# Preparation of glass-ceramic materials from granitic rocks waste

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## Abstract

*Crystallisation of glasses based on the diopside-anorthite eutectic system, containing increased amount (10–50 wt.%) of wollastonite based on granite quarries waste, was investigated for the preparation of cheap technical glass-ceramic materials. Granite quarries waste consisted of about 52 wt.% of the batch constituents depending on composition. The granite quarries waste composition was sometimes modified by adding other ingredients such as dolomite, limestone and $Al_2O_3$. Batches were melted and then cast into glass, which was then subjected to heat-treatment to induce crystallisation. The resulting glass-ceramic materials (heat-treated at 1000 °C for 3 h) were mainly composed of diopside, anorthite, wollastonite and mullite. With increasing temperature (to 1050 °C for 3 h), diopside and anorthite transformed into akermanite and mullite. It has been found that increasing the content of the diopside-anorthite eutectic in the batch constituents, resulted in increased bulk crystallisation. Samples were characterised by different techniques including differential thermal analysis, polarizing microscope, X-ray diffraction and indentation microhardness testing. The obtained glass-ceramic materials possess very high hardness, indicating high abrasion resistance, making them suitable for many applications under aggressive mechanical conditions.*

*Keywords: glass-ceramic, crystallisation, granite quarries waste, microstructure*

## I. Introduction

Granite quarries waste is an obnoxious by-product of mining operation. Recent statistics indicate that annually about 40000 tons of this very harmful by-product are disposed of by Al-Riyadh quarries in Al-Riyadh area of the Saudi Arabia. Chemical compositions of granite quarries waste indicate the possibility of their use in glass and glass-ceramics industries. Glass and glass-ceramics are known for their importance in commercial applications, for example in construction and microelectronics industry. Waste materials, such as granite quarries waste, have great economic, technological and scientific significance in production of glass-ceramic materials. The high energy consumption (1400–1500 °C) is not problematic since it is for one phase, while in the conventional ceramic production three phases are required in the process. Moreover, energy is not a big problem in some Gulf countries.

The choice of primary raw materials for the production of glass-ceramic materials is very important. Different varieties of natural rocks and various sedimentary rock mixtures are being increasingly used for the production of glass-ceramic materials. Igneous rocks such as granites, basalts and nepheline syenite are used successfully in the production of glass-ceramic materials [1–3].

Glass-ceramics are normally produced from specially formulated compositions - which usually contain a nucleating agent - melted and shaped into articles of desired geometry and then cooled to glass. After that glass articles are subjected to heat-treatments to initiate the growth of crystals in situ. Commonly, such heat-treatment process is carried out in two steps, namely at the temperature within or somewhat above the transformation range, to develop nuclei in the glass, and then followed by another higher-temperature treatment to enhance the growth of crystals on the formed nuclei. Glass-ceramics are used in a wide range of technical applications, for example in construction and for domestic purposes and in the microelectronics industry [4].

Extensive investigations have been made on the crystallisation of glasses and/or melts based on natural rocks and waste materials to obtain new crystalline glass materials (glass-ceramics) from cheap resources.

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**Table 1. Chemical analysis of the used raw materials**

| Constituent oxides | Granite quarries waste [wt.%] | Dolomite [wt.%] | Limestone [wt.%] |
|---|---|---|---|
| $SiO_2$ | 68.75 | 3.74 | 0.66 |
| $Al_2O_3$ | 14.48 | 1.06 | 0.08 |
| $Fe_2O_3$ | 2.50 | 0.88 | 0.12 |
| $TiO_2$ | 0.64 | 0.05 | - |
| CaO | 2.26 | 30.50 | 55.60 |
| MgO | 1.27 | 19.80 | 0.23 |
| $Na_2O$ | 4.21 | 0.56 | - |
| $K_2O$ | 3.49 | 0.04 | 0.09 |
| MnO | 0.05 | 0.03 | - |
| $SO_3$ | 0.06 | 0.15 | - |
| L.O.I. | 1.20 | 43.05 | 43.20 |

