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Preparation and characterization of high chemical durability and low thermal expansion borosilicate glass-ceramic composites by recycling of borosilicate glass

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Abstract

Borosilicate glass recycling is a challenge because it has high melting point and different chemical structure which makes it non-recyclable in the glass industry. This work focuses on borosilicate recycling through the preparation of a low thermal expansion and chemically durable borosilicate glass-ceramic composite (BsGC). Low thermal expansion and high chemical durability ceramics are advantageous in many applications such as lab supplies, corning ware, automobile components, and other low expansion products that are resistant to thermal shock. Kaolin and borosilicate were chosen for the preparation of glass-ceramic composite, because they have low thermal expansion and good chemical durability. BsGC was prepared by sintering borosilicate glass waste (e.g., Pyrex laboratory glassware, household glass) and kaolin at different temperatures (750-900 ° C). Water absorption method was used to measure the apparent porosity of the prepared composites. Surface morphology of the prepared BCGs was investigated using scanning electron microscopy (SEM). Phase composition of the prepared BGC samples was characterized using X-ray diffraction technique (XRD). The XRD results showed that at sintering of 750 °C a monocrystalline quartz was only existing. By increasing sintering temperature up to 800°C the quartz phase decreased, while at 850 ºC the quartz phase completely disappeared. The sintered BCG composites obtained exhibited low coefficients of thermal expansion in the range of 48 x 10-7 $^{o}C^{-1}$ and exhibited high chemical durability.

Keywords: Recycling, Borosilicate glass, Kaolin, Glass=ceramic composite.

1. Introduction

Industrial processes, manufacturing, and human activities are always accompanied by hazardous and non-hazardous waste materials. Thus, recycling and reprocess of such wastes is essential for environmental protection and maximizing economic benefits. Recycling is the selection, classification, and reemployment of waste as a raw material to produce the same, or very similar product, to the parent material. For instance, Mud waste from zinc hydrometallurgy [1], slag waste from steel production [2], ash and slag waste from incinerators [3], red mud waste from alumina production [4], glass waste from lamp, bottles, and other glass products have been used in a production of glass-ceramic composite [5].

Glass waste is abundant particularly in urban areas due to intensive usage of glass in many daily life activities. Borosilicate glass, in particular, has a wide range of applications due to its chemical durability and low thermal expansion, that vary between domestic purposes (Pyrex cooking wares), scientific purposes (laboratory glassware), medical purposes (glass ampoule), and industrial applications involving reshaping of borosilicate glass tubes [6]. Such excessive usage of borosilicate glass produces a large amount of waste [7]. Moreover, glass waste should get good attention for environmental protection, especially it takes millions for year for glass to degrade in nature. So, the recycling of borosilicate glass represents a great issue that should be studied and could have great economic and environmental impacts. In Egypt, there is no specialized industry that target the collection and recycling the waste glass. Glass waste can be utilized as fluxing material instead of common fluxes such as feldspar to reduce energy in glass ceramic production [8]. Reduction of energy consumption is an add-up advantage for using glass in the ceramic industry which will lead to reducing the

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overall cost of ceramic materials. Glass-ceramic composites are materials that are originally processed as glasses and converted to glass-ceramic composite to improve the properties of ceramics (e.g., chemical durability).

Borosilicate glass typically is composed of 70–80 wt% silica, 7–13 wt% of boron oxide, and 4–8 wt% sodium oxide or potassium oxide, and 2–8 wt% of aluminum oxide. Boron trioxide in borosilicate glass allows for a very low thermal expansion coefficient. In contrast, soda-lime glass thermal expansion coefficient is more than double that of borosilicate glass and can be easily cracked under temperature versions [9]. Therefore, recycling of borosilicate glass was our choice rather than soda-lime glass for the production of low thermal expansion glass-ceramic. It is worth mentioning that the applications of low thermal expansion ceramic are innumerous. For instance, such ceramic materials find applications in cooktop panel, laboratory crucible and hot plates. Glass ceramic could be also used in metallurgy and steel production, glass manufacturing, solid-oxide fuel cells (SOFCs), nuclear reactors, aerospace, automobile components, protective ceramic coatings, insulator, and industrial tooling [10, 11].

