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Study of Nucleation and Crystallization of SLG Mixing with SiO_2, ZnO, TiO_2 and CuO by SEM/EDX

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ABSTRACT

This study presents the progression of nucleation and crystallization from composition of soda lime glass (SLG) and oxides as 60SLG-35SiO_2-2TiO_2-2ZnO-1CuO through single step sintering at 850° C. X-ray diffraction (XRD) showed a higher degree of crystallinity and larger crystallite size of α-SiO_2 after sintering. It was also observed that plane (100) shrank to a smaller d_{100} spacing after sintering. XRD peaks from other oxides than SiO_2 decreased dramatically after sintering; possibly signifying a transition into the silica network. The microstructure of the sintered samples was analysed using scanning electron microscope (SEM) and SEM/energy dispersive X-ray spectroscopy (SEM/EDX). The SEM/EDX analysis revealed SiO_2 grains and whiskers of crystalline phase in many areas. A lower concentration of zinc and higher concentration of titanium were found to be associated with whiskers. This work has shown a possibility to utilize single-stage heat treatment for nucleation and crystallization of soda lime glass (SLG).

INTRODUCTION

Soda lime glass (SLG) is widely used as a base material for beverage bottles. Globally, SLG is consumed at a high rate, and does not degrade fast enough. For example, SLG waste, which cannot be recycled, accounts for more than 6% of all waste in Bangkok, Thailand in 2014 (equivalent to 600 tons per day) [1]. In Australia, over one million tons of glass is produced per year and only twenty thousand tons of them are recycled [2]. The remaining glass waste, if not handled properly, would basically be dumped in the environment and remain for many years before decomposing, and thus cause a long term pollution problem.

Glass-ceramic materials have a unique structure of crystalline and ceramic phases distributed in the main glass matrix. The potential of this material is based on a combination of crystalline and glass properties; for example, it is machinable, and has good optical properties like transparency and reflectance, in a single material [3]. These unique properties can be achieved by controlling nucleation and the crystallization process during heat treatment [4]. One method to ease nucleation and crystallization is by adding nucleating agents, such as metal oxides [3,4] before eventually ending the process by sintering. This sintering can be performed in quite a few different ways [5]. One such method is the usage of a single heat-treatment on a powder-compacted sample, and is preferable to other two-stage heat-treatments [6]. The sintering temperature, which can be obtained from thermal analysis, lies in the range between the crystallization temperature, T_c and the melting temperature, T_m [4,5]. SLG has a moderately low melting temperature (700-1,000 °C); it is thus interesting to be used as starting material for a glass-ceramic process. SLG contains large proportion of SiO_2 (normally >70% by weight [3]; hence it is often termed soda-lime silicate glass [7].

Zaid et al [8,9] have studied the sintering of soda lime silicate glass (SLS) in the presence of ZnO to produce glass-ceramic material. They found that Zn^{2+} from ZnO caused oxygen bonds to break and weakened the glass network in SLS. They also found significant reduction in sintering temperature and significant promotion of nucleation and crystallization, thus improving the physical properties of the glass-ceramics sample. Parra-Arciniega et al [10] have investigated the effect of adding TiO_2 as a nucleating agent to SLS. The crystallization mechanism was not promoted but rather higher strength in the material was observed. It therefore seems interesting to study the sintering process of SLS in the presence of both ZnO and TiO_2 to incorporate

both properties simultaneously. Further modification to the glass network may be anticipated with the addition of pigment oxide. It has been observed that during heating glass network became weaker and has undergone transition, the ions from pigment oxide could substitute within the network resulting in additional colour [11], which can be noticed by eyes. The transformation of crystalline phase in glass-ceramics is normally measured by using X-ray diffraction (XRD) [12]. The morphology of glass-ceramics has been characterized using scanning electron microscope (SEM) [13]. Some groups also utilized SEM along with energy dispersion X-ray spectroscopy (EDX), so-called SEM/EDX for elemental analysis of interesting phases [14].

