SYNTHESIS AND CHARACTERIZATION OF GLASS CERAMICS USING RICE HUSK ASH AS SILICA SOURCE

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Abstract

In this research, the sodium calcium silicate glass ceramics was prepared via sol-gel method utilizing rice husk ash (RHA). To prepare rice husk ash, the rice husk was treated with dilute hydrochloric acid solution to gain the high percentage silica content and then calcined at 700 °C. The high-quality rice husk ash with acid pretreatment was used as silica source for sodium silica solution to prepare silica gel. The silica gel was prepared by sol gel method with extracted rice husk ash, NaOH and Ca $(NO_3)_2.4H_2O$. The dried silica gel was calcined at 700 °C and then sintered at 900 °C to obtain glass ceramics. EDXRF was employed to study the chemical purity of the obtained silica. The structure of extracted silica and the phase purity of the prepared samples were identified by X-ray Diffractometer (XRD) analysis and it was found that the sodium calcium silicate phase was appeared. The morphology of the obtained samples was analyzed by Scanning Electron Microscope (SEM) that are depicted as aggregated particles with broad size distribution and the grain size of glass ceramics was 3.6 μm. Fourier Transform Infrared (FTIR) spectroscopy was used to detect the binding groups in the samples and Si-O-Si stretching mode and sodium calcium silicate phase were observed in both calcined glass powder and glass ceramics.

Keywords: glass ceramics, rice husk ash (RHA), sol-gel, EDXRF, XRD, SEM, FTIR

Introduction

Sodium calcium silicate glass ceramics is one of the most important biomaterials because of its bioactive property and the ability to form chemical bond with living bones and help in new bone growth [Kumar, S., 2009]. The glass ceramics has many properties with both glass and more traditional crystalline ceramics [Ravindranadh, K., 2016]. The glass ceramics have been used in different fields such as construction, optical, military, biomedical, electronics and kitchenware [Prakash Nayak, J., 2010]. The bioactive glass ceramics has found in clinical applications as coating for prostheses, bone filler, vertebral substitution and bone substitutes [Tabia, Z., et al., 2019]. Major disadvantage of bioactive glass ceramics is the high cost of fabrication [Leenakul, W., et al., 2015]. For this study, rice husk ash was used as the silica source for sodium silica solution to prepare bioactive glass ceramics. In our country, large amount of agricultural waste materials such as rice husk and rice straw are remained after rice grain milling and rice husk ash contains above 90 % of silica after complete combustion. Using RHA as a precursor can significantly reduce the cost of the bioactive glass ceramics productions and so benefits economical aspect. In this research, the glass ceramics was prepared by sol-gel method with extracted rice husk ash. The obtained samples were characterized by XRD, SEM and FTIR analysis.

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Materials and methods

Preparation of Glass Ceramics

Glass ceramics in the system of SiO_2–CaO–Na_2O with composition of 50 mol% SiO_2 -25 mol% Na_2O- 25 mol% CaO was synthesized by acid catalyzed sol-gel method. The required silica was extracted from the rice husk. The raw materials, rice husk, was firstly collected, thoroughly cleaned and then washed with tap water for several times. The cleaned rice husk was treated with 1:10 dilution ratio of HCl solution and was washed with distilled water to become pH-7 level and then dried at room temperature. The dried rice husk was calcined with 700 ˚C for 6 h to get required rice husk ash. RHA (5 g) as source of silica, NaOH (3.33 g) as source of Na_2O and Ca $(NO_3)_2.4H_2O$ (9.84 g) as source of CaO were weighted by electronic balance. The weighted NaOH and Ca $(NO_3)_2.4H_2O$ were added into 100 ml and 40 ml of deionized water, respectively. The NaOH solution was heated by temperature 70˚℃. RHA was added into this warmed NaOH solution and the resultant solution was stirred on a magnetic stirrer with temperature 100 ℃. After 1 h and 30 min of boiling, the resultant solution was filtered to obtain sodium silicate solution. 100 ml of HNO_3(conc) was mixed with Ca $(NO_3)_2.4H_2O$ solution to obtain clear solution. Titration of sodium silicate solution dropped wise very slowly into this clear solution in stirring condition. After complete addition of sodium silicate solution, gelation took 55 min for completion. The resulting gel was left for 3 days with temperature 70 ℃ for ageing to optimize the glass network formation and it was dried at 150 ℃ for 2 days. The dried gel was ground by mortar and pestle to obtain fine powder and then calcined at 700 ℃ for 2 h to remove impurities from gel powder. Finally, the calcined powder was pelletized and sintered at 900 ℃ for 2 h. The flowchart for the synthesis of bioactive glass ceramics using RHA is shown in Figure 1.

