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Synthesis of glass-ceramic glazes in the $ZnO–Al_2O_3–SiO_2–ZrO_2$ system

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Abstract

Glazes in the $ZnO–Al_2O_3–SiO_2–ZrO_2$ system with crystallization ability of gahnite ($ZnO\cdot Al_2O_3$) and β-quartz solid solution (βqss) were synthesized. The compositions were designed based on calcium and magnesium oxide replacement (from a $CaO–MgO–Al_2O_3–SiO_2$ glass-ceramic glaze system) with zinc oxide and simultaneous increasing aluminum oxide. By this replacement, diopside eliminated and co-precipitation of gahnite and zirconium silicate observed. However, a little addition of Li_2O changes the crystallization path by precipitation of βq_{ss} and willemite ($2ZnO\cdot SiO_2$) at low temperatures (800–900 °C) which dissolved into glaze by development of firing temperature. The experiments showed that while the micro-hardness of gahnite-based glass-ceramic glazes is almost equal with the diopside based one, it is more than the traditional floor tile glazes.

Keywords: Glass ceramic; Glazes

1. Introduction

Glass-ceramic materials are polycrystalline solids which are prepared by controlled crystallization.[1] The usage potential of glass-ceramic systems as glaze in comparison to traditional ones which completely forms from a glassy phase is very interesting. The mentioned glazes are coatings with high softening point, desirable chemical and erosion resistance and suitable compatibility with alumino silicate substrates. In addition, uniform dispersion of very fine crystals in glassy phase leads to smooth opaque glazes, sometimes with interesting effects.[2,3] Tailor ability of thermal expansion is one of the other important specifications of glass-ceramic glazes which come on solely by a small change in the initial glass composition, mainly through the type and quantity of nucleating agent.[4] The aim of this work is preparation of glass-ceramic glazes in the $ZnO–Al_2O_3–SiO_2–ZrO_2$ system to improve the surface quality and micro-hardness of floor tile glazes by precipitation of hard gahnite and zirconium silicate phases. Comparison of crystallization behavior of this glass-ceramic glaze system with an original $CaO–MgO–Al_2O_3–SiO_2$[5] one was also our intend. It should be noted that in spite of various valuable reports, which existed, there has not been a direct comparison between two different glass-ceramic glaze systems in the literature. We have tried also to study the possibility of preparation of a β-quartz solid solution glass-ceramic glaze for single fast firing wall tile industry that has never considered in the previous reports.

2. Experimental procedure

The raw materials used for preparation of the glazes were silica, zircon, kaolin, feldspar, dolomite, magnesium carbonate, boric acid and potassium nitrate in industrial grade. The weighted batch materials, after thorough mixing were melted in an alumina crucible in electric furnace at 1450 °C for 1 h. The fluid melt was quenched by pouring it into water to obtain a glassy frit. The glaze slips were consisted of 93 parts by weight frit, 7 parts by weight kaolin and 57 parts by weight water. The batches were fast milled for 30 min in a planetary mill. After this procedure the glaze slip particle sizes were smaller than 63 μm. The slips were then applied on 5 cm × 5 cm dried ceramic bodies. The dried samples were heat-treated from room temperature up to 1180 °C for 70 min at a steps of 100 °C. Heating rate was done according to fast firing procedure in which the total firing program was 70 min.

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For evaluation of crystalline phases which were developed in glazes during heat-treatment, X-ray diffractometer (Siemens, model D-500) with Cu Kα radiation was used. Silicon powder was used as the standard material for semi-quantitative measurements of precipitated phases. A Vickers micro-hardness tester with a diamond pyramid (MVK-H21 Microhardness) was used to measure the micro-hardness of glaze surface, by applying a load of 100 g for 30 s. The microstructure and the crystallinity were inspected using a scanning electron microscope (SEM) (Lika Cambridge Stereoscan 30).

