Structural Properties of Cullet-Paper Ash-Kaolin Clay Ceramic

K.A.Samah¹,a*, M.R.Sahar²,b and M.Yusop

¹,a*Advance Optical Material Research Group, Department of Physics, Faculty of Sciences, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

b*mrahim057@gmail.com

Abstract. This study focused on the structural properties of (x) Paper ash-(80-x) Cullet-20 Kaolin clay ceramic that are synthesized by solid state reaction due to the cullet content. The crystallinity and structure were determined using X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. The major phase of the ceramic was Wollastonite (CaSiO3) while the minor phase consisted of Dicalcium Silicate (Ca2SiO4) and Quartz (SiO2). The FTIR spectra of the S2 sample exhibited broad peak near to 1020cm⁻¹ corresponding to the stretching vibration of Si-O-Si linkage. The changes of Raman spectra linewidth of the S2 sample were observed near 575cm⁻¹, 480cm⁻¹ and 968cm⁻¹ which attributed to the Si-O-Si stretching respectively.

1. Introduction

Currently, there are two important composition based on natural recourses namely alumino-silicate-glass (ASG) and calcium-magnesium-alumino-silicate(CMAS) systems which have contributed to the excellent insulating materials. For instance, the main ingredients in cullet glass and paper ash contains ceramic network for ASG and CMAS:SiO₂, CaO, Na₂O and Al₂O₃. Thus, it is feasible to use cullet glass and paper ash as a raw materials to develop the ceramic matrices [1]. In addition, diopside, wollastonite, and melilitite can be produced from these wastes which exhibits superior mechanical, erosion, thermal and electrical properties to the parent glass [2].

Ceramic from silicate waste consists of structural units of the SiO₄ tetrahedron. It has been reported that, the SiO₄ tetrahedron can be treated as rigid units which can be linked together by their corner to form pairs, rings, chains, sheets or frameworks [3]. On the basis of IR study, a particular structure of silicate is located around 400 to 1100 cm⁻¹ which relates to bending or stretching vibration of both bridging Si-O-(Si) and terminal Si-O bond [4]. Infrared and Raman spectroscopy are well known tools to investigate the arrangement of the structural units.

Studies on cullet glasses have been introduced and grown due to their interesting behavior to improve the ceramic matrixes by incorporation of paper ash and Kaolin clay in these ceramics. Thus, in the present study, the cullet was used as host to vitrify paper ash and kaolin clay. In this study, X-ray diffraction spectra (XRD), Fourier transform infrared spectra (FTIR) and Raman spectroscopy have been used to investigate the structural aspect of cullet with paper ash and kaolin clay. The series of (x) Paper ash-(80-x) Cullet-20 Kaolin clay ceramic are prepared by using the sintering technique. The role of the cullet glass and paper ash on structural properties of ceramic has been studied.
2. Experimental
Compositions of (x)paper ash-(80-x) cullet-20 Kaolin clay, where (10 ≤ x ≤ 30) weight % were successfully prepared using modified solid-state reaction method. A proportional amount (in size 100 m) of cullet, paper ash and Kaolin clay were mixed together using ball milling for 2 hours for homogenization. Nominal composition of ceramic samples in weight percent has been enlisted in Table 3.1. These samples were then pressed into pallet using Palletizing Press Machine (HERZOG) at 40kN pressure. After that, it was sintered at 900 °C for 2 hours. Finally, ceramic samples were cut and polished for the structural measurements. The X-ray diffraction (XRD) pattern was obtained using PAN analytical X’Pert Pro with Cu Ka monochromatic radiation source at 40 kV in the 2θ range of 10-80°. The Fourier Transform Infrared (FTIR) spectra of fine powder of ceramic mixed with KBR was obtained by a Perkin Elmer Spectrum One FTIR spectrometer. The Raman spectra was obtained using a Nd:YAG laser (excitation wavelength 532nm) that operates in the range of 400 – 4000cm⁻¹.

| Sample No. | Composition (wt%) |
|------------|-------------------|
|            | Cullet powder     | Paper Ash | Kaolin Clay |
| S₁         | 50                | 30        | 20          |
| S₂         | 55                | 25        | 20          |
| S₃         | 60                | 20        | 20          |
| S₄         | 65                | 15        | 20          |
| S₅         | 70                | 10        | 20          |

3. Results and Discussion
3.1 X-Ray Diffraction (XRD)
The XRD pattern of all ceramic samples containing Cullet, Paper ash and Kaolin clay has been shown in Fig. 1 which contain multiple diffraction peaks owing to their ceramic nature. A strong peak of Wollastonite (CaSiO₃) representing the major phase of that ceramic phase. Minor phase of γ- Dicalcium silicate (Ca₂(SiO₄)) and Quartz (SiO₂) with low intensity peaks was also observed in XED pattern. The occurrence of these phases was expected since the abundance of SiO₂, Al₂O₃, and CaO in the raw material of these ceramic [5]. The formation of Wollastonite phase is probably due to coalescence particle of CaO from paper ash and SiO₂ from cullet glass and Kaolin clay [6],[7]. XRD pattern also shows that as the cullet content exceeds 55wt% (after sample 2), the intensity of wollastonite peaks decreases while the intensity of γ- Dicalcium silicate increase. Thus, some structural changes from wollastonite to γ- Dicalcium silicate and Quartz(SiO₂) were observed as cullet content exceeds from 55wt%.
Fig. 1. XRD spectra of cullet-paper ash-kaolin clay ceramic (W=wollastonite, Q = quartz, and D = γ-dicalcium silicate).

