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# Synthesis of glass-ceramics using glass cullet and vitrified industrial by-products

A. Karamberi, K. Orkopoulos, A. Moutsatsou *

*Laboratory of Inorganic and Analytical Chemistry, Chemical Engineering Department,*
*National Technical University of Athens, 9 Heroon Polytechniou Str., 157 73 Athens, Greece*

**Abstract**

This study concerns the recycling of inorganic waste materials for the production of glass-ceramics and the evaluation of the developed physical properties. Four industrial by-products were selected due to their mass production: (i) two high calcium lignite fly ashes, (ii) slag derived from the production of Fe–Ni and, (iii) steel slag. In order to examine the role of the $SiO_2$ in the crystallization process, glass cullet and Egyptian sand were added. Thermal treatment, at 1450 °C, enables the production of glasses using mixtures of these materials at appropriate proportions. The crystallization was achieved by heating at 900, 950 and 1000 °C. The produced materials were examined concerning their structure by X-ray diffraction and scanning electron microscopy (SEM-EDS). The results showed that the crystalline phase is greatly depending on the structure of the raw material and the thermal process, influencing accordingly the hardness of the final products.

*Keywords:* Vitrification; Glass; Glass-ceramics; Hardness

## 1. Introduction

Industrial development over the last decades has generated large amounts of inorganic waste such as fly ashes, slags and muds which contain significant amounts of metals. The problems related to waste production are becoming more and more significant in relation to the improvement of economical conditions, the progress of industrial development and the population and urban increase. For that reason, there is an effort in extending the application of waste mainly by innovative technologies for the production of new products. The key to management of waste products, regardless of their source, is to find means by which they can be recycled and used beneficially. Utmost care has to be taken both in terms of disposal and utilization to upgrade the environment.

During recent years, considerable research work has been devoted to the recovery and safe, useful applications of waste residues originated from industries and domestic use. The construction materials industry and especially the cement industry was the main candidate for the utilization of waste. Many attempts have been made to incorporate fly ashes, slags or domestic waste into cementitious materials.[1–5]

The production of glass, glass-ceramics can be an important application for industrial and domestic waste, bearing in mind the large quantities of raw materials needed for ceramic production. The most promising applications are based on the total use of waste for the production of new materials and the glass-ceramic applications could fulfill this demand. The aim of the present study was to test the possibility of recycling fly ashes and slags for use in glass-ceramic production.

Glass-ceramic materials are polycrystalline solids containing residual glass phase, prepared by melting glass and forming it into products that are subjected to controlled crystallization. The concept of controlled crystallization of glass designates the separation of a crystalline phase from the glassy parent phase in a form of tiny crystals. The number of crystals, their growth rate and thus their final size are controlled by suitable heat transfer. Controlled heat treatment consists of two stages: nucleation and crystal growth. The nucleation and crystallization of glasses are important in understanding the stability of glasses in practical applications and in preparing glass-ceramics with desired microstructures and properties.[6]

This technique had already used for the inertization of various radioactive industrial residues.[7–9] The main advantages of vitrification are the high chemical stability, the immobilization

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* Corresponding author. Tel.: +30 210 772 3263; fax: +30 210 772 3188.
*E-mail address:* angst@central.ntua.gr (A. Moutsatsou).

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of heavy metals and radioactive elements, the destruction of organic components and also the fact that the vitrification process usually affords a great reduction of the volume of waste.[10] Recent studies had expanded the application to other waste, which could be vitrified revealing improved materials.[11–15]

Because the selected waste are composed mainly of CaO, $SiO_2$, and $Al_2O_3$, $Fe_2O_3$/FeO with a significant amount of metal oxides which are able to act as nucleant agents for nucleation and crystallization, they can be vitrified by melting.[11,16]

In this work the results obtained from the vitrification of four industrial waste rich in $SiO_2$ content that are produced in large quantities as by products, two lignite fly ashes and two slags. In a first series of experiments the potentiality of waste vitrification without any additives was examined. Furthermore, the influence of adding melting agents was studied. In order to obtain the production of glass-ceramics the vitrified materials were subject to a de-vitrification process. The mineralogical structure and the physical properties of the material before and after the de-vitrification process were examined.

## 2. Materials and testing methods

The used fly ashes are classified as Calcareous fly ashes (C according to ASTM) and are produced in a large amount, about 11000 million kg/year, as a by-product of lignite combustion (at 1000–1050 °C) in electro-power stations at Megalopoli and Ptolemais area in Greece.

The electric furnace slag derives from the pyrometallurgical treatment of laterite ore for the production of Fe–Ni alloy, containing 18–25% Ni, in powder form. Its quantity rises up to 1500 million kg/year.

The steel slag comes from an electric arc furnace, smelting ferrous scrap as raw material and reaches the production of 9 million kg/year.

Amber and green cullet, derived from recycled glass containers, were used in the batches. The used Egyptian sand for the $SiO_2$ control consisted of 99.6% quartz.

In Table 1 are shown the values of the chemical analysis of all materials, determined by XRF analysis (PHILIPS 1606).

