

PREPARATION AND CHARACTERIZATION OF GLASS AND GLASS-CERAMICS FROM INDUSTRIAL WASTE MATERIALS INCLUDING IRON SLAG AND CEMENT DUST

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SUMMARY

Some glasses and corresponding glass ceramic samples were prepared from iron slag waste, cement kiln dust, sand and soda ash. The prepared samples were characterized by examining their chemical corrosion towards different solutions, IR spectral measurements, and X-ray diffraction measurements. The prepared samples were evaluated for their suitability for various applications.

Key Words: Glass, Glass-ceramics, Iron slag, Cement dust, IR, X-ray

1. INTRODUCTION

The production of glass and glass ceramic materials based on inorganic industrial waste generated by different industries is a promising line and has been used very successfully to prepare crystallize important crystalline phases from the glass phase. Some of these glass-ceramic materials become commercial products [1, 2] and found their applications in the field of abrasion resistance materials that is, industrial floor covering, wall facing abrasion-resistance lining and high temperature insulators. The low cost and availability of the raw materials make them very attractive economically. 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 wastes from the industry contain high concentration of toxic substances, heavy metals, organic substances and soluble salts [3]. Wastes processing by reduction of the noxious and toxic substances occupies central place for environment preservation as a method for environment protection. For protection of the environment against pollution by toxic elements, recycling of the chemical wastes is carried out [4, 5]. Methods and technologies are developed which require a minimum quantity of energy and time. The main objective of this work is to use of both iron slag waste together with cement kiln dust for the preparation of stable glasses by the additions of sand and soda ash. The prepared glassy samples were thermally heat treated to be converted to their corresponding glass-ceramic derivatives. The prepared glassy and glass-ceramic samples were chemically investigated for their corrosion

resistance to acidic HCl and alkaline NaOH solutions together with distilled water. The IR absorption spectra for the glassy and crystalline derivatives were measured to show their structural units. X-ray diffraction analyses were carried out to identify the formed crystalline phases produced during controlled heat treatment process.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Glass

The glass batches were prepared from a mixture of local blast furnace slag, cement kiln dust, sand, and soda ash and Table (1) gives their chemical compositions. Blast furnace slag was provided by Egyptian Iron and Steel Company, Helwan, Egypt. The slag was prepared by rapid cooling (X-ray examination proved its amorphicity) and pulverized and used as such (Table (2)). Cement kiln dust was provided from Beni Suef Company for Cement (Table (2)) The batches were melted in fire clay crucible of the Morganite Company, Battersae type (U.K.), for 2 hours in an electrical furnace at 1400°C and the melts were poured into a preheated stainless steel plate, and the prepared samples were transferred to a muffle furnace at 450°C for annealing and the muffle was left to cool after 1 hour to room temperature at a rate of 30°C/h.

2.2. Differential Thermal Analysis (DTA)

Differential thermal analysis was carried out utilizing an apparatus of a SETARM, labsys. tun, TG-DTA-06 model system in an argon atmosphere. A fine –grained sample from the vitrified blast furnace slag was studied with Al₂O₃ as a reference. The endothermic and exothermic temperatures were utilized to represent the appropriate temperatures for the nucleation and crystal growth temperatures necessary for the conversion of the prepared glassy specimens to their corresponding glass-ceramic derivatives.

2.3. Preparation of the Corresponding Glass-ceramics Derivatives

Bulk specimens of the prepared glasses were converted to their glass-ceramic derivatives by a controlled two-stage crystallization process. The glass samples were heated with a rate of 20°C/h in a muffle furnace up to the nucleation temperature (720°C) and held for the required time for optimum nucleation (4 hours). The nucleated glasses were further heated by rising the temperature to the crystallization temperature (930°C) and held for the required time (2 hours) to complete the crystallization process. The muffle was switched off and the samples were left to cool inside the muffle to room temperature with a rate of 25°C/hour.

2.4. X-ray Diffraction Measurements

X-ray diffraction measurements of the precipitated crystalline phases was carried out using Cu K α radiation with secondary monochromator utilizing a diffractometer, Bruker D8 Advance (Germany). The working voltage and tube current were 40 Kv and 40 mA respectively. The crystalline phases were identified by comparison of the diffraction patterns with standard files.