3. Results and discussion

Table 1 shows the chemical analysis of the investigated compositions. In this table the terms B and Z are representative of the base glass adopted as the representative of a glass-ceramic glaze based on the CaO–MgO–Al_2O_3–SiO_2 system and zinc oxide, respectively, and the numbers denote amounts of zinc oxides added to the base glass (B). Calcium and magnesium oxide was replaced by zinc oxide gradually in a manner in which the molar ratio of Al_2O_3 was kept equal to ZnO. In this way, the compositions B-Z10, B-Z12.5, B-Z15 and B-Z17.5 were obtained by replacement of 10, 12.5, 15 and 17.5 parts by weight of calcium and magnesium oxides with zinc oxide, respectively, and addition of same molar of aluminum oxide. Zirconium oxide was added in the glass compositions because it can acts as an opacifier and also nucleation agent for crystalline phases, especially β-quartz solid solution, in the ZnO–Al_2O_3–SiO_2 systems.[6–9] Fig. 1 shows the DTA curves of the base and the above-mentioned glasses. It can be observed that introducing of 10 and 12.5 parts by weight of zinc oxide and equal molar of aluminum oxide caused to obscure crystallization peaks. However, more substitution of calcium and magnesium oxides by ZnO caused to appear a broad peak again at about 1038 °C which became sharper and took place at a lower temperature (920 °C) with substitution of 17.5 parts weight ZnO.

Figs. 2 and 3 show the X ray diffraction patterns of heat treated glasses at their crystallization and glaze firing temperatures (1180 °C) for 10 min, respectively. Accordingly, the DTA crystallization peak in the base glass belongs to crystallization of diopside and in the BZ15 and BZ17.5 were due to precipitation of gahnite. It seems that zirconium oxide precipitates gradually as a minor phase in this temperature region, converts ultimately in the temperature interval of 1000–1100 °C to zirconium silicate. It can also be seen (Fig. 3) that with increasing of zinc and aluminum oxides in the glass, because the concentration

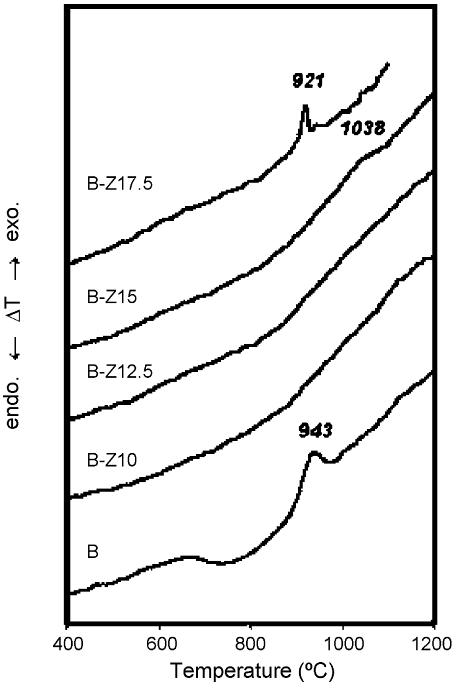

Fig. 1. DTA curves of samples B, B-Z10, B-Z12.5, B-Z15 and B-Z17.5.