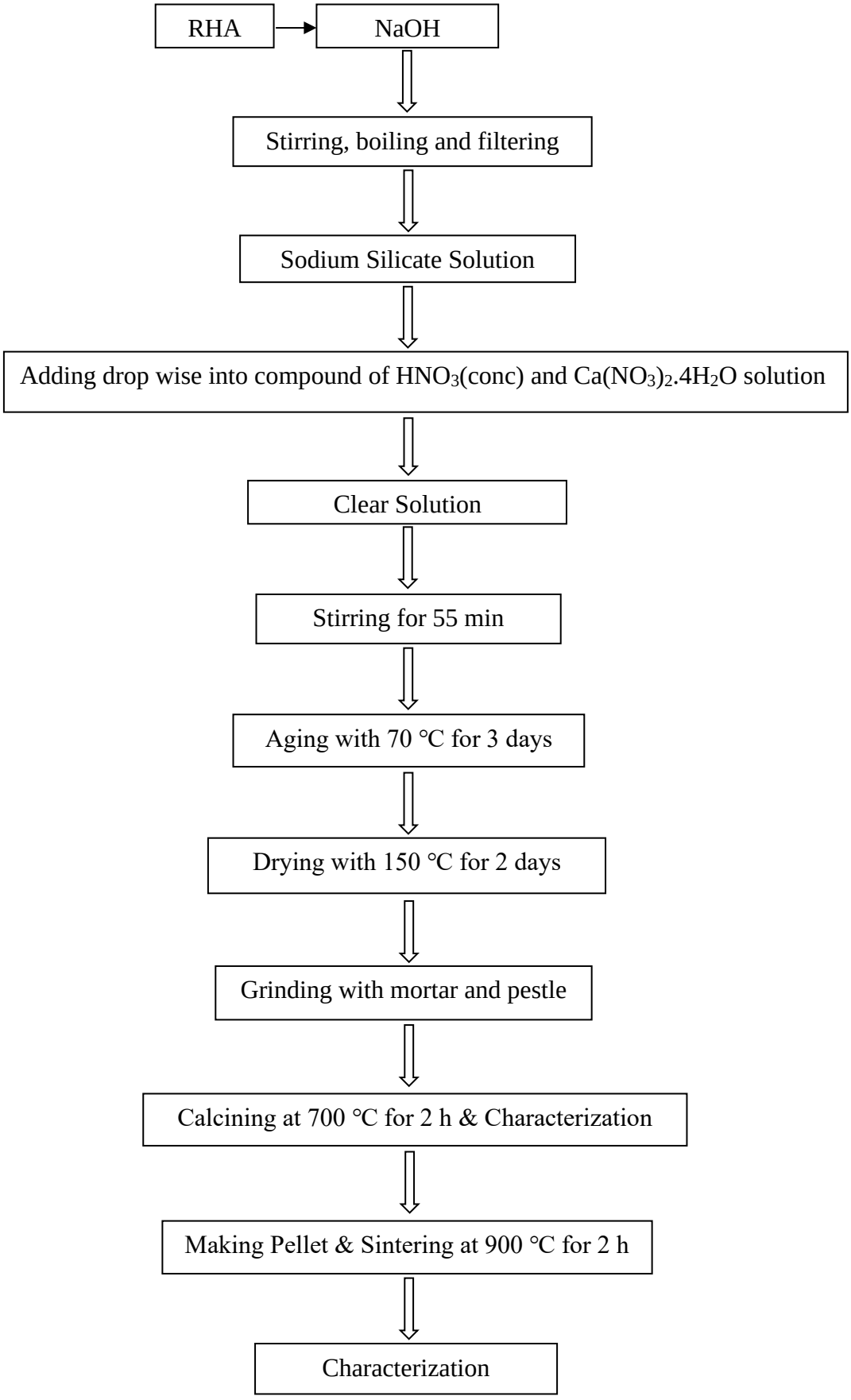

Figure 1 Flow chart for synthesis of glass ceramics using RHA

Results and Discussion

EDXRF Analysis of Rice Husk Ash

The chemical purity of the rice husk ash has been characterized by using EDXRF analysis before preparing glass ceramics. The EDXRF spectrum of rice husk ash is shown in Figure 2. The chemical composition of rice husk ash is summarized in Table 1. The EDXRF results of the rice husk ash confirmed that the main chemical component of the ash was observed as SiO_2.

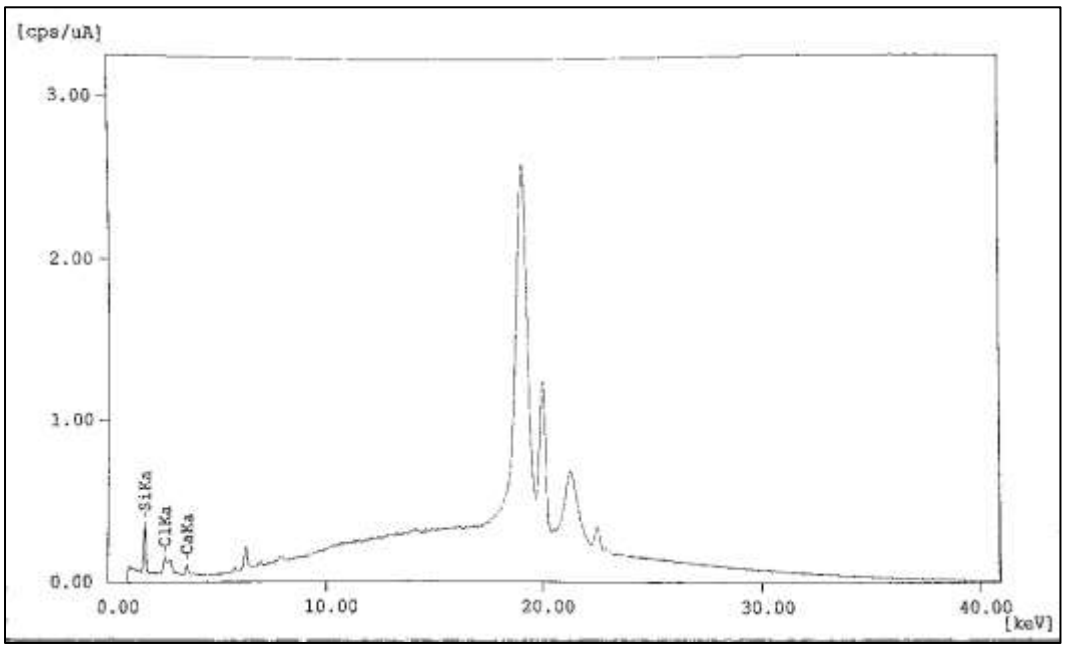

Figure 2 EDXRF spectrum of rice husk ash

Table 1 Chemical Composition of Rice Husk Ash

Compounds	Percentage of weight for Rice Husk ash
SiO_2	95.561%
Cl	3.869%
CaO	0.570%

XRD Analysis

The amorphous and crystalline form of the resultant ash has been analyzed by XRD characterization. The XRD spectrum of rice husk ash is shown in Figure 3. There is no sharp peak and the broad peak zone centered near $2\theta = 22^{\circ}$ shows the nature of amorphous silica-based materials. Therefore, the amorphous silica phase was observed in the rice husk ash.

