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# Bulk nucleated fine grained mono-mineral glass-ceramics from low-silica fly ash

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**Abstract**

$Cr_2O_3$-nucleated fine grained mono-mineral glass-ceramics of augite were produced from low-silica fly ash and additives of $SiO_2$, $Al_2O_3$ and $MgCO_3$, via two steps of heat treatment for nucleation and crystal growth. The starting glass approached the composition of $CaMg_{0.75}Al_{0.4}Fe_{0.1}Si_{1.75}O_6$, derived from $CaMg_{0.75}Al_{0.5}Si_{1.75}O_6$, which belongs to diopside – Ca-Tschermak solid solutions. The influence of $Cr_2O_3$ (up to 0.75 wt.%) on the development of crystalline phases, the properties and the microstructure of the resultant glass-ceramics crystallized at different temperatures was investigated.


*Keywords:* A. Grain growth; B. Grain size; D. Glass-ceramics; D. Glass; Fly ash

## 1. Introduction

A variety of industrial wastes, such as blast furnace slug, fly ash, filter dust from waste incinerators, different types of sludge, glass cullet etc., have been effectively converted into useful glass-ceramics (GCs) in several countries [1–10]. Nevertheless, there are only few thorough studies aiming at bulk nucleation of glasses comprising wastes to obtain fine-grain mono-mineral GCs. Fly ash (FA) is a vastly produced waste in power stations. In northern Greece, the thermal power stations of Ptolemaida (belonging to the Public Power Corporate, ''ΔΕΗ'') annually produce c.a. 7 million tones of FA from the burning process of lignite coal [11]. That particular FA, which features relatively low silica content, has been already considered for incorporation in cement and concrete [12]. Nevertheless, huge amount of FA is still dumped in landfills. Accordingly, there is high scientific challenge and strong economic and environmental motivation to develop new ways of utilizing that FA. The structure of pyroxens enables solubility of various cations in it [10]. Accordingly, a matrix of pyroxene can be suitable for accommodating cations from FA. Moreover, pyroxene-based GCs are attractive materials because of their chemical and mechanical properties [1,3,10].

Microstructure, which develops with heat treatment of parent glass, defines the final properties of GCs and thus their usefulness for particular applications. Fine grained microstructure desirably confers high strength to materials. It is usually achieved via proper selection of effective nucleating agents, which favor controlled crystallization of large number of fine crystals developed from numerous nucleation sites produced in the glass matrix [5].

In the present paper, $Cr_2O_3$, which is a typical nucleating agent used in pyroxene-based glasses [7,10,13,14], was used to produce mono-mineral augite type GCs from low-silica and high-calcium FA, whose average chemical composition (estimated by ΔEH-data, wt.%) is 30.03 $SiO_2$, 13.67 $Al_2O_3$, 38.87 CaO, 5.32 $Fe_2O_3$, 4.42 MgO, 0.63 $Na_2O$, 0.59 $K_2O$, 6.17 $SO_3$, and 0.30 $TiO_2$. We have added silica, alumina and magnesium carbonate in this FA to produce the starting glass, whose nominal composition aimed to be close to CaM-

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$g_{0.75}Al_{0.4}Fe_{0.1}Si_{1.75}O_6$. This composition actually derives from $CaMg_{0.75}Al_{0.5}Si_{1.75}O_6$, which lays in the range of diopside – Ca-Tschermak solid solutions. In our earlier study [15], we have demonstrated that a glass with similar composition crystallizes to mono-mineral GC of augite after heat treatment in the temperature range of 850–1000 °C.

## 2. Materials and experimental procedure

Fine powder of as-received FA (Ptolemaida deposit landfield, Greece, 48.24 μm) and technical grade powders of $SiO_2$ (Sibelco, Portugal, purity > 99.5%), $Al_2O_3$ (CT3000, Alcoa Chemicals, USA, purity > 99.9%), $MgCO_3$ and $Cr_2O_3$ (Aldrich-Chemie, Germany, both with purity > 99.5%) were used. Three glass compositions were prepared. The proportion (wt.%) of raw materials in the starting batch, designated as C1, was 52.78 FA, 24.96 silica, 2.68 alumina, and 19.58 magnesium carbonate. Addition of $Cr_2O_3$ in the amounts of 0.50 wt.% and 0.75 wt.% (over 100% of C1) resulted in the compositions C2 and C3, respectively.

