Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 134 (2015) 621–630

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

The effect of SiO_2/Al_2O_3 ratio on the structure and microstructure of the glazes from SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O system ☆

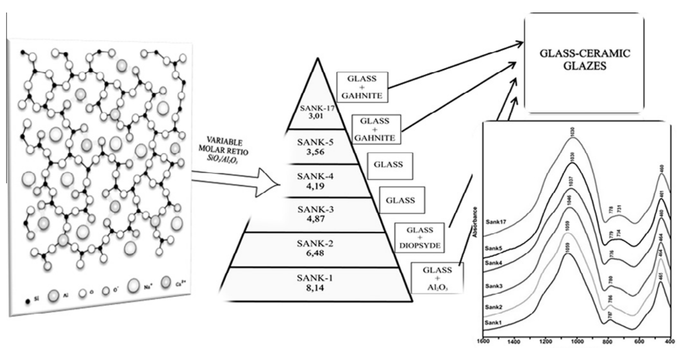
Janusz Partyka [a,*], Maciej Sitarz [b], Magdalena Leśniak [b], Katarzyna Gasek [a], Piotr Jeleń [b]

[a] AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Ceramics and Refractory Materials, Poland
[b] AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Silicate Chemistry and Macromolecular Compounds, Poland

HIGHLIGHTS

- The effect of the SiO_2/Al_2O_3 ratio on structure of ceramic glazes were examined.
- The highest SiO_2/Al_2O_3 molar ratio leads to dominance of the O—Si—O bands.
- With the highest SiO_2/Al_2O_3 ratio crystallization of diopside was detected.
- The lowest SiO_2/Al_2O_3 molar ratio leads to dominance of Si—O—Al and Si—O—Si bands.
- With the lowest molar ratio crystals of gahnite occurs – other glazes are amorphous.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 December 2013
Received in revised form 15 May 2014
Accepted 9 June 2014
Available online 3 July 2014

Keywords:
Ceramic glaze
Structure
Phase composition
FTIR analysis

ABSTRACT

Ceramic glazes are commonly used to covering of the facing surface of ceramics ware. A well-chosen oxide composition and firing conditions of glazes causes significant improvement of technical parameters of ceramic products. Modern glazes are classified as glass–ceramic composites with different crystalline phases arising during firing. The presence of crystals in the glass matrix is influenced by many factors, especially by oxides molar composition. A crucial role is played by the molar ratio of SiO_2/Al_2O_3. In this work the six composition of glazes from SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O system were examined. The only variable is the ratio of the silicon oxideto alumina at a constant content of other components: MgO, CaO, K_2O, Na_2O, ZnO. In order to determine the real phase composition of the obtained glazes research on fluorescence spectrometer (XRF) were done. For structural studies X-ray diffraction (XRD) and spectroscopic in the middle infrared (MIR) were performed. In order to determine the state of the surface (microstructure) research on the scanning electron microscope (SEM) with EDX. The research allowed to determine the influence of SiO_2/Al_2O_3 ratio on the structure and phase composition of glazes and the nature, and type of formed crystalline phases.

Introduction

Glazes are complex mixtures of various oxides systems, each of which affects the resulting properties of the vitreous coating on the surface of ceramic. Adequate selection determines compliance of the final properties with expected ones due to the destiny of products. Oxides included in the glaze can be divided into three groups:

☆ Selected paper presented at XIIth International Conference on Molecular spectroscopy Kraków – Białka Tatrzańska, Poland, September 8–12, 2013.

* Corresponding author. Address: Faculty of Material Science and Ceramics, Department of Ceramics and Refractories, AGH University of Science and Technology, Krakow, Poland. Tel.: +48 12 617 3654; fax: +48 126331593.
E-mail address: partyka@agh.edu.pl (J. Partyka).

http://dx.doi.org/10.1016/j.saa.2014.06.068
1386-1425/

- Glass-forming oxides – forming a glass framework, having a similar importance as the crystal lattice. The most commonly used glass-forming oxide in the ceramic industry is SiO_2 [1–5], although it can include a whole variety of acidic metal oxides tri-and tetra-value [1–3].
- Modifier oxides – not forming the glazes themselves but which may to some extent replace silicon cations within the glass framework of silica glazes. Their role consists in breaking bridge bonds and depolymerization of glass framework or loosening it. This group consists of alkali metal oxides (Na_2O, K_2O, Li_2O), and alkaline earth metals (CaO, MgO, ZnO, BaO, etc.) [1–3].
- Amphoteric oxides – can contribute to tetrahedral glass framework. Of these, the most common used oxide in conventional ceramic glazes is Al_2O_3 [1–6].

