

# Sintering Behavior and Machinability Properties of Industrial Waste Materials Based Glass-Ceramics

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Glass-ceramics were produced by sintering method from industrial waste materials such as fly ash, blast furnace slag and boron waste. The sintering behavior and machinability of glass-ceramic compositions were investigated. Additives were added to waste materials for enhancement of machinability and sintering properties. All starting materials were mixed by ball milling for 2 h using alumina media. The mixed and milled powders were sieved to grain sizes smaller than 75  $\mu\text{m}$  and pressed at 100 MPa. The pressed samples were sintered at 900 °C, 1000 °C and 1100 °C for 1 h in an electric furnace using a heating rate of 5 °C/min. Some characterization tests such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and machinability tests were performed on sintered samples. The results indicated that all samples exhibit good sintering and machinability properties.

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## 1. Introduction

Industrialization and urbanization brings huge amounts of waste materials. These materials are not only a burden to the industry, but also cause adverse effects on the environment. For this reason, we are interested in new technologies to recycle and convert waste materials into industrial materials again. This situation has great importance for protection of our environment. Glass-ceramics which are polycrystalline materials were obtained by controlled crystallization heat treatment process from suitable glass. This process usually involves two stages, namely a nucleation stage and a crystallization stage. Glass-ceramics can be obtained from various sources, such as pure oxides, natural rocks and industrial wastes (blast furnace, arc furnace, cupola furnace, flying ashes etc.). One of the major wastes of blast furnace slugs include high amounts of CaO, SiO<sub>2</sub> and MgO and small amounts of MnO and Fe<sub>2</sub>O<sub>3</sub>. Other major industrial waste of thermal power plants are flying ashes, which contain high amount of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Due to high amount of SiO<sub>2</sub> in industrial waste, successful production of glass-ceramic from such waste is possible. Because of brittleness of the ceramics and glass-ceramics, these are not suitable for some applications, especially when machining, such as drilling or cutting are needed. However making some modifications of glass-ceramics, such as changing chemical composition and the production methods, can provide a better machining capability [1–8]. Mica containing glass-ceramics

are preferred in some applications, such as electrical insulators and high thermal shock resist material and good machinability materials. Mica glass-ceramics are of SiO<sub>2</sub>-MgO-MgO-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-F system. They have superior properties, such as remarkable cleavage, flexibility, and elasticity, enabling therefore excellent machinability. Commercial mica-type glass-ceramic, of which the main type is the fluorophlogopite-type mica, also exhibits favorable properties like heat resistance, electrical insulating, and machinability [9–11].

In the present study, the effects of sintering/crystallization temperature on the crystal phases, the machinability and the microstructure properties of glass-ceramic, obtained from industrial waste such as fly ash, blast furnace slag and boron waste were investigated.

## 2. Experimental

The chemical compositions of the raw materials and calculated compositions of glass-ceramic used in this work are given in Table I. Initially, the main composition containing 60% fly ash, 20% blast furnace slag and 20% boron waste (wt.%) was prepared. K<sub>2</sub>O 5% and MgF<sub>2</sub> 10% (wt.%) was added to this main composition for obtaining machinability properties. The raw materials and other additives were first ground and mixed for 2 h by using an alumina ball mill. The mixture was sieved to a particle size fraction of  $75 \pm 45 \mu\text{m}$  and then uniaxial pressing was employed to shape the samples. Cylindrical samples ( $\varnothing$  25 mm) were shaped under the 100 MPa load and then sintered at several temperatures between 900, 1000 and 1100 °C, at heating rate of 5 °C/min for 2 h. XRD analysis (Rigaku D/MAX, CuK $\alpha$  radiation) was used for the crystalline phases determination.

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The micro-structural examinations were realized by using SEM (JEOL 6060) on the sample surfaces polished and etched in the solution of 5 vol.% HF for 1–2 min. Energy-dispersive spectrometer attachment (EDS) was

employed for elemental analysis. Furthermore, machinability tests were applied to the disc shaped specimens using 5 mm diamond drills with 200 rpm drilling rate under uncontrolled load.

Chemical composition of the industrial wastes and the glass-ceramic.

