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Preparation of low melting temperature, lead-free glaze by the sol–gel method

Soheila Adl, Ismail. A. Rahman*

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

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Abstract

The sol–gel method was used to prepare low melting temperature, lead-free glaze based on the Na_2O–K_2O–CaO–ZnO–B_2O_3–Al_2O_3–SiO_2 system. Tetraethoxysilane and aluminium sec-butoxide were used to replace silica and alumina, high melting constituents of the raw materials. A homogeneous gel was obtained through sequential hydrolysis by using 5 mol of water per mol of alkoxides, a mixture of ethanol and 2-butanol as solvent, and HCl as catalyst (pH $\sim$ 3). The remainder of the raw materials was processed to be coated by the gel. Gel as the coating layer was observed to be amorphous and homogeneously bonded around the raw materials particles and was very effective in lowering the melting temperature of the glaze by 30–130°C. This, however, depends on the amount of metal alkoxides used for replacement. TEM, SEM and porosimeter were used to characterize the glaze samples.

Keywords: Lead free glaze; Sol–gel preparation

1. Introduction

The thin, glassy layer on a ceramic body that results from applying a special admixture and fusing it on at high temperature is called ‘glaze’. Glaze is widely prepared by the conventional method in which the raw materials constituents are mechanically mixed and ground. However, the method is not efficient to produce a very homogeneous glaze batch that is necessary to make the glaze melts at low temperature.

One alternative to lower the melting temperature is by the introduction of modifiers in the form of alkaline and alkaline-earth oxides, but following drastic changes in thermal properties, surface tension and viscosity of the glaze put a strict limit on this method. Among alkaline oxides, lead oxide has long been a valuable component of many glazes ranging from those in the lowest melting temperature to those of the highest quality. Although glaze industry depends on the use of lead, the mounting worldwide concern about the health risk has resulted in a further tightening of lead legislation.

Many attempts have been made to seek alternatives to lead-containing glaze. [1–6] However, unleaded glaze types which have been identified as having potential for industrial take up still lack flexibility in terms of application and firing. [7]

Makishima and Nagata [8] reported lowering of melting temperature of glaze in the system Na_2O–K_2O–CaO–ZnO–Al_2O_3–SiO_2. However, the details of the sol–gel process condition and the appearance of the final glaze were not reported in their study. In this work we studied the application of the sol–gel method to lower the melting temperature of glaze by adopting the system reported by Makishima and Nagata [8]. The details of the work involve the process, heat treatment behaviour and microstructure of the glaze in order to understand the critical factor that contribute to the lowering of melting temperature of the glaze. Two glaze batches were prepared by the conventional method and by mechanically mixing of the raw materials and the dried gel in order to compare their melting behaviour and microstructure with the ones prepared by the the sol–gel method.

2. Experimental

2.1. Glaze composition

Composition of the glaze in the form of oxides and minerals percentage (glaze recipe) as adopted from

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* Corresponding author. Fax: +604-6574854.
E-mail address: arismail@usm.my (I.A. Rahman).

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Makishima and Nagata [8] are shown in Tables 1 and 2 respectively.

Composition of the G series of glazes in which silica and alumina of the raw materials were replaced partly or completely by tetraethoxysilane and aluminium sec-butoxide respectively are shown in Table 3.

Other constituents of the raw materials such as sodium oxide, potassium oxide and calcium oxide were replaced by sodium carbonate, potassium carbonate and calcium nitrate. The chemicals replacing the raw materials constituents had the same chemical composition as the ones that were replaced. The resultant glaze batches were represented by "G*n*" where "*n*" denoted the percentage of metal alkoxides (gel) used for replacement (it was assumed that metal alkoxides completely convert to gel).

Table 1
Glaze composition in the form of oxides percentage

Oxides	Content (%)
SiO_2	64.0
Al_2O_3	11.7
B_2O_3	2.6
Na_2O	3.4
CaO	10.8
K_2O	1.2
ZnO	5.0
Fe_2O_3, TiO_2, SO_3, P_2O_5	1.3

Table 2
Glaze composition in the form of mineral percentage

Raw materials	Content (%)
Feldspar	50
Quartz	10
Borosilicate glass powder	20
Lime	10
Clay	5
Zinc oxide	5

Table 3
Composition of G*n* series glaze

Raw materials		G15	G35	G50	G65	G85
Feldspar	(50%)	F[a]	F	70%F +30%gel	40%F +60%gel	gel
Quartz	(10%)	gel	gel	gel	gel	gel
Clay	(5%)	gel	gel	gel	gel	gel
Glass powder	(20%)	[d]Gp	gel	gel	gel	gel
Zinc oxide	(5%)	Z[b]	Z	Z	Z	Z
Lime	(10%)	L[c]	L	L	L	L
Total gel	(%)	15	35	50	65	85

[a] F = feldspar.

