

**Composite-like material from magnesite, fumed silica and glass cullet****<sup>1</sup>Esmat M.A. Hamzawy, <sup>2</sup>Said H. Abd El Rahim and <sup>2</sup>Ahmed A. Melegy**<sup>1</sup>Glass Research Department and <sup>2</sup>Geological Sciences Department, National Research Centre, Cairo, Egypt.**ABSTRACT**

Based on enstatite formula ( $\text{MgSiO}_3$ ), composite materials were prepared from magnesite, wastes of fumed silica and glass cullets. Augite, enstatite, forsterite and traces of cristobalite were developed in the sintered samples. The analysis of augite and enstatite grains shows the incorporation of (Na, K, Fe) in the structure. Increase of pores took place with increasing the nominal enstatite ratio and the microstructure shows rounded rods and some euhedral crystals in glassy groundmass. The densities of the sintered samples were increased by increasing nominal enstatite ratios from 1.990 to 2.672 g/cm<sup>3</sup>. In the same trend the Vicker's microhardness values were from 578 to 610 km/mm<sup>2</sup>. The coefficient of thermal expansion (CTE) were from 61.00 to 79.00 range.

**Key words:** Fumed silica, composite, pyroxene, forsterite, cristobalite.

**Introduction**

Enstatite is a low temperature modification of  $\text{MgSiO}_3$ , which, during a thermal cycle, transforms into proto-enstatite "during heating" and clino-enstatite "during cooling of proto-enstatite" (Holand and Beall, 2002). Synthetic enstatite was prepared through ceramic, glass-ceramic, composite materials. Enstatite was developed, with mullite, as secondary phase during the crystallization in gel of glass within the  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  system (Vila *et al.*, 1999; Hamzawy and Ali, 2006). In solid reaction, of the clay fired between 900 and 1150 °C, neomineralization of enstatite, gehlenite, hercynite, mullite and abundant vitreous phase took place (Jordan *et al.*, 1999). Fabrication and sintering of talc, gave enstatite ceramic which enhance the deposit of mineralized bone tissue (Goeuriot *et al.*, 1998). Transformation of proto to clino enstatite took place through using shear stress, at 96 MPa (Zhu and Kriven, 1996). By gel method, or Pechini chemical preparation, enstatite (ortho-enstatite) powder was developed after calcining at 850 °C (Huang *et al.*, 1994).

Recently enstatite ceramic foam was prepared from talc, high alumina cement and diatomaceous earth and sintering at high temperature (Petr Ptáček *et al.*, 2014). Another foamed ceramic was prepared from talc ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) and foamed glass particles (ceramic balloons, CB) with and without LiCl as a sintering acid (Okada *et al.*, 2009). Foam based on enstatite ceramic was prepared from talc using technique is based on foaming of suspension of talc.

The paper deals with the preparation of enstatite based on composite material from magnesite, fumed silica and glass cullets. This composite that based on magnesite, fumed silica ceramic / glass cullets was characterized by X-ray diffraction analysis, Scanning Electron Microscope (SEM). Some properties of the sintered composite such as coefficient of thermal expansion, microhardness value and density were measured too. Also, the microanalysis of the main crystalline materials was measured too.

**Materials and Methods**

Magnesite, in addition to fumed silica (FS) and soda-lime silica (SLS) glass wastes were the starting materials in the present work. Magnesite is the source of MgO, was collected from Hamata area in the Eastern Desert of Egypt. Fumed silica, source of  $\text{SiO}_2$ , was collected from Ferrosilicon Factory in the Upper Egypt. Wastes of SLS glass were the source of  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$  and CaO. Table 1, shows the chemical composition of the starting materials. Table 2, shows the chemical composition of the sintered composite samples.

Enstatite ( $\text{MgSiO}_3$ ) powder was prepared from magnesite and fumed silica and mixed in ball mill for 2h. The enstatite powder was subjected to firing at 1100°C for 3 hours. Different mixtures from enstatite powder and glass cullets (SLS) powder were prepared and admixed in ball mill for 5h. The mixed powders with binder (7% polyvinyl alcohol PVA) were pressed (uniaxial pressures -20KN) in pellets. The pellets were dried in dryer (up to 280 °C) then sintered in silicon carbide furnace from 750 to 1250 °C (10°C / min).