The present work aims to apply SLG as the main glass matrix in mixing with other oxides SiO_2, ZnO, TiO_2 and CuO for glass-ceramics production by the single-stage sintering method. Differential scanning calorimetry and Thermo gravimatrix analysis (DSC/TGA), XRD, and SEM/EDX techniques were used to monitor, characterize, and assess the intermediate and eventually the final product along the processing line.

METHODOLOGY

SLG powder was obtained by milling the flint SLG glass bottle on a ball mill machine. It was sieved by a #325 mesh to ensure mean particle size of smaller than 44 μm before using as starting materials. Typical composition in SLG materials are tabulated in **Table 1**.

Table 1 Starting Material composition by %weight

Composition	Percent contribution		
	Raw	Added	Total
SiO_2	42.17	-	77.17
Al_2O_3	1.33	-	1.33
Fe_2O_3	0.05	-	0.05
MgO	0.97	-	0.97
CaO	6.72	-	6.72
Na_2O	8.55	-	8.55
K_2O	0.19	-	0.19
TiO_2	0.02	2	2.02
ZnO	-	2	2
CuO	-	1	1

Sample preparation

The glass samples were prepared by mixing SLG with other oxides by weight% as follow 60SLG-35SiO_2-2TiO_2-2ZnO-1CuO. One set of powder mixture was characterized by X-ray diffraction method (XRD). The other set of powder mixture was uniaxial pressed at 10 tons to a pellet shape. The pellet was sintered in electric furnace with heating rate of 5° C/min from room temperature, held at the sintering temperature of 850°C for 2 hours, and then left for cooling to room temperature inside the furnace.

Characterization

X-ray diffraction (XRD) characterization was carried out using Bruker (D8-Advance) with Cu-K_a radiation (1.54 Å) as the X-ray source. Scanning electron microscopic (SEM) analyses were done to observe morphology on the surface of the sample, using JEOL, JSM-5410 model. The sample was sputter-coated with palladium (Pd) prior to the analysis. The SEM micrographs were carried out at ×500, ×2,000 and ×5,000 magnifications. At the ×2,000 magnification, energy dispersive X-rays spectroscopy (EDX, Oxford ISIS) were also performed in parallel for elemental distribution and phase separation.

RESULTS AND DISCUSSION

The XRD pattern of SLG mixture before sintering process is shown in the upper line in **Figure 1.** An assignment of XRD patterns to compositions in the mixture are labelled for each pattern. The major peaks belong to α-SiO_2. The lower line shows the XRD pattern after sintering at 850 °C. XRD peaks belonging to other oxides all disappeared; only those belonging to the host α-SiO_2 peaks become sharper (planes (100) and (101)) and more visible (planes (110), (102), (111), (200), (201), and (202)). Plane (100) of α-SiO_2 was significantly shifted to a higher diffraction angle (from 20.08° to 21.00°); this signified compaction in this preferred direction. Similar uniform strain has been reported [15]. α-SiO_2 is hexagonal in its crystal structure; the lattice parameters were deduced. For comparison, the

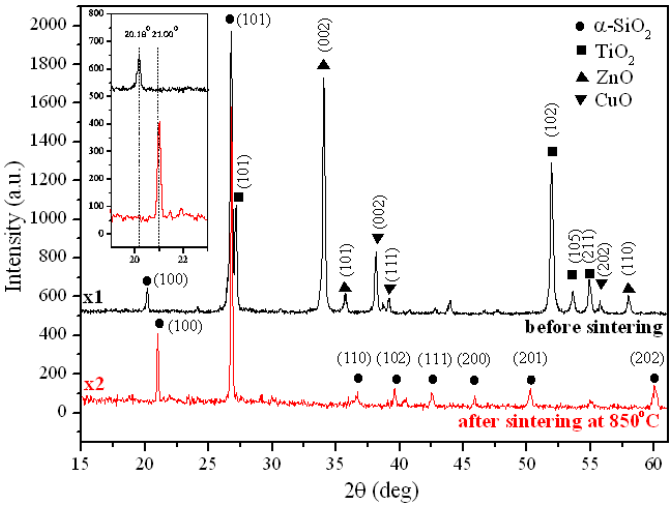

Figure 1 XRD pattern of the powder and the 850°C-sintered samples.