3.2 FTIR spectra
The structures of the obtained polycrystalline ceramic samples were also characterized using FTIR and Raman spectroscopy. These two techniques are IR-active, Raman-active or both are complementarily when react with varies vibration modes frequency in molecule. Generally, there are two types of vibration frequency known as bending or torsion vibration which have in-plane and out-of plane bending and stretching vibration. Normally, the change in the inter-atomic distance along bond axis contribute to torsion vibration. The in-plane bending of torsion vibration can be separated into two groups like scissoring and rocking relying on the atoms swing opposite or in the same directions, respectively. Then, when the atoms swing up and down it can be classified into wagging and twisting vibrations for out-of plane bending of torsion vibration. Furthermore, the angle change between bonds form bending vibration [8]. FTIR and Raman analyses yield the signature effect of cullet glass and paper ash on the vibration modes of ceramic structure.

The FTIR spectra of prepared ceramics in the range of 400-1600cm⁻¹ are shown in Fig 2. The strong absorption spectra in the range 400-800 cm⁻¹ correspond to the bending vibration, while, weak absorption spectra in the range 900 -1100 cm⁻¹ is due to stretching vibration of both bridging Si-O-(Si) and terminal Si-O bond [9], [4]. The absorption spectra appeared around 714-716 cm⁻¹ is assigned to the stretching bridging Si–O(Si) with the presence of 3-membered ring and is referred as wollastonite band [10]. The observed absorption spectra around 472-475 cm⁻¹ is allocated to the triple degenerated, stretching and bending vibration modes of the tetrahedron SiO₄ [11]. Additionally, the absorption peaks at 472, 902, 964, and 1015 cm⁻¹ confirm the existence of wollastonite phase in the structure. Interestingly, the IR spectra for samples with addition of cullet glass in the ceramic samples are in close resemblance to each other. It was also observed that the intensity of absorption spectra (900-1100 cm⁻¹) is suppressed with further addition of cullet glass. Since the intensity of an absorption
bands depends on the change in the dipole moment which contribute to the bond length and the charge difference between two atoms. Thus, more the cullet lesser is the electronegativity between Si-O-Si stretching vibration [12]. The wavenumber of the peaks shows an incremental shift from S1 to S2 at peak 472, 714, 902 and 1015 cm\(^{-1}\). However, the wavenumber remain constant with more cullet concentration. Such phenomenon indicates that the degree of polymerization improve with addition of cullet at 50 wt\%[13]. Further addition of cullet inhibits the ability of the sample to be polymerized [13], [14].

![Fig. 2. FTIR spectra of cullet-paper ash-kaolin ceramic.](image)

### 3.3 RAMAN spectra

The Raman spectra of all ceramic samples presented in Fig. 3. are selected to display in the range of 300 – 1200 cm\(^{-1}\). Each Raman spectrum is exhibiting three Raman bands centered at 480 cm\(^{-1}\), 577 cm\(^{-1}\), and 968 cm\(^{-1}\), respectively which are attributed to the fundamental vibrations of structural units/lingkages in typical Si-O structure [1]. As reported by Kingma, the peaks around 480 cm\(^{-1}\) and 575 cm\(^{-1}\) are the symmetric Si-O-Si stretching-bending mode [13, 14]. More specifically, the intensity of peak at 480 cm\(^{-1}\) increases as cullet content is increased due to the strengthening of Si-O-Si bonds. The peak around 635cm\(^{-1}\) which clearly seen in sample 2 and 4 correspond to the rings of SiO\(_4\) tetrahedra [3]. Whereas, the peaks between 960-981cm\(^{-1}\) are attributed to the Si-O stretching with 2 non bridging oxygen atoms per silicon(Q\(^2\)) [3]. Furthermore, the peak in all ceramic samples around 968 cm\(^{-1}\) are ascribed to the Ca\(^{2+}\) cation as non-bridging Si-O stretching (Q\(^3\)) atoms in the structural unit with reduction of paper ash [3],[16].
4. Conclusion

The (x) Paper ash-(80-x) Cullet-20 Kaolin clay ceramic have been successfully prepared by solid state reaction method. The variation of cullet content that strongly affect the ceramic structure are clearly revealed from FTIR spectra consisting of vibrational mode of Si-O-Si stretching units. The participation of cullet glass in ceramic matrix modifies the ceramic forming network and also responsible for changing the structure and geometry of ligands. Raman peaks around 480 cm$^{-1}$ and 575 cm$^{-1}$ are assigned as the symmetric Si-O-Si stretching-bending mode, while the peak around 968 cm$^{-1}$ referred to non-bridging Si-O stretching ($Q^2$) atoms. The obtained results suggest that our method by varying the concentration of cullet glass may constitute a basis for significant enhancement in the structural properties for potential application in electronic devices.

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