[b] Z = zinc oxide.

[c] L = lime ($CaCO_3$).

[d] Gp = glass powder.

2.2. Preparation of glaze by the conventional method

The fine powder of the raw materials of the glaze recipe were mixed and blended to produce a uniform batch, sieved through a 100 mesh sieve. The melting temperature of the resultant glaze was 1030°C. This batch was donated as reference glaze (G0).

2.3. Preparation of glaze by mechanically mixing of the raw materials and the dried gel

Tetraethoxysilane (TEOS) and aluminium sec-butoxide were hydrolysed separately with 4 and 3 mol of water per 1 mol of each alkoxide, HCl and ammonia were used as catalysts, ethanol and 2-butanol as solvents. The resultant gels were dried at 100°C, crushed into a powder form and mixed mechanically with the rest of the raw materials powder. The amount of gel was 65% of the batch. This glaze melted at 1030°C.

2.4. Preparation of glaze by the sol–gel method by sequential hydrolysis

Tetraethoxysilane (TEOS) was prehydrolysed by 1 mol of water per 1 mol of TEOS in ethanol under stirring. Then aluminium sec-butoxide dissolved in 2-butanol was added. The obtained alkoxide complex solution was hydrolysed by adding aqueous solution of sodium carbonate and alcoholic solution of calcium nitrate. After that, the remainder of the raw materials were added under vigorous stirring. HCl, 1 M, was used as the catalyst. The resultant gel was left to form a stiff gel (to shorten the gelling time, sometimes a dilute solution of ammonia was used after addition of acid, but the pH was still acidic). The pH of sol and dilute gel was measured by using pH indicator paper. Then, the gel was dried at 100°C, ground into powder and heated at 850–1030°C.

2.5. Characterization of the glaze

Heat treatment of samples was carried out in an electric furnace (Vestar, UK) in air at 850–1030°C with a heating rate of 10°C min^{-1}. The samples were soaked at each temperature for 2 h.

SEM micrographs of the gel powder and melted glaze were obtained by using a Cambridge S360 model. The sample was sprinkled (powdered sample) or attached (small piece of melted glaze) to an aluminium stub with double-sided tape and sputtered with a very thin layer of gold. Light micrographs of the glazes were obtained from a reflected microscope model Olympus BH2.

TEM observations were made by Philips type CM12. Dilute dispersion of powder of samples (0.1 g powder in 20 ml of 1:1 alcoholic mixture of ethanol and 2-botanol) were prepared ultrasonically for 10 min and a drop of suspension was evaporated on a carbon-coated copper grid.

Surface area and pore size distribution measurements were made by a porosimeter (Micromeritics model ASAP 2000). The absorption of nitrogen was measured at 100°C. X-Ray diffraction was obtained for heated glaze by a Siemens D5000 diffractometer. The Laue method [16] of XRD was used due to fusion of the melted glaze with the porcelain dish (used as the container in the melting process) and difficulty of separation of the glaze from the porcelain dish to prepare powder for common XRD measurement.

3. Results and discussion

3.1. Hydrolysis and formation of alkoxide complex solution

Hydrolysis is the main step in the sol–gel process and its rate has a significant effect on the homogeneity of the gel, structure and properties of the gel-dried product. However, the difference in reactivity of the metal alkoxides toward hydrolysis makes the preparation of homogeneous multicomponents more difficult. A huge number of studies on the preparation of homogeneous, multi-component products have been done through different approaches such as sequential hydrolysis of alkoxides, chelating reactive alkoxide by organic ligands or modification of alkoxide by organic acid [9–12]. In this work, sequential hydrolysis was adopted in order to overcome the problem of inhomogeneity due to the differences in reactivities of TEOS and aluminium sec-butoxide.