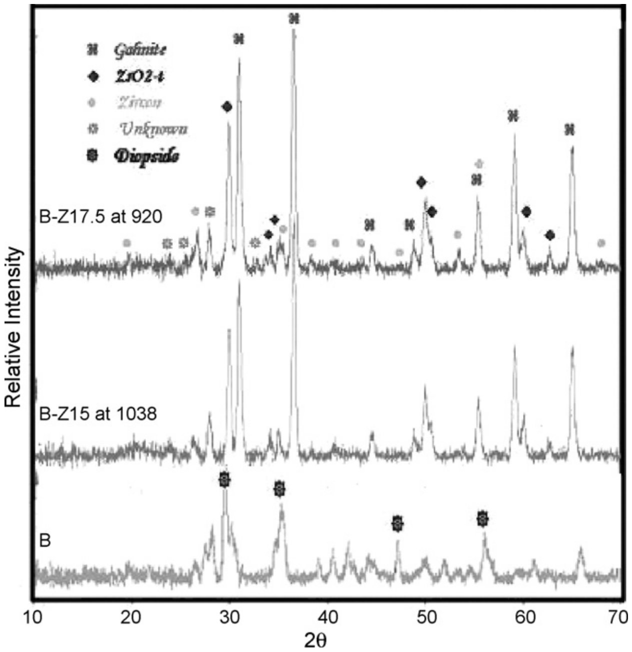

Fig. 2. XRD patterns of samples B, B-Z15 and B-Z17.5 after heat-treatment at peak temperatures for 10 min.

Table 1
Chemical analysis of the prepared compositions (parts by weight)

Composition	SiO_2	Al_2O_3	CaO	MgO	ZrO_2	Na_2O	K_2O	B_2O_3	ZnO
B	55.35	7.32	11.07	7.50	9.54	1.02	2.62	5.58	–
B-Z10	55.35	12.6	5.07	3.50	9.54	1.02	2.62	5.58	10.00
B-Z12.5	55.35	15.75	3.57	2.50	9.54	1.02	2.62	5.58	12.50
B-Z15	55.35	18.9	2.07	1.50	9.54	1.02	2.62	5.58	15.00
B-Z17.5	55.35	22.05	0.57	0.50	9.54	1.02	2.62	5.58	17.50

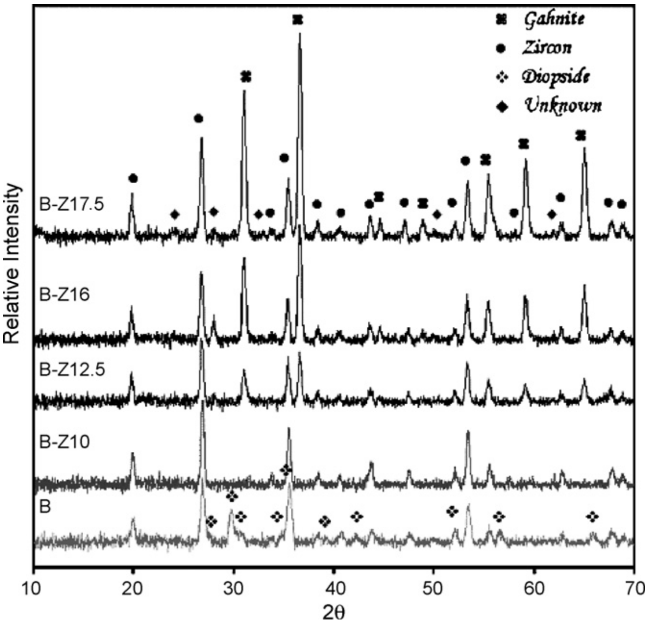

Fig. 3. XRD patterns of samples B, B-Z10, B-Z12.5, B-Z15 and B-Z17.5 after firing at 1180 °C for 10 min.

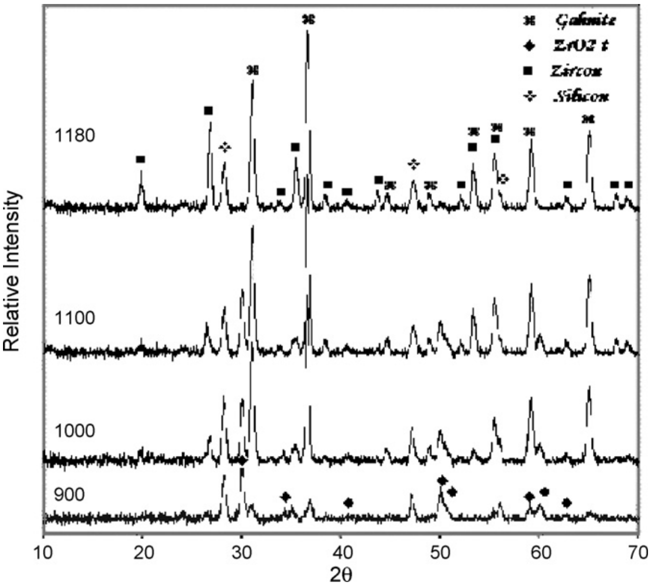

Fig. 4. XRD patterns of sample B-Z17.5 after heat-treatment at different temperatures.

of gahnite ingredients is increased; the amount of this phase is continuously enhanced.