The resistance of borosilicate glass to chemicals is so high that it is used to store nuclear waste [12]. The boron in the borosilicate makes it less soluble, preventing the leaching of any harmful materials from glass to surrounding environment [12]. Such superior property makes borosilicate glass is good choice to produce chemically durable glass-ceramic composite. Highly chemical durable ceramic and glass-ceramic composites find applications in laboratory accessories such as mortar, ceramic parts of desiccator, and ceramic proppants [6].

In this work, borosilicate glass waste was recycled through the preparation of borosilicate glass-ceramic composite (BsGC). Borosilicate glass waste was thermally treated by the sintering process of borosilicate glass and kaolin. The prepared BsGCs has the advantages of production at relatively low temperature, low thermal expansion coefficient, and high chemical durability (see below).

2. Experimental:

2.1-Preparation of glass-ceramic composite:

Kaolin was obtained as a gift from Arkan for Manufacturing and Mining company (Egypt) Laboratory broken glass (Pyrex) and Kaolin were milled separately using ball milling. Pyrex and Kaolin powders at a ratio of 3:1, respectively, with a particle size distribution of 213 nm was compressed using homemade hydraulic press as round disks and sintered in a homemade muffle furnace at different temperatures (750-900 °C) for 60 min to form glass / ceramic composites (see data depicted in **Table 1** and schematic diagram in **Figure 1**). The heating rate was 25 °C min^{-1}. This temperature range have been selected because at temperature below 750 ºC the formed composites are very brittle. On the other hand, at higher temperatures > 850 ºC the formed material are converted into glassy state and ceramic or glass-ceramic composites are not formed.

2.2-Instruments:

Thermal expansion was measured using optical dilatometry (Misura® HSM ODHT 1400, Italy,). Milling was performed using laboratory fast mill Mod Speedy from Nannetti (Italy). Morphological analysis of the prepared glass / ceramic composite was performed using field emission scanning electron microscope (FESEM) (FEI Quanta 250 FEG model). Thermal expansion was measured using optical dilatometry (Misura® HSM ODHT 1400, Italy). The crystalline phases of the glass / ceramic composites were investigated by X-ray diffraction PHILIPS®, X'Pert multi-purpose diffraction. BsGC, kaolin and borosilicate glass were analyzed by XRF using PANalytical B·V, Epsilon 3 XL.

2.3- Measurement method of chemical durability:

As recommended by the API (American Petroleum Institute Test Procedure), chemical durability was assessed by the acid solubility of glass / ceramic composites [6, 14]. According to API instructions, 5 g of ceramic glass is put into a 150 ml Teflon beaker containing 100 ml of a mixture of 12% HCl and 3% HF acid solution. The beaker containing fried glass / ceramic composite and the acid mixture is then put at 65.6 ° C for 30-35 minutes in the water bath. Stirring according to the API is avoided. Then glass / ceramic composites are filtered, washed with 20 ml of distilled water three times, and dried at 105 ºC until constant weight.

Figure. 1. Schematic diagram for the preparation of borosilicate glass / ceramic composite.