2.5. Infrared Absorption Measurements

The infrared absorption spectra of glasses were measured at room temperature in the wavenumber range (400-4000) cm^{-1} at resolution cm^{-1} using Fourier Transform Infrared Spectrometer (type Jasco FT/IR-430, Japan). The samples were pulverized into fine powder, and then mixed with KBr powder with ratio 1:100 respectively. The weighed mixture was then subjected to a pressure of 5 tons/ cm^2 in an evocable die for 2 minutes to produce clear homogeneous discs. The IR absorption spectra were measured immediately after preparing the discs.

2.6. Chemical Corrosion Studies

Experimental procedure for chemical corrosion included leaching of the samples as grains. 1 gm of the glass grains (0.3-0.4 mm) was accurately weighed in a sintered glass crucible of the G4 Jena type, which was placed into polyethylene beaker (250 ml). 150 ml of each leaching solution (0.1HCl, 0.1N NaOH, or distilled water) was introduced to cover the grains. The polyethylene beaker was fitted in a water bath regulated 95°C and after 1 hour the beaker was removed from the water bath. The sintered crucible was fitted on a suction pump and the whole solution was pumped through it. The sintered crucible was transferred to an air oven at 120°C for 1 hour. The total weight loss % from the grains was calculated. This procedure of corrosion study was recommended by ASTM specification No. C-225-73, ISO. 719-1985 and by different authors [6, 7]

3. RESULTS

3.1. X-ray Diffraction Measurements for Glass-ceramic Derivatives

The x-ray diffraction patterns of the crystalline derivatives are represented in figure (1) from which it is obvious that the base iron slag produces crystalline phases consisting of gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$, card number 35-0755) and akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$, card number 35-0592) beside some other minor phase of diopside ($\text{CaMg}(\text{SiO}_3)_2$, card number (1-659)). The crystalline phases precipitated from heat treatment of sample 2 containing additional 10 gm sand + 10 gm Na_2O + 10 gm cement dust are almost the same as the base sample. The main crystalline phases are gehlenite. The crystalline phases precipitated from heat treatment of sample no. 4 containing additional cement kiln 50 wt% are mixture of gehlenite (calcium aluminosilicate) card No. 89-1583, akermanite (calcium magnesium silicate) card No. 10-0391 and lanite (calcium silicate) card No. 73-2091

3.2. Chemical Corrosion Data

Table (3) depicts the weight loss% obtained through subjecting both the glassy and crystalline derivatives to the action of leaching solutions for 1 hour at 95°C. The corrosion data reveal the following characteristics:

- (1) Acidic HCl leaching solution is quite corrosive than water, but less than alkaline NaOH solution.
- (2) Distilled water is almost an ineffective corrosive medium on the studied samples.

- (3) It is obvious that the increase of additional amounts of silica, soda, and cement kiln dust generally improve the chemical durability of the products.
- (4) The chemical durabilities of the glass-ceramic derivatives are generally better than their original samples.

3.3. Infrared Absorption Spectra of Glassy and Crystalline Samples

Infrared absorption spectra of all prepared glassy samples and their corresponding ceramic derivatives are shown in Figures (2&3) from which it is observed that the infrared absorption spectra of the base vitrified slag resemble the familiar spectrum of commercial soda lime silica glass. The IR absorption spectrum consists of the following main bands:

- (a) A main strong band in the medium region extending from about 750 to 1250 cm^{-1} with two obvious peaks at about 997 and 905 cm^{-1} and a kink is observed at the descending lobe at about 1180 cm^{-1} .
- (b) The main strong absorption band is preceded by a medium band at about 688 cm^{-1} .
- (c) The far-infrared region shows a sharp medium band at about 506 cm^{-1} .
- (d) The previous main bands are followed by some small bands at about 1510, 1646, 2924, 3404, 3737, and 3822 cm^{-1} .

All the observed IR absorption bands are comparable to the same characteristic bands usually evolved in silicate glasses and crystals with minor variations depending on the other constituting components. They virtually represent the silicate network.

