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The effect of boron containing frits on the anorthite formation temperature in kaolin–wollastonite mixtures

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Abstract

In order to investigate the effect of boron containing frits on anorthite formation temperature in kaolin–wollastonite mixture, four different frit compositions containing boron were prepared according to Seger formulas. One of these compositions also contained lead. Four different batches composed of 40 mass% kaolin, 40 mass% wollastonite and 20 mass% frit were prepared. The linear dilatometric (LD) curves of the batches were determined and subsequently the firing schedule (FS) curves were obtained from the LD curves. Cylindrical pellets prepared from each of the batches were fired in an especially designed furnace up to respectively 950, 975, 1000, 1025, 1050 °C. The firing period including the cooling process was adjusted to 210 min. The variation of the bulk densities of the products as a function of temperature were examined. X-ray diffraction (XRD) patterns of the products were also determined and it was observed that the minimum anorthite formation temperature was 1000 °C. Since it was known that with batches not containing any frit, the minimum anorthite formation temperature was 1100 °C, it was understood that leaded or unleaded boron containing frits decreased the anorthite formation temperatures around 100 °C.

Keywords: Anorthite; Firing; Frits; Glazes; Porcelain; Wollastonite

1. Introduction

Kaolin, feldspar and quartz are used as raw materials in conventional porcelain production.[1] If the raw material ratios are changed or feldspar and quartz are replaced by some other materials, the characteristics of the prepared porcelains change.[2,3] In the conventional production processes, biscuit firing is usually carried out at temperatures between 900 and 1000 °C for 22–24 h depending on the type of the porcelain and then glazing firings are carried out at firing temperatures between 1300 and 1450 °C for another 24–36 h. The firing properties vary depending on the types of the raw porcelain batch components and their particle size distribution.[4,5] Considerable amount of energy is consumed during the conventional double firing porcelain production that is based on the formation of 3:2 mullite ($3Al_2O_3.2SiO_2$) at rather high temperatures during long periods.[6] High energy consumption as well as the deformations resulting from the variations in volume during the $\alpha \Longleftrightarrow \beta$ phase transformation of quartz that occurs at 573 °C are among the major disadvantages of double firing porcelain production. Therefore, great importance has been attributed to single firing porcelain production from raw material mixtures containing small quantities of quartz.[7–9]

Single firing porcelains are based on the formation of the anorthite phase ($CaO.Al_2O_3.2SiO_2$).[10,11] For anorthite formation, wollastonite ($CaO.SiO_2$) or similar minerals are added as a source of calcium into kaolin that is a source of aluminium and silicium.[2,12–14] Kaolinite [$Al_2Si_2O_5(OH)_4$], the major clay mineral of kaolin, transforms into metakaolinite ($Al_2O_3.\ 2SiO_2$) around 500 °C.[6,15] Examination of the temperature-mass percent phase diagram of the wollastonite–metakaolinite system shows that the minimum temperature of anorthite formation is around 1100 °C.[16] It was noted that frits were added into kaolin-wollastonite mixtures, in order to economise energy by decreasing anorthite formation temperatures.[17–19] Frits are glassy materials that

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are used for glazes in single- and double- firing porcelain productions.[20–26] Although some toxic elements such as lead might have some positive contributions towards glazing, their presence in frit compositions are usually not desired due to their toxic properties.[27] In this respect, the aim of this study was to decrease the anothite formation temperatures in kaolin–wollastonite mixtures by introducing boron containing frits into their compositions.

2. Materials and method

2.1. Materials

The Küre (Söğüt, Bilecik, Turkey) kaolin (KK) was supplied by the Mining Reseach and Exploration Institute of Turkey. The regional map of this kaolin and the rheological characteristics of its aqueous suspension were already given in a previous study.[28] The Bayramiç (Çanakkale, Turkey) wollastonite (BW) was supplied by Çanakkale Ceramic Industries. Orthoclase and quartz were supplied by Eczacıbaşı Esan Doğa Mining Corporation (İstanbuł, Turkey). Borax and boric acid were supplied by Etibank Borax and Boric Acid Industries (Bandırma, Turkey). Commercially pure potassium carbonate and sodium carbonate were used in the experiments.