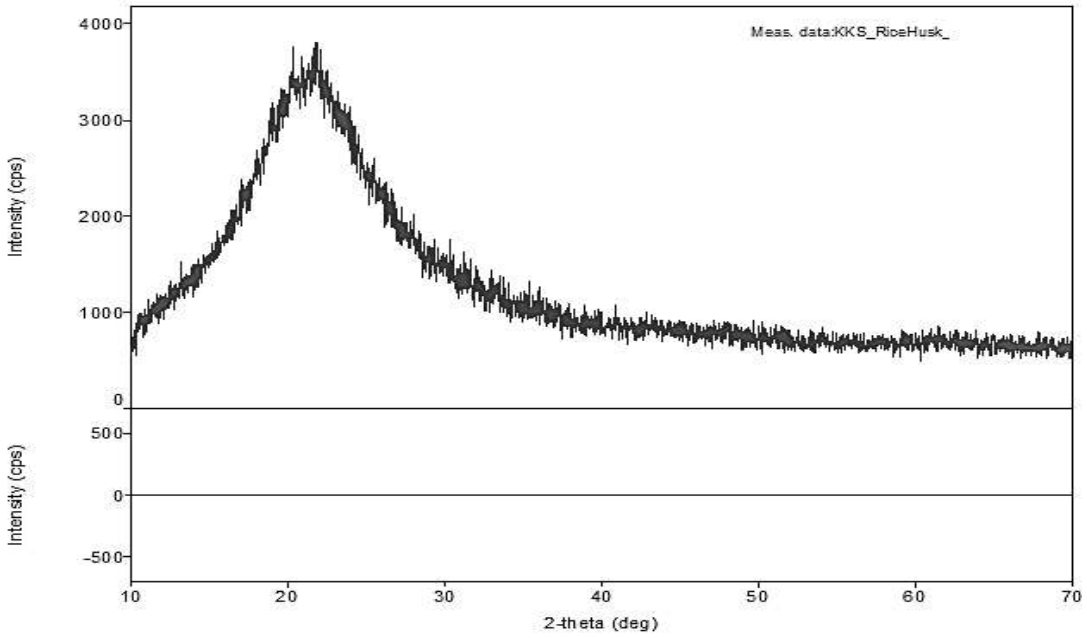

Figure 3 XRD pattern of rice husk ash (RHA)

The XRD spectra of calcined gel powder and glass ceramics are shown in Figure 4(a) and 4(b). The observed XRD profiles were confirmed with International Centre of Diffraction Data (ICDD) library file. From XRD result, sharp peaks of sodium nitrate ($NaNO_3$) were appeared around 2θ = 29.2˚, 38.8˚, 42.4˚ and 48˚ with (104), (113), (202) and (018) planes in calcined gel powder, respectively. The peaks (226) around 2θ = 32.8˚ and (040) around 2θ = 34.8˚ were also observed the present of sodium calcium silicate ($Na_2Ca_2Si_2O_7$) phase.

In XRD spectrum of glass ceramics, it was observed (104), (018) and (113) peaks at 2θ = 29.2˚, 48˚ and 38.8˚ that show the present of sodium nitrate structure. The intensity of peaks for sodium nitrate was decreased due to its decomposition after sintering at 900 ºC for 2 h. The presence of sodium calcium silicate was shown by the peaks (226) around 2θ = 32.8˚, (040) around 2θ = 34.8˚, (0012) around 2θ = 44.5˚ and (440) around 2θ = 49˚. The sample pattern of glass ceramics showed that there was the formation of sodium calcium silicate with two different crystalline phases $Na_6Ca_3Si_6O_{18}$ and $Na_2Ca_2Si_2O_7$ by two peaks around 2θ = 33˚[Prakash Nayak, J., 2010]. As the results, the main crystalline phase of the glass ceramics was the sodium calcium silicate.