The main constituents of lignite fly ashes are $SiO_2$, $Al_2O_3$ which are glass network formers and CaO, MgO, FeO which are glass modifiers. Slags have the same glass network formers and modifiers but also contain $Fe_2O_3$ which could act as glass intermediate. It is obvious that the used industrial waste, due to their oxide content, can provide by melting a useful preliminary batch for the preparation of glasses. Possibly, the addition of other ingredients to the batch will lead to lowering the glass melting temperature.

The cullet and slags were ground in ball mills under 90 μm. The fineness of fly ash is measured by Laser Granulometre (CIALAS GRANULOMETRE 715 D314) and the retained fraction on 48 μm for Megalopolis fly ash samples is 60%, while Ptolemais fly ash samples have an average retained amount of 25% on 48 μm.

The X-ray diffraction spectrums (Siemens D5000 diffractometer, Cu Kα radiation, Ni filter) of glass cullet and Fe–Ni slag revealed an amorphous material, while the spectrums of both fly ashes and electric furnace steel slag present except from the crystalline and amorphous phase. X-ray diffraction spectrums of the raw materials are illustrated in Fig. 1.

The thermal behaviour of the samples was assessed by differential thermal analysis (Mettler TGA/SDTA851$^e$). The produced glasses were ground under 45 μm in size and reheated from 25 to 1400 °C in a platinum cell at a heating rate of 10 °C/min in $N_2$ atmosphere. The results are illustrated in Fig. 2. The exothermic peak at 200–260 °C is attributed to the transition of FeO to $Fe_2O_3$. The endothermic peak at 350–500 °C is attributed to the dehydration of $Ca(OH)_2$ as well as to the unburnt carbon, while the endothermic peak at 550–750 °C is corresponding to the decomposition of $Ca^{2+}$, $Mg^{2+}$ carbonate compounds. The endothermic peak at 650–750 °C at the electric furnace steel slag referred to the presence of volatile chlorides alkalis due to the origin of the raw material. Over 1200 °C the peak is corresponding to the decomposition of $SO_4{}^{2-}$ compounds.

Former studies have shown that Ptolemais fly ash due to its CaO content achieves better retention of metals. These metals could form crystalline centres and contribute to further crystallization. Thus, at a first stage 300 g of Ptolemais fly ash were added in a 5 L solution containing 100 ppm of each of the following metals Cu, Zn, Ni, Cd, Fe, Mn, so as to simulate a real liquid waste. The mixture after half an hour stirring was filtrated

Table 1
Average chemical composition of the raw materials used

| w/w (%) | Electric furnace Fe–Ni slag | Electric furnace steel slag | Lignite Megalopolis fly ash | Lignite Ptolemais fly ash | Amber glass | Green glass |
|---|---|---|---|---|---|---|
| FeO | 41.10 | 17.00 | – | – | – | – |
| $Fe_2O_3$ | 2.60 | – | 8.44 | 5.10 | 0.35 | 0.45 |
| MnO | – | 7.50 | – | – | – | – |
| Ni–Co | 0.14 | – | – | – | – | – |
| $SiO_2$ | 33.70 | 16.00 | 51.26 | 30.16 | 71.20 | 70.50 |
| CaO | 3.30 | 41.00 | 11.82 | 34.99 | 10.35 | 10.15 |
| MgO | 3.40 | 4.50 | 2.27 | 2.69 | 2.60 | 2.75 |
| $Al_2O_3$ | 9.30 | 7.00 | 19.39 | 14.93 | 1.90 | 1.80 |
| $Na_2O$ | – | – | 0.53 | 1.01 | 13.15 | 12.95 |
| $K_2O$ | – | – | 1.81 | 0.4 | 0.60 | 0.45 |
| $Cr_2O_3$ | 4.30 | 0.56 | – | – | 0.06 | 0.25 |
| $SO_3$ | 0.85 | 6.63 | 2.91 | 6.28 | 0.30 | 0.25 |

