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Differences in densification behaviour of K- and Na-feldspar-containing porcelain bodies

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Abstract

Porcelain bodies fabricated from triaxial mixtures of clay, quartz and feldspar with different amounts of Na_2O and K_2O were investigated to study their densification behaviour on thermal treatment at which the bodies achieve full vitrification. The high temperature dilatometric study has shown a distinct behaviour in their densification rate. The degree of vitrification of the densified samples and samples separately heated at different temperatures was determined by measuring the shrinkage, bulk density (BD), percent water absorption (%WA) and flexural strength. It was found that Na-rich feldspar containing body composition achieve full vitrification at lower temperature compared to K-rich feldspar containing composition with improved flexural strength. Differential thermal analysis–thermogravimetric analysis (DTA–TGA) confirms similar reaction steps for both the compositions up to 1000 °C, beyond which feldspar forms eutectic melt and starts reacting. As the purity of raw materials has a strong influence on the colour of the fired bodies, the bodies were also subjected to colour measurement and their differences in whiteness also compared, and is discussed in this paper. The scientific and technological importance of such vitrified porcelain products has also been touched upon, highlighting their industrial application.

Keywords: Potash feldspar; Soda feldspar; Densification; Porcelain

1. Introduction

Traditionally, porcelain is defined as a glazed or unglazed vitreous ceramic whiteware and used for technical purposes, designating such products as electrical, chemical, mechanical, structural and thermal wares when they are vitreous. Triaxial porcelain, primarily composed of clay, feldspar and a filler material (usually quartz or alumina), is considered to be one of the most complex ceramic materials. Commonly, clay–feldspar–quartz porcelains are referred to as triaxial whiteware. However, alumina can be substituted for quartz to increase the mechanical strength of the fired ware and sometimes nepheline syenite also can be substituted for feldspar. On thermal treatment, the triaxial porcelain system forms a mixture of glass and crystalline phases depending upon the chemistry of the raw materials and processing science. K_2O–Al_2O_3–SiO_2 and Na_2O–Al_2O_3–SiO_2 ternary phase diagrams [1,2] provide useful information on compositions for various types of industrial porcelains. Although the primary and secondary raw materials used to produce industrial porcelains and their functions are described in the literature [3], the new introduction to these and other common raw materials are published annually [4,5]. The chemical reactions involved in a porcelain body at various stages of thermal treatment have been discussed by many authors

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[3,6–12]. Kaolinitic clay ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), the major raw material of a porcelain composition of clay–quartz–feldspar system, undergoes dehydroxylation at around 550 °C and forms metakaolin ($Al_2O_3{\cdot}2SiO_2$); and this is an endothermic process as detected in differintial thermal analysis. Then, in the temperature range of 950–1000 °C metakaolin decomposes into non-equilibrium spinal-type phases with the liberation of amorphous silica. In this temperature range itself feldspar reacts with silica and forms eutectic. The exact eutectic temperature depends on the type of feldspar (potash or soda). Beyond 1000 °C, densification starts by viscous flow sintering process followed by transformation of spinel phases to mullite ($3Al_2O_3{\cdot}2SiO_2$). Finally at around 1200 °C, a portion of quartz is transformed to cristoballite, glasses of various compositions appear and mullite grows and remains in feldspar grains. Thus, the microstructure of a porcelain body consists of quartz and mullite as major crystalline phases held in a complex glassy matrix [13,14]. The rate of viscous flow sintering process in a porcelain body is controlled by viscosity and surface tension of the glassy phase. Due to the advent of fast firing technology in the manufacturing of vitrified porcelain wares and its larger acceptance by the industries, there is a need to increase the rate of sintering process that can produce a fully vitrified ware within a very short firing cycle. Substantial amount of research has already been conducted on such type of porcelain bodies and the best firing temperatures optimized at which the bodies undergo full vitrification without producing any surface defects. The sintering behaviour of faster-firing ceramic bodies made of natural raw materials with or without a high percentage of glass ceramic frit has been recently studied by Paganelli [15] using double-beam optical dilatometer. This new technique is described to be an effective method for precise determination of the best firing profile for any porcelain composition.