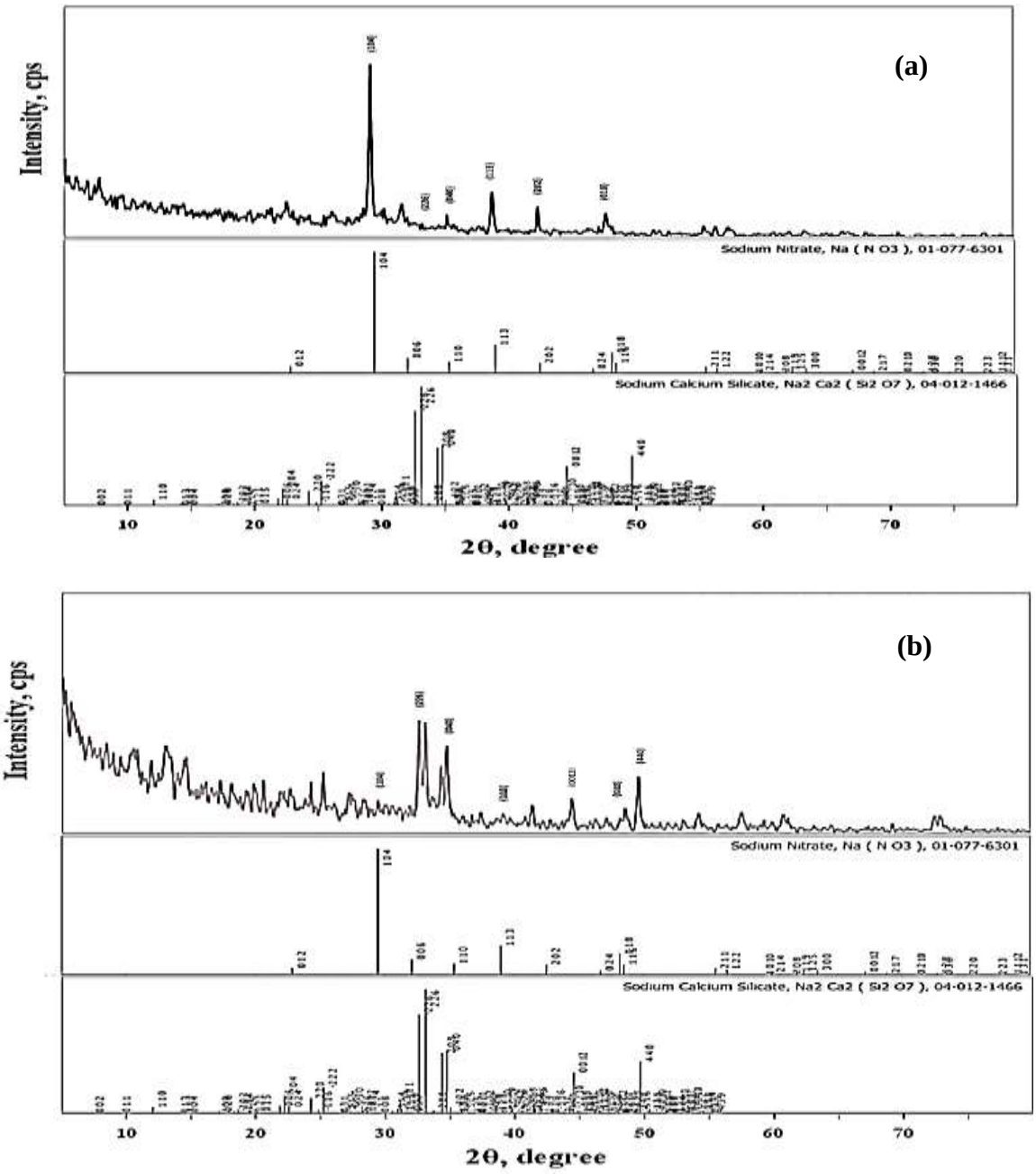

Figure 4 XRD spectrum of (a) calcined gel powder (b) glass ceramics

SEM Analysis

The microstructure and average grain size of the samples were analyzed by using SEM image. Changes in the microstructure of calcined gel powder and glass ceramics were observed in Figure 5(a) and 5(b). The morphology of both samples can be seen as aggregated particles with broad size distribution. The morphology and surface appearance of the calcined gel powder at 700 ºC corresponded to irregular agglomerates distributed heterogeneously.

