Pertanika J. Sci. & Technol. **18 (2)**: 223 – 229 (2010)
ISSN: 0128-7680

Short Communications

Preparation and Characterization of Glass-Ceramic Synthesized from Soda Lime Glass and Wastewater Sludge

Zaidan Abdul Wahab*, Syaharudin Zaibon, Khamirul Amin Matori, Norfarezah Hanim Edros, Thai Ming Yeow, Mohd Zul Hilmi Mayzan, Mohd Sabri Mohd Ghazali and Mohd Norizam Md Daud

Department of Physics, Faculty of Science, Universiti Putra Malaysia,
43400 UPM, Serdang, Selangor, Malaysia
**E-mail: zaidan@science.upm.edu.my*

ABSTRACT

This paper reports an alternative method for making glass-ceramic from disposal waste water sludge and soda lime silica (SLS) glass. The glass ceramic samples were prepared from a mixture of wastewater sludge and SLS glasses, melted at 1375°C for 3 hours and quenched by pouring into water to obtain a coarse frit. The frit glass was then crushed and sieved to 106μm before it was pressed to a pellet. The sintering process was performed at various temperatures between 700-1000°C for 2 hours and morphologically characterized with XRD, SEM, and EDX. Overall results showed the crystalline phase of diopside sodian-critobalite glass-ceramic is depending on thermal treatment process and making them attractive to industrial uses such as in construction, tiling, and glass-ceramic applications.

Keywords: Soda lime silica glass, wastewater sludge, glass-ceramic, vitrification, diopside sodian

INTRODUCTION

The industrial development in Malaysia over the last decades has generated large amount of waste and by-products such as sewage sludge, coal ashes and mud, which contain significant amounts of heavy metals. Nowadays, wastewater sludge is mostly dumped in landfills; however, suitable sites are limited in many states and furthermore, this disposal method is considered to be environmentally unfriendly (Francis *et al.,* 2004). Disposal of wastewater sludge is becoming an increasing economic and environmental burden.

Wastewater sludge contains large amounts of Fe_2O_3, P_2O_5, SiO_2 and ZnO which are glass network formers and glass network intermediates. Therefore, it serves as a raw material source for the glass-ceramic production. The recycling of by-products and waste from industry in glass-ceramic production is an effective way to reduce the amount of wastes and to immobilize the element of their heavy metals (Erol *et al.,* 2007; Zhang *et al.,* 2007; Leroy *et al.*, 2001).

Glass-ceramics have significant advantages over traditional powder-process ceramics. Among other, the flexibility and ease of forming is afforded by high speed processes such as rolling, pressing, blowing, and drawing. Meanwhile, the uniformity of microstructure and reproducibility of properties, which depend on structural consistency, are other major advantages resulting from

Received: 16 February 2009
Accepted: 17 February 2010
*Corresponding Author

the homogenous nature of the melting process (Swain *et al.,* 1994). Glass-ceramic materials are fine grained polycrystalline solids containing residual glass phase, produced by melting glass and forming it into products that are subjected to controlled crystallization (Karamberi and Moutsatsou, 2007). Controlled crystallization or heat treatments usually consist of a two-stage heat treatment, namely a nucleation stage and crystal growth stage. In the nucleation stage, small nuclei are formed within the parent glass. After the formation of stable nuclei, crystallization proceeds by growth of a new crystalline phase. The nucleation and crystallization parameters of glasses are important in the preparation of glass-ceramics with desired microstructures and properties (Zhang *et al.*, 2007). The aim of this research is to present the utilization of soda lime silica (SLS) glass and wastewater (WW) sludge in order to transform this waste to more stable and less toxic materials as glass-ceramics.

