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DEVELOPMENT OF LOW THERMAL EXPANSION COEFFICIENT (TEC) GLAZE FOR ANORTHITE-BASED CERAMICS

RINGKASAN: Produk-produk seramik terdiri daripada pelbagai jasad seramik seperti "earthenware", "stoneware", "porcelain" dan "bone china" atau "bone china" sintetik. "Bone china" atau "bone china" sintetik merupakan yang paling menyerlah kerana lebih putih, kuat dan lut cahaya. Jasad seramik berasaskan anortit yang setara dengan "bone china" sintetik atau "e-bone" di samping mempunyai sifat putih dan lut cahaya, ia juga mempunyai pekali kembangan termal (TEC) yang rendah sekitar $5.20 \times 10^{-6}/K$. Seramik berasaskan anortit dihasilkan menggunakan abu sintetik sebagai komponen major bersama lain-lain lempung. Abu sintetik dibuat daripada pengkalsinan kalsium karbonat, silika dan aluminium tri-hidroksida. Ianya mengandungi anortit sebagai fasa major, korundum dan kuarza sebagai fasa minor. Jasad seramik berasaskan anortit sukar dipadankan dengan gerlis biasa dan menimbulkan masalah keretakan dan "crazing" disebabkan "strain" yang terhasil kerana nilai 'TEC' antara gerlis dan jasad yang tidak sepadan. Gerlis dengan 'TEC' yang lebih rendah daripada $5.20 \times 10^{-6}/K$ sedang dibangunkan dengan menggunakan bahan-bahan mentah yang mempunyai nilai 'TEC' yang rendah. Lebih enam puluh (60) formula gerlis termasuk yang menggunakan bahan rendah nilai 'TEC' seperti petalit, spodumen dan litium karbonat dikaji. Tiga (3) formula gerlis berasaskan petalit menunjukkan keputusan yang memberangsangkan di mana nilai 'TEC'nya sepadan dengan jasad serta menunjukkan permukaan gerlis yang licin, berkilat dan tanpa "crazing". Kebanyakan gerlis yang rendah nilai 'TEC'nya mempunyai suhu pembakaran yang lebih tinggi dengan permukaan yang "matt". Sifat-sifat gerlis nilai 'TEC' rendah dijelaskan dalam kajian ini.

ABSTRACT: Ceramic products consist of various types of ceramic bodies such as earthenware, stoneware, porcelain and bone china or synthetic bone china. Bone china and synthetic bone china are the most impressive because of their excellent whiteness, strength and translucency. The anorthite-based ceramic body which is equivalent to synthetic bone china or e-bone with respect to their whiteness and translucency, also has a lower thermal expansion coefficient (TEC) of about $5.20 \times 10^{-6}/K$. The anorthite-based ceramic body was produced by using the synthetic ash as a major component with addition of other clays. The synthetic ash was produced by calcining calcium carbonate, silica and aluminum trihydroxide as the

starting materials. It contains anorthite as the major phase and corundum and quartz as the minor phases. The anorthite-based ceramic body has difficulty to suit with the ordinary glaze. Cracking and crazing problem caused by strain effect due to the TEC mismatch of the glaze and the body are common. A low TEC glaze of less than $5.20 \times 10^{-6}/K$ is being developed to suit the anorthite-based ceramics body by introducing low TEC glaze materials. More than sixty (60) glaze formulations including those using low TEC materials such as petalite, spodumen and lithium carbonate were studied. Three (3) petalite-based glaze formulas have shown promising results where their TEC values matched that of the body, with smooth and shining surface without crazing. Majority of the lower TEC glazes tend to have high firing temperature with matt surface. The properties of the low TEC glazes are described in this study.