Homogeneous mixtures of batches (∼100 g), obtained by ball milling, were preheated at 900 °C for 1 h for decarbonization and then melted in alumina crucibles at 1500°–1550 °C for 1 h in air atmosphere. Glasses in bulk form were produced by casting of molten glass on preheated (500 °C) bronze moulds. To release the residual stresses, the glass blocks were immediately (i.e. before cooling to room temperature) annealed at 550 °C for 1 h. Afterwards, the glass blocks were cooled down to room temperature and then were cut in prismatic blocks (0.5 cm × 1 cm × 2 cm). Conventional two-stage heat treatment at 700 °C for 1 h (for nucleation) and then at different temperatures in the range of 900 °C–1000 °C for 2 h (for crystal growth) was applied to devitrify bulk glasses to GCs. The heating rates were 4 °C/min for the first stage, and 1.5 °C/min for the second one. Small amounts of glass frit were also obtained by quenching of glass melts in water.

The following techniques and equipments were employed. Differential thermal analysis (DTA) of powders with sizes in the range of 1.000–0.415 mm, collected by sieving of glass frit, was carried out in air (Netzsch 402 EP, Germany, heating rate 5°/min). Dilatometry measurements were done with prismatic samples with cross-section of 4 mm × 5 mm (Bahr Thermo Analyse DIL 801 L, Germany, heating rate of 5°/min). The crystalline phases were identified with X-ray diffraction (XRD, Rigaku Geigerflex D/Mac, C Series, Japan, Cu $K_\alpha$ radiation, λ = 1.5406 nm, 30 kV, 25 mA, 0.02 °/s). Microstructure observations were done at polished (mirror finishing) and then etched (by immersion in 2 vol.% HF solution for 4 min) surfaces of samples by field emission scanning electron microscopy (FE–SEM, Hitachi S-4100, Japan; 25 kV, 10 μA) under secondary electron mode. Archimedes method (i.e. immersion in diethyl phthalate) was employed to measure the apparent density of the samples. Preliminary three-point bending strength tests of parallelepiped bars (4 mm × 4 mm × 50 mm) of GCs were also carried out (Shimadzu Autograph AG 25 TA; 0.5 mm/min displacement).

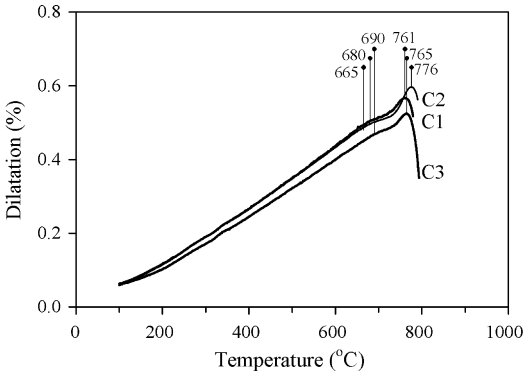


Fig. 1. Dilatation curves of the three investigated glasses.

## 3. Results and discussion

Melting at 1500 °C for 1 h effectively resulted in formation of highly homogenous dark brown molten glass C1. Higher temperatures (1550 °C) were required for obtaining the glasses C2 and C3, likely because of the low solubility of $Cr_2O_3$ in silicate melts [3]. Absence of crystalline inclusions was confirmed with XRD and SEM, afterwards.

The temperatures corresponding to glass transition ($T_g$) and softening points ($T_s$) were determined from the dilatometry curves plotted in Fig. 1. Apparently, there is no evidence of systematic influence of $Cr_2O_3$-content on these characteristic temperatures. In particular, $T_g$ ranged between 665 and 690 °C, and $T_s$ between 761 and 776 °C. A single exothermic crystallization peak ($T_p$) was registered by DTA (Fig. 2) for all investigated compositions between 900 and 1000 °C. The peak is shallow and occurs at a relatively high temperature in the case of C1 (995 °C), becoming much sharper and occurring

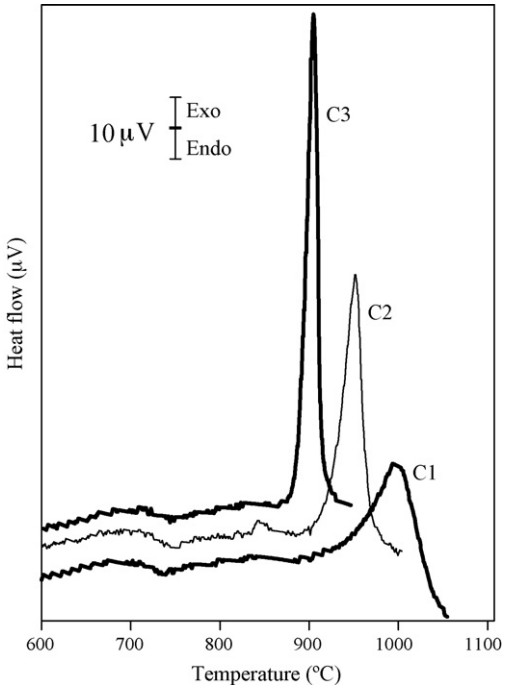


Fig. 2. DTA plots of powders (sized 1.000–0.415 mm, obtained by sieving from glass frit) of the three investigated glasses.