For the characterization of the sintered samples, X-ray diffraction analysis (XRD): Model Bruker D8, Germany with employ Ni-filtered  $\text{CuK}\alpha$  radiation was used for phase identification. Scanning Electron Microscope (SEM model FEI quanta 250 Fei-Holland) was performed, on the well polished surface etched by 1%HF-1% $\text{HNO}_3$ , to show the microstructure of the sintered composite materials. However, compositional

analyses on the fresh fracture sintered samples took place by Scanning Electron Microscope (Cam Scan – IV series) with energy dispersive spectrometer EXL (Link Analytical Ltd).

Coefficient of thermal expansion (CTE) was determined using a dilatometer (Linseis model L76/1250, Germany) with a heating rate 5°C/min. Vicker's microhardness values, are given as the average of 10 indentations per each sample, was measured on the well polished surface using (Shimadzu model HMV-Japan) microhardness tester with 100 gm/ load and 15 second / time.

Density of the composite samples were measured by a pycnometer (Quantachrome Instrument – Upyc 1200 e v5.03 US) using Helium gas.

**Table 1:** Chemical analysis of the starting materials

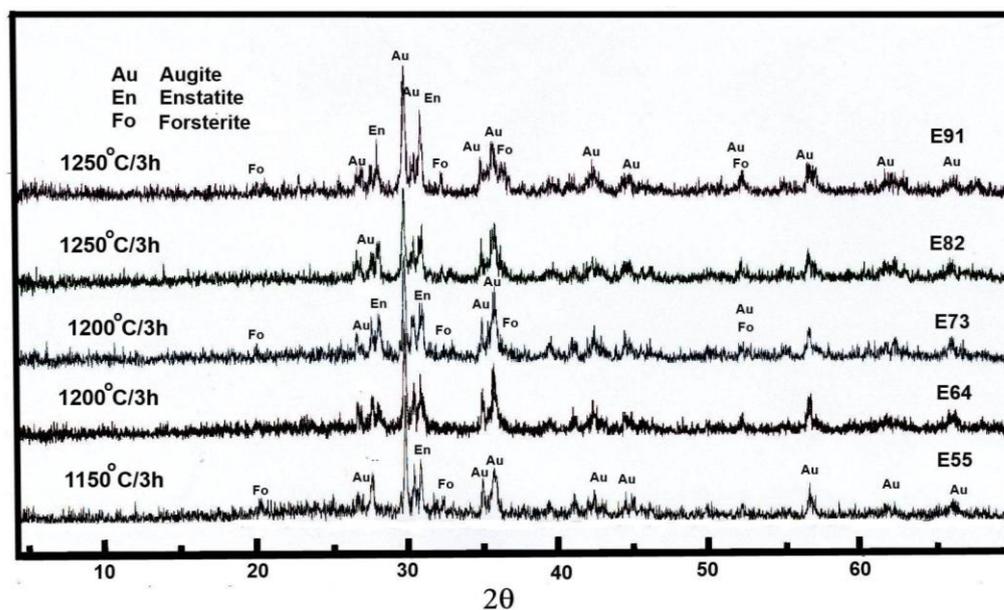
Strating Materials	Chemical Analysis (wt%)							
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	IL
Magnesite	0.80	0.05	0.74	0.98	45.91	0.00	0.00	51.52
Fumed Silica	95.18	1.08	0.23	0.68	0.23	0.40	0.40	1.80
Soda-lime-silica-glass	73.94	1.20	0.07	10.77	0.20	13.79	0.02	--

**Table 2:** Chemical composition of the sintered composite samples

Sample No	Chemical Analysis (wt%)						
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O
E55	65.82	0.95	0.43	6.00	19.67	7.00	0.13
E64	64.23	0.89	0.49	5.05	23.55	5.64	0.15
E73	62.49	0.84	0.74	4.09	27.38	4.28	0.18
E82	60.98	0.79	0.63	3.14	31.32	2.94	0.20
E91	59.36	0.74	0.70	2.19	35.18	1.60	0.23