Keywords: Petalite, anorthite, synthetic bone ash, synthetic bone china and thermal expansion

INTRODUCTION

Naturally, anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) is the end member of plagioclase feldspar with a relatively low density of 2.76 gcm^{-3} (Gautron *et al.*, 1996). Anorthite has triclinic, orthorhombic and hexagonal form. Tri-clinic phase is the most stable at all temperatures (Hong *et al.*, 1999) but all phases can be synthesized in the laboratories. Several of anorthite synthesis methods using various starting materials and process were reported (Kobayashi and Kato, 1994, Chen and Shang, 1997). Ceramic products consist of various types of ceramic bodies such as earthenware, stoneware, porcelain and bone china or synthetic bone china. In terms of appearance, bone china and synthetic bone china are the most impressive because of their better whiteness, strength and translucency.

Capoglu and Messer (2004) have worked on low-clay whiteware using coarse and fine chamotte (prefired material) and clay to design the body of white, translucent, high strength and low thermal coefficient of $4.7 \times 10^{-6}/C$. Capoglu and Kutbay (2002) studied the rheological and slip casting behaviour of low-clay containing translucent whiteware and found that it was possible to produce the body by slip casting technique with assistance of deflocculant and binder.

The anorthite-based ceramic body which is equivalent to synthetic bone china or e-bone with respect to their high degree of whiteness and translucency, also has a lower thermal expansion coefficient (TEC) of about $5.20 \times 10^{-6}/K$ (Doll Said and Saidin, 2007). The anorthite-based ceramic was formulated using 80 % synthetic bone ash or pre-fired material, which was locally produced, as a major component together with 12 % clay and 8 % fluxing material. The body is composed of anorthite and

corundum as a major phase with cristobalite, mullite and glass as minor phase. It was designed to reduce the problems of anisotropic shrinkage and also to be stronger, more translucent and whiter, with similar appearance to bone china.

Glazes are used on a wide diversity of ceramic products and can be regarded as a form of decoration. Essentially, a glaze is a continuous layer of glass, coating the ceramic surface that provides a hard, non-absorbent, impermeable, easily clean surface and allows for variety of colours and surface textures (Watson, 1980). Besides enhancing the aesthetic-artistic worth of the finished ceramic product, it also adds strength to the ware and helps prevent chipping.

Three important elements in glaze are silica, flux and refractory. Silica is the principal glass forming material. Silica alone would form a glaze, but its melting point is high, about 1700°C. To lower the high melting point of silica, flux materials must be added. Flux is a compound of which gives the effect of lowering the melting point of the glaze. In fact, a better melt is obtained if more than one flux is used (Ryan and Radford, 1987). The flux materials for this glaze are ZnO from zinc oxide, CaO from calcium carbonate, K₂O from feldspar, Al₂O₃ from feldspar and SiO₂ from silica and feldspar.

Glaze has direct influence upon the mechanical strength of the ceramic body which is glazed. Every failure of bodies always appears first on the surface. The state of the body is determined by the nature of its surface. The effect of glaze on body strength can be considered by chemical and physical factors. Chemical factor is the relationship between chemical composition of glaze and body. The physical factor is the effect of thermal coefficients of glaze and body. The linear thermal coefficient of expansion is the change of length per unit temperature (Dinsdale, 1993). The value of thermal expansion coefficient represents the degree to which a glaze will expand and contract in firing process. It is an indicator of amount of crazing (or shivering) which might be expected of glaze fired on particular body. In an ideal state, if the glaze and the body has equal coefficient of thermal expansion, the glaze and the body will have the same amount of expansion. However, if moisture expansion occurs due to the penetration of moisture into porous body, the glaze will eventually craze. If the glaze expands more than the body, the glaze will shrink more than the body and results in tensile stress on cooling. The stress will cause crazing on glaze and reduced mechanical strength. If the glaze has lower expansion than the body, the glaze contracts less than the body and result in compression on cooling. If the compression stress is high, the phenomena of "shivering" occurs where the glaze peels-off from the edge of the ware. If the glaze has a slightly lower coefficient of thermal expansion than the body, the glaze will be in compression and the strength improved.

Since the anorthite-based ceramic body has an average value of low thermal expansion coefficient of about $5.20 \times 10^{-6}/K$ (at 100 °C to 1200 °C), it has difficulty to match with the ordinary glaze. Cracking and crazing problem caused by strain effect due to the TEC mismatch of the glaze and the body are common.