In sintered glass ceramics at 900 ºC, one can also see irregular agglomerates but the distribution of grains is homogeneous than the calcined gel powder sample. After the sintering process, it was possible to observe fine grains in the microstructure. Increasing the volume of crystallization after sintering process was observed by the microstructural features of the samples. SEM ruler base on line intercept method was used to determine the average grain size of the glass ceramics sample. From the results, the grain size of the glass ceramics was 3.6 μm.

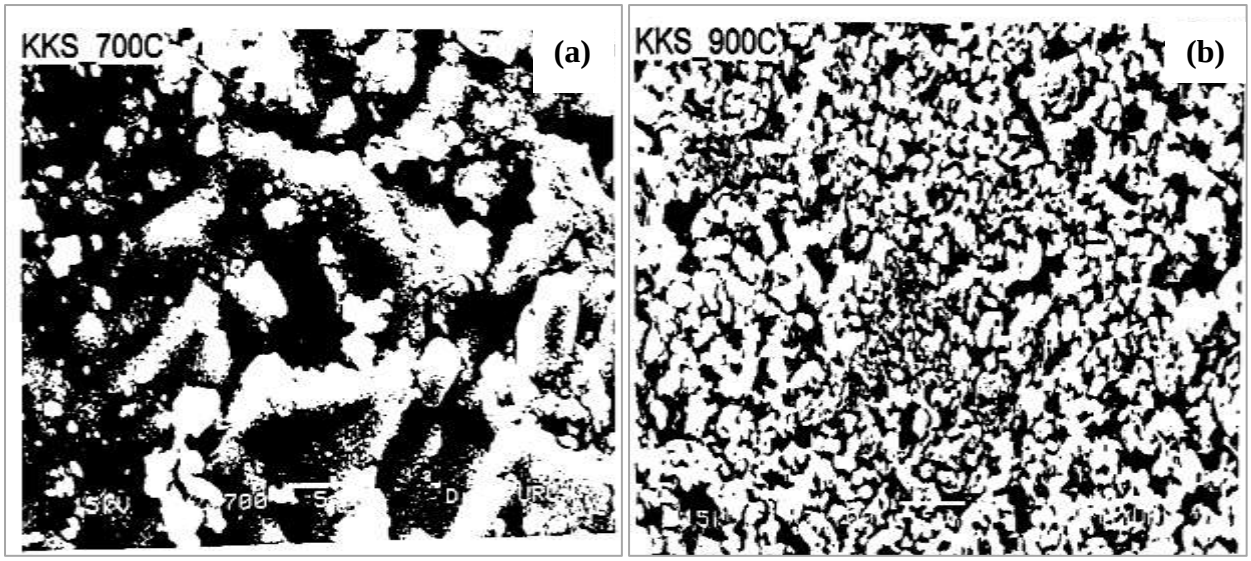

Figure 5 SEM image of (a) calcined gel powder (b) glass ceramics

FTIR Analysis

The FTIR spectrum of the calcined gel powder and glass ceramics were shown in Figure 6(a) and 6(b). The explanations for FTIR transmission bands of samples were shown in Table 2. From FTIR analysis, Si-O-Si bending vibration was strongly found in both samples. The bands at 947.46 cm^{-1} in calcined gel powder and 959.52 cm^{-1} in glass ceramics were indication of Sodium Calcium Silicate phases [Michailova, I., et al., 2015]. C-O stretching mode in both samples was considered to the absorption of carbonate group [Kazeli, K., et al., 2021]. Observing of O-H bond in these samples was associated with the presence of moisture in the samples [Ikotun, B. D., et al., 2014].