Table 2 Lattice parameters of α-SiO_2 from XRD result

Condition	Lattice parameters			d_{100} (Å)
	a (Å)	c (Å)	V (Å^3)	
Before sintering	4.85	5.48	111.71	4.40
After sintering	4.81	5.52	110.53	4.23

lattice parameters before and after sintering are summarized in **Table 2.**

A SEM image of the sintered sample surface is presented in **Figure 2**. The crystalline phase of SiO_2 on the SiO_2 glass residual is shown in **Figure 2(a)**. In some areas, several whisker forms are obvious (as shown in **Figure 2 (b)**). This development is understandable as one dimensional crystallization and also self-nucleation out of the glass matrix.

Moreover, other crystalline zones, visible as small-sized crystallites, aggregated to form irregular shapes distributed over the surface in **Figure 2(b)**. Therefore, our proposed single-stage sintering temperature at 850°C has driven the sample to nucleate and crystallize

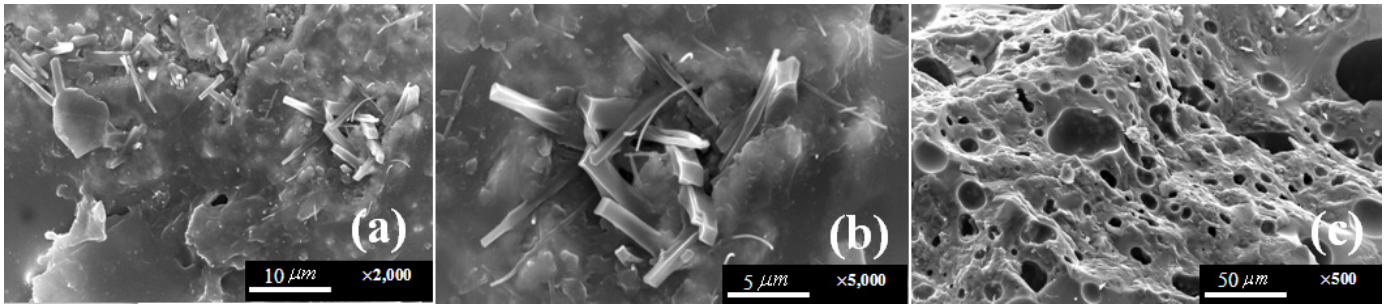

Figure 2 SEM micrograph of 850°C sintered sample at top surface (a)2,000 and (b)5,000 magnification and at inside sample (c)500 magnification