The present study is to develop low thermal expansion coefficient glaze of less than $5.20 \times 10^{-6}/K$ designed for the anorthite-based or synthetic bone china body by using low thermal expansion coefficient materials such as petalite, spodumen and lithium carbonate. Petalite is a compound of lithium-aluminum-silicate that has low thermal expansion coefficient.

More than sixty (60) glaze formulations using various low thermal expansion coefficients materials were studied. Three (3) petalite-based glaze formulas showed promising results where their TEC values matched that of the body, with smooth and shining surface without crazing. The properties of the low TEC glazes are described in this paper.

MATERIALS AND METHOD

The materials used in formulating the glaze were zinc oxide, calcium carbonate, potash feldspar, silica, petalite, aluminum, magnesium carbonate, kaolin and talc as listed in Table 1.

Table 1. List of raw materials used in glaze formulation

No.	Materials	Origin	Supplier
1	Zinc oxide (Readseal)	China	Concord Chemical
2	Calcium Carbonate (UNICO)	Malaysia	Concord Chemical
3	Potash Feldspar (Thunitak)	India	Concord Chemical
4	Silica (SM325)	Malaysia	Sibelco
5	Petalite (Standard)	Zimbabwe	Concord Chemical
6	Alumina (Martoxid)	Germany	Concord Chemical
7	Magnesium carbonate (light)	China	Concord Chemical
8	Kaolin (CKI)	Malaysia	Concord Chemical
10	Talc	China	Concord Chemical

The key raw materials chemical composition is shown in Table 2. Chemical analysis of the glaze key materials were conducted using Shimadzu X-ray Fluorescence Spectrometer. Petalite material chemical content was received from the supplier.

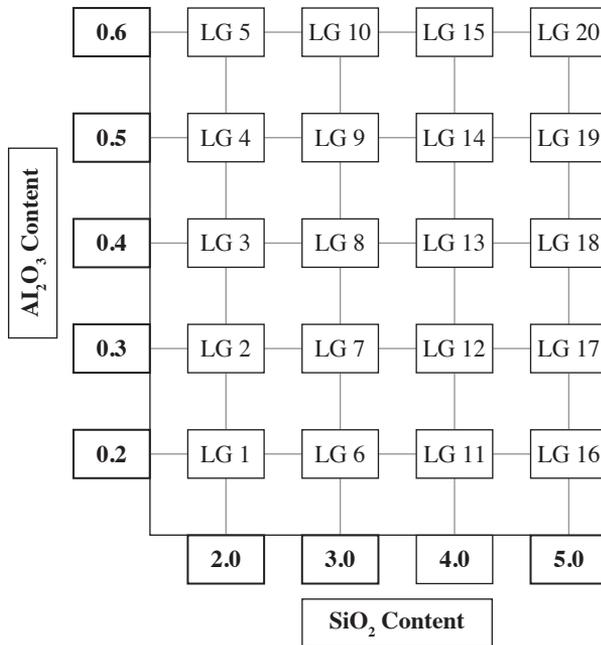
Test specimens of anorthite-based body with size of 4 cm x 4 cm x 3 cm were prepared by slip casting technique. The specimens were dried first before being fired at 1300 °C for 1 hour.

Table 2. List of raw materials used in glaze formulation

Composition (%)	Zinc Oxide (ZnO)	Calcium Carbonate (CaCO ₃)	Potash Feldspar (K ₂ O.Al ₂ O ₃ .6SiO ₂)	Silica (SiO ₂)	Petalite (Li ₂ O.Al ₂ O ₃ .8SiO ₂)	Kaolin (Al ₂ O ₃ .6SiO ₂ .2H ₂ O)
SiO ₂		0.01	65.32	99.7	77.0	78.3
Al ₂ O ₃		0.01	18.26	0.16	17.5	17.4
K ₂ O		0.02	11.52	0.01		0.22
Na ₂ O		0.11	2.58	0.11		2.21
TiO ₂		0.01	0.01	0.05		0.07
Li ₂ O					4.30	
ZnO	99.5					
Fe ₂ O ₃	0.01	0.09	0.19	0.11		0.37
PbO	0.05					
CdO	0.01					
CaO		54.78	0.74			1.23
MgO		1.13	0.62	0.01		0.18
Other oxides	0.43				0.30	
LOI		43.8	0.77	0.01	0.90	9.22