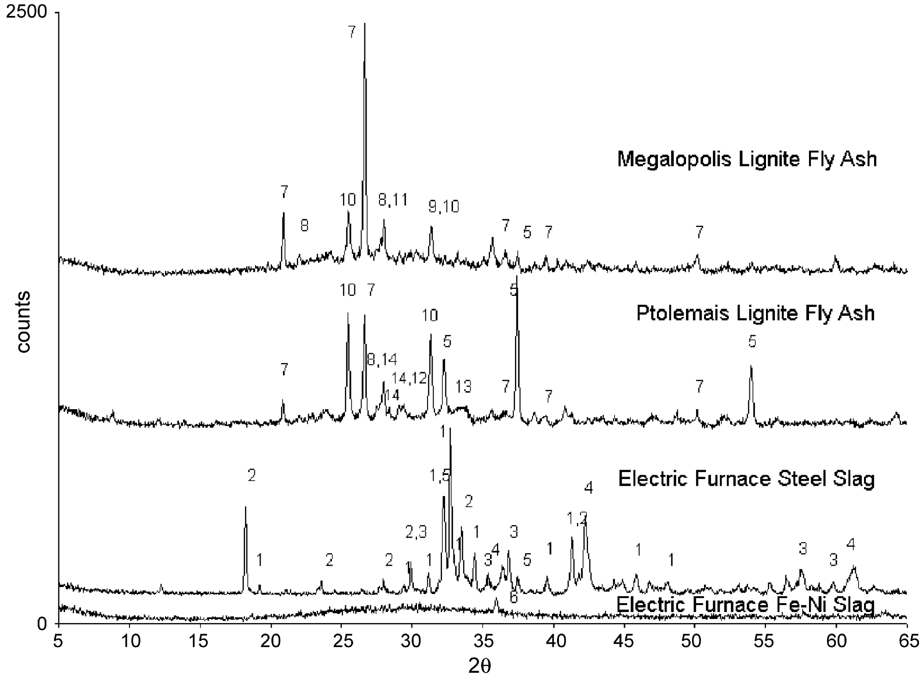


Fig. 1. X-ray spectrum of raw materials: 1. $Ca_2SiO_4$ (PDF:29-0371), 2. $Ca_5Al_6O_{14}$ (PDF:03-0149), 3. $Fe_3O_4$ (PDF:02-1035) 4. FeO (PDF:01-1223), 5. CaO (PDF:37-1497), 6. 2(Mg, Fe)O·$SiO_2$ (PDF:02-1060), 7. $SiO_2$ (PDF:46-1045), 8. $CaAl_2S_2O_8$ (PDF:41-1486), 9. $Ca_2Al_2SiO_7$ (PDF:35-0755), 10. $CaSO_4$ (PDF:37-1496), 11. $NaAlSi_3O_8$ (PDF:01-0739), 12. $CaCO_3$ (PDF:29-0371), 13. $Ca(OH)_2$ (PDF:04-0733), 14. $CaAl_2Si_2O_8 \cdot 4H_2O$ (PDF:38-0382).

and the sediment was dried at 100 °C. The % retention of metals was calculated by measuring the metals content in the filtrate by atomic absorption spectroscopy (Perkin-Elmer 3300). The results were 98, 99, 85, 85, 99, and 80% respectively.

Ten different glasses were prepared from all the industrial waste by melting at 1450 °C for 2 h. Fire resistant ceramic crucibles were used for the vitrification process. After fusion the glass was casted in a metallic mould and the material was solidified. The annealing of the glasses took place at 550 °C for 2 h.

In order to estimate the influence of $SiO_2$, a series of samples were prepared by mixing the raw materials so as a $SiO_2$ enrichment could occur, either deriving from a waste material or a primary raw material as it is shown in Table 2. Moreover, in sample G-6 the Ptolemais fly ash, as described above, is enriched by metals ions. Every specimen was subjected to devitrification thermal treatment at 900, 950, 1000 °C for 2 h in platinum crucibles.

In order to examine the produced glass and glass-ceramics based on their mechanical characteristics, samples hardness was measured. The microhardness has been tested by the Vickers indentation method. The calculated results were mean values for at least five measurements.

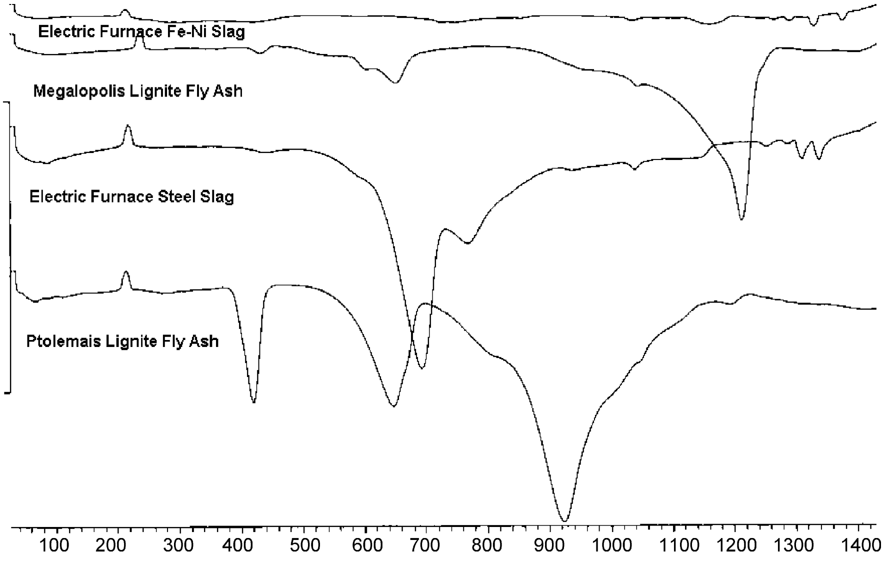


Fig. 2. DTG curves of the waste materials.

Table 2
Percentage of the raw materials used in every specimen

| | G-1 (%) | G-2 (%) | G-3 (%) | G-4 (%) | G-5 (%) | G-6 (%) | G-7 (%) | G-8 (%) | G-9 (%) | G-10 (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Lignite Megalopolis fly ash | 100 | 80 | 60 | | | | | | | |
| Lignite Ptolemais fly ash | | | | 100 | 80 | 100 | | | | |
| Electric furnace Fe–Ni slag | | | | | | | 100 | | | |
| Steel slag | | | 40 | | | | | 100 | 60 | 77 |
| Amber glass | | 20 | | | | | | | 40 | |
| Green glass | | | | | 20 | | | | | |
| Egyptian sand | | | | | | | | | | 23 |
| Metals | | | | | | + | | | | |

The ability of produced glassy materials to be crystallized is assessed by differential thermal analysis. The crystalline phase composition of the produced glasses and glass-ceramics was investigated using X-ray powder diffraction.