Locsei [5] prepared glass-ceramic materials characterised by high resistance and chemical durability from glasses based on blast furnace slag, sand and clay with some additions of crystallisation catalysts. Zhunina *et al*. [6] studied the crystallisation of glasses based on fusible calcareous clays. They obtained crystalline materials composed mainly of pyroxene. They found that $Cr_2O_3$ and $TiO_2$ were the most effective catalysts. Khater [7] obtained a glass ceramic material characterised by low thermal expansion coefficient from glasses based on Egyptian clay, sand, $MgCO_3$ and $Li_2CO_3$ with some additions of catalysts. Khater [8] synthesized basalt melt cast ceramic materials composed of monomineralic pyroxene. The outstanding strength, excellent abrasion and chemical resistance are the most valuable features of these materials. In addition, Khater *et al*. [9–13] studied the crystallisation of glasses and preparation of glass-ceramics from different raw materials. Morsi *et al*. [14] obtained a glass-ceramic from glass based on industrial waste materials. Khater [15] prepared glass-ceramic materials from bypass cement dust that possess very high hardness, indicating high abrasion resistance and making them suitable for many applications under aggressive mechanical conditions. Omar and Salman [16] studied the crystallisation process of molten granite and dolomite mixtures. Materials composed of alkali

aluminous pyroxene, melilite and olivine assemblages were obtained. El Shenawi *et al*. [17] studied the crystallisation of monopyroxenic basalt-based glass-ceramic. The obtained crystalline materials composed of pyroxene. Khater and Hamzawy [18] managed to obtain glass and glass-ceramics from raw materials such as cement kiln dust, granite and magnesite.

The present work aims at studying the crystallisation of some glasses based on the diopside ($CaMgSi_2O_6$) - anorthite ($CaAl_2Si_2O_8$) eutectic composition containing successive increased amount of wollastonite ($CaSiO_3$) from 10 to 50 wt.% based on granite quarries waste. Emphasis is based on the effect of the base glass composition and heat treatment conditions on the crystalline phases and microstructures of the resultant materials.

## II. Experimental

### 2.1. Glass compositions and batch preparation

The choice of a base composition of a glass suitable for conversion into glass-ceramics depends on the conditions of preparation and crystallisation and on the expected properties of the crystalline phases. Moreover, the microstructure of the material is an important factor determining the technical properties of the glass-ceramics. In the light of the chemical analysis of granitic quarries waste, it was decided to modify the present granite quarries waste composition in order to make it more suitable for obtaining glass-ceramic materials.

Granitic quarries waste, dolomite and limestone from Al-Riyadh area were used as starting materials in batch preparations of a technical glass-ceramics. Chemical analyses by atomic absorption data of raw materials used for batch preparations are listed in Table 1. Five meltable glass compositions, according to the nominal phase and actual chemical analyses (Tables 2 and 3) were selected for this study; they are designated as G1 to G5. About 10 kg of representative samples of each ingredient (granite quarries waste, dolomite and limestone), were collected, crushed and ground into less than 100 mesh powders. An adequate representative quantity for all stages of the laboratory investigation was obtained using the quartering technique.

Batches corresponding to these compositions were prepared by calculating the appropriate proportions of

**Table 2. Chemical composition of the investigated glasses according to the nominal phase**

| Glass No. | Nominal phase composition [wt.%] | | | Calculated composition [wt.%] | | | | Batch ingredient [wt.%] | | | | Note excess $Al_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Woll.* | Di.* | An.* | $SiO_2$ | $Al_2O_3$ | CaO | MgO | Granite | Dolomite | Limestone | $Al_2O_3$ | |
| G1 | 10 | 52.20 | 37.80 | 50.49 | 13.87 | 25.98 | 9.67 | 52.17 | 31.35 | 14.18 | 2.30 | - |
| G2 | 20 | 46.40 | 33.60 | 50.62 | 12.33 | 28.46 | 8.59 | 52.02 | 27.30 | 19.51 | 1.18 | - |
| G3 | 30 | 40.60 | 29.40 | 50.77 | 10.79 | 30.93 | 7.52 | 51.89 | 23.35 | 24.70 | 0.07 | - |
| G4 | 40 | 34.80 | 25.20 | 50.90 | 9.25 | 33.41 | 6.44 | 51.20 | 19.21 | 29.59 | - | 1.47 |
| G5 | 50 | 29.00 | 21.00 | 51.04 | 7.71 | 35.89 | 5.37 | 48.85 | 18.02 | 33.13 | - | 3.04 |