4. DISCUSSION

4.1. Interpretation of the Crystallization Data

It is generally accepted that glass-ceramics are fine-grained polycrystalline materials formed by controlled thermal crystallization of specific glasses with suitable compositions [8-10]. It is evident that blast furnace slag consists of CaO, SiO₂ and MgO in decreasing order as the main constituents, together with minor constituents such as MnO, Fe₂O₃ and S.

The first prepared "slagceram" was produced by conventional two-stage heat treatment method [1]. The addition of low titania (2-5 wt% TiO₂) was observed to show surface crystallization as the predominant mechanism [10] while with extra TiO₂ bulk crystallization was the main mechanism. Several authors [11-13] have conducted and examined crystallization of basic pure blast slag or with other additives and numerous crystalline phases such as gehlenite, merwinite, akermanite, diposide are formed depending on the introduced additions. Recent work by Hudon and Baker [14] reviewed the nature of phase separation in silicate melts and glasses. They reached the conclusion that the tendency towards phase separation increases with a decrease of the basicity (or the capacity to give electrons) of the modifier cation (i.e. Cs<R<K<Na<Li<Ba<Ca<Mg) [15]. Warren and Pincus [16] earlier proposed that immiscibility arises due to the fact that the melts are composed of network former and network modifier cations that compete for the

nonbridging oxygens in order to be properly charge-balanced by oxygens. The stronger the bond between a network modifier and an oxygen, the greater is the possibility for this network modifier to be surrounded by non-bridging oxygen and the greater is the tendency towards immiscibility. From all these previous assumptions, it is thus expected that the presence of noticeable amounts of oxides such as MgO and CaO initiates the immiscibility and phase separation tendency in the base silicate slag wastes. Also, the combined presence of transition metal oxides MnO and Fe₂O₃ support the mentioned phase separation and immiscibility mechanism. The output is the final separation of the gehlenite or similar phases containing the oxides CaO, MgO, and the sharing other oxides present or added. The different phases formed in the studied glass-ceramics of samples 2-4 can be realized by considering the additional oxides introduced in their basic constituents in the glasses. The introduction of additional sand, soda ash, and cement dust produces different percentages in the basic glasses. Such new compositions are expected to give different crystalline phases according to the final percent of the constituent oxides. The formed crystalline phases are mainly consisted of silicates of calcium, magnesium and aluminum, the oxides of which are the main constituents of iron slag and cement dust and generated by the immiscibility tendency proposed by numerous authors [9, 14-17]

4.2. Interpretation of the Corrosion Results

It is known that binary alkali silicate glasses are attacked by aqueous solutions through ion exchange and the possible dissolution of the separated glass constituents especially at compositions with high alkali content. The introduction of B₂O₃, Al₂O₃ or divalent oxides such as CaO, MgO to binary alkali silicate glasses is accepted to increase the chemical durability of the resultant glasses [17-19]. This enhancement is believed to be due to several reasons:

- (a) The formation of additional structural building units such as AlO₄ and BO₃ or BO₄ which strengthen the glassy network and hence retard the corrosion process and the strong attachment of these groups by neighboring modifier cations to compensate for the residual negative charges. These modifier cations aren't easily released by aqueous solutions.
- (b) The presence of mixed cations including differently charged cations obviously interferes with the diffusion process through the percolation channels proposed by Greaves [20], for the diffusion mechanism during the corrosion process.
- (c) The possible formation of sparingly soluble or precipitates during the progress of the corrosion process (e.g. sparingly soluble or insoluble hydroxides or sulphates, etc.)

The difference in the effect of leaching solutions can be realized and interpreted on the following basis:

- (1) Hydrochloric acid is strong and completely ionized in water and can thus furnish plenty of hydronium ions capable of ion exchange with modifier ions from the surfaces of the glass. Also, the leached modifier ions are easily dissolved in hydrochloric acid solution and thus this acid is observed to corrode the glasses with higher rate than other solutions.