EXPERIMENTAL PROCEDURE

The raw material used in this study were SLS glass obtained from KFC Holdings (Malaysia) Bhd. Seri Serdang, and WW sludge from the water treatment plant, Hitachi Air-Conditioning, Bangi, Malaysia. In order to dry the waste, the WW sludge was heated in an oven at a temperature of 120°C for 24 hours. Later, both the SLS and WW sludge were crushed and sieved to106µm. The chemical compositions of SLS and WW sludge were determined by Shimadzu energy dispersive X-Ray fluorescence Spectrometer EDX-720 under vacuum condition.

Meanwhile, the glass ceramics were prepared from mixtures of 95-75 wt% SLS glass and 5-25 wt% WW sludge, as shown in Table 1. All samples batches were dry milled for 24 hours to ensure thorough and homogeneous mixing before they were melted in an alumina crucible at 1375°C in air at a heating rate of 10ºC min^{-1} for three hours in an electrically heated furnace. The melted material was poured into water and allowed to cool. Then, it was crushed and sieved to 106µm, and pressed into a 14 mm diameter pellet without any binders under a pressure of 3 tones. All pellets were sintered at various temperatures between 700-1000ºC for two hours at 100ºC intervals with heating and cooling rates of 2ºC min^{-1}.

TABLE 1
The composition of the prepared samples

SLS glass (wt%)	WW sludge (wt%)
95	5
90	10
85	15
80	20
75	25

The density of the samples was measured by using Archimedes principle with acetone as buoyant liquid using the relation, $\rho_s=(W_a/W_{ac})\rho_{ac}$, where ρ_s is the density of the sample, ρ_{ac} is the density of the acetone, W_a is the weight of the sample in air and W_{ac} is the weight of the sample in acetone. All the weights were measured with a digital balance.

XRD was used to identify the crystalline phases which occurred in all the samples, before and after sintering by using a Philips X'Pert XRD model PW3040/60 operating at 40 kV and 30 mA utilizing Cu Kα radiation. The detector was scanned over a range 2θ from 10 to 90° with 0.001° step size. The resulting diffraction patterns were analyzed using X'Pert HighScore software.

The microstructures were investigated by Scanning Electron Microscope (SEM) model LEO 1455 Variable Pressure attached with Energy Dispersive X-Ray (EDX). Selected pellet surface was ground on 600, 800, and 1200 grit abrasive paper (Buehler Silicon Carbide) and polished to obtain a flat and mirror surface. The polished samples were thermally etched at 100°C below their sintered temperature and gold coated using a Sputter Coated Baltec SCD 005.

RESULTS AND DISCUSSION

The chemical compositions of the SLS glass and WW sludge are shown in Table 2. The main elements of the SLS glass are SiO_2, Al_2O_3, which are categorized as glass network formers and CaO, Na_2O as glass modifiers. The WW sludge also contained SiO_2, Al_2O_3 along with P_2O_5 as a glass network formers but it also contained higher Fe_2O_3 which could act as a glass network intermediates. The presence of these glass network formers and modifiers clearly suggests that both the SLS glass and WW sludge have great potentials for the glass-ceramic preparation.

TABLE 2
Chemical composition of the tested soda lime silica glass and wastewater sludge in terms of oxide contents

Oxides	SLS glass	WW sludge
	wt% ± 0.01	wt% ± 0.01
SiO_2	66.50	6.07
CaO	26.00	2.30
Fe_2O_3	0.38	56.78
P_2O_5	0	10.86
ZnO	0.01	5.14
NiO	0	4.48
Al_2O_3	2.12	4.47
MnO	0	3.02
SO_3	2.22	2.98
Na_2O	1.43	0
MgO	0.63	1.78
TiO_2	0	1.64
K_2O	0.29	0
Sc_2O_3	0.27	0
ZrO_2	0.07	0.24
PbO	0.06	0.03
SrO	0.04	0.02
CuO	0	0.13
Cr_2O_3	0	0.08

TABLE 3
Density and sintering temperature of (85% SLS+15% WWS) glass ceramic

Samples	Sintering temperature (ºC)	Density ρ (g/cm^3± 0.01)
A	700	2.58
B	800	2.60
C	900	2.64
D	1000	2.68