*\* Woll. - Wollastonite; Di. - Diopside; An. - Anorthite*

**Table 3. Actual chemical analyses of glass compositions from raw materials**

| Constituent oxides | Glass compositions [wt.%] | | | | |
|---|---|---|---|---|---|
| | G1 | G2 | G3 | G4 | G5 |
| $SiO_2$ | 47.29 | 47.34 | 47.29 | 46.70 | 46.11 |
| $CaO$ | 23.56 | 25.88 | 28.12 | 30.04 | 31.90 |
| $MgO$ | 8.77 | 7.81 | 6.84 | 5.79 | 4.77 |
| $Na_2O$ | 3.03 | 3.02 | 3.00 | 2.95 | 2.90 |
| $K_2O$ | 2.32 | 2.34 | 2.35 | 2.32 | 2.30 |
| $Fe_2O_3$ | 2.02 | 1.98 | 1.95 | 1.88 | 1.83 |
| $TiO_2$ | 0.43 | 0.43 | 0.43 | 0.43 | 0.43 |

granite quarries waste, dolomite and limestone, with a little amount of pure chemical reagent $Al_2O_3$ which served as starting materials (the purity of the $Al_2O_3$ is 99.9%). After being thoroughly mixed, the weighed powdered batch materials were melted in fire clay crucibles in a globar furnace at temperature ranging from 1450 to 1500 °C for 1 to 2 hours depending on the composition of the melt. Homogeneity of the melt was achieved by swirling of the melt-containing crucible several times at about 30 minutes intervals. After melting and refining, the bubble-free melt was cast onto a hot steel marver into button and rods. The hot glass samples were then transferred to a pre-heated electrical muffle furnace for annealing at 600 °C, which was



**Figure 1. Differential thermal analysis patterns of the investigated glasses**

then switched off immediately after the samples are transferred.

*2.2. Thermal treatment*

The obtained glass samples were heated in a muffle furnace from room temperature to the required temperature and kept at the intended temperature for 3 h, after which the furnace was switched off and the samples were allowed to cool inside it to room temperature.

A double-stage heat-treatment schedule was used to study its effect on the microstructure. Glass samples were first heated at 750 °C for 1 h and then 1000 °C for 3 h.

*2.3. Sample characterisation*

Thermal analysis was carried out using a Shimadzu DTG60 micro differential thermoanalyser using 40 mg of powdered glass sample, having particle size less than 0.60 mm and larger than 0.2 mm, against $Al_2O_3$ powder as a reference material. A heating rate of 10 K/min was maintained for all the runs.

The identification of crystals precipitating in the course of crystallisation was conducted with the X-ray diffraction analysis of the powdered samples. X-ray diffraction patterns were obtained using a Bruker D8 Advance, Germany, adopting Ni-filtered CuKα radiation. Instrument settings were maintained for all analyses, using a Si disk as an external standard. This was necessary to make the measurements based on the peak height more accurate.

Mineralogical constitution and microstructure of almost all the heat-treated specimens were examined optically in thin sections using a polarizing Carl Zeiss research microscope.

Indentation microhardness was determined for the obtained glasses and corresponding glass-ceramics. The Vicker's hardness values were measured using a Shimadzu microhardness tester of the M-type under a load of 100 g. and loading duration of 15 seconds. Three Vicker's measurements were made for each condition.

**III. Results and discussion**

Differential thermal analysis patterns of glasses (Fig. 1) are similar in their general characteristics, but have minor variations in peak positions and intensities. They show endothermic effect between 730–739 °C, which corresponds to a precrystallisation stage [19], and is followed by exothermic effect due to crystallisation with a
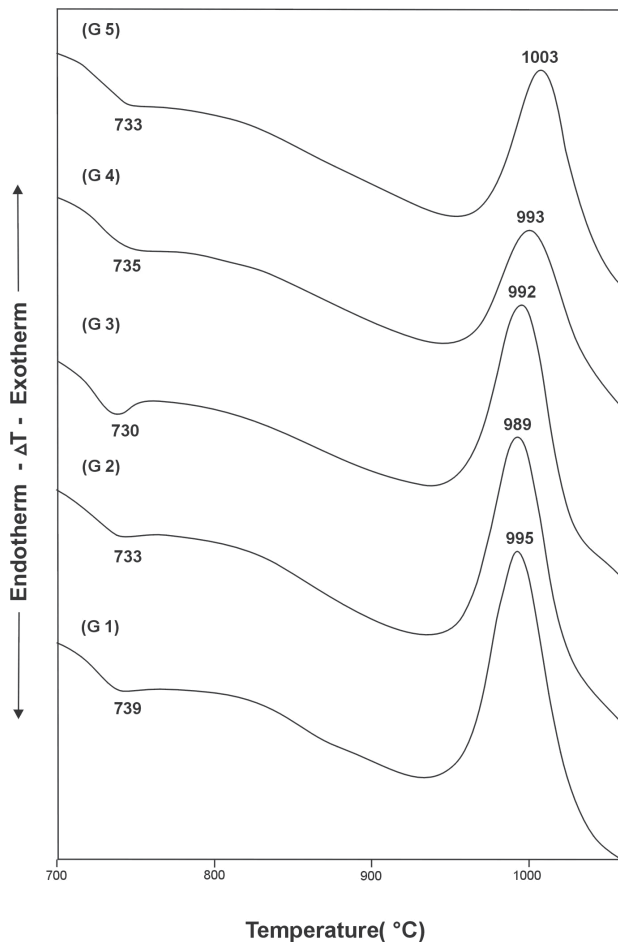
maximum heat at 989 to 1003 °C. As the wollastonite content was progressively increased or granite waste decreased the peak temperature of exothermic crystallisation increased while the endothermic effects mentioned above were slightly displaced towards lower temperatures. These effects may be ascribed to the viscosity-temperature relations of the glasses since the downward shift of the endotherms may indicate lower viscosities, which was noted during melting and casting.