- (2) Water is a feebly ionized liquid and thus the ion exchange process is governed by the presence of easily ionized alkali ions and their ability directly to dissolve into water. The continuation of these collective mechanisms is expected to be slower than with acidic solutions.
- (3) Sodium hydroxide solution is efficient leaching solution towards alkali earth silicate glasses because it attacks both glass constituents, namely the silicate network and modifier ions, respectively. So, the corrosion weight loss is higher by NaOH solution due to its combined action on both silicate network and modifier ions.

4.3. Interpretation of the Infrared Absorption Spectroscopy of Glassy Samples

The realization and interpretation of the IR absorption spectra have been carried out in agreement with the concept adopted by Tarte [21] about independent vibrations of different groups. Also, it is born in mind the detailed published infrared spectra of multi component silicate glasses [22-24]. The structure of silicate glasses is originally similar to silicate crystals and consist of SiO_4 tetrahedra but in glasses the groups are in non-periodic arrangement. In the glass, the SiO_4 tetrahedra are linked at the vertices to form a network, while the various modifiers such as alkali and alkaline earth ions occupy interstices or holes within the networks. Some oxygen atoms are bonded to only one silicon and are called non-bridging oxygen atoms (NBOs). These latter atoms form coordination polyhedra for the modifiers. The infrared absorption peaks at 1114 cm^{-1} and 1024 cm^{-1} are assigned to the asymmetric stretching vibrations of the silicate tetrahedral network. The peak at about 930 cm^{-1} is assigned to the Si-O- stretching vibration with non-bridging oxygen (NBO). The content of the NBO in the glass is increased by the increase of the alkali and alkaline earth oxides of sodium and calcium. When the content of sodium oxide increases relative to the former oxide (SiO_2) the amount of NBO increases. Therefore, the peak at 930 cm^{-1} becomes more prominent by increasing sodium oxide. The weak band at ($800\text{-}600\text{ cm}^{-1}$) can be assigned to Si-O-Si symmetric stretching of bridging oxygens between tetrahedral. Merzbacher et al. [23] reported that infrared spectra of aluminosilicate glasses show a shift of the stretching mode to longer wavenumber with increasing Al/Si ratio. The increase of the silica content in samples other than the base sample makes the Al/Si ratio decreases and so, the peak is seen to shift to the higher energy. The band at $600\text{-}400\text{ cm}^{-1}$ in the base sample can be assigned to the bending motions of the aluminosilicate network.

It is known that alkaline earth aluminosilicate glasses and melts make up a large and important group of materials, with a wide range of commercial applications, as well as being representative of the voluminous basaltic natural system and rocks in the crust of the earth [25]. The studied wastes used for the prepared glasses are known to consist of calcium and magnesium aluminosilicates. Alkaline earth cations (especially Ca^{2+} or Mg^{2+}) can obviously act as either charge balancer or network modifier in the same glass. They can balance all the tetrahedral Al with the excess serving to depolymerize the structure.

It is evident that inspection of all the IR spectra indicates that the main features of all the spectra are a high-frequency band at $900\text{-}1050\text{ cm}^{-1}$ and a mid-frequency band at $400\text{-}500\text{ cm}^{-1}$. Also, a weak band is observed at $\sim 680\text{ cm}^{-1}$ in most of the spectra. These same spectral features are in agreement with previous results by several authors [26-28].

It is accepted that IR as well as Raman modes at 800-1200 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of the tetrahedral silicate network. Aluminum is assumed to replace Si in tetrahedral coordination and hence acts as a network former. The net negative charge due to this substitution is neutralized by a nearby network divalent modification (Ca^{2+} or Mg^{2+}). If Mg is acting in part as a network former, then the glasses would be more polymerized than predicted and the more polymerized stretching frequencies occur at higher wavenumbers. Our studied glasses contain appreciable content of CaO and minor content of MgO and therefore the effect of Ca^{2+} cations is more pronounced. The strong main band (750-1250 cm^{-1}) may contain the sharing of AlO_4 units as it is known that these units vibrate between 700 and 900 cm^{-1} . The observed shift of the high-frequency band can be correlated with a possible superposition of discrete bands due to $\text{Si}(\text{OAl})_x$ units, where x is the number of aluminate tetrahedral adjacent to a silicate tetrahedral. The band near 400-600 cm^{-1} is accepted to be associated with bending vibrations of the silicates network