## Results and Discussion

After sintering all the five samples, in the 750 to 1250 °C temperature range, the vitreous phase appear as white pellets that help in polishing and microhardness measurements ( Table 3 ). The X-ray diffraction analysis of the sintered samples gives augite "(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)<sub>2</sub>O<sub>6</sub>" (Clark, *et al* 1969), enstatite "Mg SiO<sub>3</sub>" (Arima and Onuma, 1977) and forsterite "Mg<sub>2</sub>SiO<sub>4</sub>" (Brodholt and Refson, 2000), however, little low cristobalite (ICSD #76-0935) was developed at 1100 °C in addition to the later phases ( Fig.1).

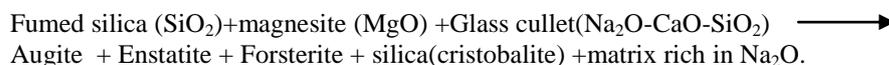


**Fig. 1:** X-ray diffraction patterns of the sintered composite samples heat-treated at different temperatures.

Increasing of the nominal enstatite portion in the composite samples concomitant with increasing of the intensity of enstatite lines (2.88 and 3.13 Å). However, pyroxene augite exists as the major phase even in low percentage on the incorporated calcium (i.e. decreasing of glass fraction), this means that in the crystallization of the composite samples, the heat of formation of augite < enstatite < forsterite. The reported data revealed that enthalpies of formation at 1073 are enstatite: -8.10 ± 0.42 kcal; forsterite: -14.23 ± 0.45 kcal (Brousse *et al*, 1984). Also, in nature the first crystallization of the amorphous magma was olivine, since it needs higher

energy, whereas pyroxene was developed after it ("Bowen's reaction series" ,Deer *et al*, 1978). However, crystallization of cristobalite was initiated by presence of sufficient alkali or alkaline earth elements (Table 3).

Stability of the developed crystalline phases even at 1250 °C in all compositions were prone to good homogeneity, easy casting and resulted in the partial re-melting of the glass. The following equation shows the reaction that has happened in the heat-treatment process:



**Table 3:** Crystalline phases developed in the sintered composite samples heat-treated at different temperatures.

Sample No	Mix composition wt%			Heat-treatment Parameters °C/3h	Crystalline Phases	Morphology
	Enstatite powder	Glass powder	cullet			
E55	50	50	1100	Au+En+Fo+Crist (t)		
			1150	Au+En+Fo (t)		
E64	60	40	1100	Au+En+Fo+Crist (m)		
			1200	Au+En+Fo (t)		
E73	70	30	1100	Au+En+Fo+Crist (m)		
			1200	Au+En+Fo (t)		
E82	80	20	1100	Au+En+ Crist+ Fo		
			1250	Au+En+Fo (t)		
E91	90	10	1100	Au+ Crist+ En+Fo		
			1250	Au+En+Fo (t)		

Au: Augite / En:enstatite/ Fo:forsterite/ Crist:cristobalite/t:trace/ m:minor.

Figure 2 shows the microstructure of the crystalline E55, E73 and E91 sintered composite samples heat-treated at different temperatures. Some pores were appeared on the polished surface of the samples and through these pores the crystalline phases were appeared. Increasing of the pores was with increasing of the nominal enstatite phase (decreasing of glassy fraction). Dissminated round and rod like crystals were embedded in glassy ground mass in the sample E55 heat-treated at 1150 °C, whereas clear euhedral crystals of augite and enstatite in sample E73 heat-treated at 1200 °C was shown. In the sample containing high nominal enstatite, fine spheres and rods were appeared in sample E91 heat-treated at 1250 °C.