TEOS was first prehydrolysed with 1 mol of water per 1 mol of TEOS to form a single chain siloxane oligomer. After addition of aluminium sec-butoxide and an equivalent amount of water, a cloudy complex solution which was believed to contain a linear polymer of an Al–O–Si– bond was formed [10,13]. Makishima and Nagata [8] reported that a clear solution was formed at this stage by using aluminium iso-butoxide. This may be attributed to the low reactivity of aluminium iso-butoxide toward hydrolysis in comparison with aluminium sec-butoxide. Yamane et al. [14] emphasized that a homogeneous gel is obtainable once a clear complex solution was formed. By adopting a technique of Pancrazi [15], a clear solution was obtained when hydrolysis was carried out under flowing nitrogen.

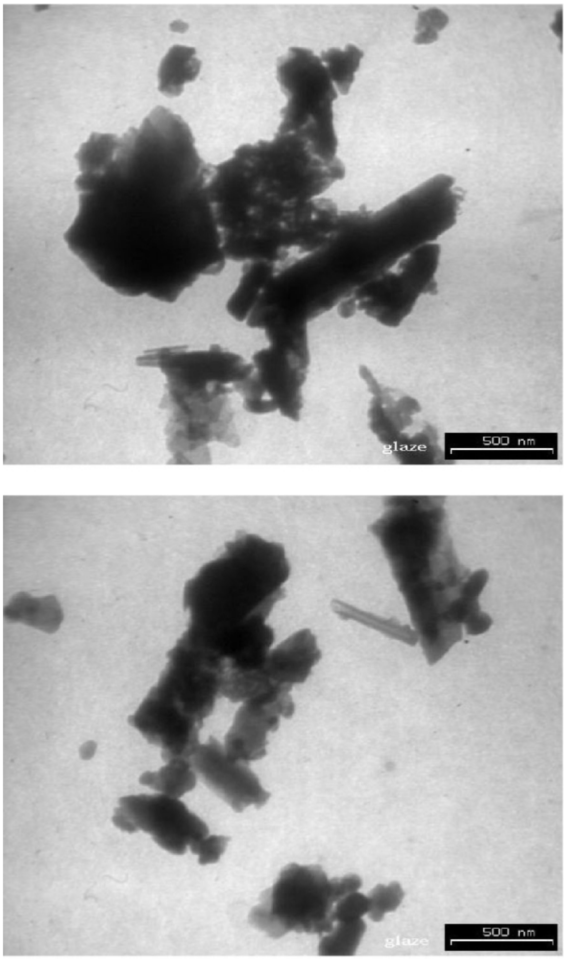

Fig. 1. Transmission electron micrographs of reference glaze (prepared by conventional method).

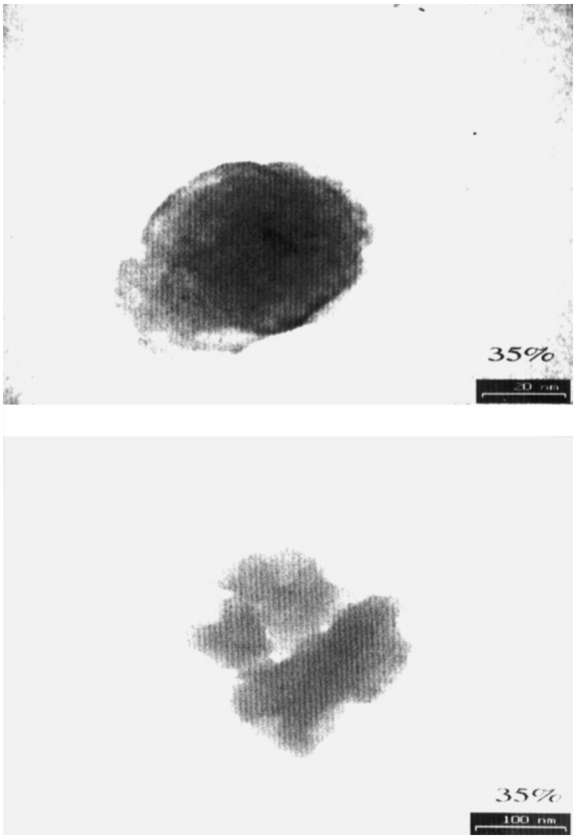

Fig. 2. Transmission electron micrographs of glaze with 35% gel (G35).

Based on the above arguments, it was first believed that a clear solution contributed to the formation of an homogeneous gel which would lower the melting temperature the glaze. However, melting temperatures of the glaze batches (G50) prepared from clear and cloudy solutions were the same (970°C). Thus, it shows that the formation of either a clear or cloudy complex solution does not effect the homogeneity of the gel.