The suspension obtained by the self dispersion of kaolin in water was stirred at a rate of 1700 min^{-1} and homogeneized and its wet sieve analysis was made. Its fraction which passed through a 0.053 mm (270 mesh) sieve was dried at 105 °C until it attained costant mass and its particle size distribution (PSD) was determined by an Andreasen pipette according to the literature.[29] The total of wet kaolin fraction that passed through a 0.125 mm sieve was used in the experiments.

Wollastonite was crushed into pieces smaller than 5 mm successively in jaw and conical crushers and then dry ground in a ball mill such that all of it would pass through a 0.125 mm sieve. The PSD was determined as for kaolin. Similarly, wollastonite that passed through a 0.125 mm sieve was used in the experiments.

The X-ray diffraction patterns (XRD) of kaolin and wollastonite were determined by a PW 1730 Philips diffractometer after being dried at 105 °C for 24 h. $\text{Cu}K_\alpha$ X-rays and a Ni filter were used for the determinations. The differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) curves of the same materials were determined by a Netzsch instrument (Simultaneous Thermal Analysis, Model 429); Heating rate 10 K min^{-1} and $\alpha\text{-Al}_2\text{O}_3$ as inert material. The chemical analysis (CA) of kaolinite, wollastonite and quartz was made by an atomic absorption spectrophotometer (Hitachi Z-8200), according to the standard procedure applied to silicate minerals.

2.2. Preparation of the frits

Some of the raw materials used in glazing are soluble in water. If certain amounts of these materials are mixed and melted and then cooled, amorphous frits that are insoluble in water are obtained. The optimum molar amounts of the metal oxides contained in frits are given by the Seger formulas.[25, 30–33] For this study, the molar amounts of four frits, one of them leaded (F1) and three of them unleaded (F2, F3 and F4) were determined together with their stoichiometric mass percents and presented in Table 1.

The raw frit mixtures were dry ground in a ball mill and homogenized, then melted in quartz crucibles at 1050 °C. The molten masses were abruptly poured into distilled water to obtain a solid that was amorphous to a large extent. The frits were dried at 105 °C until they attained constant mass and then they were ground to pass through a 0.125 mm sieve by a Fritsch Planetary Mill Pulverisette 5 instrument. Their true densities were measured according to standard procedure ASTM C-188 CE 110 by a picnometer by using kerosene ($\rho = 0.76$ g cm^{-3}). They were then humidified by an aqueous carboxymethylcellulose solution and pressed to obtain pellets whose diameters and heights were respectively 1 and 0.5 cm. The softening and half-sphere temperatures of the prepared pellets were determined by heating in a furnace that was designed to contain a lens system that permitted the observation of the interior of the furnace.

2.3. Batch preparation and firing

The chemical formula of the anorthite phase can be represented as $\text{CaO.Al}_2\text{O}_3\text{.2SiO}_2$. According to this formula it contains 43.2 mass% SiO_2, 36.6 mass% Al_2O_3

Table 1
The Seger formulas used in the preparation of frits and the mass percents of chemicals in the mixtures

