

PRODUCTION OF GLASS-CERAMIC FROM SLS GLASSES AND WASTEWATER SLUDGE

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ABSTRACT

This project presents an alternative method for disposal sludge from industrial waste water treatment plants and SLS glass via converting them to glass-ceramic materials. The sludge was initially characterized for its chemical composition using EDXRF and XRD. The glass-ceramics were prepared from a mixture of waste water sludge and SLS glasses and 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 and press to a pellet. The sintering process was performed at from 700-1000°C for 2 hours and were 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 make them attractive to industrial use such as in construction, tiling and glass-ceramic applications.

INTRODUCTION

In Malaysia, industrial development over the last decades has generated large amount of waste and by-products such as sewage sludge, coal ashes and muds, which contain significant amounts of heavy metals. Nowadays, wastewater sludge mostly dumped in landfill sites, but in many states there is limited number of suitable sites and furthermore this disposal method is considered to be environmentally unfriendly [1]. 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 can be a candidate for the glass-ceramic production as a raw material source. 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 their heavy metals element [2].

Glass-ceramic usually has superior mechanical and erosion properties to the parent glass and also exhibit unique thermal and electrical properties [4]. 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 [5]. 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 [4].

The aim of this research concentrate on the production of glass-ceramic material from soda lime silica (SLS) glass and wastewater sludge in order to reduce waste materials volume and to produce a new marketable product and leads to a better potential for industrial applications.

EXPERIMENTAL PROCEDURE

The raw materials used in this study were SLS glass obtained from KFC Holdings (Malaysia) Bhd. Seri Serdang, and wastewater (WW) sludge was obtained from the water treatment plant, Hitachi Air-Conditioning, Bangi, Malaysia. To remove the humidity of the waste, the WW sludge was desiccated in oven at temperature 120°C for 24 hours. Later, the SLS and WW sludge were crushed and sieved to 106µm. The chemical compositions of SLS and WW sludge were determined by Shimadzu Energy dispersive X-Ray fluorescence Spectrometer EDX-720. Samples had been analyzed under vacuum condition to detect the light elements in the samples.

The glass ceramics were prepared from mixtures of 95-75 wt% SLS glass and 5-25 wt% WW sludge as shown in Table 1. To aid homogeneity, all batches were dry milled for 24 hours. All batches were melted in an alumina crucible at 1370-1380°C in air with heating rates of 10°Cmin⁻¹ for 3 hours in an electrically heated furnace. Later, the melted was poured into water and crushed and sieved to 106µm and form to a pellet without any binders with 14 mm in diameter under a pressure of 3 tones. All pellets were sintered at 700-1000°C for 2 hours at 100°C intervals with heating and cooling rates of 2°Cmin⁻¹.

XRD has been used to identify the crystalline phases occur in all samples before and after sintering by using Philips XRD model PW3040/60 operated at 40 kV and 30 mA utilizing Cu K α radiation. The detector was scanned over a range $2\theta = 10-90^\circ$ with 0.001° in step sized. The data then analyzed by utilizing software X'Pert HighScore.

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

Table 1: The composition of prepared samples

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

Table 2: Chemical composition of tested soda lime silica glass and wastewater sludge in terms of oxide contents.

Oxides	SLS glass	WW sludge
	wt%	wt%
SiO ₂	66.498	6.068
CaO	25.995	2.301
Fe ₂ O ₃	0.381	56.778
P ₂ O ₅	0	10.861
ZnO	0.011	5.142
NiO	0	4.478
Al ₂ O ₃	2.12	4.467
MnO	0	3.015
SO ₃	2.215	2.98
Na ₂ O	1.426	0
MgO	0.632	1.784
TiO ₂	0	1.637
K ₂ O	0.29	0
Sc ₂ O ₃	0.266	0
ZrO ₂	0.074	0.238
PbO	0.056	0.029
SrO	0.036	0.015
CuO	0	0.128
Cr ₂ O ₃	0	0.078

RESULT AND DISCUSSION

The chemical compositions of SLS glass and WW sludge was shown in Table 2. The main elements of SLS glass are SiO_2 , Al_2O_3 which are glass network former and CaO , Na_2O which are glass modifier. WW sludge also contain SiO_2 , Al_2O_3 along with P_2O_5 as a glass network formers but also contain higher Fe_2O_3 which could act as a glass network intermediates. It is shown that SLS glass and WW sludge have great potentials for the preparation of glasses.