3.2. Microstructure of the gels

Fig. 1 shows TEM of the reference glaze powder which was prepared by mechanically mixing the raw materials. The particles of the raw material are clearly seen. The nature of the glaze powder as obtained by sequential hydrolysis of tetraethoxysilane and aluminium sec-butoxide, after drying at 100°C, are shown in Figs. 2–4. The results show that the gel formed a coating layer around the raw material particles. The coating gel is a thin, low density layer of very fine amorphous material which adheres to the raw material particles. With a small

Table 4
Melting results of glaze

Glaze batch	Gel (%)	Temperature (°C)						
		850	870	900	930	970	1000	1030
Reference glaze G0	0	s/p[c]	s/p	s/p	s/p	s/p	s/p	g[a]
G15	15	s/p	s/p	s/p	s/p	pm[b]	g	g
G35	35	s/p	s/p	s/p	pm	g	g	g
G50	50	s/p	s/p	s/p	pm	g	g	g
G65	65	s/p	s/p	pm	g	g	g	g
G85	85	pm	pm	g	g	g	g	g
Raw materials + dried gel	65	s/p	s/p	s/p	s/p	s/p	pm	g

[a] g = Glass.
[b] pm = Partly melted.
[c] s/p = Sintered or powder.

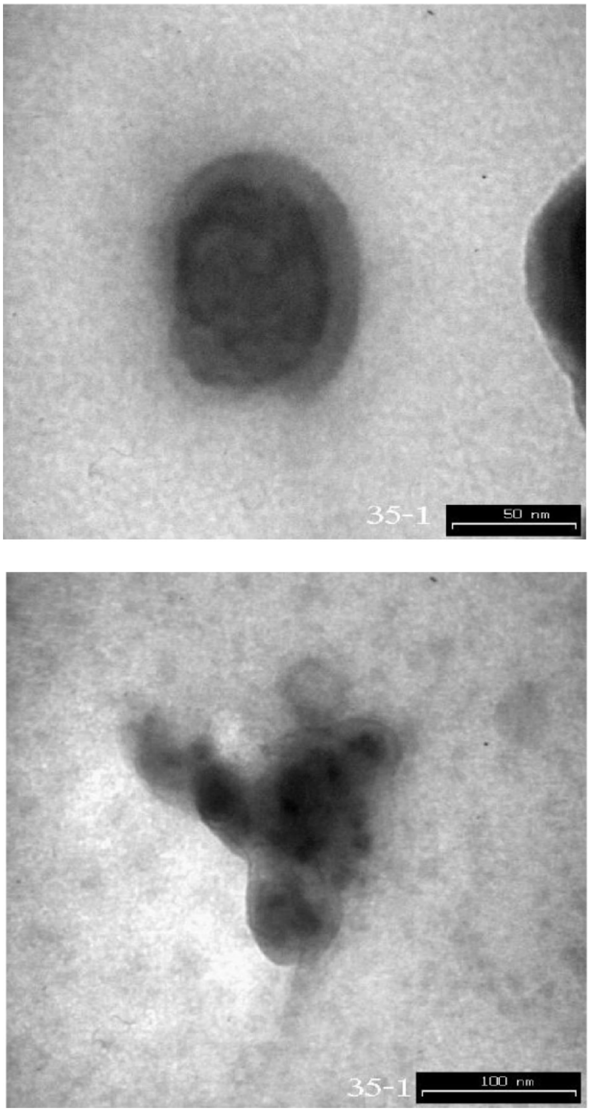

Fig. 3. Transmission electron micrographs of glaze with 50% gel (G50).