Frit labels	Seger formulas (as mole)	Chemicals in the mixture (as mass%)
F1	1 PbO	48.3% Pb_3O_4
	2 SiO_2	25.4% SiO_2
	1 B_2O_3	26.3% H_3BO_4
F2	1 NaO	32.0% SiO_2
	3 SiO_2	68.4% $\text{Na}_2\text{B}_4\text{O}_7\text{.10H}_2\text{O}$
	2 B_2O_3	
F3	1 K_2O	31.7% SiO_2
	3 SiO_2	43.7% H_3BO_4
	2 B_2O_3	24.5% K_2CO_3
F4	0.45 Na_2O	8.9% SiO_2
	0.45 K_2O	34.2% $\text{Na}_2\text{B}_4\text{O}_7\text{.10H}_2\text{O}$
	0.10 CaO	7.4% K_2CO_3
	0.20 Al_2O	41.4% KAlSi_3O_8
	1.80 SiO_2	3.4% CaSiO_3
	0.60 B_2O_3	

and 20.2 mass% CaO. In order to achieve the formation of anorthite it was determined stoichiometrically that the mass percents of kaolinite [$Al_4Si_4O_{10}$ $(OH)_8$] and wollastonite ($CaO.SiO_2$) had to be approximately equal in the raw batch. In this respect, primarily a batch consisting of 50 mass% kaolin and 50 mass% wollastonite was prepared and labeled as P0. Then, several batches were prepared by mixing 40 mass% kaolin, 40 mass% wollastonite and 20 mass% frit. The mixtures that were prepared by F1, F2, F3 and F4 frits were respectively labeled as P1, P2, P3 and P4. The raw batches were dry ground in a ball mill, homogeneized and put in the form of pellets under a pressure of around 100 MPa without using any binder. The diameters of the pellets were 1 and 5 cm. First, the pellets of 5 cm diameter and 2–3 mm height were cut in a direction parallel to the cylindrical axis and rods of at least 30 mm length were obtained. The linear dilatometric curves of the raw batches were determined by using these rods. A Netzsch STA 429 instrument was used for these determinations. The firing schedule (FS) curves were derived from the LD curves.[5,23,32] A rotating furnace was especially designed and built in order to realize the firing according to the FS curves[33]. Then, the raw porcelain pellets of 1 cm were heated up to the respective maximum temperatures 950, 975, 1000, 1025, 1050 and 1075 °C according to the FS curves. The firing period including the cooling period was chosen as 210 min. The bulk densities of the obtained P1, P2, P3 and P4 products were determined by taking the volumes of the products as equal to the volumes of mercury that they displaced. The P0 batch was fired at 1000 °C and P0 product was obtained. To understand whether anorthite has been formed or not, the P0–P4 products were dry ground to form powders and their XRD patterns were determined. The adsorption and desorption isotherms of nitrogen at 77 K on the P0 and P2 products that were obtained by firing the corresponding batches at 1000 °C were determined. A volumetric adsorption instrument connected to high vacuum [34] was used for the determinations.

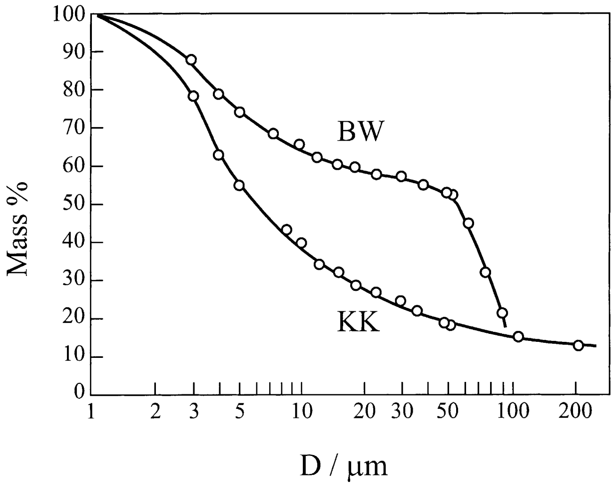

Fig. 1. The particle size (D) distributions of the Küre kaolin (KK) and Bayramiç wollastonite (BW).