In the present study, two porcelain compositions were formulated, using potash feldspar in one and soda feldspar in another, keeping other raw materials same. The densification behaviour of these two bodies was studied using high temperature dilatometer, and the degree of vitrification was assessed by their shrinkage, bulk density (BD), percent water absorption (%WA) and flexural strength data. The brightness of vitrified porcelain is one of the important technological requirements in the manufacture of vitrified ceramic tiles of natural granite finish in various colour shades and designs. In the present investigation, colour measurement was also conducted and the variation in whiteness is also discussed in this paper.

2. Experimental

One-kilogram batch of each were weighed out as per the composition provided in Table 1.

Each batch was wet-ground in a pot mill for a duration of 18–20 h till the residue on 200 mesh BS sieve reduced to less than 1.5 wt.%. The slip thus produced was allowed to dry, then powdered and made into rectangular samples of dimension 66 mm × 15 mm × 4 mm and cylindrical samples of 25 mm length, 4 mm diameter using a hydraulically operated compacting press. A specific pressure of 450–500 kg/cm^2 was applied according to normal industrial practice. The pressed samples were oven-dried till the moisture content was reduced to less than 0.5%. The dried cylindrical samples were thermally heated in a high temperature dilatometer furnace (Orton 1600D) at a rate of 10 °C/min to study their densification behaviour. Rectangular samples were heated in the temperature range of 1160–1200 °C in an electric furnace at the rate of 18 °C/min, with a holding time of 45 min at the peak temperature. The heated samples were subjected to tests such as bulk density (BD), linear shrinkage, percent water absorption (%WA) and flexural strength (Instron 5500R). The vitrified samples obtained from dilatometer were also tested for shrinkage, BD and %WA, and the results are compared with the samples heated in electric furnace. The resulting vitrified samples were investigated by colour measurement according to ASTM-C609-71 using a colorimeter instrument

Table 1
Batch compositions

Raw materials	Composition (wt.%)	
	C1	C2
Clay (kaolin)	60	60
Potash feldspar	30	Nil
Soda feldspar	Nil	30
Quartz	10	10

type Hunter Lab with attached standard colours. The green powders were subjected to differential thermal analysis–thermogravimetric analysis (DTA–TGA) (Netzsch STA-490C) at a heating rate of 10 °C/min.

3. Results and discussion

The raw materials used to prepare vitrified porcelain bodies play a vital role in ultimate product quality. All the raw materials used in the study were chemically analysed, and the results are given in Table 2. The chemical composition of C1 and C2 bodies (Table 1) is given in Table 3.

It may be observed from Table 3 that the C2 body contain comparatively less amounts of Fe_2O_3 and TiO_2 due to the purer grade of soda feldspar used, and this is advantageous for white-based vitrified porcelain as its presence in extra amounts leads to colouration in the fired body [16]. Johnson and Pask [17] also observed that impurities such as Fe_2O_3 and TiO_2 affect the kinetics and morphology of mullite formation. DTA–TGA curves for both C1 and C2 are presented in Fig. 1. The DTA–TGA curve indicates endothermic peaks at ~113 °C due to removal of physically adsorbed water followed by dehydroxylation of kaolin (clay) initiated at almost similar temperatures (~536 °C) for both C1 and C2, and by this process kaolin transforms to metakaolin (as observed by other authors also [6–12]). The nature of the peak further indicates that dehydroxylation is an endothermic process. The exothermic peak at ~985 °C is due to the transformation of metakaolin to a spinel-type structure, which is reported to be a γ-Al_2O_3 and alumino-silicate spinel [6]. These measurements are very important in optimizing fast-fired porcelain bodies' profiles.

Table 2
Chemical analysis of the raw materials

Constituents (wt.%)	Raw materials			
	Clay	Potash feldspar	Soda feldspar	Quartz
SiO_2	45.41	66.81	70.23	98.66
Al_2O_3	34.39	18.08	18.11	0.39
Fe_2O_3	1.13	0.24	0.05	0.07
TiO_2	0.89	0.11	0.04	0.01
CaO	1.07	1.03	0.91	0.10
MgO	0.76	0.23	0.23	0.02
K_2O	0.42	10.94	0.31	0.12
Na_2O	0.87	1.69	9.95	0.09
L.O.I.	14.67	0.58	0.20	0.37