TABLE I

	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	CaO	Cl	Fe <sub>2</sub> O <sub>3</sub>	FeO	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	S	SiO <sub>2</sub>	SO <sub>3</sub>	SrO	TiO <sub>2</sub>	MgF <sub>2</sub>	L.O.I.
Fly ash	17.27		1.68	0.002	12.44		1.26	4.67		0.62			56.06	0.6				2.31
Blast furnace slag	10.82		35.32			0.3	0.7	6.47	2.13			0.56	44.1			0.5		
Boron waste	2.55	14.6	25.1		0.73		1.22	14		8.43			11.42	0.9				20.1
Glass-ceramic	11.081	2.482	10.96	0.001	6.469	0.1	5.97	5.86	0.36	1.75	0	0.095	39.56	0.5	0.95	0.09	10	4.5951

### 3. Results and discussion

The XRD patterns of the samples sintered at temperatures in the range from 900 to 1100 °C are shown in Fig. 1. Ca(Mg,Fe)Si<sub>2</sub>O<sub>6</sub> [Augite (ASTM card no:24-0203)], CaCO<sub>3</sub> [Calcite (ASTM card no:47-1743)], Mg<sub>9</sub>F<sub>2</sub>(SiO<sub>4</sub>)<sub>4</sub> [Clinohumite (ASTM card no: 14-0009)], KMg<sub>3</sub>(Si<sub>3</sub>Al)O<sub>10</sub>F<sub>2</sub> [Fluorophlogopite (ASTM card no: 16-0344)] and K<sub>2</sub>Mg<sub>6</sub>(Si<sub>0.75</sub>Al<sub>0.25</sub>)<sub>8</sub>O<sub>20</sub>(OH)<sub>1.8</sub>F<sub>2.2</sub> [Phlogopite (ASTM card no: 73-0224)] phases were determined by XRD in the sample of controlled crystallization, heat treated at 900 °C (Fig. 1a). When the same phases as Augite, Clinohumite and Phlogopite were detected in heat treated samples at 1000 °C, the Calcite and Fluorophlogopite phases were not determined, as seen in Fig. 1b. In literature Calcite phase can be stable up to 950 °C, this phase can transform into other phases at suitable conditions [5, 12]. In Fig. 1c, Augite, (K, Na)AlSiO<sub>4</sub> [Nepheline (ASTM card no:12-0198)], MgSiO<sub>3</sub> [Magnesium Silicate (ASTM card no:47-1750)], Ca<sub>4</sub>Fe<sub>14</sub>O<sub>25</sub> [Calcium iron oxide (ASTM card no:13-0395)] and Ca(Mg,Al)(Si,Al)<sub>2</sub>O<sub>6</sub> [Diopside (ASTM card no:41-1370)] phases have appeared but the Clinohumite, Fluorophlogopite and Phlogopite phases have disappeared. Fluorophlogopite phase has great importance for machinability. Increase in sintering temperature caused formation of weak Fluorophlogopite peaks. This phase was observed in the XRD patterns of the samples sintered at 900 and 1000 °C. Above 1000 °C, intensities of these peaks, but also intensities of all other peaks have decreased with temperature. Machinable glass-ceramic under the commercial trademark of MACOR consists of Fluorophlogopite mica in a borosilicate glass matrix. The XRD results are in good agreement with the literature [13]. The crystallization temperatures of Fluorophlogopite and Phlogopite phase were around 900–1000 °C and it is probable, that the increase in temperature has caused melting of these crystalline phases and their transformation into other phases.

Table II exhibits detected crystalline phases and the macro images before and after machinability tests. As seen from Table II, machinability test was performed for all samples, successfully. As can be seen in the macro images, firing shrinkage and also darkening of color was observed clearly with the increase of temperature.