## 3. Results and discussion

In Fig. 3 the XRD spectrums of the produced glasses are illustrated. XRD analysis verified that all the vitrified specimens were amorphous materials except from Fe–Ni slag (sample G-7). For sample G-7 the main crystalline phases that are presented were Augite aluminian (Ca(Mg, Al,Fe)$Si_2O_6$), Diopside aluminian (Ca(Mg, Fe, Al) $(Si,Al)_2O_6$), Chromite ($FeCr_2O_4$), and Magnetite ($FeFe_2O_4$).

In Fig. 4, it is shown the differences which resulted from the de-vitrification at 1000 °C of the various glasses. Regarding sample G-7 no changes can be observed during the de-vitrification process since it is crystalline from the beginning. Vitrified Megalopolis Lignite fly ash (sample G-1) could provide glass-ceramics. The main crystalline phases that could be recognized from the XRD spectrums are anorthite ($CaAl_2Si_2O_8$), quartz ($SiO_2$) and augite (Ca(Fe,Mg)$SiO_6$). Nevertheless, the addition of glass cullet seems to deduct the crystallization, as could be revealed from the spectrum of G-1 sample compared with sample G-2. This phenomenon may occur due to the presence of $Na_2O$ and $K_2O$ in the glass cullet as fluxes which it is possible to suppress crystallization.[17] All the vitrified mixtures of steel slag (samples G-8, G-9, G-10) have shown crystalline formation. The main crystalline phases were diopside (Ca(Mg,Al)$(Si,Al)_2O_6$), anorthite ($CaAl_2Si_2O_8$), albite calcian ((Na,Ca)$(Si,Al)_4O_8$). The resulted glass-ceramic from the mixture of Lignite Megalopoli fly ash and steel slag (samples G-3) was alike to that made from steel slag. On the other hand the presence of Egyptian sand (sample G-10) favours the production of anorthite and the presence of glass cullet (sample G-9) promote the production of albite calcian.

Concerning Ptolemais Lignite fly ash specimens, sample G-6 seems to have the higher tendency towards crystallization as XRD analysis verified. It is obvious that the presence of a variety of metals even in small quantities favours crystallization. Thus, the crystallization degree is clearly a function of the composition. From the examining of G-6 XRD pattern

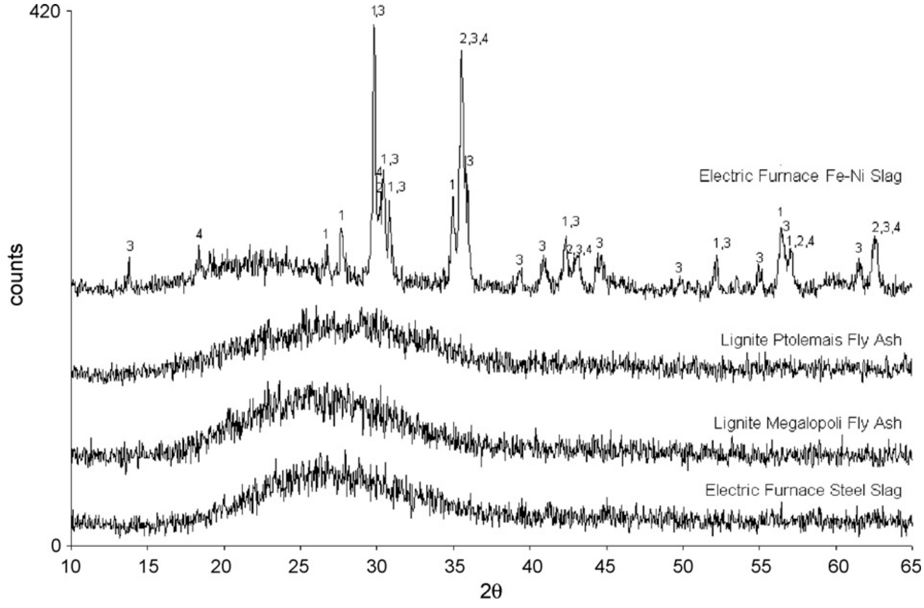


Fig. 3. XRD spectrums of the produced glasses: 1. Augite aluminian (Ca(Mg, Al,Fe)$Si_2O_6$) (PDF:24-0202), 2. Magnetite ($FeFe_2O_4$) (PDF:19-629), 3. Diopside aluminian (Ca(Mg, Fe, Al) $(Si,Al)_2O_6$) (PDF:38-0466), 4. Chromite ($FeCr_2O_4$) (PDF:34-0140).