The broad nature of the exothermic peaks indicates the wide temperature span over which crystallisation may take place in these glasses, but the low peak height indicates that relatively long heating times are needed to achieve a reasonable degree of crystallisation. The stronger and narrower exotherms exhibited by G1 and G2 may indicate that such diopside-anorthite-rich glasses have higher crystallisabilities, a possibility which was confirmed during heat-treatment.
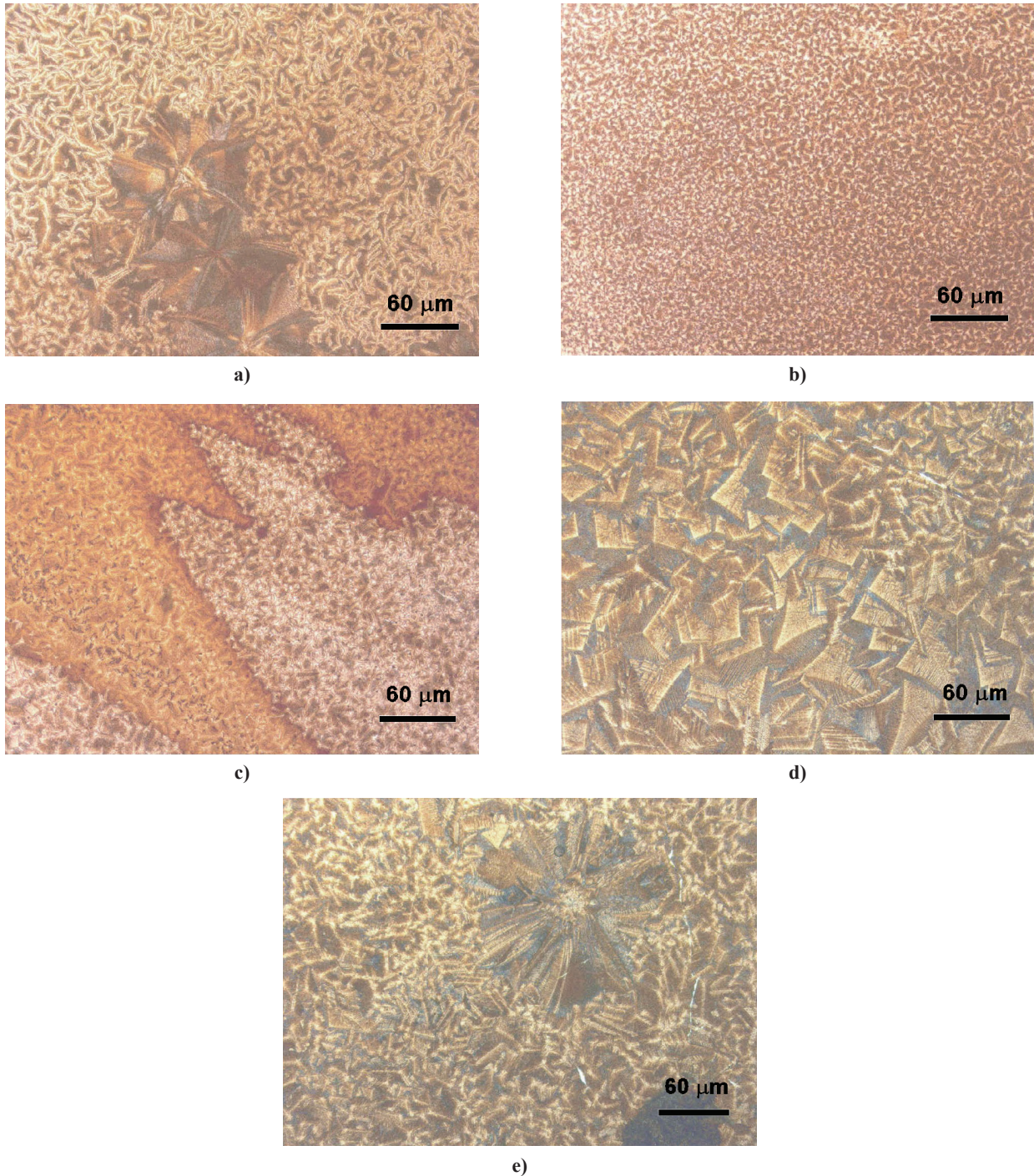


