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Glass-ceramics in the $CaO–MgO–Al_2O_3–SiO_2$ system based on industrial waste materials

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A R T I C L E I N F O

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A B S T R A C T

Cement kiln dust from Rabigh plant in Saudi Arabia was examined for use in the preparation of glass-ceramic materials. The cement kiln dust made up about 70 wt.% of the batch constituents depending on the composition. The cement kiln dust composition was sometimes modified by additions of other ingredients such as silica sand, granite and magnesite. The batches were melted and then casted into glass which was subjected to heat treatment to induce crystallization. Different techniques were used in the present study, including differential thermal analysis, polarizing microscope, X-ray diffraction and indentation microhardness. The colored glass and glass-ceramic materials obtained, possess very high hardness indicating high abrasion resistance, which make them suitable for many applications under aggressive mechanical conditions.

1. Introduction

Glass-ceramic materials, prepared by the controlled crystallization of glasses, have a variety of established uses that depend on their uniform reproducible fine-grained microstructures, absence of porosity and other wide-range of properties, which can be tailored by an adjustment of composition and the heat treatment procedure applied.

Recently, glass-ceramics based on chain silicate structures have been developed [1,2]. Some work has been done on the diopside ($CaMgSi_2O_6$)–anorthite ($CaAl_2Si_2O_8$)–celsian ($BaAl_2Si_2O_8$) system [3–5]. Khater [6] studied the crystallizing phases from multi-component silicate glasses in the system $K_2O–CaO–MgO–Al_2O_3–SiO_2$ and the conclusion drawn that diopside and anorthite were the primary crystalline phases present, with a small amount of microcline.

The nature and character of the crystalline phases and the microstructure of the material were reported [7,8] to be the most important factors affecting the technical properties of the glass-ceramic.

Controlled bulk crystallization is the method most frequently used for producing glass-ceramics through controlled crystallization. Since Stookey's [9] discovery of the controlled and catalytic crystallization of glasses, a large volume of work has been undertaken on this aspect. Researches in this branch have been mainly restricted to glasses in systems such as $SiO_2–Al_2O_3$ [10], $CaO–Al_2O_3–SiO_2$ [11–14], and $MgO–Al_2O_3–SiO_4$ [15,16]. To avoid uncontrolled crystallization, controlled surface crystallization was carried out on these types of glass for systems $CaO–Al_2O_3–SiO_2$ and $MgO–Al_2O_3–SiO_2$ [17]. The main crystalline phases present were anorthite, cordierite, spinel and forsterite.

The study of the $CaO–MgO–Al_2O_3–SiO_2$ system was also important for understanding the reactions taking place in rocks, blast furnace slags and MgO refractories [18]. In most cases, published phase diagrams are related to equilibrium conditions that are not usually encountered in glass-ceramic preparations [19]. Therefore, it is necessary to determine the relationship between the compositions of glass-ceramics and the crystal phases developed under conditions in which such polycrystalline materials were actually produced. In a previous paper Khater [20] managed to obtain a glass-ceramic material based on by-pass silica sand and magnesite. From cement kiln dust which made up about 57 wt.% of the batch constituents depending on the composition. Cement kiln dust is generated in the cement kiln and associated equipment. Dust from the raw mix and the surroundings of the plant is normally suppressed with closed systems and through water sprays. During the burning process, the gas flows entrain a substantial quantity of dust that forms part of the kiln exit gasses. The production of cement kiln dust strongly depends upon the chemistry of raw materials, type of process and the design of gas velocities in the kiln. Other factors such as kiln performance and dust collection systems also play vital roles in kiln dust generation.

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Table 1
Chemical analyses of the raw materials used in glass-ceramics.

Constituent oxides (wt.%)	Cement kiln dust	Silica Sand	Granite	Magnesite
SiO_2	12.90	99.10	68.75	3.12
Al_2O_3	3.22	0.28	14.48	0.05
Fe_2O_3	2.35	0.03	2.50	0.06
TiO_2	0.23	Trace	0.64	0.02
CaO	42.98	0.10	2.26	2.45
MgO	1.22	Trace	1.27	44.60
Na_2O	3.35	Trace	4.21	0.08
K_2O	2.10	Trace	3.49	0.02
MnO	0.03	Nil	0.05	0.01
SO_3	4.50	Nil	0.06	0.02
L.O.I.	27.38	0.40	1.20	49.12

The production of alkaline-earth aluminosilicate glasses in the system SiO_2–Al_2O_3–MgO–CaO has been broadly investigated in the past decade. Crystalline phases such as cordierite, diopside, wollastionite, mellite, etc., have been precipitated from glasses under controlled conditions resulting in glass-ceramics with attractive dielectric properties and high mechanical and chemical resistance [21,22].

Khater and Hamzawy [23] studied the effect of different nucleation catalysts on the crystallization behavior, within the CaO–MgO–Al_2O_3–SiO_2 system. They found that glass-ceramics containing CaF_2, Cr_2O_3 and TiO_2 is characterized by fine-grained textures, whereas glass-ceramics containing LiF is characterized by coarse grain texture.

