Preparation of glass–ceramic glazes for fast firing applications by CaF$_2$ substitution with B$_2$O$_3$ in the CaO–CaF$_2$–Al$_2$O$_3$–SiO$_2$ system

S. Banijamali*

Ceramic Department, Materials & Energy Research Center, Alborz, Iran

Abstract

The present work aims to obtain glass–ceramic glazes for floor tile applications. In this regard, CaF$_2$ was gradually replaced by B$_2$O$_3$ in the glass compositions belonging to the CaO–CaF$_2$–Al$_2$O$_3$–SiO$_2$ system. This substitution led to a noticeable decrease of crystallization peak temperatures and to an alteration of the crystallization trend. In the B$_2$O$_3$ bearing glazes, anorthite and gehlenite were identified as the major and minor crystalline phases, respectively. During concurrent crystallization and sintering based on the fast firing program, glass–ceramic glazes containing 9 weight parts of fluorine and 12 weight parts of boron oxide showed the most desirable sinterability. The optimized glass–ceramic glazes offered acceptable micro-hardness, whiteness and thermal expansion behavior after fast firing heat treatment.
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Keywords: Glass–ceramic; Crystallization; Glaze

1. Introduction

Recently, a developing interest has been focused on glass–ceramic glazes which are compatible with fast firing technology commonly used in tile industry [1]. A glass–ceramic glaze comprises a homogeneous distribution of crystalline phases dispersed in a residual glass matrix [2]. Controlled crystallization process based on the fast firing program guarantees adequate crystallinity as well as sufficient flow-ability and maturing of the glass–ceramic glazes [1,3–5]. In comparison with traditional glazes, glass–ceramic ones present superior chemical durability and mechanical properties such as micro-hardness and abrasion resistance. Furthermore, formation of crystalline phases leads to the achievement of appropriate opacity and whiteness without using zircon, zirconium oxide and tin oxide as opacifiers. The growing costs of these materials necessitate fabrication of glass–ceramic glazes with improved properties [1].

In the light of superior properties of glass–ceramic glazes and possibility to reduce raw materials' costs, various glass–ceramic systems have been proposed for floor tile glaze applications. For this purpose, various glazes containing different crystalline phases like mullite, diopside, cordierite, gahnite, spinel, etc. have been investigated [6–13].

The present work reports the results concerning the substitution of CaF$_2$ by B$_2$O$_3$ in the CaO–CaF$_2$–Al$_2$O$_3$–SiO$_2$ glass–ceramic glazes. It should be noted that the glass–ceramic bodies of the prototype CaO–CaF$_2$–Al$_2$O$_3$–SiO$_2$ system had been suggested for unglazed floor tiles applications, previously [14]. Due to the high cost of fluorine (CaF$_2$) and general potential of boron oxide as a glaze constituent such as lowering thermal expansion and improving both mechanical strength and scratch resistance [15], CaF$_2$ was gradually replaced by B$_2$O$_3$ in the glaze compositions. Hence, the starting glass frits containing various amounts of CaF$_2$ and B$_2$O$_3$ were prepared. The relevant glazes were exposed to a crystallization heat treatment scheduled according to the fast firing program. Crystallization behavior and sinterability of specimens were evaluated throughout simultaneous sintering

*Tel.: +98 9122132080; fax: +98 2636201888.
E-mail address: banijamalis@yahoo.com

Table 1
Chemical composition of the initial glasses (weight ratio).

Composition	CaO	Al_2O_3	SiO_2	CaF_2	B_2O_3
F9	23.5	42.8	33.7	9	–
B3F6	23.5	42.8	33.7	6	3
B6F3	23.5	42.8	33.7	3	6
B9	23.5	42.8	33.7	–	9
B12	23.5	42.8	33.7	–	12

and crystallization process. The arising changes in crystallinity, micro-hardness, whiteness index and coefficient of thermal expansion as well as the microstructural features of the optimized glazes were also characterized.