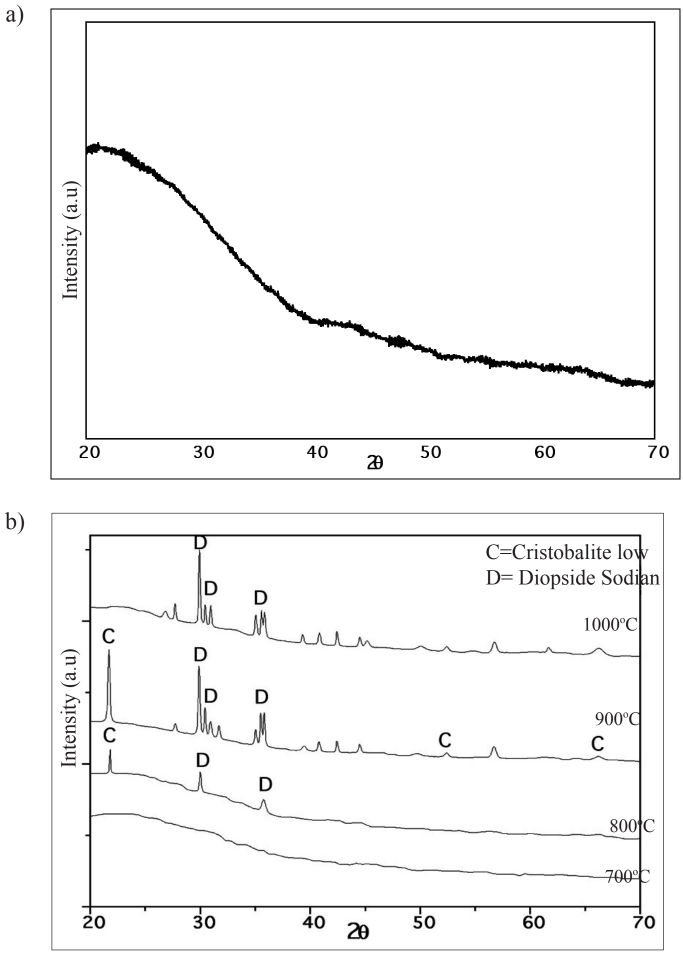

Fig. 1: a) XRD pattern of the untreated (SLS-WW sludge) glass; b) XRD patterns of the produced glass-ceramics indicating the presence of diopside sodian phases (ICSD code: 69702) and cristobalite low phases (ICSD code: 34931)

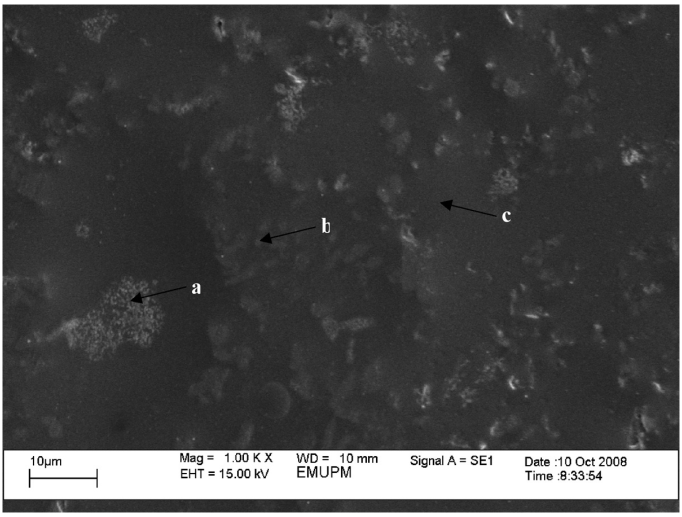

Fig. 2: SEM micrograph of 1000°C sintered glass-ceramic, Sample D

Table 3 shows the density of the produced glass-ceramic for the 85% SLS 15% WWS sample sintered from 700ºC to 1000ºC. It can be seen that the density of glass-ceramic increases with an increasing sintering temperature (Karamanov and Pelino, 1998). The produced glass containing 85 wt% of SLS glass and 15 wt% WW sludge was selected for this study, based on their basic processing characteristics such as ease of melting and ease to pour into water.