3. Results and Discussion:

Tons of glass are produces yearly worldwide. For instance, 36 million tons were produced in the European union in 2017 [15]. and high volume of glass is disposed on yearly bases. For example, 10 million tons of glass are disposed yearly in the united states. Unfortunately, most of the disposed glass finds its way to trash [16]. This makes glass recycling an essential part of the glass industry. In particular, the real challenge in the glass recycling is the recycling of borosilicate glass which is sold under different commercial names (e.g., Borosil, Pyrex, Heatex, Suprax, Kimax, etc.), because it has high melting temperatures and different chemical compositions. Therefore, it is not possible to recycle borosilicate through soda-lime glass recycling process. Borosilicate should not exist in the soda-lime glass cullet in the process of glass recycling. Existence of borosilicate within the glass disposal makes it unusable waste. Consequently, tons of high-quality borosilicate glass are discarded to landfills yearly occupying precious land space and wasting material (i.e., borosilicate) with favorable properties such as low thermal expansion and high melting point that suits may applications. This makes the recycling of borosilicate a challenge and opportunity at the same time from environmental and economical perspectives. To meet this challenge, different research groups attempted to recycle glass through the production of glass-ceramic composites. For instance, borosilicate glass-ceramic was prepared using different materials such as calcined Valoxy [17], Sr-cordierite [18] and, $A1_2O_3$ [19]. Such glass ceramic materials were prepared at sintering temperature ranges of 850-1350 ºC. Different properties of such prepared glass-ceramic composite were studied such as compression strength, mechanical strength, and electrical property. Herein we utilize borosilicate glass and kaolin mixture to prepare borosilicate glass / ceramic composite. The sintering temperature was relatively low (750 to 850) compared to the previously reported glass-ceramic [14-16], which could achieve good economic feasibility. This study is focused on the characterization of prepared glass / ceramic composites in terms of thermal expansion and chemical durability according to the American Petroleum Institute test procedure (API method) [20].

Table 1. Sintering temperatures for glass / ceramic composite prepared using a fine powder (230 nm) of mixed Pyrex glass and Kaolin. The sintering temperature is 60 minutes.

BsGC	Sintering Temperature, ºC
A	750
B	800
C	850
D	900

The borosilicate glasses waste (e.g., broken laboratory glassware) of the following chemical composition (SiO_2 71.2 wt%, Al_2O_3 6.14 wt%, CaO 1.5 wt%, Na_2O 8.1, wt% Fe_2O_3 0.03 wt%, TiO_2 0.03 wt%, and B_2O_3 13 wt%) was mixed, milled, and fired at different temperature with kaolin of the following chemical composition (SiO_2 53.05 wt%, Al_2O_3 35.9 wt%, CaO 0.1 wt%, Na_2O 0.3 wt%, Fe_2O_3 0.35 wt%, TiO_2 0.85 wt%, and B2O3 9.454 wt%). The percent compositions of the raw material were studied using XRF technique (**Table 2**). The XRF data in **Table 2** indicated that prepared BsGCs have the same metal oxides as the raw materials with a percent composition closer to the raw material with higher oxide percent. Borosilicate glass and kaolin were chosen as raw material for the preparation of glass / ceramic composite because they have good chemical durability and low thermal expansion. And the produced glass-ceramic composite is expected to inherit those properties from Kaolin and Pyrex. The mixture was sintered at different temperatures and characterized using XRD, SEM. In addition, thermal expansion coefficient and chemical durability of the produced glass-ceramic composite were assessed as described below.

3.1-Water absorption

There are different methods to examine the porosity of ceramic material such as BET surface method, and Archimedes method. The simplest method is water absorption that reflects the porosity of ceramic. Glass ceramic porosity can be calculated using (JIS A 5209) method [21, 22]. In this method water absorption is dependent on open pores [21]. When ceramic material was soaked in water, water impregnate and retained in open pores that are easily filled. It was observed that upon increasing the sintering temperature, water absorption was decreased. As sintering temperature increase, the amount of water impregnation and retention in open pores was decreased due to the decreasing of porosity. Water absorption was highest for BsGC (A) (13.0 %) and decreased in case of BsGC (B) (3%) and BsGC (C) (1%). At high temperatures (900 ºC) glass / ceramic composite material was totally fused and water absorption of 0% is reached for BsGC (D) (see data depicted in **Table 3**).

Table 2. XRF analysis of BsGC composites prepared at different temperatures, Kaolin, and borosilicate glass.