**Figure 2. Photomicrographs of investigated glasses heat-treated at 750 °C, 1 h and then 1000 °C, 3 h: a) G1 (volume crystallisation of fine fibrous growth of anorthite and wollastonite together with spherulites of diopside), b) G2 (fine texture of tiny diopside, anorthite and wollastonite), c) G3 (similar to G2 but somwhat coarser texture), d) G4 (very well shaped pyroxene growths with anorthite and wollastonite) and e) G5 (spherulites of diopside with fine fibrous growth of anorthite, wollastonite and mullite)**

**Table 4. Calculated composition of the investigated glasses**

| Glass No. | Calculated composition [mol%] | | | |
|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | RO* | RO/SiO$_2$* |
| G1 | 50 | 8.33 | 41.67 | 0.83 |
| G2 | 50 | 7.14 | 42.86 | 0.86 |
| G3 | 50 | 6.27 | 43.73 | 0.87 |
| G4 | 50 | 5.29 | 44.70 | 0.89 |
| G5 | 50 | 4.70 | 45.30 | 0.90 |

*RO represents total of the divalent oxides MgO+CaO mol %

Visual and petrographic investigations (Figs. 2) of the heat-treated glasses show the crystallisation at the surface of G4 and G5 with some residual glass (wollastonite-rich glasses). However, G1, G2 and G3 (wollastonite-poor glasses) showed both surface and volume crystallisation, with the latter predominating in G1-G3 and emerging readily throughout the entire volume of these glasses.

The above observations, therefore, indicate an increase in the diopside-anorthite eutectic or granite quarries waste content in the glasses up to a certain limit. It is desirable for enhancing the crystallisability of the glass through bulk nucleation and for lowering the temperature of the onset of crystallisation which in turn favours the formation of crystalline products.

Visual and optical microscopic examinations of the heat-treated glasses indicated that crystallisation in some of these glasses started from the surface of the specimens with internal growths. Diopsidic pyroxenes are found to be characterised by strong birefringence oblique extinction (about 40°) and biaxial positive optic figure. Diopsidic pyroxene crystals began to grow as thin needles from the surface of the glass specimen towards its centre. Three-hour heat-treatment at 1000 °C temperature showed that almost complete crystallisation occurred (Fig. 2a). Bladed aciculars of anorthite and fine wollastonite are observed (Fig. 2) in the samples with higher content of wollastonite (G4 and G5). Change in the texture of glass-ceramic specimens from fine- to coarse-grained may be attributed to the expected decrease in the viscosity with decreasing MgO and $Al_2O_3$ contents (Tables 2 and 3); a condition which opposes crystal growth.

The aforementioned results show that, as the MgO and $Al_2O_3$ in the glass increase, so the tendency of the glass to crystallise throughout the bulk increases.

$Al^{3+}$ ions may likewise be responsible for promoting bulk crystallisation when moving from G5 to G1 as the result of a possible change in its coordination from four to six. The coordination state of $Al^{3+}$ ions in silicate glasses has been the subject of considerable debate. Physical property measurements on alkali silicate glasses [20] and alkaline earth silicate melts [21] suggested that $Al_2O_3$ acts amphoterically over a wide range of compositions; i.e. aluminium can occur in both network forming and network modifying positions and