Firing experiments showed that in exception of B-Z17.5 the other glazes bore suitable white and glossy appearance. The surface quality of glaze B-Z17.5 was undesirable, consisted of crawled regions which easily chipped from the substrate. This appearance was indicative of an unfired glaze and a weak bond in the glaze–substrate interface, originated probably from high amounts of aluminum oxide added into the glaze and so decreasing of its fluidity and reactivity. Thus, it seems that B-Z15 was the best glaze in the gahnite series glazes.

To get ride of these defects, improvement of fusibility and also to prepare conditions for obtaining a new type of glass-ceramic glaze with a lower thermal expansion and perhaps suitable for lower firing temperatures, through precipitation of βquartz$_{ss}$,[10] 2.5 parts by weight of lithium oxide was added to B-Z17.5 composition. Figs. 4 and 5 show the XRD patterns of the initial (B-Z17.5) and resulted glasses (B-Z17.5 Li2.5) after firing at 800, 900, 1000, 1100 and 1180 °C for 10 min. Comparison of these figures indicate that with addition of Li_2O, the types of crystalline phases precipitates at 800 °C changed to tetragonal zirconia and β-quartz solid solution. With increasing of temperature up to 900 °C, willemite and gahnite also crystallized. It seems that Li_2O helps to prepare conditions, kinetically, for crystallization of β-quartz and willemite, through reduction of glass viscosity. In this way, ZrO_2 acts as a nucleating agent. However, with more rising of temperature, the intensity of former phase's decreases gradually, eliminates finally at 1100 °C. During this procedure ziconia was converted to zircon which remains stable even after final firing temperature (1180 °C). Furthermore, addition of Li_2O led to degradation of gahnite amounts and so easer fluidity of the glaze at this temperature. It seems as the crystallization of β-quartz solid solution and willemite were occurred prior to gahnite, consumption of Zn^{2+} ions in the glaze by the formers reduced the chance for gahnite formation through decreasing of its constituents at lower temperatures.

Fig. 6 shows the SEM microstructure of glaze B-Z17.5 Li2.5 in two different magnifications, after firing at 1180 °C. The crystalline phases are visible as cubic and fibrous forms. Figs. 7 and 8 also depict EDAX analysis of the cubic and fibrous particles, respectively. With attention to XRD patterns and these analysis it can be said that the fibrous particles are zircon and the cubic ones are gahnite. The crystalline particles of gahnite and zirconium silicate were respectively smaller than 5 and 10 μm, which should guarantee the glossiness and smoothness of glass

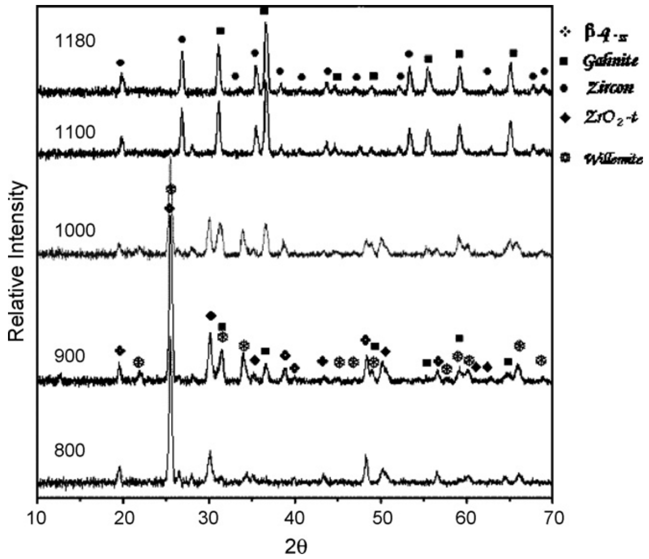

Fig. 5. XRD patterns of sample B-Z17.5 Li2.5 after heat-treatment at different temperatures.