The produced glass containing 85 wt% of SLS glass and 15 wt% WW sludge was selected for study based on their basic processing characteristics such as ease of melting and ease to pour into water.

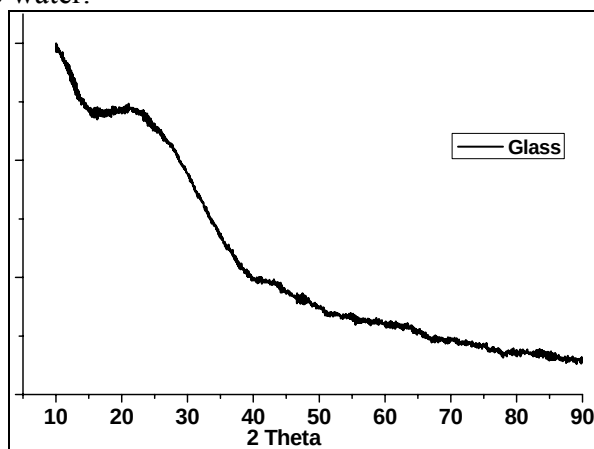


Figure 1: XRD pattern of the produced glass.

Figure 1 shows XRD spectrums of glass frit revealed that an amorphous material confirming the mixture of SLS glass and WW sludge can be used to form glass.

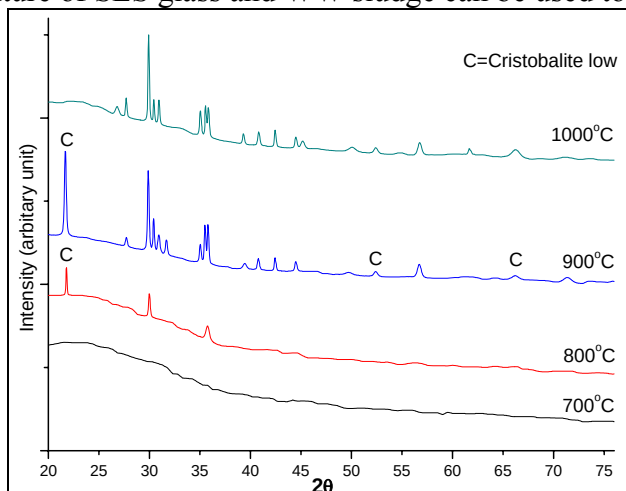


Figure 2: XRD patterns of the produced glass-ceramics indicating the presence of diopside sodian phases (not label peaks) (ICSD code: 69702) and cristobalite low phases (ICSD code: 34931)

Figure 2 shows XRD patterns from glass produced powder heat treated at different temperatures ranging from 700°C to 1000°C for a constant time of 2 hours. The XRD scans verified that for glass-ceramic sintered at 700°C was an amorphous material. There is no significant heat effect below 700°C for these compositions.