Table 1
Density (g/cm$^3$) of the parent glasses and the resultant glass-ceramics crystallized at different temperatures for 2 h in air (each value is the average from five different measurements; the standard deviation of the presenting values is less than 0.01 g/cm$^3$)

| Composition | Density (g/cm$^3$) | | | |
|---|---|---|---|---|
| | Glass | 900 °C | 950 °C | 1000 °C |
| C1 | 2.91 | 2.93 | 2.93 | 2.96 |
| C2 | 2.91 | 3.05 | 3.04 | 3.04 |
| C3 | 2.92 | 3.11 | 3.08 | 3.08 |

at lower temperatures in C2 (952 °C) and more pronouncedly in C3 (905 °C).

The effect of the $Cr_2O_3$ on nucleation (promoted by heat treatment close to $T_g$, ~700 °C, for 1 h) and crystallization (promoted by heat treatment in the range of $T_p$ for 2 h) can be evaluated by the difference of density between the parent glasses and the GCs. This difference, calculated from the density values of Table 1, reflects the extent of the conversion the parent glasses into crystalline phases [7]. Accordingly, for the same temperature of heat treatment, C3 features the highest degree of crystallization.

The diffractograms of Fig. 3 show that heat treatment at 900 °C predominantly result in single crystalline phase GCs of augite, (Ca,Mg,Fe,Na)(Mg,Fe,Al,Ti)(Al,Si)$_2O_6$, which belongs to the family of pyroxenes [2,3]. Increasing $Cr_2O_3$ improves crystallinity (i.e. increasing intensity of peaks). Furthermore, the peaks at $2\theta = 19.18^\circ$ and at $2\theta = 59.32^\circ$, registered in the $Cr_2O_3$-free C1 (whose assignments were not firmly resolved), decay in the composition containing 0.5% $Cr_2O_3$ (C2) and totally vanished for 0.75% $Cr_2O_3$, suggesting C3 as a mono-mineral augite-containing GC.

The influence of $Cr_2O_3$ on the microstructure of GCs is shown in Fig. 4. The $Cr_2O_3$–free GC C1 crystallized at 1000 °C exhibited the structure of Fig. 4a, which comprised coarse crystal layers sandwiched in high chemical resistant (to HF etching) glassy phase. Observation at the edges of samples confirmed that crystallization starts from the surface. These findings agree fairly well with literature. In particular, with no

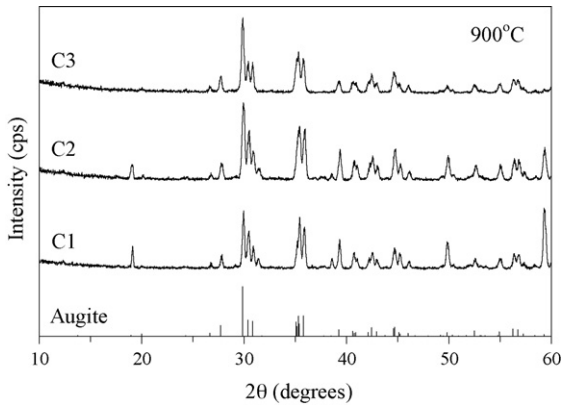


Fig. 3. X-ray diffractograms of the three investigated glass-ceramics crystallized at 900 °C for 2 h in air. The patterns of augite (ICDD card 01-088-0856) are also marked. (The diffractograms have not been normalized. Full scale of intensity axis is 6000 cps.)