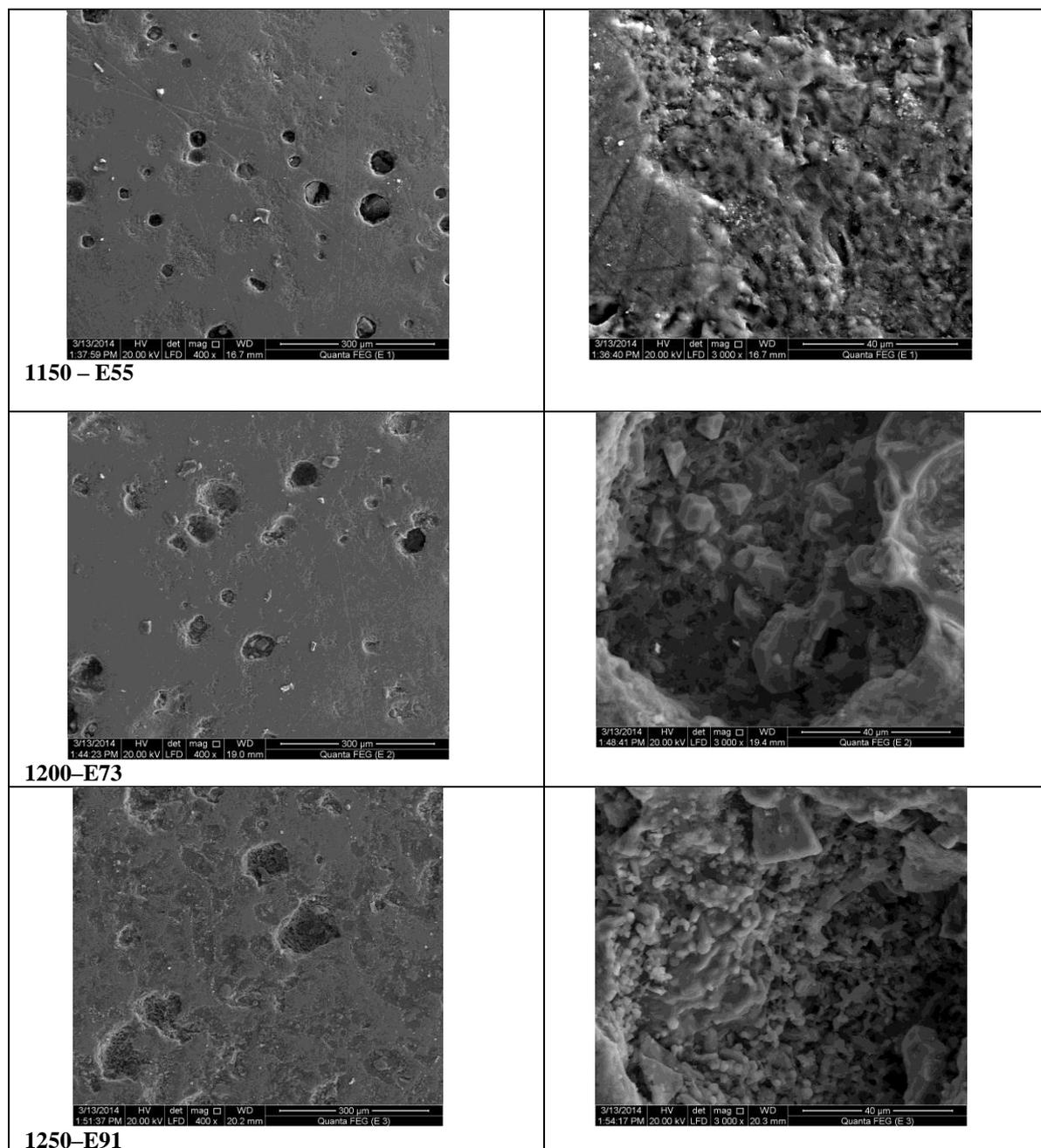
Table 4 shows the properties of the sintered composite samples which compares, thermal properties (CTE) and physical properties (density g/cc and microhardness kg / mm<sup>2</sup>). It can be seen that the density increases from 1.894 to 2.670 g/cc, with decreasing the glass ratio and in the same manner the Vicker's microhardness values were increased from 578 to 610 kg/mm<sup>2</sup> ( Table 4). Also, the CTE values show relative increase from 6.1 to 7.9 x 10<sup>-6</sup> °C<sup>-1</sup>.