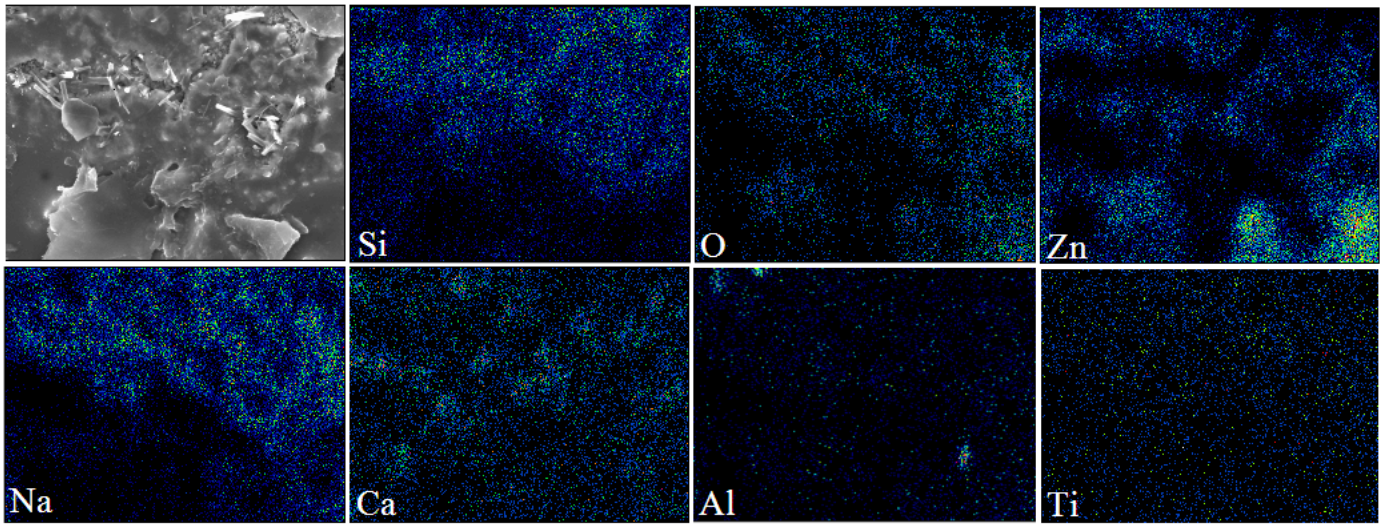

Figure 3 SEM image and elemental distribution of 850°C sintered sample

in the SLG glass matrix [16,17]. The SEM micrograph at lower magnification (× 500) shows the gross structure after sintering.

Pores of a few micrometers in size are seen very clearly in **Figure 2(c)**. The large degree of porosity is believed to originate during pellet formation, for example, as a consequence of uniaxial pressing of the powder mixture. The presence of such porosities would unavoidably affect mechanical and optical properties [18]. Further optimization for better densification and lower porosity is necessary. One way to get around this problem is probably using isostatic pressing. Another reason for the observed porosity was probably a boiling of a certain composition in the mixture during the sintering process which consequently left bubbles or voids behind. Calcination of SLG before pulverizing may also help eliminate contaminants but at the cost of involving a higher working temperature.

Figure 3 shows a SEM/EDX image of the corresponding region in **Figure 2(a)**. Elemental distributions as deduced from energy dispersive X-ray spectroscopy are shown. Silicon (Si) and Oxygen (O) are found throughout the whole area, due to the presence of SiO_2. Zinc (Zn) is concentrated in the lower left corner. Sodium (Na) and calcium (Ca) are found copiously as they would be in soda-lime glass. On the other hand, aluminium (Al) is found much less than Na and Ca. Titanium (Ti) is also much less than Na and Ca. Focusing on the whisker area, where nucleation and crystallization were a dominating process, we found less zinc and more titanium in this area. This finding is a bit contrary to the observation of Zaid et al [8,9], who observe a significant promotion in nucleation and crystallization when adding ZnO to the sintering process of soda lime silicate glass. In addition, Parra-Arciniega et al [10] have observed that TiO_2 played very little role in crystallization but rather promoted higher strength. We have noted, however, in these two cases, ZnO and TiO_2 were added separately, not simultaneously as in our case. A more detailed study of the synergy of their effects is necessary.

CONCLUSION

Glass-ceramics were successfully produced from soda lime glass waste. The nucleation and crystallization of SiO_2 at the sintering temperature 850° C was observed by SEM and SEM/EDX. The morphology of crystalline phase in whisker shape is observed implying that the crystallization progress in one-dimensional growth. However, the sample still contains quite a large pore density. Further improvements are expected from purifying SLG by additional heat treatment and/or using isostatic pressing. Also a detailed study of the nucleation and crystallization in this system of SLG and SiO_2, ZnO, TiO_2 and CuO is envisaged.

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