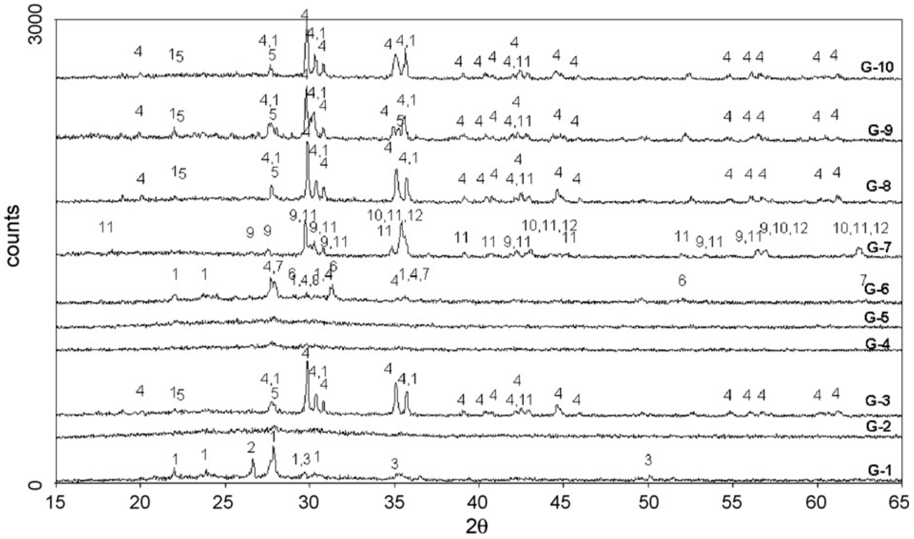


Fig. 4. XRD spectrums of the produced glass-ceramics (de-vitrification at 1000 °C). 1. PDF:41-1486-$CaAl_2Si_2O_8$, 2. PDF:33-1161-$SiO_2$, 3. PDF:4-0201-Ca(Fe,Mg)$SiO_6$, 4. PDF:41-1370-Ca(Mg,Al)(Si,Al)$_2O_6$, 5. PDF:20-548-(Na,Ca)(Si,Al)$_4O_8$, 6. PDF:35-0755-$Ca_2Al_2SiO_7$, 7. PDF:39-1346-$Fe_2O_3$, 8. PDF:43-1460-$CaSiO_3$, 9. PDF:24-0202-Ca(Mg, Al,Fe)$Si_2O_6$, 10. PDF:38-0466-Ca(Mg, Fe, Al) (Si,Al)$_2O_6$, 11. PDF:34-0140-$FeCr_2O_4$, 12. PDF:19-0629-$FeFe_2O_4$.

(Fig. 4) it could be stated that the major phases presented are: anorthite ($CaAl_2S_2O_8$), diopside (Ca(Mg,Al)(Si,Al)$_2O_6$), Gehlenite ($Ca_2Al_2SiO_7$), Maghemite ($Fe_2O_3$) and Wallastonite ($CaSiO_3$). All the other specimens comprising of Plolemais Lignite fly ash had shown no crystallization at all temperatures during the de-vitrification process. The ability of sample G-6 towards crystallization is also obvious through the differential thermal analysis of the produced glasses, which was carried out in order to determine the transition temperature and the crystallization temperature which verifies the tendency of the produced glass to be transformed into semicrystalline material. In Fig. 5 the DSC curve of G-6 in comparison to the DSC curve of glass cullet are illustrated. The intense peak at 800–1000 °C of G-6 curve is obvious; however, glass cullet has actually not presented any tendency to be crystallized.

The XRD spectrums of the glass-ceramics derive from lignite Megalopoli fly ash (sample G-1) showed that the glass sample could not be de-vitrified at 900 °C and is gradually crystallized at higher temperatures (Fig. 6c). There is no significant heat effect from 900–1000 °C for steel slag glass-ceramics (Fig. 6b and e). The main crystalline phases were diopside, anorthite, albite calcian. The presence of lignite Megalopoli fly ash or Egyptian sand has not significantly changed the final products. Nevertheless,