Increasing of the nominal enstatite lead to increase of the density, hardness and CTE. In the fact the reported density of enstatite was in the 3.2- 3.9g/cc (Deer *et al*,1978) whereas the density of the SLS glass was 2.53 g/cc. The hardness of enstatite or the SLS glass was 5-6 (in Moho scale). Also, the CTE of the enstatite was 65.0-85.0×10<sup>-7</sup>°C<sup>-1</sup>(Holand and Beall, 2002) whereas, it was 8.3 x 10<sup>-6</sup>°C<sup>-1</sup>for the SLS. These reported data show the behaviour of the developed crystalline phases in the composite samples.

The microanalysis of the sintered composite samples shows the possible replacement in the developed pyroxene(Augite and Enstatite)and olivine (Forsterite) phases (Table 5). However, in comparison of the general formula of pyroxene (Ca,Mg,Fe,Na) (Mg,Fe,Al)(Si,Al)<sub>2</sub>O<sub>6</sub> and olivine (Ca, Fe, Mn, Ni, Mg) SiO<sub>4</sub> with comparison of the present microanalysis, it can be seen that the possible solid solution phases that give a good mechanical properties of the composite samples.

**Table 4:** Properties of the sintered composite samples at different temperatures

Sample No	Thermal Properties	Vickers microhardness	Density	Developed phases at different temperatures	
	CTE 20 – 500 °C $\alpha \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$	Kg/mm <sup>2</sup>	g/cc	Heat-treated at °C/3h	Crystalline phases
E55	7.00	578	1.894	1150	Au+En+Fo(t)
E64	6.1	588	1.895	1200	Au+En+Fo(t)
E73	7.4	599	2.170	1200	Au+En+Fo(t)
E82	7.9	594	2.189	1250	Au+En+Fo(t)
E91	7.9	610	2.672	1250	Au+En+Fo(t)

**Fig. 2:** SEM of the sintered composite samples heat-treated at different temperatures.

**Table 5:** Microanalysis of the developed phases (pyroxene and olivine) in wt %.

Constituents Oxides	Amount (wt%)					
	Augite <sup>1</sup>		Enstatite <sup>2</sup>		Forsterite <sup>3</sup>	
	Stoichiometric	Calculated	Stoichiometric	Calculated	Stoichiometric	Calculated
SiO <sub>2</sub>	48.30	58.64	59.85	48.65	57.29	45.55
Al <sub>2</sub> O <sub>3</sub>	8.63	0.23		0.40		0.53
Fe <sub>2</sub> O <sub>3</sub>	6.08	0.33		0.44		1.60
MgO	15.35	19.39	40.15	47.03	42.71	45.94
CaO	21.35	19.15		1.81		5.89
K <sub>2</sub> O		0.13		0.12		0.07
Na <sub>2</sub> O	1.31	1.52		1.16		0.28
TiO <sub>2</sub>	3.38	0.13		0.09		0.06
MnO		0.08		0.10		0.09

<sup>1</sup> Clark *et al* (1969), <sup>2</sup> Arima and Onuma. (1977), <sup>3</sup> Brodholt and Refson (2000)

### Conclusion:

Composite material based on enstatite ceramic / soda-lime-silica glass were prepared from magnesite, fumed silica and glass cullet. Augite, enstatite, forsterite and little cristobalite were the developed phases that appeared during sintering process. The microcrystalline structure shows rounded rods and some euhedral crystals in glassy matrix. Increasing of nominal enstatite leads to increase of density, microhardness and the coefficient of thermal expansion up to 7.9 g/cc, 610 kg/mm<sup>2</sup> and 7.9 x 10<sup>-6</sup> C<sup>-1</sup>, respectively. The chemical microanalysis supports and confirms the possible solid solution in the developed phases.

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