Various methods are used to capture the dust, such as electrostatic precipitators and bag filters. If cement kiln dust contains low proportions of chemicals such as alkali and chlorides, then it is possible to regenerate cement kiln dust into the kiln as part of the raw mix. Cement kiln dust not reused in this manner can be used in a variety of industrial applications, such as: an additive to cement in the grinding process; a sub-base in road construction given its hydration properties, a source of alkalis in chemical processing, for example, potassium sulfate for the extraction of potassium oxide, according to the equation $K_2SO_4 \rightarrow K_2O + SO_3$ and a backfill material in mining.

Cement dust is an obnoxious by-product of the cement industry. It is usually retained behind filters (rather than discharged into the atmosphere), as a fine, active particulate residue. Recent statistics indicate that about 1000 tons/day of this very harmful by-product is disposed of by one major cement manufacturer in the Rabigh area. The factories efforts to recycle cement dust result in a maximum utilization of about 7–10%, the remaining enormous amount from Rabigh cement plant located in the Rabigh area, is generally loaded on trucks and dumped in nearby open space surface impoundments or used simply as land refills. This vulnerable disposal method allows huge quantities of the erosive, light weight, fine powder to be recycled into the atmosphere as the wind blows, posing serious environmental problems and health hazards. Recent research showed the cement dust can be used in various applications as mentioned above. From these applications, it was found that the percentage of by-pass cement dust is not more than 57% of the batch constituents. The chemical analyses of cement kiln dust indicate the possibility of its uses in glass and glass-ceramic industries (Table 1).

Because glass and glass-ceramics are known to have many commercial applications, the transformation of waste into glass or glass-ceramics provides an opportunity for making use of products out of waste, even hazardous wastes.

The use of waste materials such as cement kiln dust for the production of glass-ceramic materials is of great economic technological and scientific importance with proper adjustment of the chemical composition.

The present work aims at the usability study of cement kiln dust for the production of glass-ceramic materials.

Table 2
Chemical composition of the base glasses.

Glass No.	Nominal glass-ceramics (wt.%)				Raw materials (wt.%)			
	SiO_2	Al_2O_3	CaO	MgO	Cement dust	Silica sand	Magnesite	Granite
K60	51.16	6.16	38.36	4.32	61.28	16.47	6.65	15.60
K70	51.30	4.62	40.84	3.24	66.61	25.59	5.09	2.71
K80	51.45	3.08	43.32	2.16	69.88	26.76	3.36	–
K90	51.58	1.54	45.80	1.08	72.44	25.92	1.64	–
K100	51.72	–	48.28	–	74.92	25.08	–	–

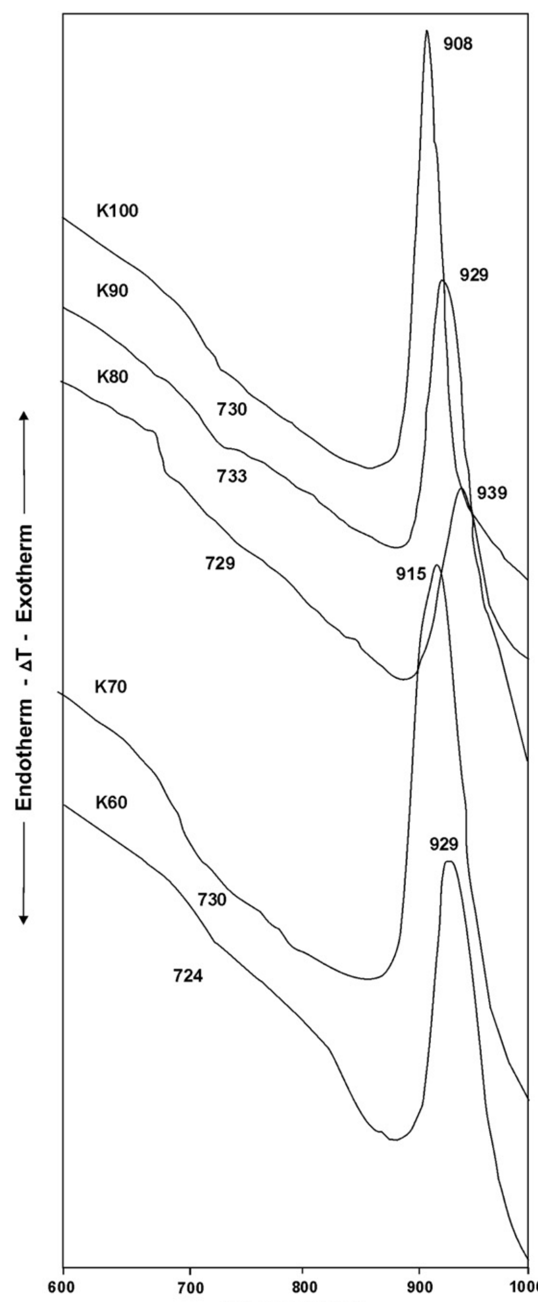

Fig. 1. Differential thermal analysis of the investigated glasses.