that $Al^{3+}$ ions would therefore exist in both four-fold and six-fold coordination. These coordination states depend, to some extent, on the alkalinity or basicity of the silicate. Accordingly, in glasses with high RO/SiO$_2$ mol ratios (Table 4), $Al^{3+}$ ions being in four-fold coordination, form $(AlO_4)^{5-}$ tetrahedral which enters the glass network and takes part in the formation of a strong aluminium-silicon-oxygen framework. The formation of such closely packed tetrahedral structural groups reduces the propensity towards devitrification. This may explain why the samples G4 and G5 (which contain less than 5 mol% $Al_2O_3$ and have RO/SiO$_2$ ratios higher than 0.89) are somewhat difficult to crystallise. With further increases in $Al_2O_3$ and corresponding decreases in the alkaline earth oxides (from G1 to G3), the share of $Al^{3+}$ in six-fold coordination increases, and these ions move from the network forming sites into the less closely packed interstitial octahedral sites in the glass structure. This may create a condition which is more favourable for crystallisation, thus increasing the crystallisation tendency throughout the interior of granite-rich glasses.

X-ray diffraction (Fig. 3 and Table 5) showed that diopside, anorthite and wollastonite were the main crystalline phases developed after being treated at 1000 °C for 3 h in the investigated glasses. Their portion depends on base composition.

Figure 3 depicts the X-ray diffraction patterns of the samples G1-G5 treated at 1000 °C for 3 h. In the sample G1 diopside ($CaMgSi_2O_6$), anorthite ($CaAl_2Si_2O_8$) and wollastonite ($CaSiO_3$) phases were crystallised. In the samples G2-G4 the wollastonite was developed better, especially in G2. Increase in the intensity of wollastonite lines can be noticed (e.g. lines 3.85, 3.08, 2.07 and 1.78 nm). In the sample G5 (Fig. 3 and Table 5) diopside is a major crystalline phase with anorthite and wollastonite having appearance of mullite phases (notice lines 3.98, 3.42 and 2.229 nm). The strong intensities of diopside diffraction lines and their slight shift to higher $2\theta$ values indicate a solid solution character.

X-ray diffraction (Fig. 4 and Table 5) showed that akermanite ($Ca_2MgSi_2O_7$), mullite ($3Al_2O_3 \cdot 2SiO_2$) and wollastonite ($CaSiO_3$) were the main crystalline phases developed after being treated at 1050 °C for 3 h in the investigated glasses G1-G5. After treatment at a higher temperature (1050 °C, 3 h), the picture of the X-ray became more explicit.
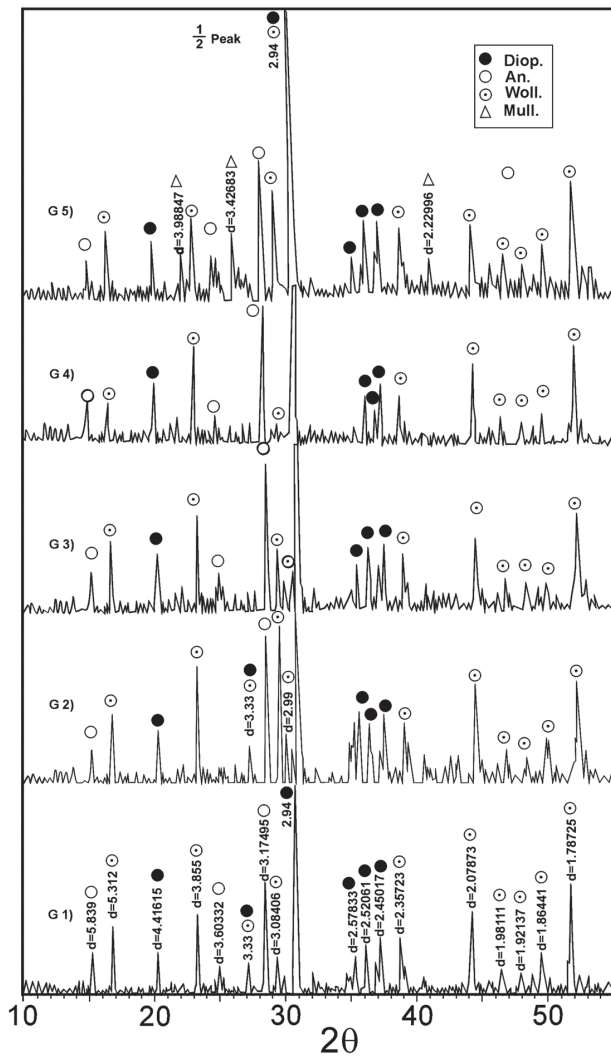
**Figure 3. X-ray diffractions of the investigated glasses heat-treated at 1000 °C/3 h**