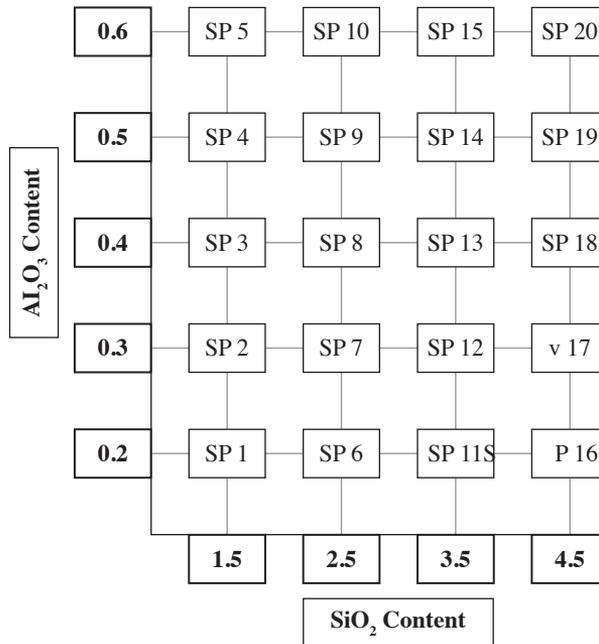
Fifty six various glaze formulations were prepared from the following three groups: (1), (2) and (3). Twenty lime-based glaze formulations from Group 1, denoted as LG 01 to LG 20 were prepared by varying the mole equivalent of alumina and silica as follows:

0.2 K ₂ O	0.2 - 0.6 Al ₂ O ₃	2 - 5 SiO ₂	(Group 1)
0.8 C ₂ O			



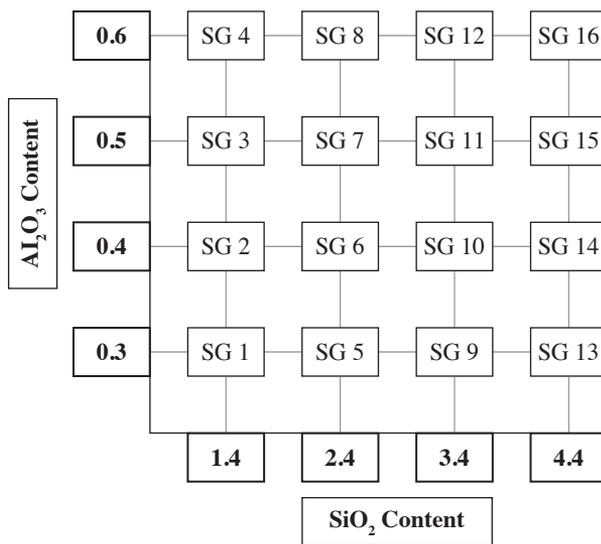
Twenty zinc-based glaze formulations with petalite and limestone from Group 2, denoted as SP 01 to SP 20 were prepared by varying the mole equivalent of alumina and silica as follows:

0.2 Li ₂ O			
0.2 CaO	0.2 - 0.6 Al ₂ O ₃	1.5 - 4.5 SiO ₂	(Group 2)
0.6 ZnO			



Another 16 formulations of zinc-based glaze with petalite, limestone and magnesium carbonate from Group 3, denoted as SG 01 to SG 16 were prepared by varying the mole equivalent of alumina and silica as follows:

0.3 Li ₂ O			
0.324 CaO	0.3 – 0.6 Al ₂ O ₃	1.4 - 4.4 SiO ₂	(Group 3)
0.176 ZnO			
0.2 MgO			



The glazes were prepared by milling the raw glaze materials in the jar mill. The specific gravities were maintained at about 1.6 and the viscosity of the glazes was adjusted by addition of deflocculant. After ageing for an overnight, the glazes were applied by dipping the anorthite-based body specimens. After the specimens had dried, they were fired at 1280 °C for 30 minutes. Out of 56 glazed body specimens, some showed an acceptable glaze appearance but with the crazing effect.