Table 3
Chemical composition of porcelain bodies used in the study

Constituents (wt.%)	Body	
	C1	C2
SiO_2	61.83	62.86
Al_2O_3	29.64	29.65
Fe_2O_3	0.92	0.81
TiO_2	0.73	0.59
CaO	1.07	1.03
MgO	0.60	0.61
K_2O	3.58	0.40
Na_2O	1.12	3.60

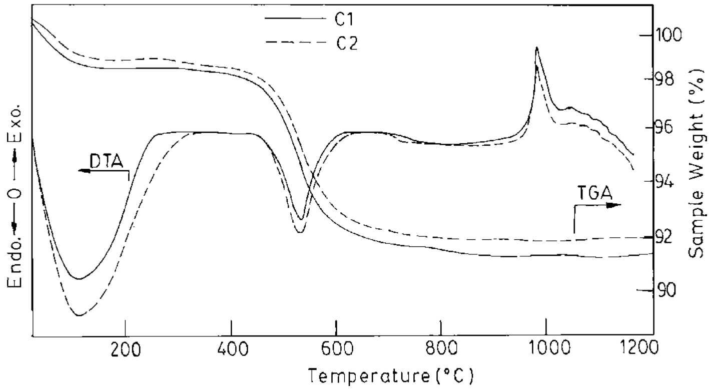

Fig. 1. DTA–TGA curve of the compositions.

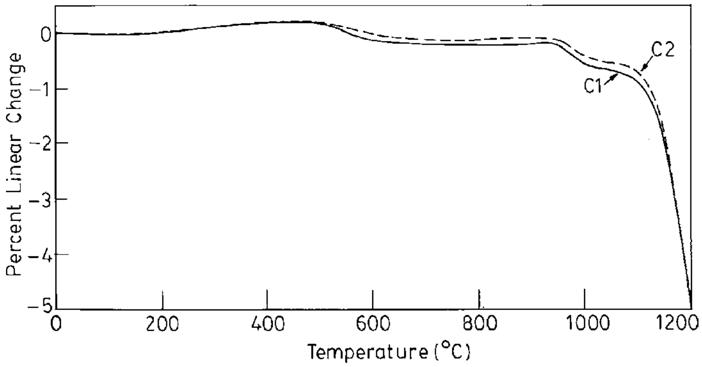

Fig. 2. Variation in percentage linear change of the compositions with temperature.

The plot of percent linear change with temperature (Fig. 2) illustrates the densification behaviour of compact green samples of C1 and C2 compositions with temperature. The test is conducted at a constant heating rate (10 °C/min) up to 1200 °C. Initial increase in length is observed due to thermal expansion of the material. Then distinct changes in the curves are seen at around 530 °C when kaolin transforms to metakaolin by the dehydroxylation process. After removal of lattice water, the clay matrix starts shrinking, followed by its conversion into a spinel-like structure at around 980 °C. These observations are also supported by the results of DTA–TGA discussed earlier. Slow and steady shrinkage of the clay matrix continued up to 980 °C, beyond which a rapid shrinkage is observed due to formation of liquid phases when feldspar starts to melt. As the temperature further continues to increase, porosity is eliminated by the viscous flow of glassy phases, which finally results in densification.

The differential shrinkage plot (Fig. 3) indicates the rate of densification achieved at a specific temperature. For both the compositions, a remarkable increase in densification rate is observed at above 1100 °C. Comparison of two compositions shows that C2 (soda-feldspar-containing composition) undergoes maximum densification at 1171 °C compared to a higher temperature (1195 °C) for C1 (potash-feldspar-containing composition). Hence, soda-feldspar-containing porcelain composition can be densified at a temperature of 1171 °C, which is 24 °C lower than the temperature required for the

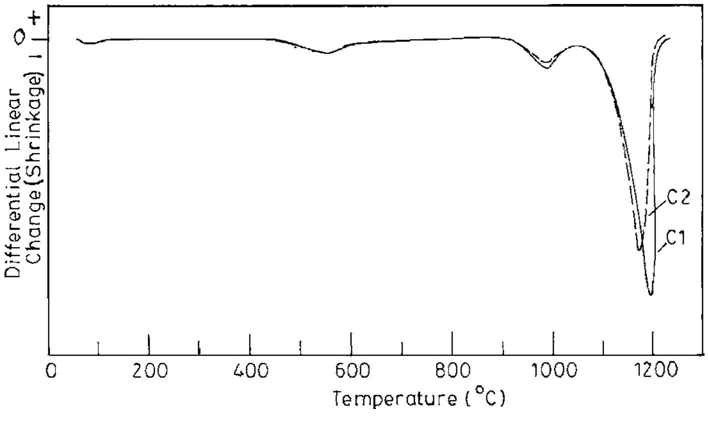

Fig. 3. Differential shrinkage plot of the compositions.

potash-feldspar-containing composition. The densified samples of dilatometric study were tested for BD and %WA to verify their degree of vitrification. The results are given in Table 4.

