EFFECT OF ADDING ALKALINE EARTH OXIDES TO ZnO-MgO-Al_2O_3-SiO_2 GLASS-CERAMIC GLAZES

Berkay YAZIRLI[1,2], Hasan SARI[1], Kağan KAYACI[1], Ferhat KARA[2]

[1]Kaleseramik Çanakkale Kalebodur Seramik San. A.Ş., Çanakkale, Turkey

[2]Eskisehir Technical University, Department of Materials Science and Engineering, Eskişehir, Turkey

ABSTRACT

Glass-ceramic materials are produced by controlled crystallization of glass articles. In the tile industry, glass-ceramic glazes are especially preferred for some special surface effects such as a satin or matte appearance and high abrasion resistance. Also, crystallization of some phases such as spinel and gahnite in traditional firing conditions, using appropriate compositions, enables opacity to be achieved due to their high refractive index (n=1.76-1.86) which is close to that of zircon (n=1.95).

In this study, CaO, SrO and BaO were used in order to regulate the ZnO-MgO-SiO_2-Al_2O_3 glass-ceramic system. For this purpose, the equimolar amount (2 and 4%) of alkaline earth oxides was substituted for SiO_2. Optical and microstructural properties were characterized.

The results show that the addition of alkaline earth oxide instead of SiO_2 reduced sintering temperature. Also, with the addition of these oxides to the compositions, another crystallization was seen such as that of anorthite, celsian and strontium aluminium silicate. Replacing SiO_2 by alkaline earth oxides reduces oxygen bridging and connectivity of glass structures. As a result of a loosened network, glaze viscosity decreased at elevated temperatures and pore coarsening occurred.

1. INTRODUCTION

A glass-ceramic is produced by controlled crystallization, which consists of the growth of one or more crystalline phases in the vitreous mass. These systems can therefore be optionally modified within a large range by the variation of network modifiers and intermediates in the glass structure. In this study, the effects of alkaline earth oxides (BaO, CaO, SrO) on the crystallization of the $ZnO-MgO-SiO_2-Al_2O_3$ glass-ceramic system was investigated.[1-2]

2. EXPERIMENTAL PROCEDURE

Quartz, alumina, magnesite, sodium and potassium feldspar, zinc oxide, calcium carbonate, barium carbonate, strontium carbonate and boric acid were used as raw materials. The chemical composition ranges are shown in table 1. Seven compositions were formulated with different alkaline earth oxides. The frits were prepared by melting the required amount of batch in an alumina crucible at 1500°C with a 10°C/dk heating rate and 1 hour soaking time in an electrically heated furnace. The frits were mixed and milled with 5% kaolin. The mixture was then applied on a porcelain body and fired in an industrial kiln cycle.

	SiO_2	Al_2O_3	MgO	ZnO	Na_2O	K_2O	B_2O_3	CaO	SrO	BaO	MgO/ZnO
G1	50-55	20-25	5-10	5-10	<5	<5	<5	-	-	-	3
G1C2	45-50	20-25	5-10	5-10	<5	<5	<5	2	-	-	3
G1C4	45-50	20-25	5-10	5-10	<5	<5	<5	4	-	-	3
G1S2	45-50	20-25	5-10	5-10	<5	<5	<5	-	2	-	3
G1S4	45-50	20-25	5-10	5-10	<5	<5	<5	-	4	-	3
G1B2	45-50	20-25	5-10	5-10	<5	<5	<5	-	-	2	3
G1B4	45-50	20-25	5-10	5-10	<5	<5	<5	-	-	4	3

Table 1. *Molar compositions of G1 series.*

3. RESULTS AND DISCUSSION

Figure 1(a-d) shows the XRD results obtained from the glazed surfaces of the tiles. For sample G1S4, XRD analysis cannot be performed due to the surface of glaze which contains a high amount of surface defects. In glaze G1, which does not contain any alkaline earth oxides, cordierite, mullite and spinel phases are detected with an amorphous phase hump between 15°-30°. In all samples with the 2% mole addition of alkaline earth oxides instead of SiO_2, cordierite and mullite crystallization were suppressed in all samples. Strontium aluminium silicate crystallization was detected in the SrO addition (Figure 1-d), while no different crystalline phases were observed in the BaO and CaO addition (Figure 1-b and c). On increasing the alkaline earth addition to 4% mole, anorthite and celsian formations were detected.

The main base composition changed due to the surface defects of G1S4 glazes. In the new compositions, the MgO/ZnO ratios were changed. In all compositions, 4 mole of alkaline earth oxide were added instead of SiO_2. Hot stage microscopy results showed that the compositions with CaO, BaO and SrO additions had similar sintering temperatures. But thermal behaviour of compositions was different at higher temperatures. Also, with the addition of these oxides instead of SiO_2, sintering temperatures will reduce due to the looser glass network. Also, glass transition temperatures are similar in the compositions with alkaline earth oxide additions. In G2, glaze spinel and mullite phases were observed in the XRD results, cordierite phase does not crystallize due to the low amount of MgO. In all compositions with alkaline earth oxide additions, alumina silicate phases of related oxides with spinel phases were seen. In SEM analysis of the glazes with alkaline earth oxides, two types of crystalline phases were observed.