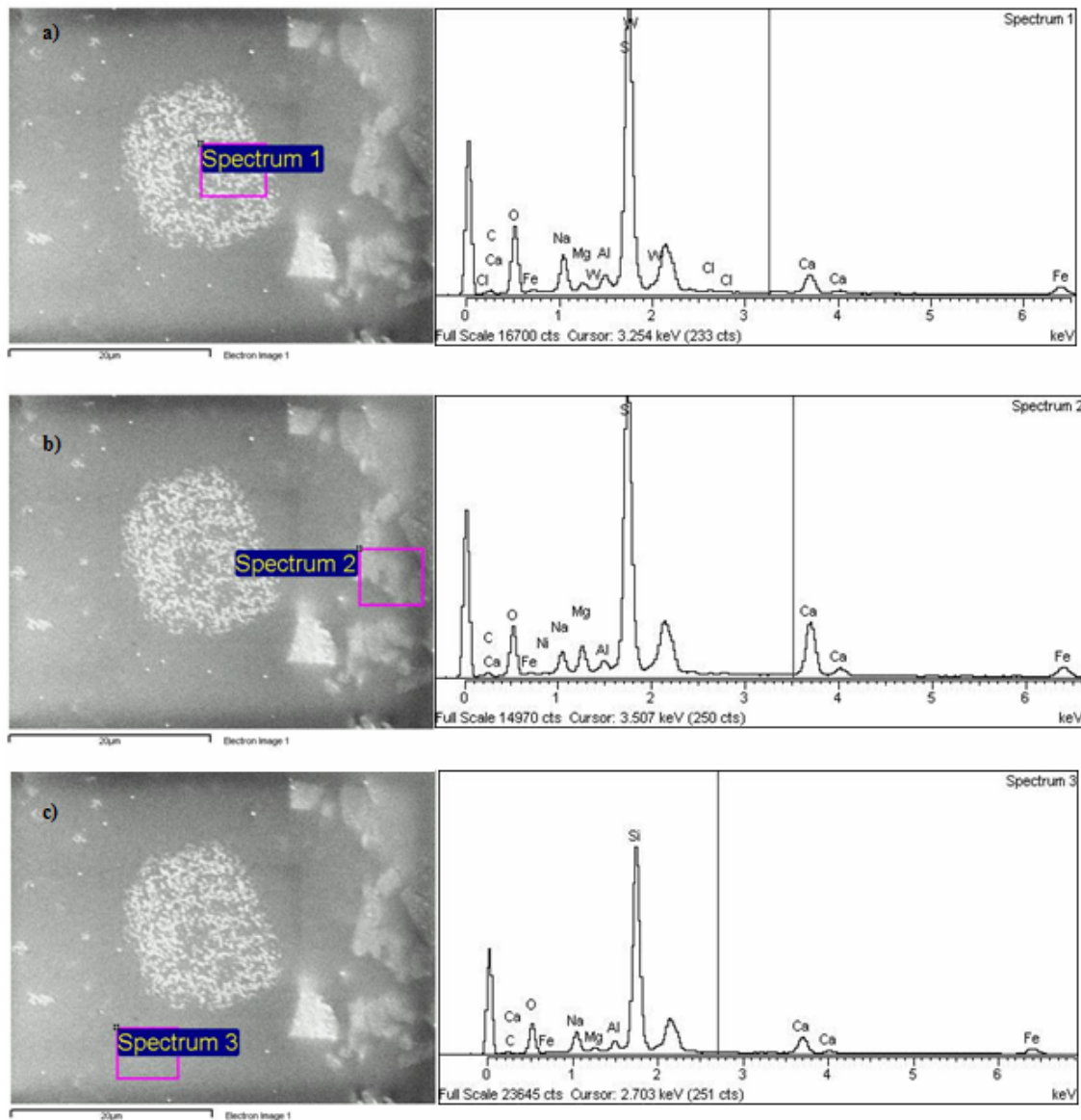


Figure 3: SEM micrographs and EDX analyses of 1000°C sintered glass-ceramic.