The variation in physico-mechanical properties and colour of the samples fired in an electric furnace at different temperatures are graphically represented in Fig. 4a–e.

It may be seen from Fig. 4a that there is no significant difference in shrinkage value between the two

Table 4
Bulk density and percent water absorption of the samples densified in dilatometer

Composition	Peak densification temperature (°C)	BD (gm/cc)	%WA
C1	1195	2.39	0.45
C2	1171	2.41	0.27

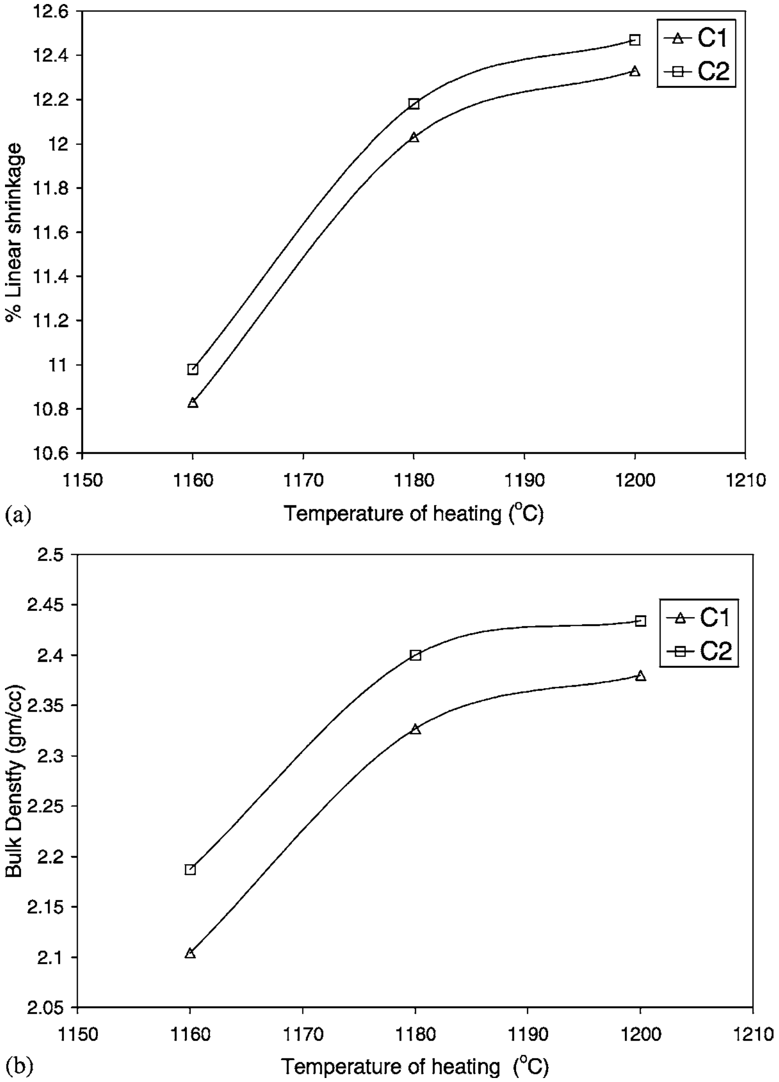

Fig. 4. Variation in physicomechanical properties and *L*-value of C1 and C2 bodies with heating temperature: (a) vs. % linear shrinkage; (b) vs. bulk density; (c) vs. % water absorption; (d) vs. flexural strength; (e) vs. *L*-value.