In order to overcome the problem of crazing, the theoretical TEC values of the formulated glazes were calculated using their oxide component, TEC values obtained from literature and using INSIGHT software. Only glazes with TEC values below the body TEC values, $5.20 \times 10^{-6} \text{K}^{-1}$, were considered and prepared. These constitute another 8 additional formulations and denoted as P-1 to P-8 as shown in Table 3:

Table 3. Glaze formulation according to oxides mole equivalent

Oxides	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8
(mole equivalent)								
Li ₂ O	0.42	0.34	0.56	0.27	0.41	0.16	0.14	0.41
MgO	0.08		0.27	0.39	0.39	0.46	0.41	0.03
ZnO	0.50	0.52					0.40	0.44
CaO		0.14	0.09	0.22	0.17	0.25	0.03	0.09
K ₂ O			0.08	0.04	0.01	0.04		0.02
Na ₂ O				0.08	0.018	0.09		0.01
Al ₂ O ₃	0.55	0.57	0.85	0.73	0.57	0.73	0.17	0.66
SiO ₂	3.55	3.69	7.15	7.90	4.32	7.90	4.00	4.39
Calculated TEC (x 10 ⁻⁶ K ⁻¹)	4.95	5.13	4.57	4.57	4.50	4.78	4.39	4.99

The glazes P-1 to P-8 were prepared, applied and fired by the same method as the previous glazes. Out of 8 glazed specimens, only P-1, P-2 and P-3 showed an acceptable result when fired at 1280 °C where they can create suitable glaze coating layer on the body as shown in Figures 1 to 6.

As only glazes P-1, P-2 and P-3 showed acceptable results, more amount of these glazes were prepared to study further on the method of application onto the prototype products. The suitable thickness of the glazes applied before and after firing was monitored by measuring the glaze thickness gauge (before fired) and also by Scanning Electron Microscopy (SEM) for the fired thickness. These glazes were characterized by measuring their actual thermal expansion coefficient, thermal shock resistant and the microstructure. The surface morphology and cross section microstructure were observed by using SEM. Out of three glazes, the P-1 glaze showed the best surface appearance with smooth and shine surface. Glaze P-2 and P-3 showed the smooth surface but was less shiny and developed crystallite structure. Thermal shock test was conducted only on Glaze P-1 (best surface) by heating the specimens from 30 °C to 250 °C with the interval of 50 °C in the oven. The heated specimen was then quenched in cold water at room temperature and the surface properties observed. If no crack was observed, the test was repeated at every interval temperature until the cracks phenomena occur.

The TEC of the glaze samples were prepared by melting it in the alumina crucibles at 1500 °C to 1550 °C in a glass-melting furnace. The molten glazes were then poured into rectangular shaped graphite mould. While the molten glazes had cooled slightly and hardened in the mould, they were immediately transferred into an annealing furnace operating at 500 °C to 600 °C for at least one hour before further cooling to room temperature. After they had cooled, the samples were cut to 1 mm by 1 mm by 20 mm for thermal expansion coefficient test at temperature ranging from 100 °C to 700 °C using Linseis L75/1550 Dilatometer at heating rate of 10 °C/min. Thermal expansion coefficient of the anorthite-based body was also measured.

RESULTS AND DISCUSSION

The formulated glaze P-1, P-2 and P-3 showed reasonably good results where their surface were matured and smooth without cracking problem after being fired at 1280 °C for 30 minutes. Glaze P-4, P-5, P-6, P-7 and P-8 although did not crack but at the same firing temperature, their surface appearance were matt and rough as they were underfired. SEM micrograph shows that Glaze P-1 (Figure 1) showed the best surface appearance; smooth shiny and the glaze spread-out evenly. The surface of Glaze P-2 (Figure 3) was smooth but less shiny with some pinholes. Glaze P-3 (Figure 5) surface was smooth but matt and with more fine pin-holes. Both Glaze P-2 and P-3 showed the development of crystallite structure.

