015)

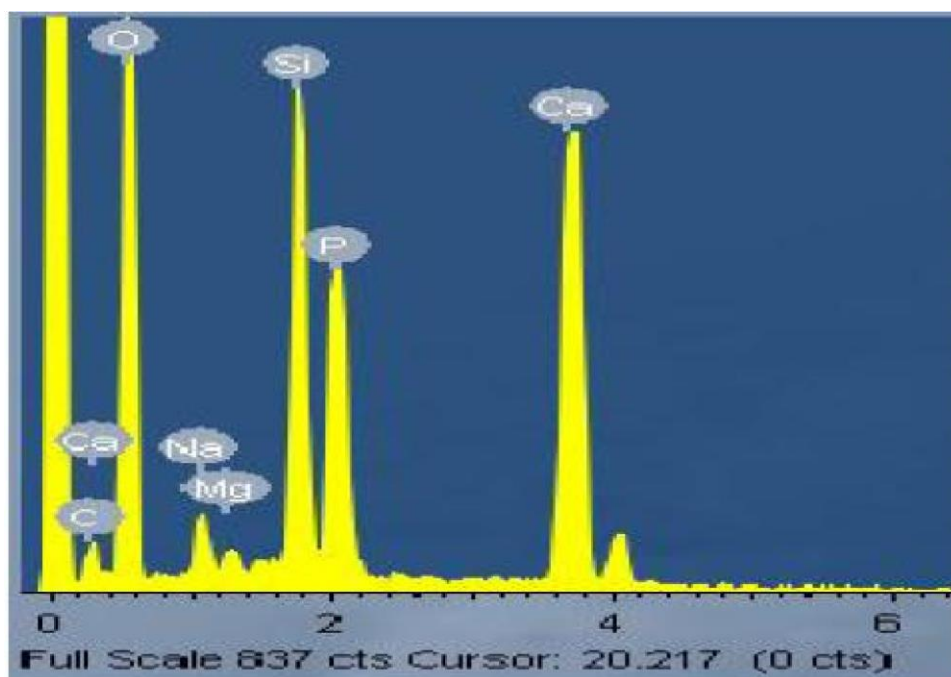


Plate II: EDS of the Sintered Glass Product, Source: Gideon, (2015)

Conclusion

From the results and discussion of the study, the following conclusion can be drawn:

1. By analyzing the RHA it was found that it contains compounds such as 79.98% SiO_2 and the rest 20.02% which includes 1.80% P_2O_3 , 0.42% Na_2O , 1.54% CaO , 0.05% BaO , 0.11% TiO_2 that can be used for glass and glass ceramics formulation and production.
2. It was also found that a solution can be prepared with the ash, gel the same solution with a solution of Calcium trioxonitrate (iv) tetrahydrate and trioxonitrate (v) acid.
3. The sinter crystallisation of the powder obtained from drying of the gel was also possible, specimens were sintered at a temperature of 700°C .
4. The sintered powder mainly contains combeite ($\text{Na}_6\text{Ca}_3\text{Si}_6\text{O}_{18}$) crystalline phase dispersed in amorphous glass matrix from the result of its characterisation by XRD and Scanning Electron Microscope (SEM).
5. The presence of crystalline phases confirmed by XRD and the morphology shown by SEM confirm both crystalline and amorphous phases as seen in the microscopy identify the material as that of glass ceramics.
6. The outcome has been found to be good energy and time saving methods of glass ceramics production. This method has no regards to the composition of the starting raw materials, with a promising future in Nigeria, especially with respect to agricultural waste materials in glass ceramics production with advantage of promoting safe environment. This has shown that the un-utilized abundant and growing biomass RHA that is an environmental problem in terms of pollution and disposal can be used to produce glass ceramics. This research will contribute to other research to be carried out on glass ceramics. It also increased the knowledge of the advantage of using local agricultural waste raw materials rather than imported ones. It also has advantage of using a low energy consuming process.

Finally, it can be concluded that rice husk ash may be a low-cost raw material for the preparation of glass ceramics materials through simple sol-gel route.

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