Table 2
Vickers hardness of prepared glass-ceramic glazes

	B	B-Z10	B-Z12.5	B-Z15	B-Z17.5	B-Z17.5 Li2.5	Normal glaze
Hardness (VHN)	649 ± 2	617.6 ± 6	655.3 ± 28	642.6 ± 20	–	651.6 ± 11.5	600

surface.[11] However, It should be noted that lithium oxide caused glaze surface widely marred by numerous pinholes after firing at 1180 °C. It seems that as lithium oxide is a powerful flux and reduces viscosity of the glaze, as already predicted it amplified the reactivity at glaze–body interface, led to evolution of gas and so pinholes. Therefore, with attention to this effect and instability of β-quartz solid solution in firing temperatures higher than 1000 °C, it seems that B-Z17.5 Li2.5 can be used only as a low thermal expansion glaze in double fast firing schedules, in wall tile industry, up to1020 °C.

Micro-hardness of the examined glazes and a customary one used usually in the floor tile industry are shown in Table 2. As it can be observed while the micro-hardness of glass-ceramic glazes is more than the conventional glaze one, they, i.e. the original one (which belongs to the CaO–MgO–Al_2O_3–SiO_2 system) and the other (which belongs to the ZnO–Al_2O_3–SiO_2 one), show approximately equal values themselves. It is known that the glass-ceramic hardness is related to both crystalline and residual glassy phases. In the present gahnite based glazes, the decreasing of glassy phase hardness due to replacement of calcium and magnesium oxides with zinc oxide is compensated by higher percentage of crystalline phases, deduced from relative intensities of crystalline phases to silicon.

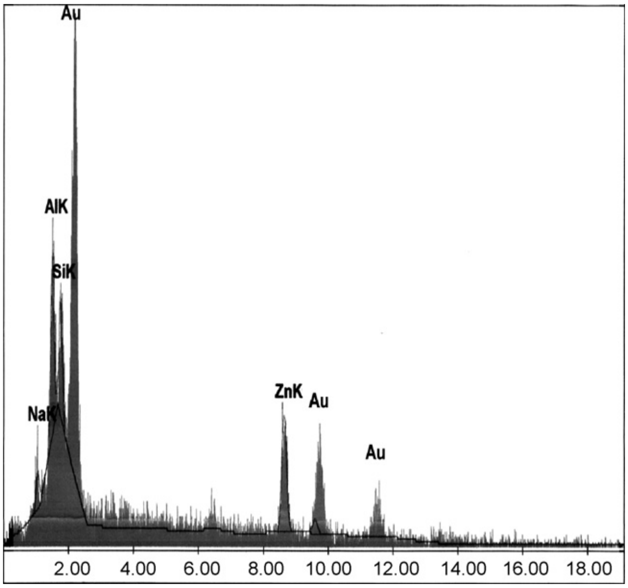

Fig. 7. EDAX analyses of the cubic shape particles.