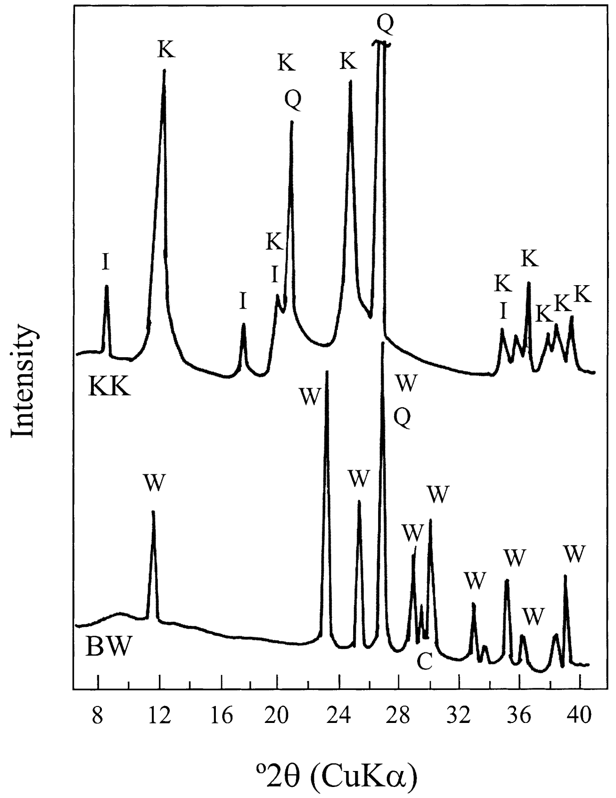

Fig. 2. The XRD patterns of kaolin (KK) and wollastonite (BW) (K: kaolinite, I: ıllite, Q: quartz, W: wollastonite, C: calcite).

3. Results and discussion

3.1. Characterization of raw materials

The particle size (D) distribution curves of kaolin and wollastonite are shown in Fig. 1. It was observed that wollastonite particles were coarser and the curves were rather close to each other. From the XRD patterns shown in Fig. 2, it was observed that kaolin (KK) contained kaolinite (K) as the major clay mineral as well as quartz (Q) and a small amount of illite (I). BW contained wollastonite and small amounts of calcite (C), and quartz (Q). The exothermic peak between 200 and 400 °C in the DTA curve of kaolin (Fig. 3) resulted from combustion of organic materials, determined as 4 mass% from the TGA curve. The endothermic peak between 500 – 600 °C in the DTA curve resulted from the dehydroxylation of kaolinite, and the associated mass loss was determined as 6% from TGA. The exothermic peak between 900 and 1000 °C resulted from the recrystallization of kaolinite without any mass loss. The DTA curve of wollastonite showed an endothermic peak between 700 and 800 °C resulting from decomposition of

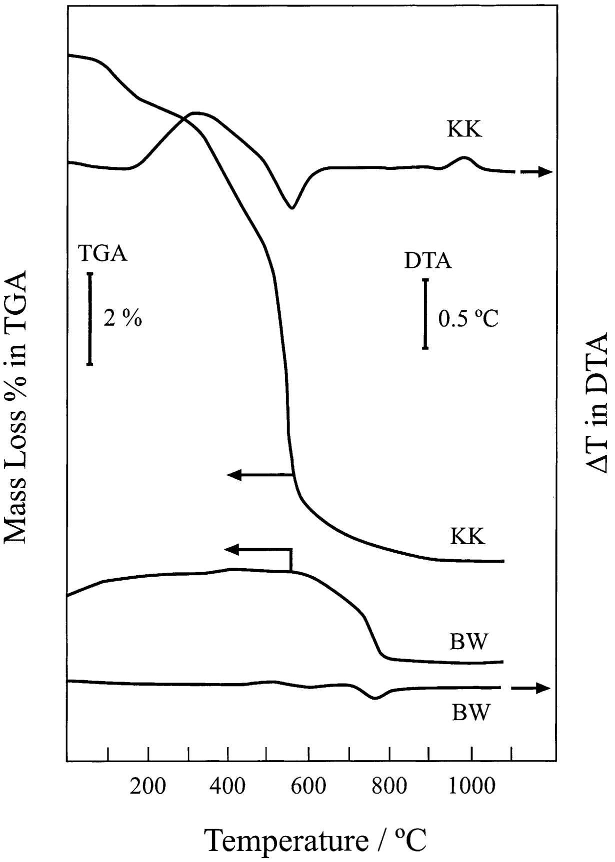

Fig. 3. The TGA and DTA curves of kaolin (KK) and wollastonite (BW).