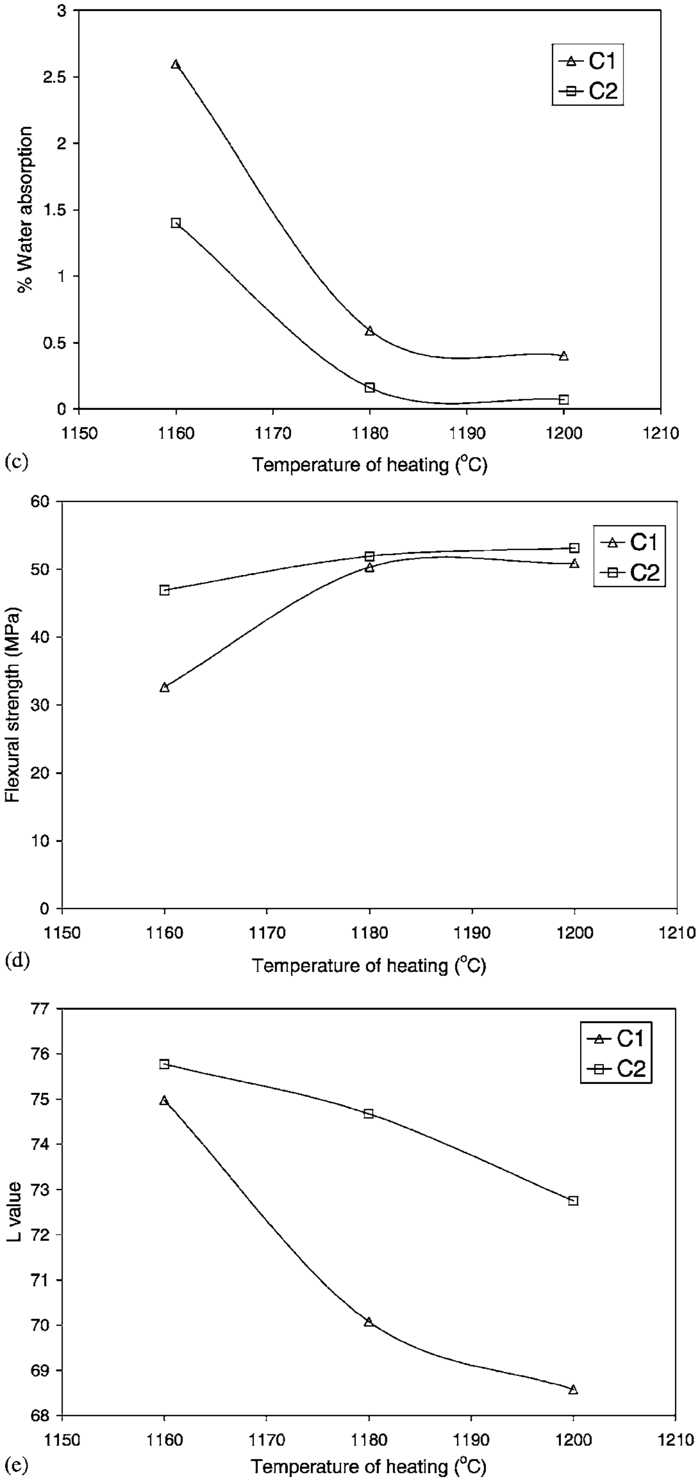

Fig. 4. (*Continued*).

compositions. Fig. 4b displays the variation in bulk density with heating temperature. The value continued to increase, and reached a maximum value at 1200 °C in both the cases. The C2 body achieved higher bulk densities at all temperatures. As expected, %WA decreases with increase in heating temperature (Fig. 4c) due to elimination of pores through liquid phase sintering. The figure further indicates that C2 achieved vitrification (%WA $\sim$ 0.16) at 1180 °C compared to 1200 °C for C1 (0.59% WA). This result also supports the observations made from dilatometer studies (Table 4). This is probably due to increased mobility of glass when sodium oxide is included at the expense of potassium oxide. The same phenomenon of glass mobility is also observed in case of K_2O- and Na_2O-containing glazes during firing [18]. This difference of 20 °C is of great importance technologically to the manufacturers of vitrified porcelain ware in order to save thermal energy. Fig. 4d shows the flexural strength of the samples fired in the range of 1160–1200 °C. The flexural strength increased with an increase in firing temperature and reached maximum values of around 51 MPa for C1 and 53 MPa for C2 composition. The increase in flexural strength with increase in bulk density was also observed by other authors [19] for triaxial porcelain compositions. Theoretically, flexural strength developed in a porcelain body is maximum when apparent porosity decreases to zero. A similar trend is observed in the present study also. In modern day technology for the production of vitrified porcelain ware, particularly for tiles, greater attention is paid to the industrial development of white base body. The resulting vitrified porcelain samples obtained in the present investigation were subjected to colour measurement using the opponent-colour coordinate system developed by Hunter [20]. In this system, the third coordinate describes the lightness of colour and is usually denoted by L. The results are graphically represented in Fig. 4e. It may be observed that the L-value decreases as the body approaches vitrification at higher temperatures. This is probably due to increased intensity of colour-forming oxides Fe_2O_3 and TiO_2 present in the raw materials at higher temperatures. It may also be noted that the soda-feldspar-containing composition (C2) showed higher L-value (whiter) due to the presence of lower amounts of Fe_2O_3 and TiO_2 compared to the potash-feldspar-containing composition (C1).