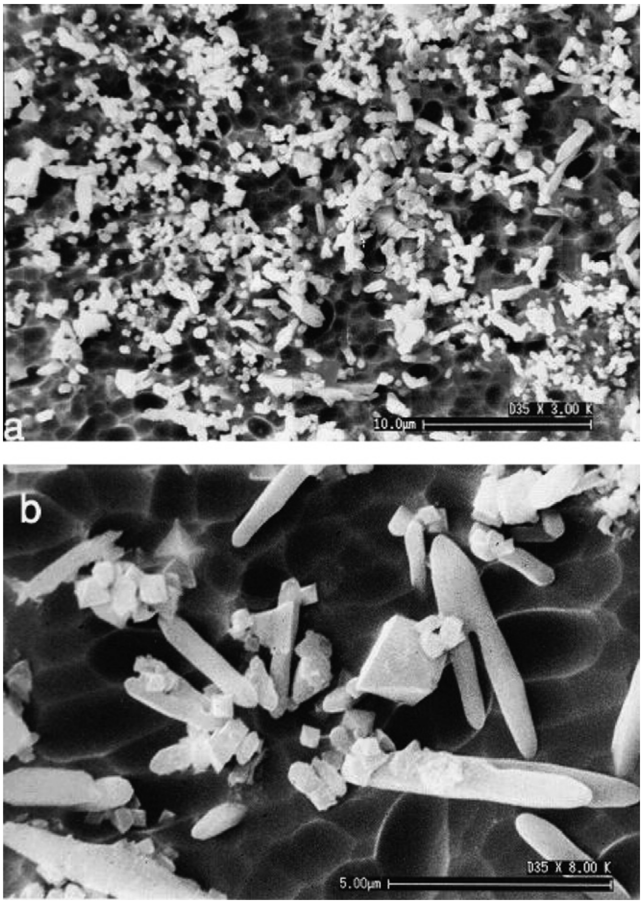

Fig. 6. SEM micrographs of sample B-Z17.5 Li2.5: (a) magnification ×3000; (b) magnification ×8000.

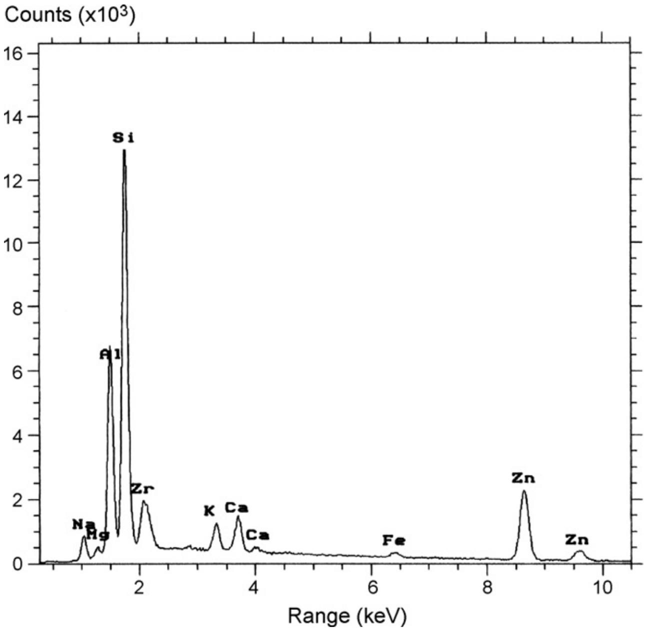

Fig. 8. EDAX analyses of the fibrous shape particles.

4. Conclusions

1. The amount of precipitated gahnite in the glazes depends on the amounts of zinc and aluminum oxides. It seems that precipitation of gahnite in the free-Li_2O glazes is happened directly from the initial glass phase. Zirconium silicate was another crystalline phase precipitated in the glazes, which increasing of its intensity associated with decrease of pre-existence zirconium oxide crystalline phase with temperature. Addition of Li_2O altered the above mentioned crystallization path. A little amount of lithium oxide led to precipitation of β-quartz solid solution and willemite as the initial zinc containing crystalline phases, hereby decreased the amount of gahnite at the maturing temperature through spending of zinc oxide and available times for its formation.
2. Besides of a better surface quality, micro-hardness of the prepared glass-ceramic glazes was more than the traditional floor tile glaze and more smooth than the base glass-ceramic one. The former advantages confirms previous reports by the others.
3. With attention to instability of β-quartz solid solution above 1000 °C, it seems that Li_2O bearing glaze can be used as a glaze with low thermal expansion coefficient in double fast firing programs in the wall tile industry.
4. During firing procedure a fine microstructure composed of cubic gahnite and fibrous zirconium silicate particles immersed in glass matrix was developed.

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