calcite with a mass loss of 2% from TGA. The chemical compositions of kaolin, wollastonite and quartz are presented in Table 2. The LOI values of kaolin and wollastonite correspond approximately to the respective total mass loss values determined from the TGA curves.

3.2. Characterization of frits and firing properties

Concerning the four frits, the true density (ρ), softening point (t_1) and half-sphere point (t_2) and the difference between these temperatures ($\Delta t = t_2 - t_1$) are presented in Table 3. The fact that the temperature differences were large and half-sphere temperatures were around 850 °C showed that the prepared frits were suitable for liquid phase sintering.

Table 2
The chemical analysis results of kaolin, wollastonite and quartz (LOI represents the loss on ignition)

Raw materials	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
Kaolin	63.10	21.42	1.13	0.90	0.95	0.50	0.40	0.75	10.35
Wollastonite	52.00	0.50	0.01	0.30	45.00	0.80	–	–	1.39
Quartz	99.10	0.20	–	0.10	0.20	0.10	0.10	0.20	–

Table 3
The densities, softening temperatures (t_1) and half-sphere temperatures (t_2) of the frits

Frits	ρ/ g cm^{-3}	t_1 /°C	t_2 /°C	Δt/°C
F1	3.78	775	850	75
F2	2.40	780	850	70
F3	2.89	728	830	102
F4	2.73	788	820	132

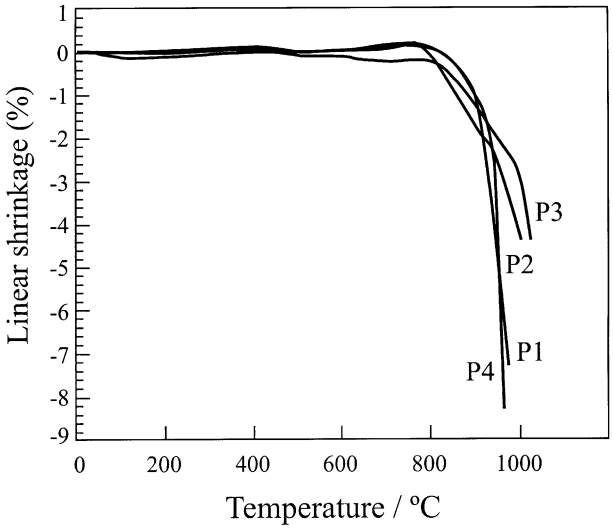

Fig. 4. The linear dilatometric (LD) curves of the batches.

The LD curves of raw batches are shown in Fig. 4. An important shrinkage or elongation was not observed between 25 and 800 °C. Over 800 °C, due to the melting of frits and their flow towards the pores between the particles, a viscous sintering occurs and a linear shrinkage between 4 and 8% is observed at 1000 °C.

It was observed that the LD curves of the products almost fitted one into another up to 900 °C. The theoretical firing schedule (FS) curves derived from those curves are shown in Fig. 5. The FS curves show the relationship between the firing temperature and firing period. The raw batches were fired according to these

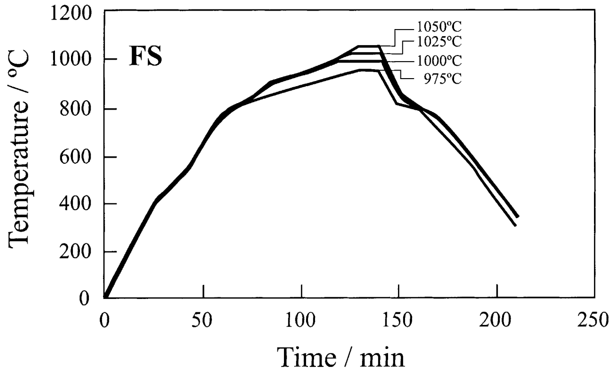

Fig. 5. The firing schedule (FS) curves that have different maximum temperatures.