Studies on the effect of SiO_2 to Al_2O_3 ratio on the properties of ceramic glazes were conducted at the beginning of the twentieth century by Stull [4] and Seger [5]. This work focused mainly on simple oxide systems where alkali oxides most frequently are represented by K_2O and alkali earth metal oxides, mainly by CaO. The results showed that the change in the silicon oxide to aluminum oxide ratio has an evident effect on the characteristic temperatures of glazes. The research was continued by a number of other researchers as Parmeele [3] Eppler and Eppler [1], Taylor and Bull [2] and Carty et al. [6]. The results of their work show that in more complex oxide systems, which are used in modern glazes, there is no simple relationship between the molar composition and properties.

Studies on the structure of glazes are also conducted for some time now. The first works of Zachariesen [7] defined the way to create a silico-oxygen and alumino-silico-oxygen framework, as well as the existence of two types of spatial arrangement, short- and long-range. Further work [7–10] explain the mechanisms of binding of modifiers cations with alumino-silico-oxygen framework by non-bridged oxygens. Modern research work is focused on the possibilities of modifying the properties of the glazes by influencing the degree of amorphization of the glass framework and controlled crystallization [10–19]. The influence of grain size distribution on selected surface parameters was discussed by Partyka and Lis [20]. Presented experimental results concern the influence of SiO_2 to Al_2O_3 ratio on the phase composition and structure of porcelain glazes of the SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O.

Table 1
Oxides molar composition of glazes SANK 1–5 and 17.

Oxides	Na_2O	K_2O	CaO	MgO	ZnO	SiO_2
Molar fraction	0.22		0.30	0.21	0.27	3.37

Table 2
Molar ratio of SiO_2 to Al_2O_3 SANK glazes.

SiO_2/Al_2O_3	SANK-1	SANK-2	SANK-3	SANK-4	SANK-5	SANK-17
	8.14	6.48	4.87	4.19	3.56	3.01

Experimental

Six sets of porcelain glazes designed for firing temperature of 1220–1240 °C were selected for the study. The oxide composition of glazes marked from SANK-1 to SANK-5 and SANK-17 were based on multiple system of SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O. Modifier oxide content was constant and the only variable in the composition was SiO_2/Al_2O_3 molar ratio.

Pure raw materials were used for the preparation of glazes: carbonate (Na_2CO_3, K_2CO_3, chalk and dolomite) and oxide (quartz flour, alumina and zinc oxide). Milling was carried out in planetary mills during 30 min and the resulting suspension was applied by spraying the airbrush into 50 mm diameter disks made of porcelain VC mass. Part of raw dried glaze were compacted in porcelain crucibles with a capacity of about 90 cm^3. Rings and crucibles with enamel were fired together in an electric laboratory furnace at a

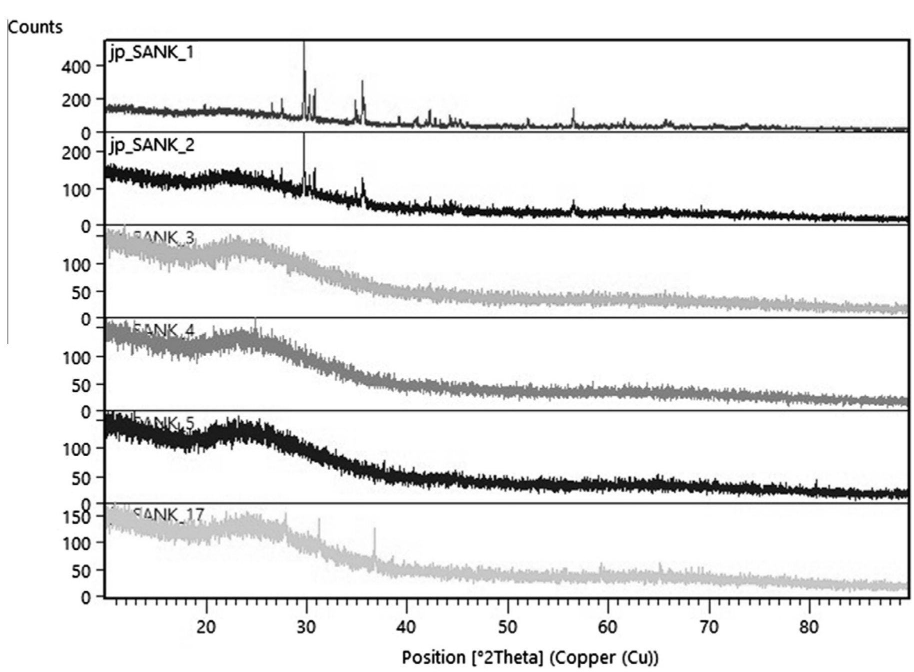


Fig. 1. XRD patterns of SANK-1 to SANK-5 and SANK-17 glazes.