Oxide	Material		
	Borosilicate glass, wt%	**Kaolin, wt%**	**BsGCs[a], wt%**
SiO_2	71.2	53.05	66.4
Al_2O_3	6.14	35.9	14.70
CaO	1.50	0.10	1.11
Na_2O	8.10	0.30	6.00
Fe_2O_3	0.03	0.35	0.13
TiO_2	0.03	0.85	0.27
B_2O_3	13.00	9.45	11.30

3.2-SEM micrographs:

To investigate the morphology of glass / ceramic composites, scanning electron microscopic analysis (SEM) was performed. As can be seen in **Figure 2**, the ceramic sample fusion increased as the sintering temperature of glass / ceramic composite samples increased from 750 to 900 ºC. For glass / ceramic composites BsGC (A) and BsGC (B), the surface appears in the form of flakes (**Figure 2 A and B**). While The flakes disappeared completely in the case of the glass / ceramic composite sample BsGC (C), and the surface appeared as a semi-fused ceramic (**Figure 2 C**). The sintering temperature for glass-ceramic composite BsGC (D) was high enough to achieve the maximum degree of fusion (**Figure 2 D**). such analysis agrees with water absorption test. For BsGC (A) and BsGC (B) the morphology of surface(flaks) indicated that the porosity is high, so the water absorption was also high. While in BsGC (C) and the porosity decreased, and the water absorption decreased. In case of BsGC (D) the surface was fully fused, and the water absorption reaches zero percent.

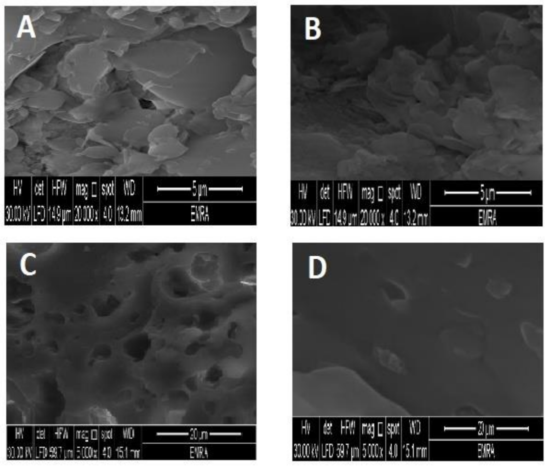

Figure 2. SEM micrographs of glass / ceramic composite prepared at different sintering temperatures (GC from A to D).

3.3- XRD Analysis:

XRD is an analytical technique used for the identification of crystalline material phases and can provide details on the dimensions of unit cells [23]. XRD is also used to compare the change in mineralogical, composition after sintering. The glass / ceramic composite was sintered at 750 °C, 800 °C, 850°C, and 900 ºC. Before XRD analysis BsGC materials were finely grounded and homogenized. From XRD pattern of samples (**Figure 3**), we can see that there is a descending trend of quartz peaks (Reference code: 01-078-152) which is the only detected crystalline phase in the investigated samples and it is originated from kaolin that composed mainly of kaolinite mineral and quartz as reported literature [6, 24, 25]. This observed trend is correlated to the rising in the sintering temperature of glass / ceramic composite samples from 750 to 900 ºC. This can be attributed to the reaction of silica with other oxide components in the glass / ceramic composite [26]. The quartz crystalline phase exists obviously in BsGC at 750 ºC and 800 ºC. At 850 ºC the crystalline phase had almost disappeared. While in case of 900 ºC the crystalline phase had completely disappeared, and the glass / ceramic composite material converted to amorphous borosilicate (**Figure 3**).

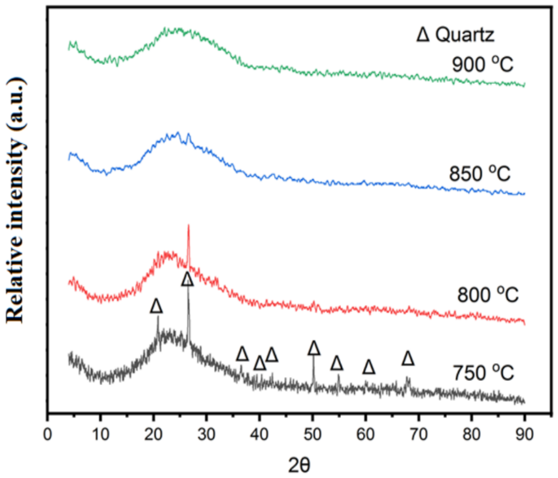

Figure 3. XRD patterns of glass / ceramic composite sintered at different temperatures.