4. Summary

The sequence of chemical reactions during thermal heating of potash- and soda-feldspar-containing triaxial porcelain compositons has been studied using DTA–TGA technique. Both the compositions followed similar reaction steps up to1000 °C, beyond which feldspar forms eutectic melt and starts reacting. The difference in their densification behaviour has been studied using high temperature dilatometer. The soda-feldspar-containing composition exhibits maximum densification rate at 1171 °C compared to 1195 °C for the potash-feldspar-containing composition. A separate set of pressed samples heated in an electric furnace to temperatures of 1160–1200 °C showed almost similar densification behaviour. The soda-feldspar-containing composition achieved higher BD (2.43 gm/cc), lower %WA (0.07%) and highest flexural strength (53.14 MPa) at 1200 °C compared to potash-feldspar-containing composition. The whiteness of potash-feldspar-containing body is poorer than soda-feldspar-containing body due to increased amount of Fe_2O_3 and TiO_2 impurities present in it.

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References

[1] W.D. Kingery, Introduction to Ceramics, Wiley, New York, 1976, pp. 78, 532.
[2] J.F. Schairer, N.L. Bowen, Am. J. Sci. 245 (1947) 196, 199, 201.
[3] W.M. Carty, U. Senapati, J. Am. Ceram. Soc. 81 (1) (1998) 3.
[4] Annual minerals review, Am. Ceram. Soc. Bull. 76 (6) (1997) 65.
[5] Materials handbook, Ceram. Ind. 146 (1) (1997) 41.
[6] G.W. Brindley, M. Nakahira, J. Am. Ceram. Soc. 42 (7) (1959) 311, 314, 319.

[7] H.B. Johnson, F. Kessler, J. Am. Ceram. Soc. 52 (4) (1969) 199.
[8] G.W. Brindley, M. Nakahira, J. Am. Ceram. Soc. 40 (10) (1957) 346.
[9] K.J.D. Mackenzie, I.W. Brown, R.H. Meinhold, M.E. Browden, J. Am. Ceram. Soc. 68 (6) (1985) 293, 298.
[10] K. Okada, N. Otsusa, J. Ossaka, J. Am. Ceram. Soc. 64 (10) (1986) C-251.
[11] B. Sonuparlak, M. Sarkiaya, L.A. Aksay, J. Am. Ceram. Soc. 70 (11) (1987) 837.
[12] K.H. Schiller, Trans. Brit. Ceram. Soc. 63 (1964) 102.
[13] S.T. Lundin, NBS Misc. Publ. 257 (1964) 93.
[14] Y. Iqbal, W.E. Lee, J. Am. Ceram. Soc. 82 (12) (1999) 3584.
[15] M. Paganelli, Am. Ceram. Soc. Bull. 81 (11) (2002) 25.
[16] S. Kumar, K.K. Singh, P. Ramachandra Rao, J. Mater. Sci. 36 (2001) 5917.
[17] S.M. Hohnson, J.A. Pask, Am. Ceram. Soc. Bull. 61 (1982) 838.
[18] J.R. Taylor, A.C. Bull, Ceramics Glaze Technology, Pergamon Press, New York, 1986, p. 22.
[19] O.I. Lee, Z. Nakagawa, Ceram. Int. 28 (2002) 131.
[20] R.S. Hunter, J. Opt. Soc. Am. 32 (1942) 509.