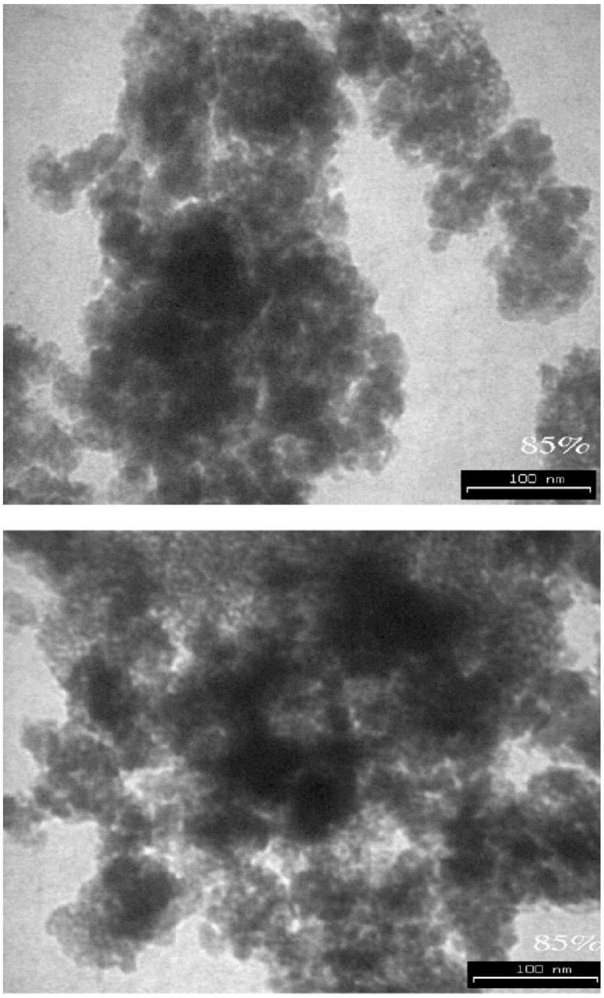

Fig. 4. Transmission electron micrographs of glaze with 85% gel (G85).

amount of gel (15%) it is very difficult to observe the coating gel in the mass of glaze raw materials. It is possible that at this stage, a very thin coating layer forms around the raw material particles, and to observe it, more powerful equipment is required. As the amount of gel increases, the thickness of the coating gel layers increases. Larger amounts of the gel (G85, 85% gel, Fig. 4) lead to the development of clump of agglomerated coated particles which bind together. At this stage, the remaining raw material is only 15% of very fine zinc oxide and calcium carbonate in the mass of the gel lumps. The coating gel increases the specific surface area of the samples. For example, BET measurements for G35 give specific surface area of 122 m^2/g as compared to 6 m^2/g for the reference glaze. The presence of coating materials in a very fine amorphous, and homogeneously distributed form and well-bonded on the particles of high melting temperature raw materials contributes to the lowering of melting temperature of the glaze. From the point of view of "coating", the glazes with 35–50% of gel are sufficiently coated to the raw material particles (feldspar, quartz, zinc oxide and lime) to give a reasonable comparison with the reference glaze (Figs. 2 and 3). In other samples such as G65 and G85, a large amount of raw materials were replaced by the gel. Although the fineness of the particles is one of the most important factors to lower the melting temperature, the role of the coating layer around the raw material particles seem to be more important. It can be seen from the melting result of

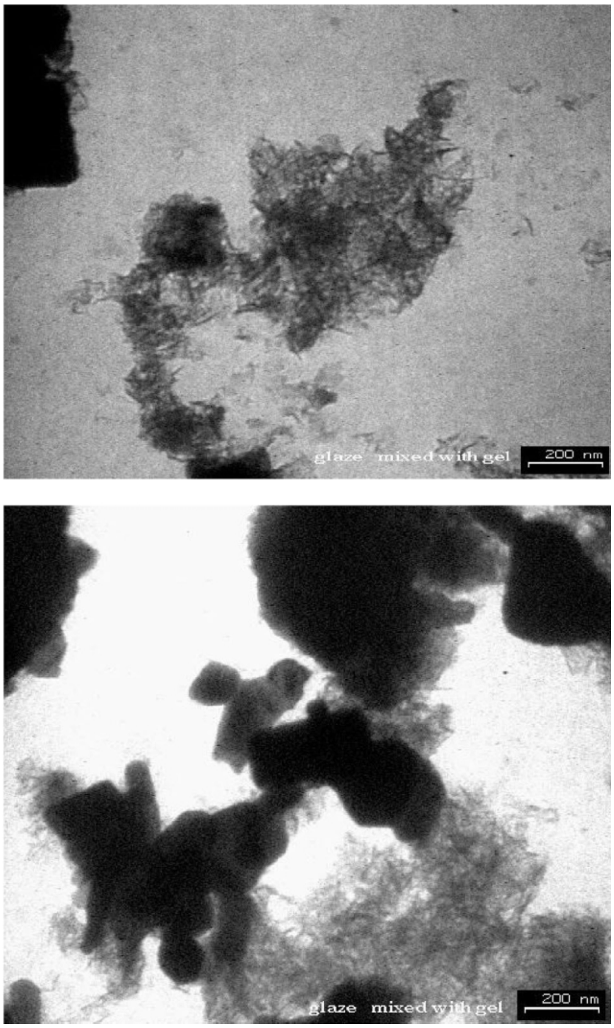

Fig. 5. Transmission electron micrographs of glaze prepared by mechanical mixing of raw materials and 65% dried gel.