Fig. 1 (a) shows the XRD spectrums of glass frit that reveals the amorphous nature of the mixture of SLS glass and WW sludge which can be used to form glass. *Fig. 1 (b)* shows the XRD patterns from the glass-ceramic produced powder that had been heat treated at different temperatures ranging from 700ºC to 1000ºC for a constant time of 2 hours. The XRD scans verified that the glass-ceramic sintered at 700ºC was an amorphous material. Nevertheless, there is no significant effect of heat below 700ºC.

Glass-ceramic sintered at 800ºC contained diopside sodian ($Al_{0.06}Ca_{0.91}Fe_{0.11}Mg_{0.9}Na_{0.05}O_6Si_{1.97}$) as the main crystalline phase and minor amount of cristobalite low (SiO_2). Glass-ceramic sintered at 900 ºC had a similar mineral content as that of glass-ceramic sintered at 800ºC. Diopside sodian was the principal crystalline phase together with cristobalite low.

The XRD analysis of glass-ceramic sintered at 1000ºC showed that diopside sodian was the only crystalline phase occurred. In a crystallization study of the glasses produced from similar industrial wastes by Erol *et al*. (2007), diopside was reported as the predominant crystalline phase, especially at a heat treatment temperature of around 900ºC. Hence, it is observed that a higher sintering temperature leads to the increment of crystalline diopside phase in the samples, as depicted by the XRD spectrums in *Fig. 1 (b)*. In addition, the presence of a variety of metals (even in small quantities) in these samples probably favours crystallization as well (Karamberi and Moutsatsou, 2007).

The results from the XRD analysis are strongly supported by the SEM observations. The SEM examinations were conducted to get a better understanding of the micro structural morphology. *Fig. 2* shows the SEM image of sample D glass-ceramics, while the EDX analyses on the surface of sintered glass-ceramics is shown in *Fig. 3*. The crystallized microstructure is divided into 3 groups: a) the small rounded crystals, b) cube-like crystals, and c) glassy surface. The EDX analysis shows