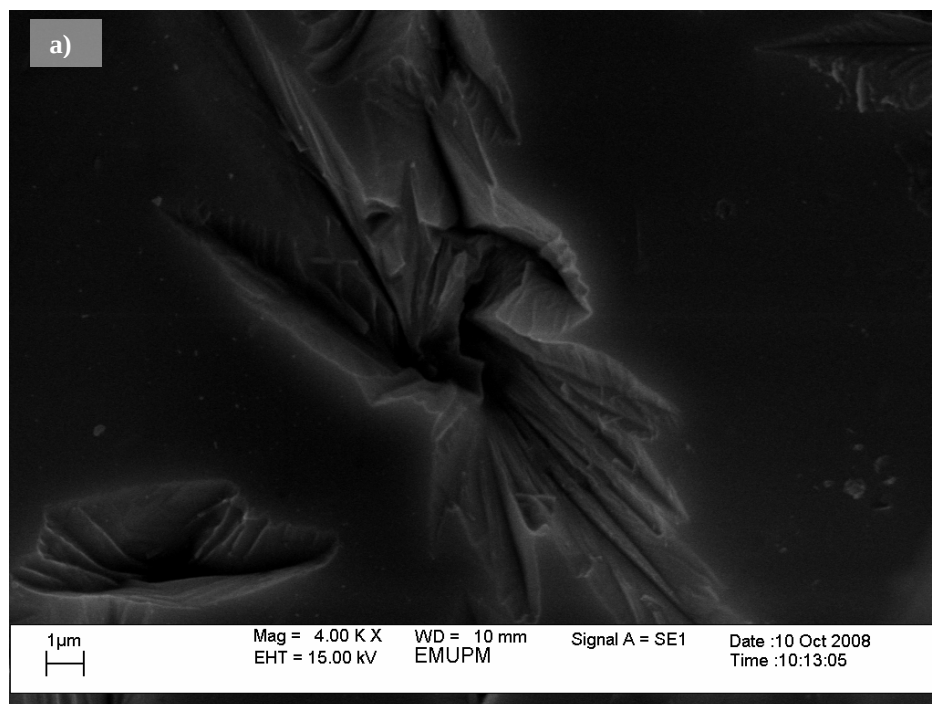
Glass-ceramic sintered at 800°C contained diopside sodian ($\text{Al}_{0.06}\text{Ca}_{0.91}\text{Fe}_{0.11}\text{Mg}_{0.9}\text{Na}_{0.05}\text{O}_6\text{Si}_{1.97}$) as the main crystalline phase and minor amount of cristobalite low (SiO_2). Glass-ceramic sintered at 900°C had similar mineral content as of glass-ceramic sintered at 800°C. Diopside sodian was the principal crystalline phase together with cristobalite low. XRD analysis of glass-ceramic sintered at 1000 °C

showed that diopside sodian was the only crystalline phase occurred. Nevertheless, higher sintering temperature leads to the increment of crystalline phase occurred in the samples as depicted by the XRD spectrums in Figure 2. It is obvious that the presence of a variety of metals even in small quantities favours crystallization [5].

The results from XRD are strongly supported by the SEM observations. SEM examinations were conducted in order to get a better understanding of the micro structural morphology [2].

Figure 3 shows that the SEM images of glass-ceramics are illustrated accompanied with EDX analysis on the surface of sintered glass-ceramics. The crystallized microstructure is divided into 3 groups, the small rounded crystals, glassy surface and feather-like crystals. The EDX analysis shows that the small rounded crystals contain high SiO_2 , Na_2O , Fe_2O_3 and CaO . There are no significant differences between the compositions of 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 crystallize diopside sodian.

In Figure 4 the SEM observations revealed that a significant number of leaf-shaped crystals occurred in the glass-ceramic sample. Figure 4 b) shows that the crystalline phase grows from the porosity resided on the glass-ceramic surface.