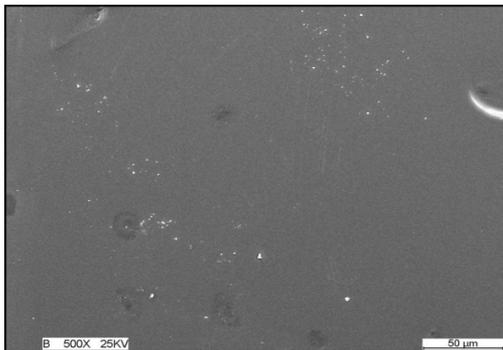


Figure 1. Glaze P-1 surface appearance fired at 1280 °C. Magnification 500x

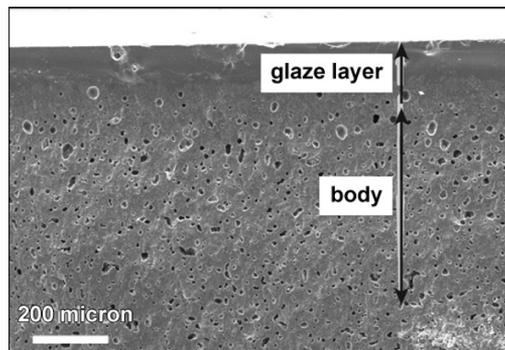


Figure 2. Cross section at glaze-body interface of glaze p-1 fired at 1280 °C. Magnification: 100x

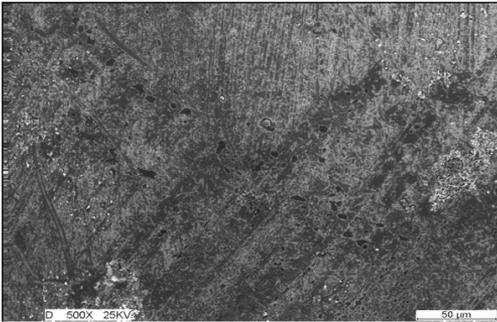


Figure 3. Glaze P-1 surface appearance fired at 1280 °C. Magnification 500x

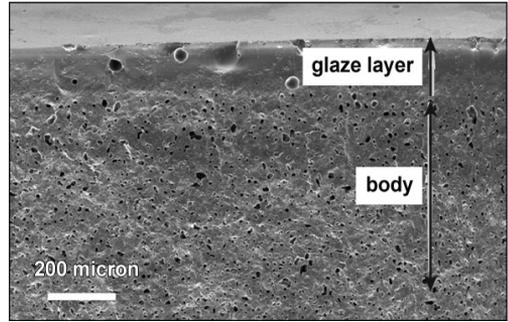


Figure 4. Cross section at glaze-body interface of glaze P-1 fired at 1280 °C. Magnification: 100x

SEM micrographs of the cross section at the glaze-body interface showed that glaze P-1 (Figure 2) was denser and fully melted to form smooth and matured surface. Glaze P-2 (Figure 4) and P-3 (Figure 6) contained more pores and had not fully melted. This showed that they were not fully matured and need to be fired at a higher temperature.

Thickness of glaze and application technique influenced the fired surface behavior. Cracking problem can be avoided by controlling the glaze thickness (P-1 to P-8) of less than 200 μm (0.2 mm) during application by spraying or dipping technique onto the biscuits body.