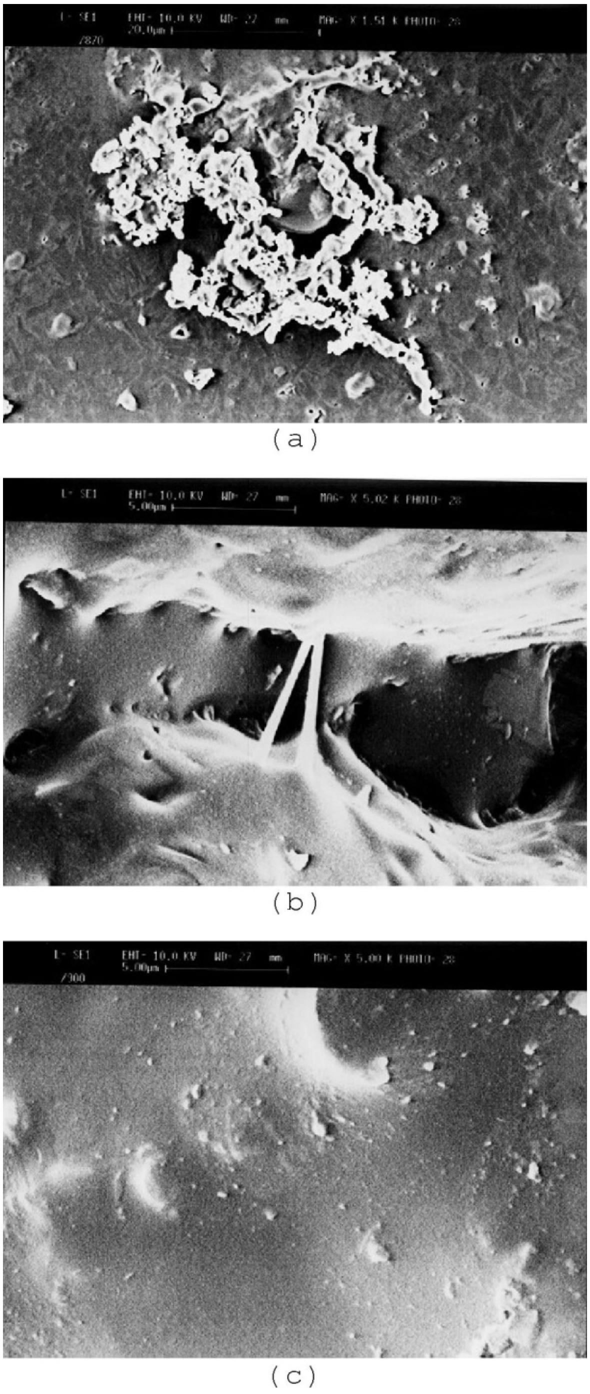

Fig. 6. Scanning electron micrographs of melted glaze with 85% gel: (a) at 870°C; (b) and (c) at 900°C.

the glaze batch prepared by mechanically mixing the raw materials and dried gel (Table 4). In this batch, the overall particle sizes are finer than the reference glaze due to the replacement of the clay, glass powder, quartz and part of the feldspar by dried gel, but the melting temperature is the same as the reference glaze. TEM in Fig. 5 shows the sample consists of separated aggregate of raw material particles and the gel.

Fig. 6 shows SEM micrographs of the G85 glaze melted at 870 and 900°C. For G85 heated at 870°C, the surface of the glaze is not smooth and the unmelted part of the glaze is clearly seen (Fig. 6a), which means a temperature of 870°C is not high enough to melt the batch completely. The formation of glass in fibrous shape (Fig. 6b) and smooth surface of the glaze (Fig. 6c) are definitely representative of the complete melting and vitrification of the sample during the heating and cooling process of the glaze.