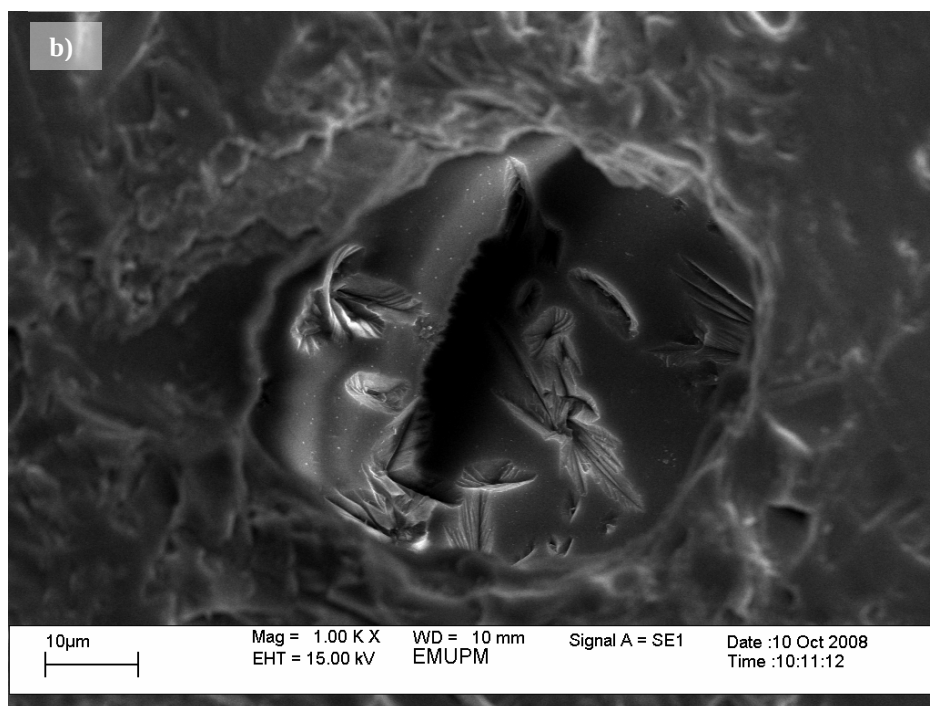


Figure 4: SEM micrographs of Glass-ceramics 85SLS 15WWT - 800°C a) magnification at 4.0K, b) magnification at 1.0K.

CONCLUSIONS

The wastewater sludge from industrial waste water treatment plant was successfully vitrified by adding 85% of soda lime silica glass as a former glass network. Diopside sodian- cristobalite low glass-ceramics can be produced at temperatures between 800°C to 900°C via sintering and crystallization of glass powder compact. So this glass-ceramic has a potential as an added material for industry such as construction and engineering.

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REFERENCES

- [1]. A.A. Francis, R.D. Rawlings, R. Sweeney, A.R. Boccaccini. Crystallization Kinetic of Glass Particles Prepared from A Mixture af Coal Ash and Soda-Lime Cullet Glass. *Journal of Non-Crystalline Solids* **333** (2004) 187–193
- [2]. M. Erol, S. Kucukbayrak, A. Ersoy-Mericboyu. Production Of Glass-Ceramics Obtained From Industrial Wastes By Means Of Controlled Nucleation And Crystallization. *Chemical Engineering Journal* (2007).

- [3]. M. Erol, S. Kucukbayrak, A. Ersoy-Mericboyu, M.L. Ovecoglu. Crystallization Behaviour Of Glasses Produced From Fly Ash. *Journal of the European Ceramic Society* **21** (2001) 2835–2841.
- [4]. Jian Zhang, When Dong, Juan Li, Liang Qiao, Jingwu Zheng, Jiawei Sheng. Utilization of Coal Fly Ash In The Glass Ceramic Production. *Journal of Hazardous Materials* **149** (2007) 523-526.
- [5]. A. Karamberi and A. Moutsatsou. Vitrification of Lignite Fly Ash And Metal Slags For The Production of Glass and Glass Ceramics. *China Particuology* Vol. **4**, no. 5, 250-253, 2006.
- [6]. P. Colombo, G. Brusatin , E. Bernardo , G. Scarinci . Inertization and Reuse Of Waste Materials By Vitrification And Fabrication Of Glass-Based Products. *Current Opinion in Solid State and Materials Science* **7** (2003) 225–239.
- [7]. P. Kavouras, Ph. Komninou, K. Chrissafis, G. Kaimakamis, S. Kokkou, K. Paraskevopoulos, Th. Karakostas. Microstructural Changes of Processed Vitrified Solid Waste Products. *Journal of the European Ceramic Society* **23** (2003) 1305–1311.
- [8]. Francesco Dellisanti, Piermaria L. Rossi, Giovanni Valdrè. Mineralogical And Chemical Characterization Of Joule Heated Soil Contaminated By Ceramics Industry Sludge With High Pb Contents. *Int. J. Miner. Process.* **83** (2007) 89–98.
- [9]. L. Asquini, E. Furlani , S. Bruckner, S. Maschio. Production and Characterization of Sintered Ceramics From Paper Mill Sludge And Glass Cullet. *Chemosphere* **71** (2008) 83–89
- [10]. P. Appendino, M. Ferraris, I. Matekovits, M. Salvo. Production of Glass–Ceramic Bodies from the Bottom Ashes Of Municipal Solid Waste Incinerators. *Journal of the European Ceramic Society* **24** (2004) 803–810.