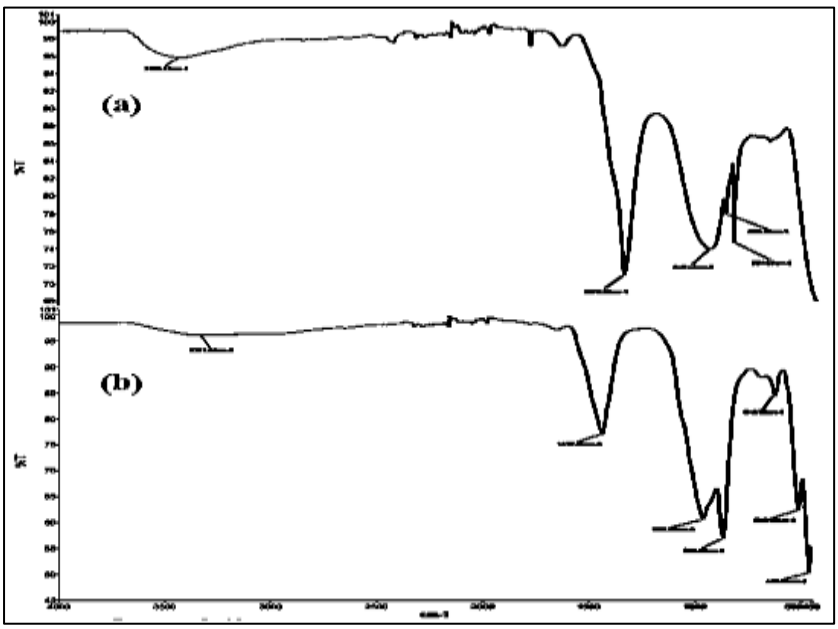

Figure 6 FTIR spectrum of (a) calcined gel powder (b) glass ceramics

Table 2 FTIR Transmission bands of calcined gel powder and glass ceramics sample

Functional Group	Wavenumber (cm^{-1})		Explanation
	Calcined gel powder	Glass ceramics	
Si-O-Si bending vibrations	-	458.71, 510.82	confirmed silica strongly found
Si-O vibration	-	619.75	presence of cristobalite phase and most likely arise from sodium calcium silicate phase
Symmetric stretching vibration of Si-O-Si	834	-	confirmed silica strongly found
Stretching vibration of SiO_4	872.76	864.38	confirmed silica strongly found
Asymmetric stretching vibration of Si-O-Si	947.46	959.52	indication of sodium calcium silicate phase
C-O stretching mode	1348.20	1437.4	absorption of carbonate group
O-H bond	3428.22	3321.66	showed water trapped in sample

Conclusion

The required silica was prepared by combustion of rice husk at 700 ˚C for 6 h with acid pre-treatment. From the results of EDXRF and XRD analysis, the obtained rice husk ash is suitable to use as silica source for preparation glass ceramics. The silica gel was synthesized by sol-gel method utilizing the extracted silica, sodium hydroxide and calcium nitrate tetrahydrate. The prepared silica gel was calcined at 700 ºC for 2 h. The calcined powder was pelletized and sintered at 900 ℃ for 2 h to prepare sodium calcium silicate glass ceramics.

From XRD results, the peaks of sodium nitrate and sodium calcium silicate were observed in both samples. However, the intensity of peaks for sodium nitrate was decreased due to its decomposition and there was formation of sodium calcium silicate with two different crystalline phases $Na_6Ca_3Si_6O_{18}$ and $Na_2Ca_2Si_2O_7$ in glass ceramics.

According to SEM images, both samples corresponded to irregular agglomerates distributed heterogeneously but the particles began to be homogeneous in glass ceramics sample due to sinter. The grain size of the glass ceramics was 3.6 μm.

By FTIR analysis, the peaks for the Si-O-Si group, CO_3^{2-} group and sodium calcium silicate phase were strongly found in both samples. In the prepared samples, the detected peaks for O-H groups indicated that some water molecules were trapped inside both samples. The above results showed that the glass ceramics containing the sodium calcium silicate as main crystalline phase was prepared in this research.

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