**Figure 4. X-ray diffractions of the investigated glasses heat-treated at 1050 °C/3 h**

Figure 5 shows a comparison between the X-ray diffraction patterns of G3 after being treated at different temperatures. At 1000 °C for 3 h diopside, anorthite and wollastonite were formed (Fig. 5, pattern *a*). At 1050 °C diopside ($CaMgSi_2O_6$) and anorthite ($CaAl_2Si_2O_8$)
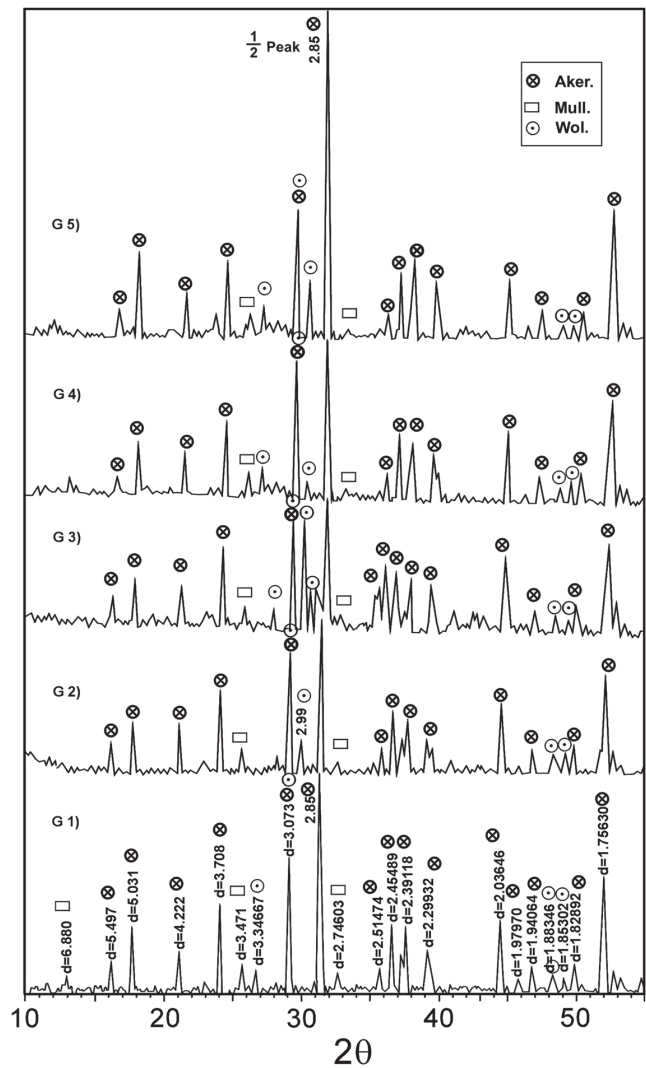
were altered into akermanite ($Ca_2MgSi_2O_7$) and mullite ($3Al_2O_3 \cdot 2SiO_2$) (Fig. 5, pattern *b*).

It can be said that heat treatment at 1050 °C for 3 h leads to crystallisation of akermanite mullite and wollastonite in all investigated glasses (G1-G5). Table 5 gives

**Table 5. X-ray identification of the crystalline phases and Vicker`s hardness numbers of the investigated glasses**

| Glass No. | Heat-treatment parameters | Phases developed* | Vicker hardness No. |
|---|---|---|---|
| G1 | 1000 °C, 3 h | Diop., An., Woll. | 1008 |
|    | 1050 °C, 3 h | Aker., Mull. ,Woll. | -- |
| G2 | 1000 °C, 3 h | Diop., An., Woll. | 1015 |
|    | 1050 °C, 3 h | Aker., Mull., Woll | -- |
| G3 | 1000 °C, 3 h | Diop., An., Woll. | 995 |
|    | 1050 °C, 3 h | Aker., Mull.,Woll | -- |
| G4 | 1000 °C, 3 h | Diop., An., Woll. | 988 |
|    | 1050 °C, 3 h | Aker., Mull., Woll. | -- |
| G5 | 1000 °C, 3 h | Diop., An., Woll., Mull. | 976 |
|    | 1050 °C, 3 h | Aker., Mull. ,Woll. | -- |