X-ray diffraction (Laue method) analysis of G85 and G65 batches heated at 900 and 930°C respectively, verified the amorphous nature of the glazes (Fig. 7). Although the melted glazes did not quench immediately after soaking time, crystal formation did not occur, that shows the batch is resistant to devitrification caused by crystallization.

3.3. Heat treatment of the glaze

Fig. 8 shows the appearance of melted glaze with different amount of gel as compared to the reference glaze (no gel). The melted glaze with 85% gel, G85, (Fig. 8b) appears whiter in colour, more bright, transparent and fluid than the one with 35% gel, G35, and reference gel, G0, (Fig. 8c and a). It is observed that a slight darker colour of G35 and G0 samples is attributed to the

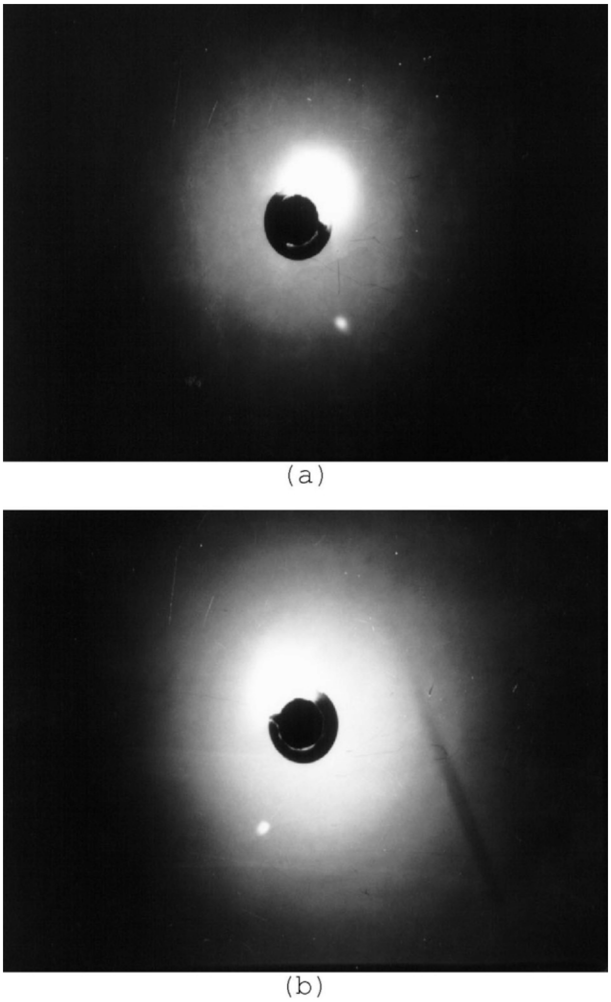

Fig. 7. X-ray diffraction of (a) glaze with 85% gel heated at 900°C and (b) glaze with 65% gel heated at 930°C.