3.4-Thermal expansion study:

The prepared glass / ceramic composite BsGC (A-D) thermal expansion coefficient is found to be in the range of 4.79 x 10^{-6} to 4.81 x 10^{-6} ºC^{-1} for all prepared BsGCs (see data depicted in **Table 2**). The observed low thermal expansion coefficient of the prepared glass / ceramic composite is attributed to the low thermal expansion of borosilicate and kaolin components [27, 28]. The thermal expansion coefficient of prepared glass / ceramic composite was near to the thermal expansion coefficient of borosilicate glass 3.2x10^{-6} – 4.0x10^{-6} ºC^{-1}. The thermal expansion coefficient of the prepared glass-ceramic composites (BsGCs) is comparable with the thermal expansion of low thermal expansion MgO/Al2O3/SiO2 glass- ceramic (4.5x10^{-7} ºC^{-1}). The thermal expansion coefficients of glass-ceramic composites in the paper report [28] were 4 to 5 × 10^{-6} ºC $^{-1}$ doped with expensive zirconium oxide and prepared at much higher temperatures (up to 1150 ºC) [29]. Moreover, the prepared glass-ceramic composite has the advantage of recycling borosilicate glass. It is worth mentioning that the thermal expansion of the prepared BsGC is much smaller than the high thermal expansion machinable glass-ceramic (1.2x10^{-5}-1.6x10^{-5} ºC^{-1}) [30]. The prepared low thermal expansion glass / ceramic composite may have different application such as laboratory supplies, ceramic cooking ware, and other low expansion products that resist thermal shock. This may be good for welding of such glass-ceramic composite with borosilicate glass tubing without cracking which essential criteria in manufacturing of electrochemical reference electrode.

3.5-Chemical durability

Chemical durability is a property of a substance that prevents the corrosive action of aqueous acidic or basic solution. The chemical durability of glasses is superior to most metals and polymers [31]. In terms of total performance, borosilicate glass is far superior to normal glass [12]. The amount of weight loss due to acid contact was measured. The chemical durability of prepared glass / ceramic composites was found to be high with very limited acid solubility (0.21-0.83 w/w%) (see data depicted in **Table 2**). It could be found that with rising sintering temperature, the acid solubility of glass / ceramic composite decreased. This may be attributed to increasing the degree of fusion and density, as well as closing of the pores with increasing the temperature. The prepared glass / ceramic composites from BsGC A to BsGC D have much lower acid solubility compared to other ceramics with high acid solubility (1.6-6.9 w/w%) [20, 31, 32].

Table 3. Properties BsGCs composites prepared at different sintering temperatures.

Property	**Borosilicate glass / ceramic composite (BsGC)**			
	(A)	**(B)**	**(C)**	**(D)**
Water absorption, (w/w%)	13.0	3.0	1.0	0.0
Acid solubility, (w/w%)	0.83	0.41	0.36	0.21
Thermal expansion coefficient (ºC^{-1}) (50 -600 ºC)	4.79 x 10^{-6}	4.82 x 10^{-6}	4.81 x 10^{-6}	-

This high chemical durability may be inherited from the chemical nature of the materials used in the preparation of glass / ceramic composites (Pyrex and Kaolin), which are distinguished by their high chemical durability [32].

2. Conclusions

Herein, borosilicate was recycled through the preparation of glass / ceramic composites using borosilicate and kaolin. The prepared borosilicate glass-ceramic composites (BsGC) were fabricated and characterized using XRD, SEM micrographs. The prepared BsGC was assessed in terms of thermal expansion, water absorption, and chemical durability. The results showed that the glass / ceramic composite possess amorphous structure when sintering temperature was 850 ºC. While at lower temperature 750 ºC and 850 quartz crystals were observed. The water absorption test showed that by increasing sintering temperature from 750 until 850 ºC the water uptake decreases and at 900 ºC the glass / ceramic composite was completely fused and there was no water uptake. SEM micrographs also confirmed the results observed from the water absorption test. The prepared BsGC exhibited high chemical durability compared to the previously reported ceramic materials.

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