Figure 2 shows the SEM images of the samples sintered

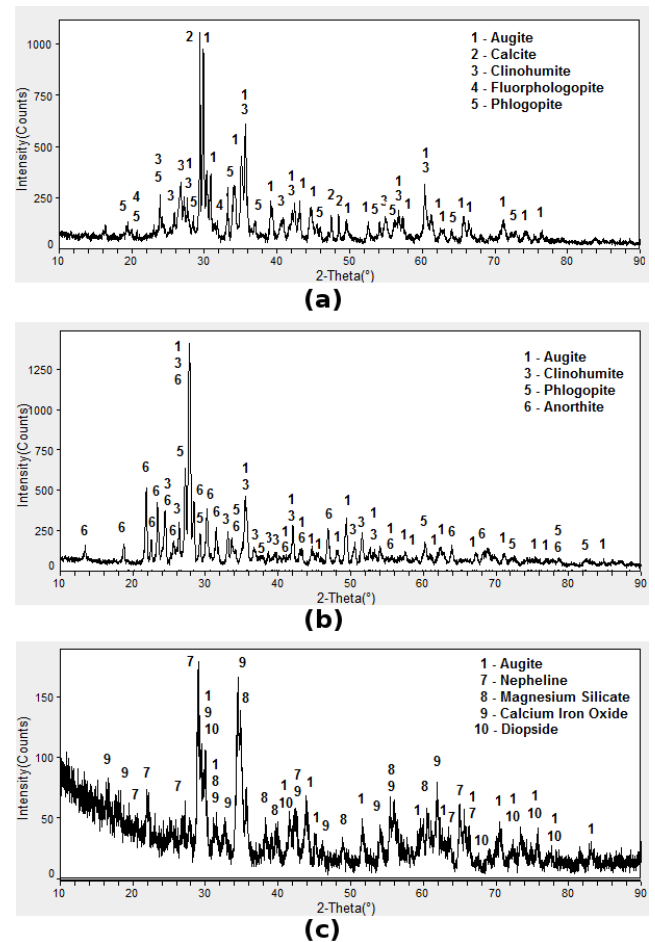


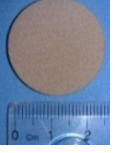
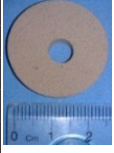
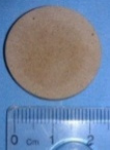
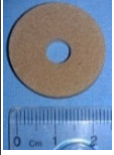
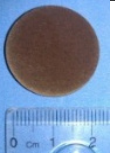
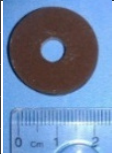
Fig. 1. XRD patterns of the samples sintered at temperatures of a) 900 °C, b) 1000 °C and c) 1100 °C.

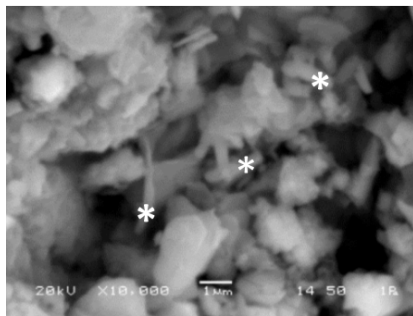
at 900 and 1000 °C. The results obtained from EDS analysis are in good agreement with the XRD analysis results. The grains marked with (\*) in both Fig. 2a and 2b are common images for mica glass-ceramic, including flour, it was presented by Höche as mica plates [14].

### 4. Conclusion

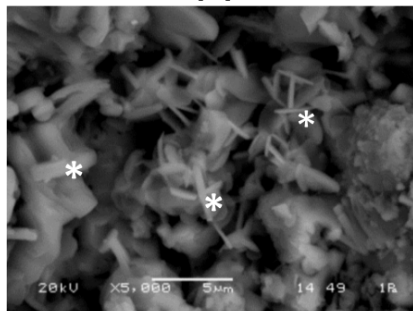
The main objective of this study was to produce machinable glass-ceramic materials from industrial wastes, such as fly ash, blast furnace slag and boron

TABLE II  
The macro images and detected crystalline phases of samples according to sintering temperature.

Sintering temperature	Detected phases	Machining test	
		Before	After
900 °C	Augite, Calcite, Clinohumite, Fluorphlogopite, Phlogopite		
1000 °C	Anorthite, Augite, Clinohumite, Phlogopite		
1100 °C	Augite, Diopside, Calcium Iron Oxide, Magnesium Silicate, Nepheline		



(a)



(b)

Fig. 2. SEM images of the samples sintered at a) 900 and b) 1000 °C.

waste, by sintering method. Whereas Fluorphlogopite, Phlogopite and Clinohumite phases were obtained in the sample sintered at 900 °C, the Phlogopite and Clinohumite phases were determined in samples sintered at 1000 °C. These phases disappeared at 1100 °C and Augite, Diopside, Calcium Iron Oxide, Magnesium Silicate and Nepheline phases have occurred. Machinability test was performed successfully for all samples. When macro images of samples were scrutinized, firing shrink-

age and also darkening of color was observed, which were clearly depending on increase in sintering temperature.

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