4.4. Interpretation of the Infrared Absorption Spectroscopy of Glass-ceramic derivatives

By comparing the IR absorption peaks of crystalline samples with the IR absorption peaks of gehlenite, melilite, diopside and wollastonite (the crystalline phases proved to be existed in glass-ceramics by X-ray diffraction), the following points can be reached:

- (a) The main IR vibrational modes are generally accepted to be the same in silicate crystals and glasses of equivalent compositions.
- (b) The main silicate network modes are generally vibrating in the range of about 500-1400 cm^{-1} .
- (c) The modifier ions are vibrating in the range 50-500 cm^{-1} if present in interstitial sites.
- (d) The IR absorption bands in the range of 1640-3800 cm^{-1} are virtually related to different water, OH, silanol (SiOH) or similar groups as postulated by Efimov et al. [28]

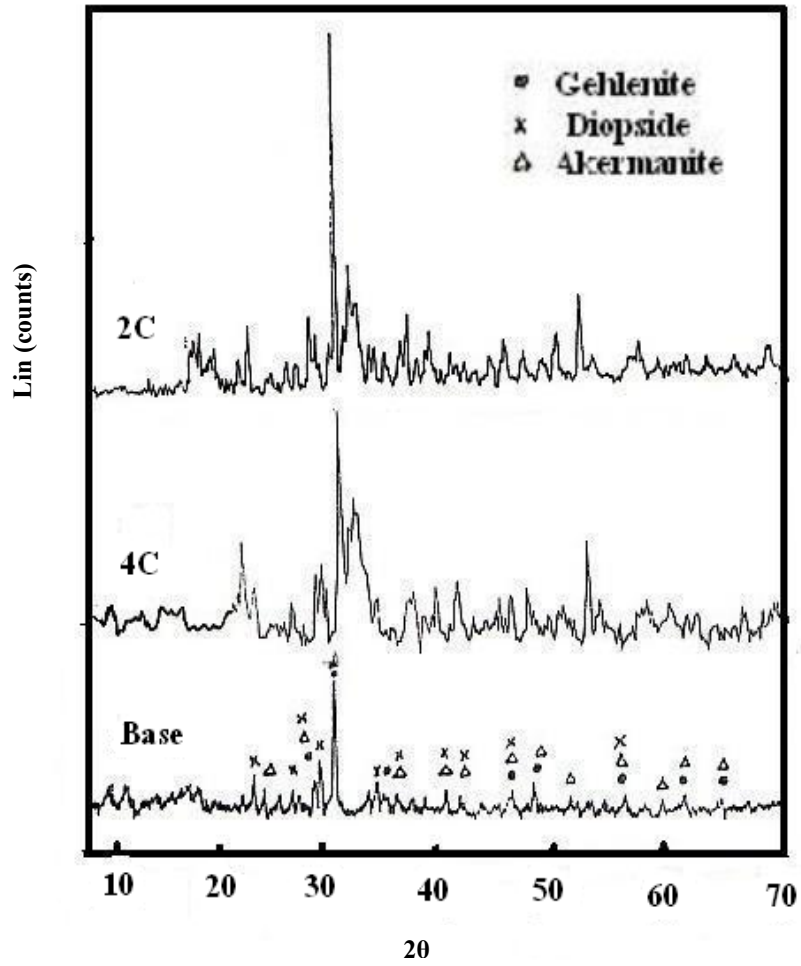


Fig (1) X-ray diffraction patterns of some glass-ceramics

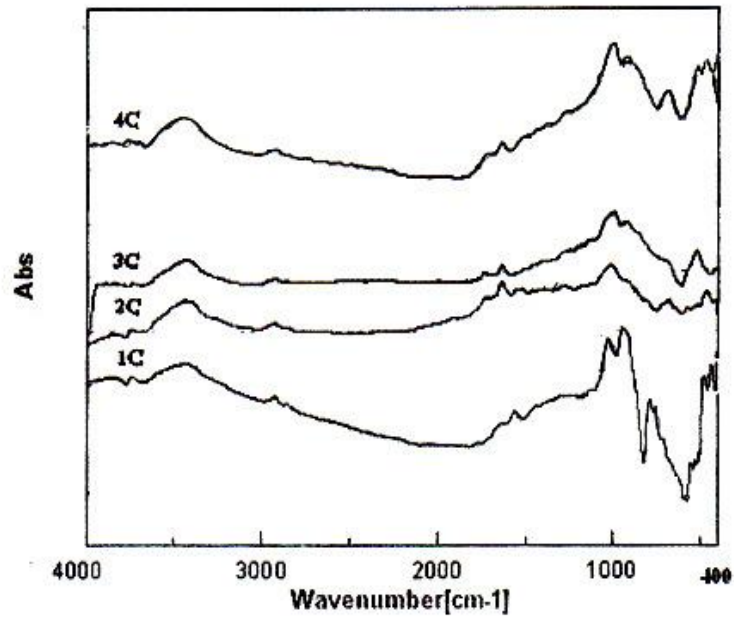


Fig (2) Infrared absorption spectra of glasses