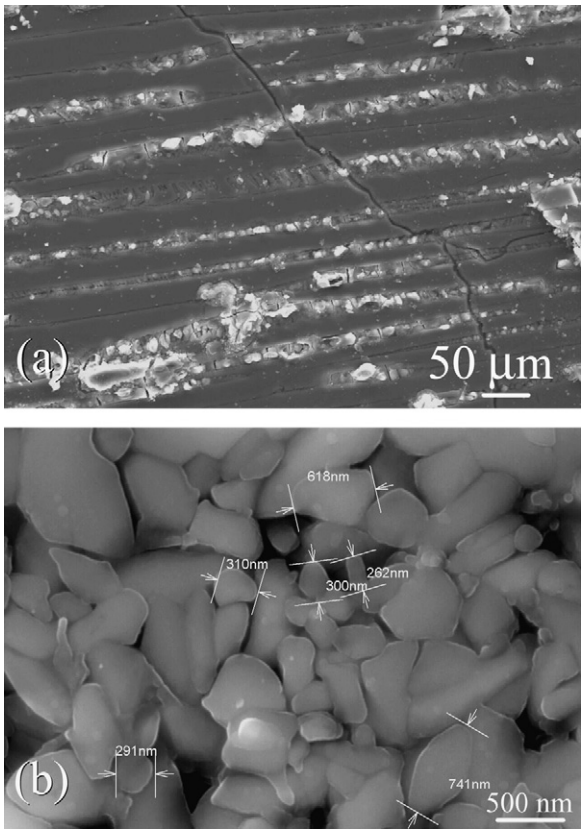


Fig. 4. Microstructure of (a) the $Cr_2O_3$-free glass-ceramic C1 crystallized at 1000 °C, and (b) the 0.75% $Cr_2O_3$-containing glass-ceramic C3 crystallized at 900 °C, both for 2 h in air.

use of nucleation agent, pyroxene-based systems are generally prone to surface crystallization because of the big difference between the density of crystals and glassy phase [16–18].

Addition of $Cr_2O_3$ resulted in fine grained GCs, bulk-crystallized after heat treatment at a temperature as low as 900 °C, which agrees with the results of DTA. Fig. 4b shows the microstructure of C3 (0.75% $Cr_2O_3$) crystallized at 900 °C, where submicron crystals are perfectly bordered one to the other. Observations in the bulk and at the surface of C2 and C3 samples did not show evidence of surface crystallization. These results confirm that the $Cr_2O_3$-free C1 glass is prone to surface crystallization, while $Cr_2O_3$ favors bulk crystallization, which was observed in both C2 and C3 GCs [1].

Earlier studies [7,10,18–20] have demonstrated that $Cr_2O_3$ considerably increases the crystallization rate of Fe-containing compositions. The crystallization mechanism involves formation of spinels, which effectively catalyze the formation of pyroxene phases. Formation of magnesium–iron–chromium spinel, $Mg(Cr,Fe)_2O_4$, whose lattice parameters match better those of pyroxene phase than pure $MgCr_2O_4$ [19], seems to play a key role at promoting bulk nucleation. The fine spinel crystals act as nuclei for epitaxial pyroxene growth [18]. In the present study, both glass production and ceramization processes occurred under air atmosphere, which should favour the $Cr^{3+}$ state. The results of XRD of C2 and C3 samples (Fig. 3), heat treated at temperatures close to crystallization peak (i.e. 900 °C), did not indicate formation of spinel crystals, which may be accommodated in

pyroxene structure [7]. Certainly, further investigation in the temperature range $T_g$–$T_p$, using XRD and/or other techniques (e.g. neutron diffraction), will shed light in the role of spinel in formation of pyroxene structure.

As mentioned in the introduction, fine microstructure (Fig. 4b) and formation of mono-mineral GC (Fig. 3) anticipate high mechanical properties of the resultant materials. Preliminary flexural tests have shown that the 3-point bending strength of the GC C3 crystallized at 900 °C is about 200 MPa. This value is comparable with the bending strength of the conventional GC ''Siliceram'' (174 MPa), produced from blast furnace slag via one stage heat treatment, but considerably higher than GC ''Slagsital'' (80–120 MPa), developed in the former Soviet Union at Konstantinov plant [1,3,6].

In general, the GCs produced in the present study possess attractive properties as building materials for usage as construction and architectural components. As far as other potential specific technical applications are concerned, investigations towards the influence of the amount of $Cr_2O_3$ (also beyond 0.75%) on mechanical, thermal, and chemical properties of the resultant GCs are required. Meanwhile, there is also a challenge for replacing the technical grade powders, used in this study as additives to FA, with alternative inexpensive natural materials or wastes, but with no compromise of GCs properties, to reduce the production cost.

## 4. Conclusions

Glasses, made of low-silica fly ash and additives of $SiO_2$, $Al_2O_3$ and $MgCO_3$, were successfully converted into fine grained mono-mineral augite (pyroxene) GC materials. $Cr_2O_3$, as nucleating agent, favors bulk-crystallization mechanism. The difference of density between the parent glasses and the GCs, assumed to be an index of the degree of devitrification and the formation of the crystalline phases, is well correlated with $Cr_2O_3$-content. Accordingly, the composition containing the highest amount of $Cr_2O_3$ (i.e. 0.75%, C3) featured the highest degree of crystallization among the investigated compositions, upon heat treatment at the same temperature and time. The high flexural strength of the GCs C3 should result from the fine microstructure of well arranged submicron crystals in the residual glass.

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