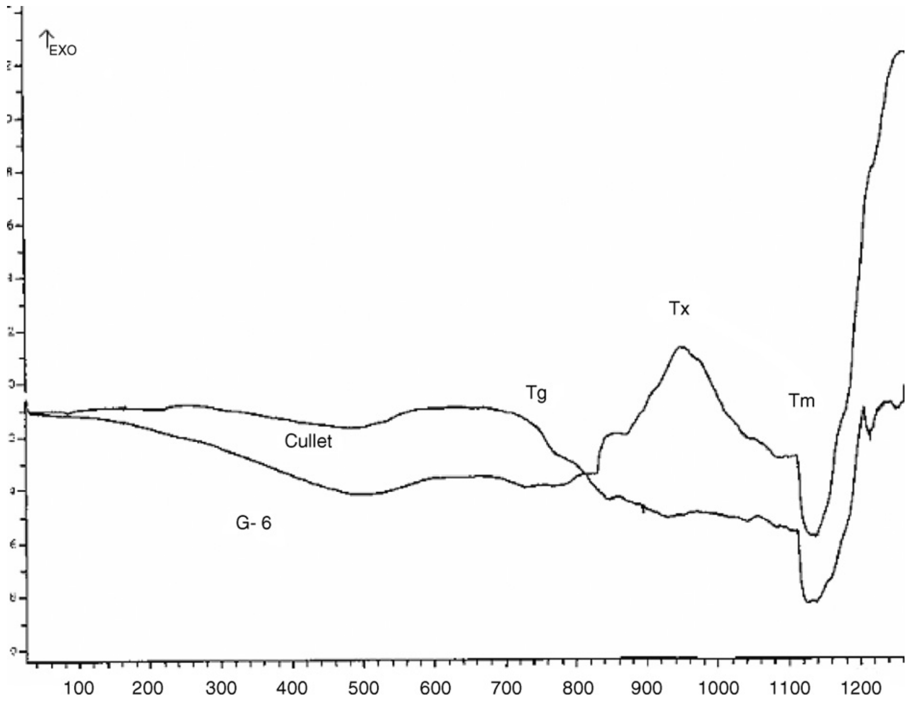


Fig. 5. DSC curves of flint glass and G-6 specimen.

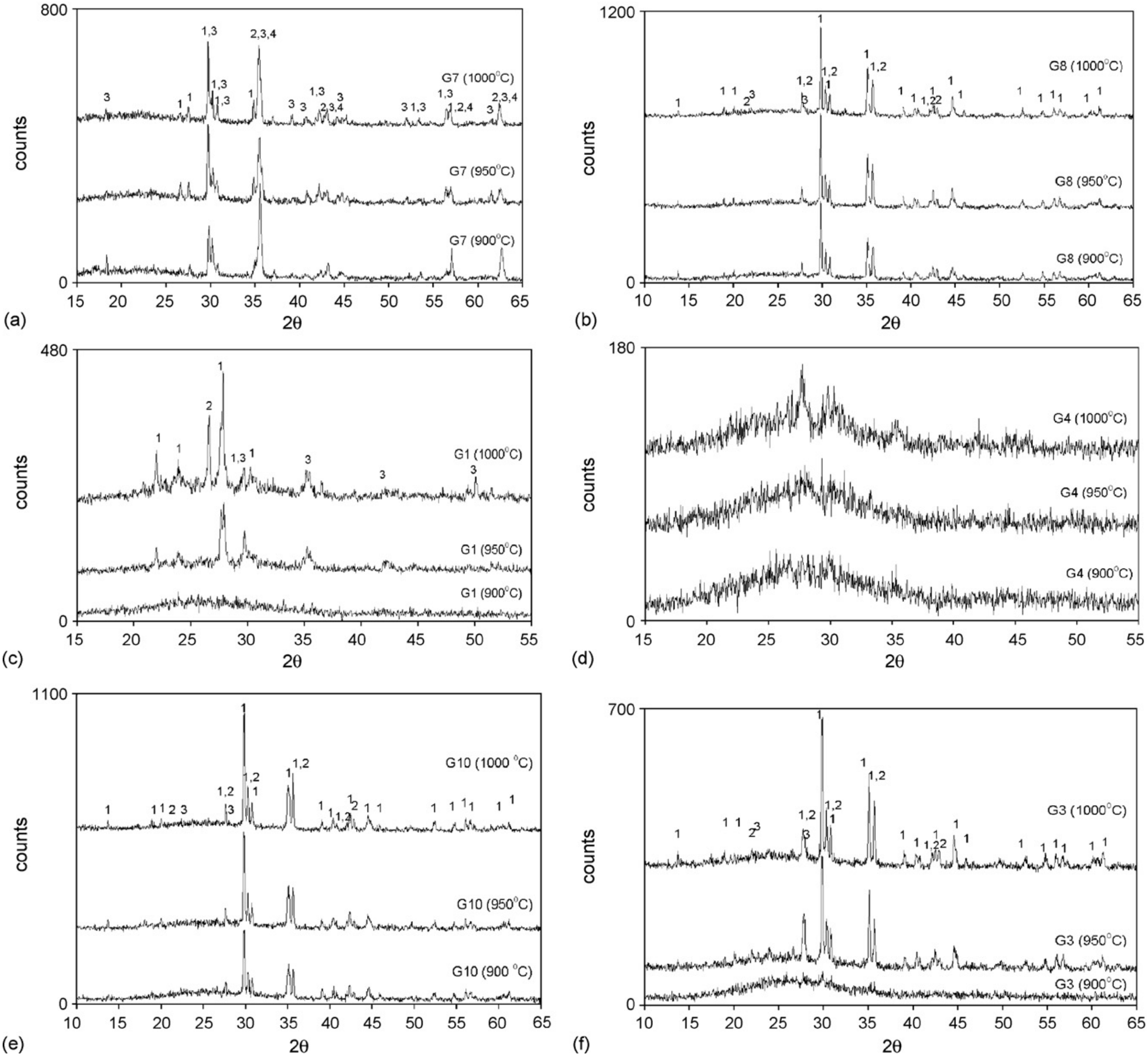
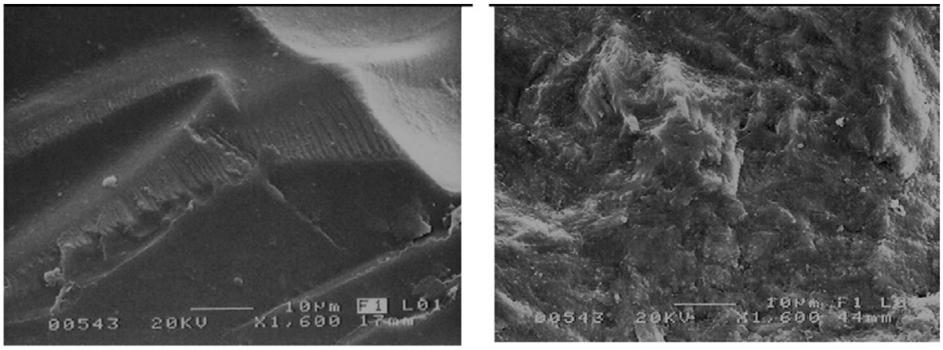
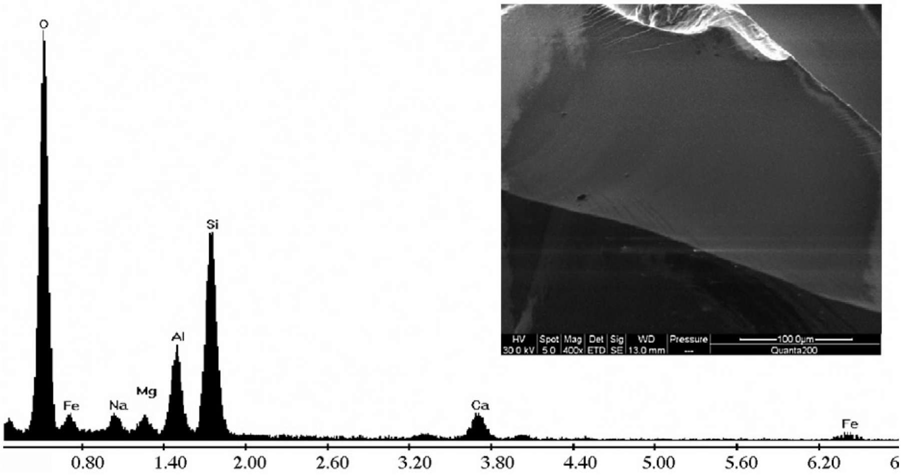