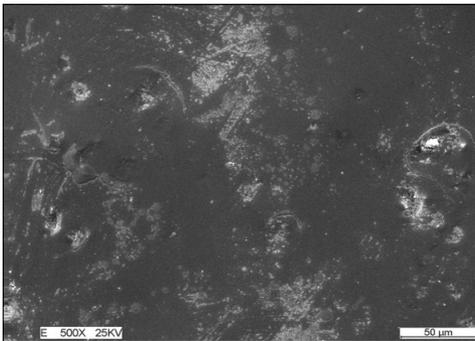


Figure 5. Glaze P-1 surface appearance fired at 1280 °C. Magnification 500x

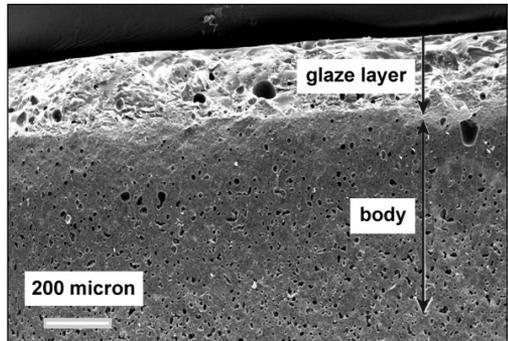


Figure 6. Cross section at glaze-body interface of glaze P-1 fired at 1280 °C. Magnification: 100x

Figure 7 showed that the fired thickness of the glaze (P-1) of less than 100 μm (or less than 200 μm before firing) could avoid the glaze from cracking. Thermal shock resistant test on Glaze P-1 result showed that the glaze could stay at temperatures up to 200 °C before it started to crack (Figure 7).

The results of thermal expansion coefficient of glazes and the anorthite-based body are shown in Figure 8. The average values of thermal expansion coefficient at 30 °C to 700 °C of glaze P-1 was $5.12 \times 10^{-6}/K$ and the glaze P-2 was $4.72 \times 10^{-6}/K$, while the TEC of the anorthite-based body at temperature range 30 °C to 1200 °C was $5.20 \times 10^{-6}/K$. TEC of glaze P-3 cannot be measured because the test specimen cannot be prepared as the sample cannot be fully melted at 1500 °C and was too viscous to pour.

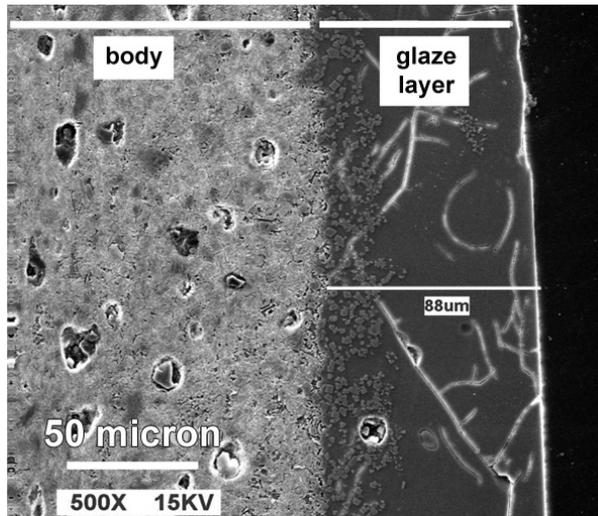


Figure 7. SEM image for 0 wt. % of Silica in Si-BCP after immersion in SBF

Plot of coefficient of thermal expansion against sintering temperature of glazes P-1, P-2 and anorthite-based ceramic body is shown in Figure 8. On cooling state, at temperatures of 550 °C (point A) and 300 °C (point B) respectively, both glazes P-1 and P-2 have their thermal expansion coefficient values turning to below the value of the body. At temperatures about 100 °C to 200 °C (point C) for both glazes P-1 and P-2, thermal expansion coefficient values were at the lowest and have the higher thermal shock resistance property as shown by the thermal shock resistant test (Figure 7). But then at temperature of 50 °C and below, the thermal expansion coefficient values was drastically increased again above the body thermal expansion coefficient values (point D) to a maximum value of $7 \times 10^{-6}/K$. At room temperature (point D), the glaze has potential to crack as it was under strained situation due to the mismatch in thermal expansion coefficient.