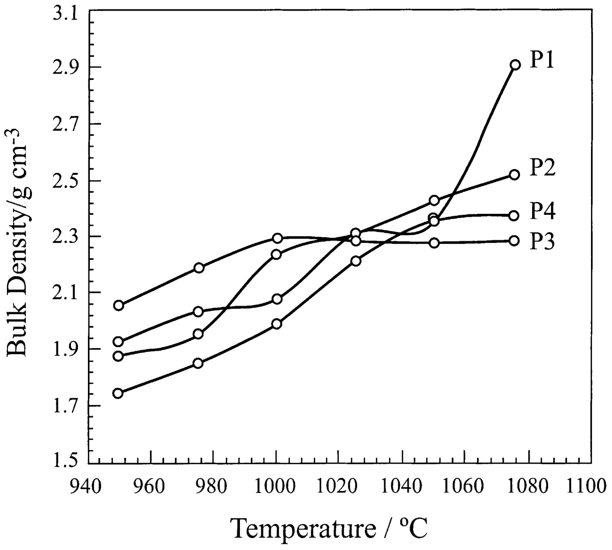

Fig. 6. The variation of the bulk densities of the batches as a function of the firing temperature.

FS curves and the variations of their densities as a function of maximum firing temperatures are shown in Fig. 6. The fact that the densities increased as the firing temperatures increased showed that liquid phase sintering has occured. The XRD patterns of the P0 product that was obtained by the firing of P0 sample that did not contain any frit were similar to the XRD patterns of wollastonite shown in Fig. 2. In these patterns, there was no peak indicating the presence of either kaolinite or anorthite therefore, it was understood that kaolin was recrystallized and anorthite was not formed at 1000 °C. The XRD patterns of the other products that contained frits that were fired for 210 min by varying the maximum temperatures between 950 and 1050 °C were examined and it was understood that the formation of anorthite began at 1000 °C. Since the XRD patterns of all of the frit containing fired products were similar to each other, only the XRD patterns of the P2 product that was fired respectively at 1000, 1025 and 1050 °C are presented as examples in Fig. 7. It was observed that anorthite (A), quartz (Q) and β-wollastonite (βW) were contained in the fired products. It was thought that excess quartz that was contained in KK was left unchanged during sintering and wollastonite-metakaolinite phase diagram [16] indicates that if the mass% of metakaolinite is smaller than 65%, βW is formed between 1000 and 1200 °C. The intensity of the characteristic anorthite peak observed at $2\theta \approx 28°$ did not change appreciably as the firing temperature increased between 1000 and 1050 °C. Such a behaviour indicates that the formation of the anorthite phase has been completed at 1000 °C and leads to the conclusion that boron containing products that are based on anorthite phase formation may be produced by a single and fast firing process whose maximum temperature is 1000 °C.