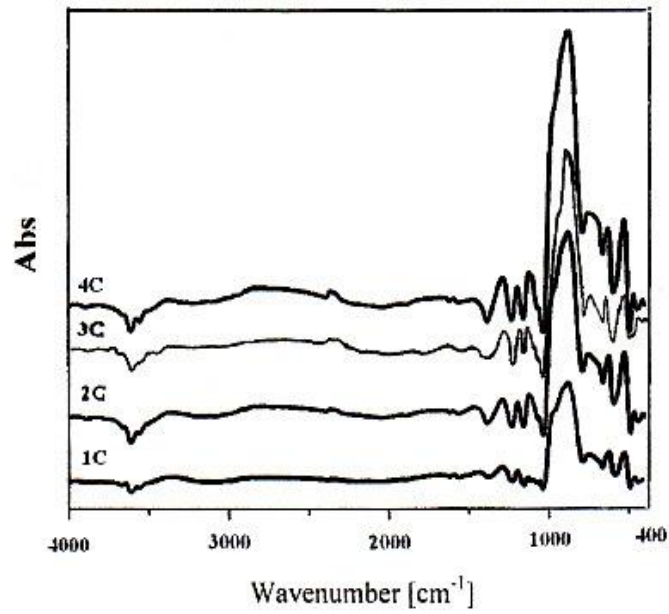


Fig (3) Infrared absorption spectra of glass-ceramics

Table (1) Chemical Composition of studied glasses

weight (gms)	Slag	Sand	Na ₂ CO ₃	Cement kiln dust	Glass Cullet
1C	100	--	---	---	---
2C	100	10	17.1	10	---
3C	100	20	34.2	20	---
4C	100	--	---	50	50

Table (2) Chemical composition of blast furnace slag and cement kiln dust

Slag composition	weight%	Cement composition	weight %
SiO ₂	38.21	SiO ₂	11.45
AL ₂ O ₃	10.45	AL ₂ O ₃	3.22
Fe ₂ O ₃	1.27	Fe ₂ O ₃	1.88
CaO	37.70	CaO	45.14
MgO	2.05	MgO	0.53
MnO	3.5	SO ₃	5.14
Na ₂ O	1.61	K ₂ O	3.73
K ₂ O	0.71	Na ₂ O	2.72
SO ₃	3.52	Cl	2.59
Loss on Ignition	0.43	Loss on Ignition	23.60

Table (3) Chemical corrosion % for glass and glass -ceramics

corrosion %	0.1N HCl		0.1N NaOH		distilled water	
	glass	Glass-ceramic	glass	Glass-ceramic	glass	Glass-ceramic
1C	0.33	0.090	25.5	0.56	0.16	0.31
2C	0.26	0.031	13.21	0.64	0	0.01
3C	0.25	0.01	33.33	0.01	0.17	0
4C	0.18	0.02	0.16	0.83	0.06	0.01

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