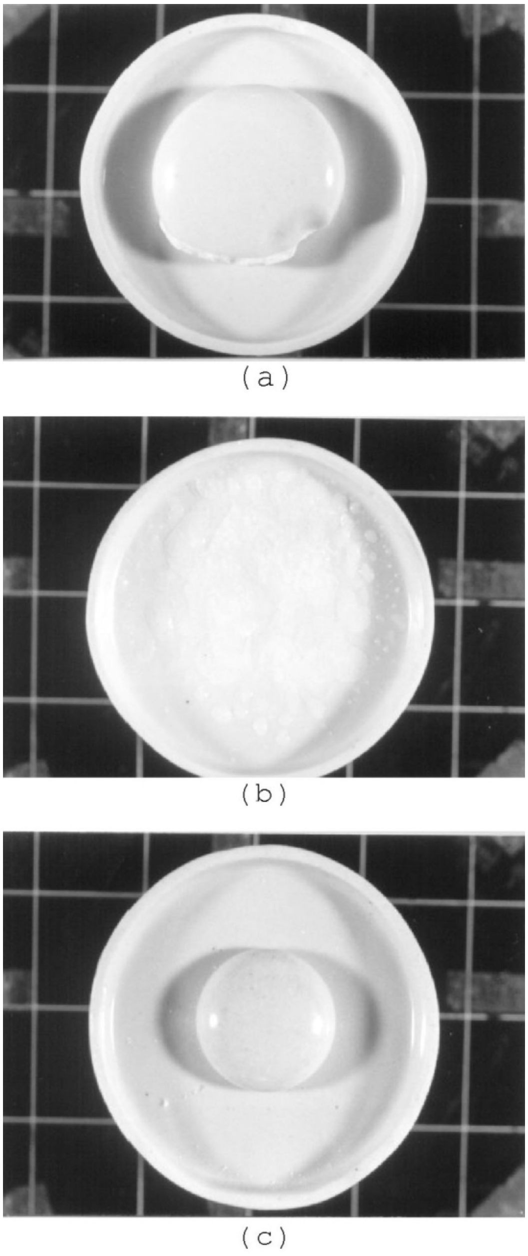

Fig. 8. Appearance of melted glaze (a) reference glaze, G0, (b) glaze with 85% gel, G85, and (c) glaze with 35% gel, G35.

presence of iron and chromium oxides in the feldspar. This shows that replacement of the raw materials by appropriate alkoxides produced a glaze with improved colour, brightness and transparency. Some researchers [9–11] reported that heat treatment often brought about blackening of the gel due to incomplete hydrolysis or residual organic compounds which could not easily be evaporated out of the gel.

Table 4 shows melting results of the G*n* series glazes, the reference glaze and glaze with mechanically mixing of the raw materials and the dried gel. Overall observation shows that increases in the amount of metal alkoxide reduces the glass formation temperature (the melting temperature) of the glaze by 30–130°C with the maximum amount of alkoxide replaced by raw materials up to 85%. However, the melting temperature of the glaze batch which was prepared by mechanically mixing the raw materials and the dried gel was similar to the reference glaze. Makishima and Nagata[8] succeeded in lowering the melting temperature of a series of glaze batches by 50–150°C by replacement up to 100% of the glaze components with metal alkoxides and metal salts. However, the appearance (colour) of the glaze was not mentioned in their study.

4. Conclusion

It was found that the sol–gel process was effective to lower the melting temperature of lead-free glaze. The prepared glaze showed some valuable properties of the leaded glaze such as brilliant appearance, low melting temperature and resistance to devitrification. It was observed that the glaze batch series were prepared by the sol–gel process in which powder of the raw materials was coated by gel, melted at a lower temperature than the one prepared by the conventional method and the one by mechanically mixing of the raw materials and the dried gel.

These observations suggested gel-coated particles of the raw materials took on surface characteristics of the coating material and then showed improved characteristics in the heating state. The melting temperature lowered by 30–130°C depending on the amount of the metal alkoxides used for replacement up to 85%.

Acknowledgements

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References

[1] P. Thometzek, UK Patent Application GB 2265619 A, 1993.
[2] V.K. Marghusian, Y. Eftekhari, Br. Ceram. Trans. 93 (2) (1994) 61–64.
[3] P.R. Jackson, Br. Ceram. Trans. 94 (4) (1995) 171–173.
[4] R.A. Eppler, Glazes and enamels, in: Ulhmann, Kreidl (Eds.) Glass Science and Technology, Vol. 1, Academic Press, New York, 1983, pp. 301–337.
[5] R.A. Eppler, D.R. Eppler, Am. Ceram. Soc. Bull. 75 (9) (1996) 62–65.
[6] R.O. Knapp, Br. UK Pat. Appl. GB2294261, April 1996.
[7] S. Alsop, Br. Ceram. Trans. 93 (2) (1994) 77–79.
[8] A. Makishima, T. Nagata, J. Non-Cryst. Solids 100 (1988) 519–522.
[9] B.E. Yoldas, J. Non-Cryst. Solids, 38- 39 (1980) 81.
[10] S. Saka, K. Kamiya, J. Non-Cryst. Solids 42 (1980) 403.
[11] M. Guglielmi, J. Carturun, J. Non-Cryst. Solids 100 (1989) 243.
[12] S. Doeuff, M. Henry, C. Sanchez, J. Livage, J. Non-Cryst. Solids 89 (1987) 206.
[13] M. Nagami, J. Non-Cryst. Solids 178 (1994) 320.
[14] M. Yamane, S. Inoue, K. Nakazawa, J. Non-Cryst. Solids 178 (1994) 320.
[15] F. Pancrazi, J. Phalippou, F. Sorrentino, J. Zarzycki, J. Non-Cryst. Solids 63 (1984) 85.
[16] R.A. West, Solid State Chemistry and its Applications, John Wiley & Sons, 1984, p. 143.