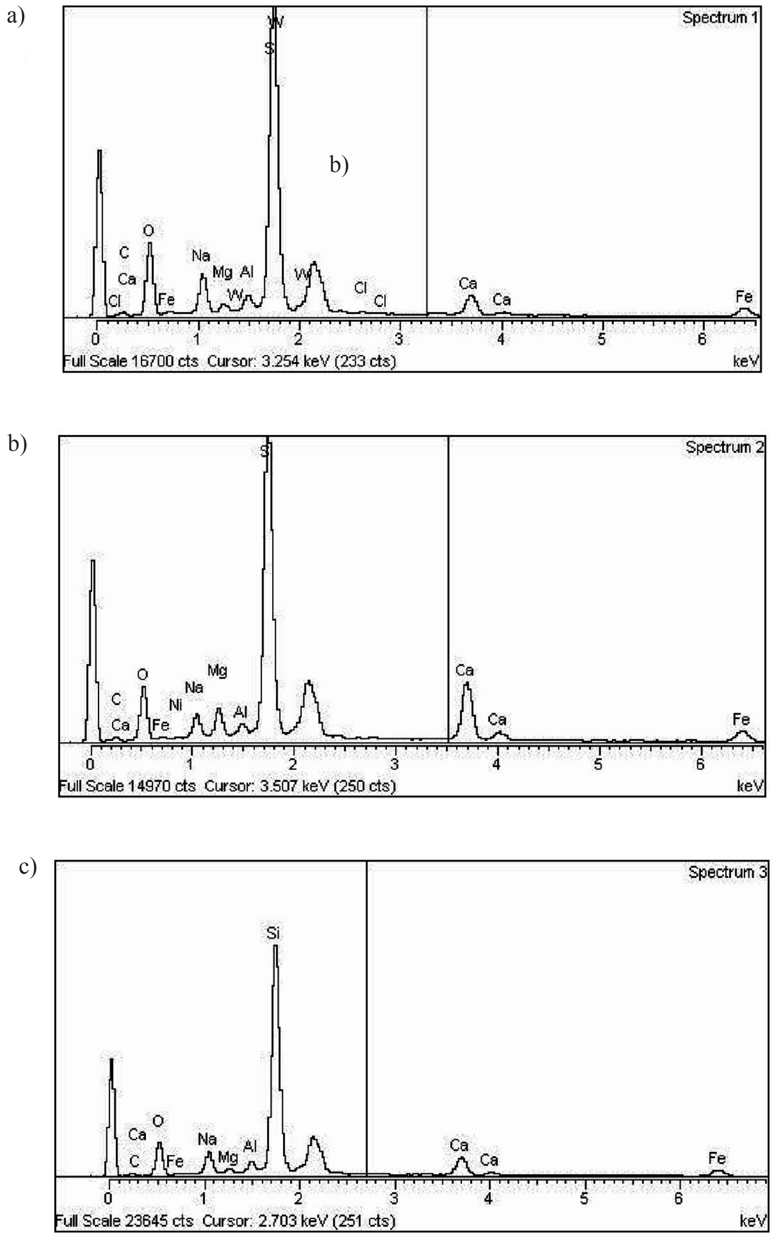

Fig. 3: EDX analyses of 1000°C sintered glass-ceramic, Sample D at 3 spectrum (a) small rounded crystal, (b) cube-like crystal, and (c) glassy surface

that the small rounded crystals contain high Si, Na, Fe, and Ca. There are no significant differences between the compositions of the glassy phase surrounding with two types of crystals. Thus, both crystalline phases grow from the same parent glass and the XRD results indicate that the peaks of spectrum correspond to crystallized diopside sodian.

CONCLUSIONS

The wastewater sludge from the industrial waste water treatment plant was successfully vitrified by adding 85% of soda lime silica glass as a glass network former. Diopside sodian-cristobalite low glass-ceramics can be produced at relatively 800°C to 900°C via sintering and crystallization of glass powder compact.

ACKNOWLEDGEMENT

The authors thankfully acknowledge the financial support from the Ministry of Higher Education, Malaysia, through the Fundamental Grant 01-10-07-312FR (5523312).

REFERENCES

Erol, M., Kucukbayrak, S. and Ersoy-Mericboyu, A. (2007). Production of glass-ceramics obtained from industrial wastes by means of controlled nucleation and crystallization. *Chemical Engineering Journal*, *132*, 335 – 343.

Francis, A.A., Rawlings, R.D., Sweeney, R. and Boccaccini, A.R. (2004). Crystallization kinetic of glass particles prepared from a mixture of coal ash and soda-lime cullet glass. *Journal of Non-Crystalline Solids*, *333*, 187–193.

Karamanov, A. and Pelino, P. (1998). Evaluation of the degree of crystallisation in glass-ceramics by density measurements. *Journal of the European Ceramic Society*, *19*, 649-654.

Karamberi, A. and Moutsatsou, A. (2007). Vitrification of lignite fly ash and metal slags for the production of glass and glass ceramics. *China Particuology*, *4*, 250-253.

Leroy, C., Ferro, M.C., Monteiro, R.C.C. and Fernandes, M.H.V. (2001). Production of glass-ceramics from coal ashes. *Journal of the European Ceramic Society*, *21*, 195-202.

Swain, M.V., Cahn, R.W., Haasen, P. and Kramer, E. J. (1994). Structure and properties of ceramics. *Materials Science and Technology*, *11*, 267-294.

Zhang, J., Dong, W., Li, J., Qiao, L., Zheng, J. and Sheng, J. (2007). Utilization of coal fly ash in the glass ceramic production. *Journal of Hazardous Materials*, *149*, 523-526.