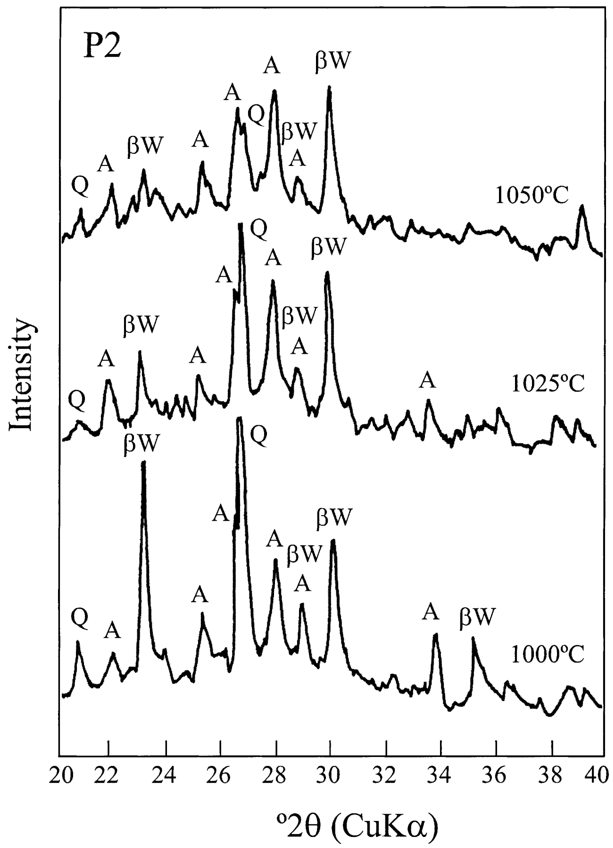

Fig. 7. The XRD patterns of the P2 products that were fired up to different maximum temperatures (A: anorthite, βW: β-wollastonite, Q: quartz).

According to the Brunauer, Emmett, Teller procedure,[35,36] the specific surface areas (A) of the P0 and P2 products were calculated respectively as 3.24 and 0.25 $m^2\ g^{-1}$ by using the data of adsorption of nitrogen at 77 K.The volume of liquid nitrogen that was not yet desorped at a relative equilibrium pressure of $p/p^0 = 0.96$ was taken as the micro-mesopore volume in the solid.[37,38] The specific micro-mesopore volumes (V) of the P0 and P2 products were calculated respectively as 0.023 and 0.014 $cm^3\ g^{-1}$ by using the data of desorption. Since, the A and V values of the P2 product were within the error limits of measurement it was understood that sintering had occured.

4. Conclusion

In this study, it was determined that leaded and unleaded boron containing frits decreased the anorthite formation temperature from 1100 to 1000 °C in kaolin-wollastonite mixture. It was observed that introduction of lead into the frit composition had no favorable effect towards a decrease in anorthite formation temperature. This observation is favorable considering the possible disadvantages of lead such as toxicity in porcelain batches. A decrease of 100 °C in anorthite formation temperature is prone to lead to considerable energy economy in single firing porcelain production.