Fig. 6. XRD spectrums of the produced glass-ceramics (a) G-7—1. PDF:24-0202-Ca(Mg, Al,Fe)$Si_2O_6$, 2. PDF:24-0202-$FeFe_2O_4$, 3. PDF:38-1423-Ca(Mg, Fe, Al) $(Si,Al)_2O_6$, 4. PDF:30-0140-$FeCr_2O_4$, (b) 1. PDF:41-1370-Ca(Mg,Al)$(Si,Al)_2O_6$, 2. PDF:41-1486-$CaAl_2Si_2O_8$, 3. PDF:20-548- (Na,Ca)$(Si,Al)_4O_8$., (c) G-1—1. PDF:41-1486-$CaAl_2Si_2O_8$, 2. PDF:46-1045-$SiO_2$, 3. PDF:4-0201-Ca(Fe,Mg)$SiO_6$, (d) G-4, (e) G-10: 1. PDF:41-1370-Ca(Mg,Al)$(Si,Al)_2O_6$, 2. PDF:41-1486-$CaAl_2Si_2O_8$, 3. PDF:20-548-(Na,Ca)$(Si,Al)_4O_8$., (f) G-3—1. PDF:41-1370-Ca(Mg,Al)$(Si,Al)_2O_6$, 2. PDF:41-1486-$CaAl_2Si_2O_8$, 3. PDF:20-548-(Na,Ca)$(Si,Al)_4O_8$.