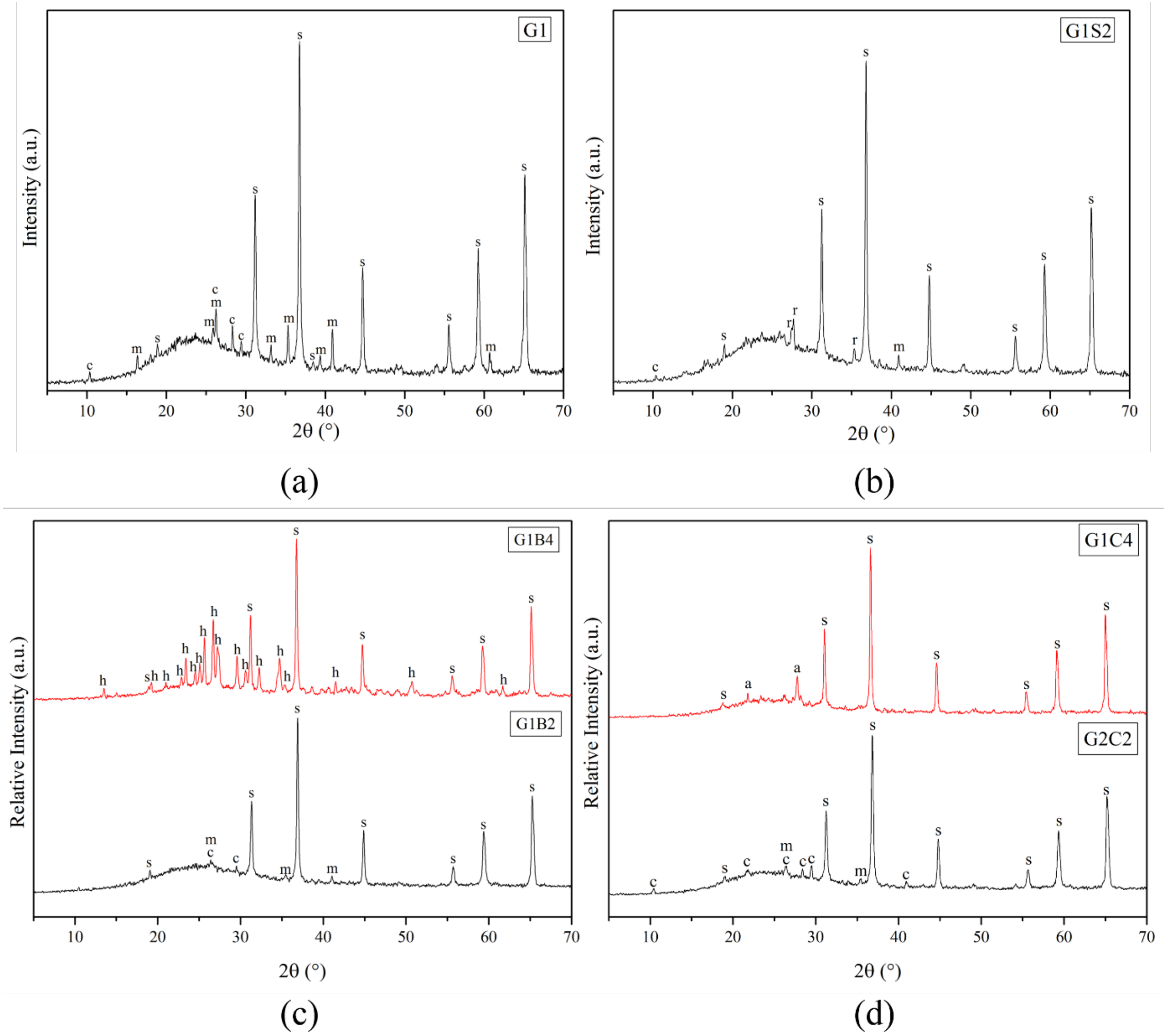

Figure 1. *XRD patterns of samples a) G1 glaze b) G1S2 glaze c) G1B2 and G1B4 glaze d) G1C2 and G1C4 glazes (c: cordierite, m: mullite, s:spinel, r strontium aluminium silicate, h:celsian, a:anorthite)*

	SiO_2	Al_2O_3	MgO	ZnO	Na_2O	K_2O	B_2O_3	CaO	SrO	BaO	MgO/ZnO
G2	50-55	20-25	5-10	5-10	<5	<5	<5	-	-	-	1
G2C4	45-50	20-25	5-10	5-10	<5	<5	<5	4	-	-	1
G2S4	45-50	20-25	5-10	5-10	<5	<5	<5	-	4	-	1
G2B4	45-50	20-25	5-10	5-10	<5	<5	<5	-	-	4	1

Table 2. *Molar compositions of G2 series.*

4. CONCLUSION

The results showed that the addition of alkaline earth oxide instead of SiO_2 reduces sintering temperature. Also with addition of these oxides to the compositions, another crystallization was seen, such as anorthite, celsian and strontium aluminium silicate phases. Replacing SiO_2 by alkaline earth oxides reduces oxygen bridging and connectivity of glass structure.

5. REFERENCES

[1] R.Casasola, J.Ma. Rincón, M. Romero. Glass-ceramics glazes for ceramic tiles – a review *Journal of Material Science, 47 (2012) 553-582*

[2] H. Mao, X. Chen, F. Wang, W. Zhang, Effects of alkaline earth oxides on the densification and microwave properties of low-temperature fired BaO-Al_2O_3-SiO_2 glass-ceramics /Al_2O_3 composites, *Journal of Material Science, 54(2019), 12371-12380*