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References

1. Shüller, K. H., *Porcelain, in Ceramic Monographs—A Handbook of Ceramics*. Verlag Schmidt GmbH, Freiburg, 1979.
2. Kurczyk, H. G., Synthetic diopside and synthetic wollastonite—new raw materials for ceramics. In *Advances in Ceramics*, ed. P. Vincenzini. Faenza, Italy, 1976, pp. 22.
3. Reiger, K. C., *Ceram. Eng. Sci. Proc*, 1996, **17**, 180.
4. Villagas-Palacio, S. and Dinger, D. R., *Am. Ceram. Soc. Bull.*, 1996, **75**, 71.
5. Villagas-Palacio, S. and Dinger, D. R., *Am. Ceram. Soc. Bull.*, 1996, **75**, 79.
6. Restrepo, J. J., Dinger, D. R. and Funk, J. E., *Ceram. Eng. Sci. Proc*, 1993, **14**, 116.
7. Sladek, R., *Interceram*, 1986, **35**(4), 35.
8. Grosjean, P., *Interceram*, 1986, **35**(5), 23.
9. Kirsch, M., Berger, G., Banach, U. and Hübert, T., *Interceram*, 1988, **37**(3), 34.
10. Sletson, L. C. and Reed, J. S., *Am. Ceram. Soc. Bull.*, 1988, **67**(8), 1403.
11. Lepkova, D., Vassileva, V. and Ionchev, Hr., *Interceram*, 1990, **39**(6), 24.
12. Sainamthip, P. and Reed, J. S., *Am. Ceram. Soc. Bull.*, 1987, **66**, 1760.
13. Sandoval, F., Ibanez, A., Beltran, V., Gonzalez Pena, J.Ma. and Amoros, J. L., *Interceram*, 1990, **39**(6), 24.
14. Mihailescu, M., Emandi, M., Vancea, V. and Marcu, M., *Interceram*, 1990, **39**(6), 17.
15. Chakravorty, A. K. and Ghosh, D. K., *J. Am. Ceram. Soc.*, 1991, **74**, 1401.
16. Levin, E., Robins, C. and Murdie, H.Mc., *Phase Diagrams for Ceramists*. Am. Ceram. Soc. Inc, Columbus, OH, 1964.
17. Gonzalez Pena, J.Ma., Coma Diaz, C. and Alvarez-Estrada, D., Wollastonite based porcelains of low firing temperature. In *Energy and Ceramics*, ed. P. Vincenzini. Elsevier Scientific Pub, Amsterdam, 1980, pp. 125.
18. Bridger, K. E., *Interceram*, 1985, **34**(3), 15.
19. Mörtel, H., *Ber. DKG*, 1986, **63**(1-2), 9.
20. Lorici, L. and Brusa, A., *Ceram. Eng. Sci. Proc*, 1991, **12**(1-2), 183.
21. Benlloch, A. E., *Ber. DKG*, 1992, **69**(1-2), 210.
22. Benlloch, A. E., *Ber. DKG*, 1992, **69**(7-8), 258.
23. Bittner, H. G., Halex, G. and Kobras, U., *Ber. DKG*, 1992, **69**(11-12), 481.
24. Ghorra, G. J., *Ceram. Eng. Sci. Proc*, 1993, **14**(1-2), 77.
25. Norton, F. H., *Elements of Ceramics*, 2nd edn. Addison Wesley Pub, London, 1974.
26. Taylor, J. R. and Bull, A. C., *Ceramics Glaze Technology*. Pergamon Press, Oxford, UK, 1986.
27. Eppler, R. A. and Eppler, D. R., *Ceram. Eng. Sci. Proc*, 1997, **18**(2), 150.
28. Yıldız, N., Erol, M., Baran, B., Sarıkaya, Y. and Çalımlı, A., *Appl. Clay Sci.*, 1988, **13**, 65.
29. Patat, F. and Kirchner, K., *Praktikum der Technischen Chemie*. Walter de Gruyter, Berlin, 1968.
30. Singer, F. and Singer, S., *Industrial Ceramics*. Chapman and Hall, London, 1979.
31. Eppler, R. A. and Eppler, D. R., *Am. Ceram. Soc. Bull.*, 1996, **75**(9), 62.
32. Baran, B., Sarıkaya, Y., Alemdaroğlu, T. and Önal, M., *Commun. Fac. Sci. Univ. Ank.*, 2001, **B47**(1-2), 1.
33. Baran, B., *Glazes and Self Glazing Porcelain*. Ankara University, Graduate School of Natural and Applied Sciences, Ankara, 1988.
34. Sarıkaya, Y. and Aybar, S., *Commun. Fac. Sci. Univ. Ank.*, 1978, **B24**, 33.
35. Brunauer, S., Emmett, P. H. and Teller, E., *J. Am. Chem. Soc.*, 1938, **60**, 309.
36. Gregg, S. S. and Sing, K. S. W., *Adsorption, Surface Area and Porosity*. Academic Press, London, 1982.
37. Sarıkaya, Y., Ada, K., Alemdaroğlu, T. and Bozdodan, Í., *J. Eur. Ceram. Soc.*, 2002, **22**, 1905.
38. Ada, K., Sarıkaya, Y., Alemdaroğlu, T. and Önal, M., *Ceram. Int.* (in press).