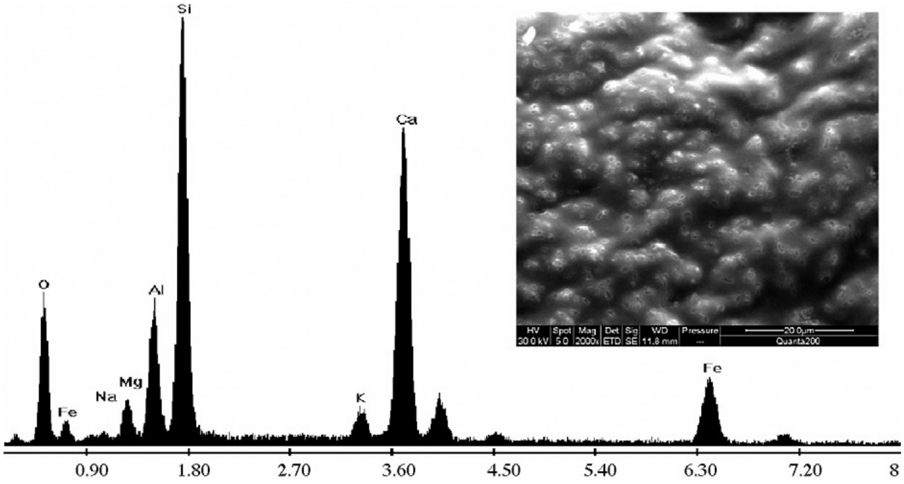


(a) Produced glass x1600 (b) Produced glass -ceramic x1600

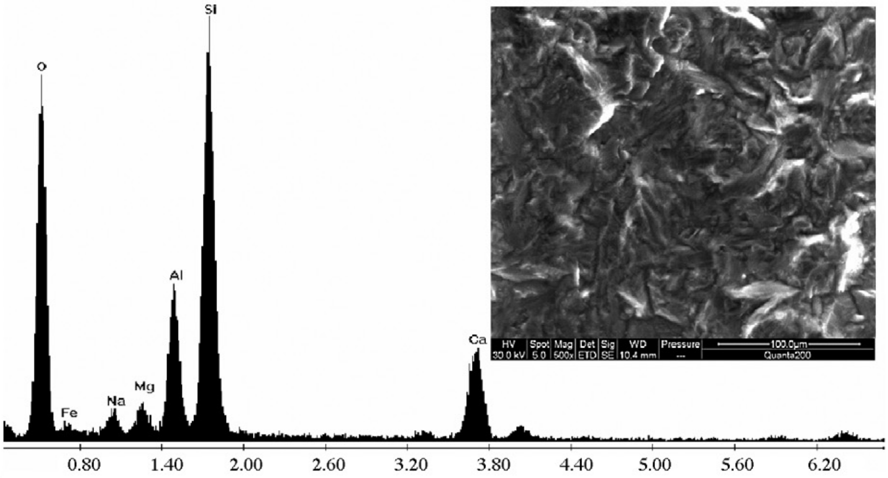
Fig. 7. SEM observations of the produced glass and glass G-6: (a) produced glass ×1600 and (b) produced glass-ceramic ×1600.



(a) Vitrified sample G-1



(b) Glass-ceramic G-1



(c) Glass-ceramic G-8

Fig. 8. SEM-EDS of glass and glass-ceramics samples: (a) vitrified sample G-1; (b) glass-ceramic G-1; (c) glass-ceramic G-8.

the presence of lignite Megalopoli fly ash increases the needed de-vitrification temperature (Fig. 6f).

The results from XRD are reinforced by the scanning electron microscopy observations. In Fig. 7a an amorphous vitrified material is illustrated. At SEM Fig. 7b the formation of crystalline phase could be observed. In Fig. 8 the SEM images of glass and glass-ceramics are illustrated accompanied with EDS analysis.

The results of the Vickers Hardness are presented in Fig. 9. The glasses derived from the slags exhibited higher hardness

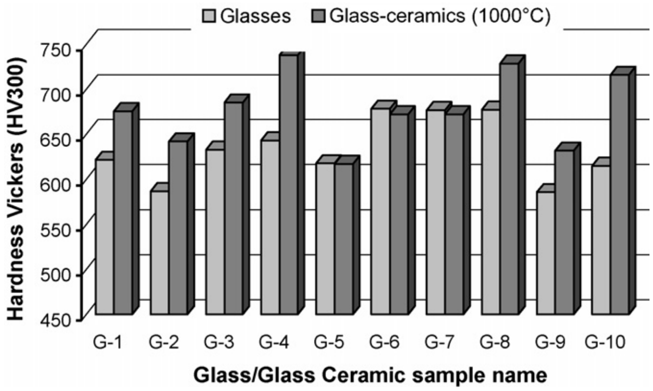


Fig. 9. Comparative hardness values of glass and glass-ceramics.

values. The de-vitrification process seems to favours the hardness of the final product. The crystal growth during the heating accounts for the increase in hardness value. Therefore, as it was prospective, it was not observed any alteration of the Fe–Ni Slag (sample G-7) hardness during the de-vitrification process. The presence of glass seems to decrease the hardness values of glass-ceramics (samples G-2, G-5, G-9); this phenomenon is attributed to the depression of crystallization due to the presence of glass cullet. Moreover, the presence of diopside as a major crystalline phase has a beneficial effect on the hardness of the materials (samples G-3, G-8, G-10) compared to the samples that have anorthite as the major crystalline phase (sample G-1, G-6). It is, therefore, found that diopside is a more preferable crystalline phase than anorthite from the viewpoint of the mechanical properties of these glass-ceramics. A similar tendency was also reported by Park et al.[18] in glass-ceramics prepared from sewage sludge fly ash. Diopside is also suggested to be a more preferable crystalline phase in glass-ceramics compared with wollastonite in glass-ceramics[19] though the amount of wollastonite is less than diopside.

## 4. Conclusions

The formation of vitrified materials from mainly industrial waste was accomplished by thermal treatment at 1450 °C. Further heat treatment transformed the produced glass-like materials into glass-ceramics at different temperatures depending on the structure of the glassy material. The de-vitrification of the glasses had a beneficial effect on the hardness of the glass-ceramics which in most of the cases performed higher values in comparison to the produced glass. Electric furnace Fe–Ni Slag had not performed any capability to be vitrified and consequently de-vitrified for the production of glass and glass-ceramics. Its use as a secondary raw material in adequate proportions needs further investigation.

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