*Diop. - Diopside; An. - Anorthite; Woll. - Wollastonite; Mull. - Mullite; Aker. - Akermanite
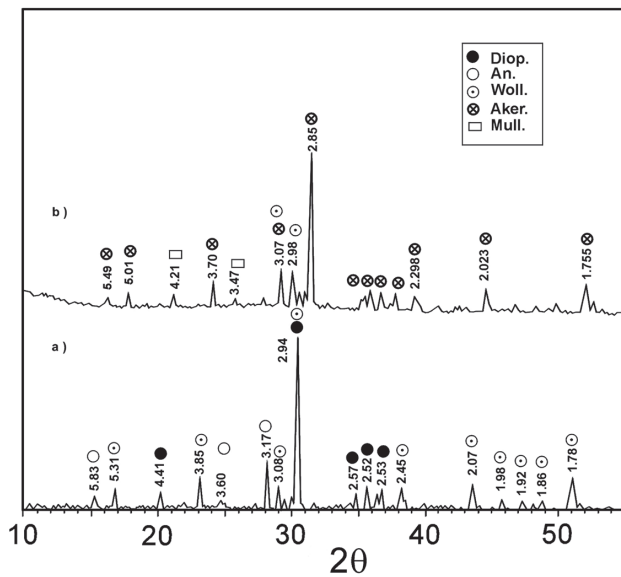
**Figure 5. X-ray diffraction patterns of G3 subjected to different heat treatment schedule: a) 1000 °C for 3 h, b) 1050 °C for 3 h**

summaries of the crystalline phases developed after the various heat treatment conditions as identified by XRD.

Owing to the fundamental differences between the structures of the three crystallised phase, monoclinic pyroxene (diopside), triclinic plagioclase (anorthite) and monoclinic wollastonite, almost no solid solution can occur between any two of them, but it could exist within each mineral species, especially the pyroxene.

$Al^{3+}$ ions can be easily shared in building up the complex aluminous pyroxene under non-equilibrium conditions such as that obtained in Tschermak's molecule, $CaAl_2SiO_6$. The extent of solid solution was largely dependent on the crystallisation parameters, and increases as the deviation from equilibrium conditions increases. Under non-equilibrium conditions of crystallisation, the maximum solubility of Tschermak's molecule in diopside ranges between 40 and 48% [21,22].

The strong tendency of $Al^{3+}$ to share in building up the complex pyroxinic solid solutions can be explained by the ability of $Al^{3+}$ to take four-fold and six-fold coordination in crystalline silicates. Aluminium share in these different structural positions is controlled by the ratio between its ionic radius and those of the oxygen (0.43), which is approaching the geometrical limits of stability between four-fold and six-fold coordination [23].

The development of mullite in G5, may be due to the breaking down of the metastable diopsidic solid solution firstly formed, which exsolved the elements of Tschermak's molecule, and the subsequent reaction with $Al_2O_3$, that may be present essentially in the residual interstitial glass (G5 contains excess $Al_2O_3$ than nominal composition).

The measurement of the indentation micro-hardness were carried out on glass samples G1-G5 treated at 1000 °C, 3 h, where bulk crystallisation was noticed.

Vicker's indentation micro-hardness numbers were found to range from 976 to 1015 (Table 5). Vicker's hardness numbers increase as the diopside-anorthite eutectic or granite quarries waste contents increase. Thus indicating the high abrasion resistance nature of these materials, which make them suitable for many applications under aggressive mechanical conditions. Thus, it can be concluded that the granite quarries waste can be successfully used for making glass-ceramic materials that possess valuable properties. These glass-ceramics can be used for different purposes such as floor and wall tiles, bench tops, sewer pipes and many others.

Microstructure and microhardness results showed that the G2 glass is better than other glasses investigated in this paper.

## IV. Conclusions

Present results show that the increase in the content of diopside-anorthite phase in glass results in increased bulk crystallisation. This effect is accompanied by a change in the texture of the glass-ceramics specimens from coarse to fine grained diopside, anorthite, wallastonite and mullite formed at 1000 °C, 3 h. After being heated at 1050 °C, 3 h diopsiode and anorthite altered into akremanite and mullite.

Thus, it can be concluded that the granite quarries waste, dolomite and limestone from Al-Riyadh area can be successfully used to create glass-ceramic materials possessing valuable properties. This may pave the way for disposal of these wastes in a friendly way to the environment. These glass-ceramics can be used for different purposes, such as floor and wall tiles, bench tops, sewer pipes and many others. Microstructure and microhardness results showed that the best the glass sample tested was G2, with the composition 50.62 wt.% $SiO_2$, 12.33 wt.% $Al_2O_3$, 28.46 wt.% CaO and 8.59 wt.% MgO.

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