2. Experimental procedure

The studied glaze compositions, formulated with different amounts of CaF_2 and B_2O_3, are presented in Table 1. The starting raw materials were reagent-grade chemicals of calcium carbonate (Merck 2066), fluorine (Merck 2840), boric acid (Merck 160), aluminum hydroxide (Merck 1093) and silica (Setabran, purity > 99%). The homogeneous mixtures of glass batches were melted in alumina crucibles at 1450–1480 °C in an electric furnace for 3h followed by rapid quenching in cold water to obtain frits. All frits were dry milled in an agate mortar for 30 min to reach the mean particle size of 10 μm. Crystallization behavior of glass frits was monitored by a differential thermal analyzer (Polymer Laboratories, STA-1640). Each DTA run was carried out in air atmosphere with alumina reference sample, using a heating rate of 20 ° C/min. Crystalline phases precipitated during heat treatment were identified by X-ray diffractometer (Siemens D500) with Cu-$K\alpha$ radiation. The quantitative determination of the crystalline phases in the optimized glass–ceramic glazes was performed from X-ray diffraction data by using the Ohlberg and Strickler method as Eq. (1):

$$X_c = (I_g - I_x)/(I_g - I_b) \times 100 \tag{1}$$

In this equation, I_g, I_x and I_b are the XRD intensity scattered by the parent glass, the partially crystallized glass and a mechanical mixture of oxide powders having the same composition as the parent glass, respectively [16].

The sinterability of glass–ceramic specimens was evaluated during sintering at several temperatures up to 1210 °C. Thereof, glass frits were mixed by 0.1 wt% CMC (carboxy methyl cellulose) and uniaxially pressed under a pressure of 5 MPa to obtain loosely compacted glass pellets with 2 cm in diameter. To simulate the condition of fast firing program, the glass pellets were heat treated according to Fig. 1.

In order to confirm the complete maturing of the selected compositions as glazes, they were applied as glaze slips on a conventional floor tile support. Glaze slips comprised frit and kaolin with weight ratio of 93/7 were mixed by 0.1 wt% carboxy methyl cellulose as a binder, 0.3 wt% sodium tripolyphosphate as a dispersant and 35 wt% water in a planetary mill for 30 min. The glazed specimens were also
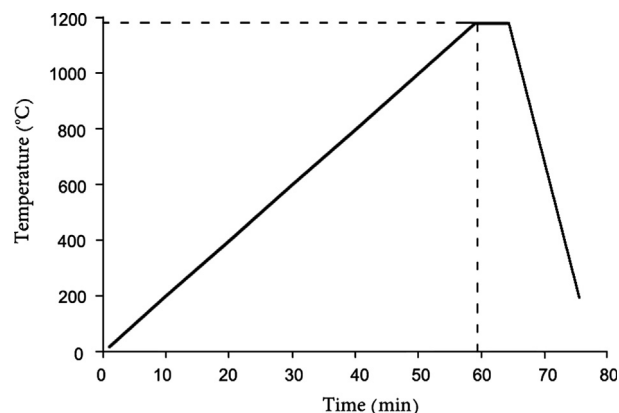

Fig. 1. Heat treatment regime scheduled according to the fast firing program.
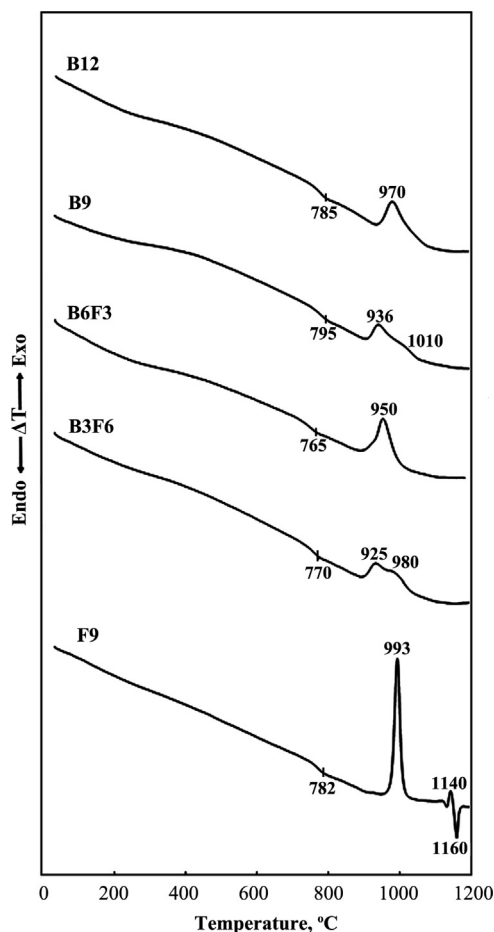

Fig. 2. DTA thermographs of glass particles (< 63 μm) at the heating rate of 20 °C/min.

heat treated according to Fig. 1. The Vickers micro-hardness was measured utilizing the indentation method [17]. This test was carried out by applying a 100 g f load of a diamond indenter (Akashi, MVK-H21) for 30 s.

To examine the consistency between thermal behavior of the glass–ceramic glazes and the support, thermal expansion coefficients of the most promising glazes and that of the support were measured by dilatometer (Netzsch 402E). This examination was performed at the heating rate of 10 °C/min in