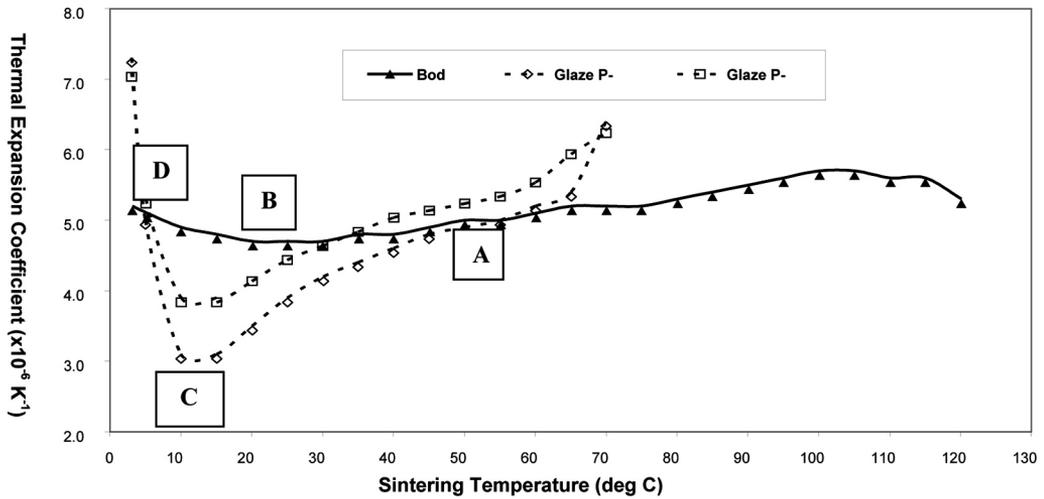


Figure 8. Plot of coefficient of thermal expansion of glazes and anorthite-based ceramic body at temperature from 30 °C to 700°C and 1200°C

CONCLUSION

Low thermal coefficient glaze can be prepared by using petalite, zinc oxide, magnesium carbonate, kaolin and silica based materials in glaze P-1 formulation. Glaze P-1 gives the best surface appearance with smooth and shine surface. To overcome glaze cracking problem, the thickness of the glaze applied should be controlled thin, which is less than 200 µm (0.2 mm) and apply by spraying or dipping onto the biscuits body.

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REFERENCES

- Capoglu, A. and Messer, P. F. (2004). Design and development of a chamotte for use in low-clay translucent whiteware. *Journal of European Ceramic Society*, 24(7), pp. 2067-2072.
- Capoglu, A. and Kutbay, I. (2002). Rheological and slip casting behavior of low clay containing translucent whitewares. *Key Engineering Materials* Vols. 206-213 pp.1739-1742.
- Chen, Y, Xie Y. and Shang, Y. (1997). Crystallization behaviour of sol-gel derived anorthite powders. Selected papers of Engineering Chemistry and Metallurgy China, vol. 8, pp. 117-123.
- Dinsdale, A. (1993). Sains Tembikar, Bahan, Proses dan Hasil. Translation by Radzali Othman and Ahmad Fauzi Mohd. Noor. Pulau Pinang. Universiti Sains Malaysia, pp. 189-201.
- Doll Said N. and Saidin K (2007). Development of pre-fired material as a precursor to anorthite-based ceramic. *Malaysian Journal of Microscopy*, vol. 3, pp 94-99.
- Gautron, L, Kesson S.E., and Hibberson (1996). Phase relations for $\text{CaAl}_2\text{Si}_2\text{O}_8$ in the system $\text{CaOAl}_2\text{O}_3\text{SiO}_2$ at 14 GPA. *Physics of the earth and planetary interiors 97, Elsevier Science*, pp71-81.
- Hong S.H., Young F, Yu P. and Kirkpatrick R.J. (1999). Synthesis of anorthite by Pechini process and structural investigation of the hexagonal phase. *Journal of Material Research*, 14(5), pp1828-1833.
- Ian Watson, (1980): Minerals for frit and glazes - value in variety, *Industrial Minerals*, pp, 23-35.
- INSIGHT Ceramics Chemistry Software by Digitalfire Corporation. Online trial. <http://digitalfire.com/insight>
- Kobayashi Y. and Kato E. (1994). Low temperature fabrication of anorthite ceramics. *Journal American Ceramic Society*, 77(3), pp. 833-34.
- Ryan, W and Radford, C. (1987): *Whitewares, Production, Testing and Quality Control*, Pergamon Press, pp. 9-11.