

Doll Said Ngah*

Engineering Materials Section
Advanced Materials Research Centre (AMREC)
SIRIM Berhad, P.O. Box 7035
Shah Alam, Selangor

*(said@sirim.my)

SYNTHETIC ANORTHITE CERAMIC FROM LOCAL RAW MATERIALS

RINGKASAN: "Bone china" bersama "soft porcelain" dan "fine translucent china" adalah kumpulan tembikar putih lut-cahaya komersial. Tembikar putih lut-cahaya adalah bersifat tumpat, putih dan membenarkan sebahagian cahaya menembusnya. "Soft porcelain" dan "fine translucent china" dibuat daripada campuran kaolin, feldspar dan kuarza, walaupun merupakan jasad lut-cahaya tetapi kekuatan dan ketahanan pecahnya tidak tinggi kerana kandungan kacanya yang tinggi. "Bone china" adalah lebih kuat dan tahan daripada seramik putih lut-cahaya yang lain kerana kandungan bahan hablurannya. Kajian ini adalah untuk membangunkan bahan anortit sintetik ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) atau abu tulang sintetik sebagai bahan alternatif kepada bahan abu tulang asli serta mempunyai ciri-ciri yang setara. Anortit sintetik ini dibuat menerusi proses pengkalsinan campuran kalsium karbonat (CaCO_3), silika (SiO_2) dan aluminium tri-hidroksida ($\text{Al}(\text{OH})_3$) bersama dengan magnesium karbonat (MgCO_3) sebagai fluks. Bahan anortit sintetik ini mengandungi 90 % habluran anortit dan 10 % habluran korundum. Anortit terbentuk seawal suhu 1200 °C. Purata ketumpatan bahan anortit sintetik ialah 2.77 gcm^{-3} semasa disinter pada suhu antara 1240 °C dan 1280 °C dan adalah sangat hampir dengan nilai ketumpatan anortit asli iaitu 2.76 gcm^{-3} . Bahan anortit sintetik ini boleh digunakan sebagai bahan penyediaan untuk produk seramik seperti "bone china" sintetik.

ABSTRACT: Bone china together with soft porcelain and fine translucent china is grouped as a main commercial translucent whiteware. Translucent whiterwares are dense, white and allow some light to pass through them. Soft porcelain and fine translucent china are made from a mixture of kaolin, feldspar and quartz, although they have a translucent body, their strength and fracture toughness are not very high as the glass content is higher. Bone china is stronger and tougher than other translucent wares because it is a crystalline material. The present work on synthetic anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) material or synthetic bone ash is designed to provide an alternative to natural bone ash materials. It is also designed to have equivalent properties of natural bone ash. The anorthite was prepared by calcining the low-iron containing materials, such as local calcium carbonate (CaCO_3), silica (SiO_2) and commercial aluminium trihydroxide ($\text{Al}(\text{OH})_3$) together with a little magnesium carbonate (MgCO_3) as a fluxing agent. The synthesized anorthite materials

contained about 90 % anorthite and 10 % corundum. Anorthite phase was formed as early as 1200 °C. The average density of the synthetic anorthite was 2.77 gcm⁻³ when sintered at 1240 °C to 1280 °C that was very close to the theoretical value of natural anorthite density of 2.76 gcm⁻³. The synthetic anorthite can be used as precursor material for ceramic products such as synthetic bone china.

Keywords: Anorthite, synthetic bone ash, bone china

INTRODUCTION

Naturally, anorthite (CaAl₂Si₂O₈) is the end-member plagioclase feldspar with a relatively low density of 2.76 gcm⁻³ (Gautron *et al.*, 1996). Anorthite has triclinic, orthorhombic and hexagonal form. Triclinic phase is the most stable in all temperatures (Hong, 1999) but all phases can be synthesized in the laboratories. Some methods of anorthite synthesis using various starting materials and process were reported. Kobayashi and Kato (Kobayashi & Kato, 1994) have developed low temperature fabrication of anorthite for substrate usage from kaolin and calcite. Yunfa (Yunfa *et al.*, 1997) used tetraethyl orthosilicate (TEOS), calcium nitrate and ethyl acetoacetate (etac) to undertake sol-gel processing of anorthite. Capoglu and Messer (Capoglu & Messer, 2004) have developed chamotte using commercial calcium carbonate, silica and aluminium trihydroxide. The chamotte contained anorthite, as major phase used in low-clay translucent whiteware that has a similar appearance to bone china.

Bone china together with soft porcelain and fine translucent china is grouped as a main commercial translucent whiteware. Translucent whiterwares are dense and white and allow some light to pass through them. Soft porcelain and fine translucent china are made from a mixture of kaolin, feldspar and quartz, although they have a translucent body, their strength and fracture toughness are as high as the glass. Bone china is stronger and tougher than other translucent wares because it is a crystalline material but it is not very serviceable in the severe conditions where the glaze can be easily scratched.

Apart from the above-mentioned factors, these whiterwares have clays as substantial constituent in their bodies and this commonly creates a problem due to alignment of platelet particles during forming process. This can lead to anisotropic shrinkage during drying and firing. Preferred alignment of the clay particles on the large scale of size as occurs in plastically formed and slips casting wares, lead to shape distortion both during drying and firing.

The present work on synthesis of anorthite or synthetic bone ash is for low-clay whiteware body, designed to reduce the problems arising from anisotropic

shrinkage. It is also designed to be more translucent and whiter. The synthetic anorthite material was prepared by calcining the low-iron containing materials, such as local calcium carbonate (CaCO_3), silica (SiO_2) and commercial aluminium trihydroxide ($\text{Al}(\text{OH})_3$) together with a little magnesium carbonate (MgCO_3) as a fluxing agent.

The products that are made using the synthetic anorthite material or synthetic bone ash can also be formed by powder pressing, slip casting and injection moulding (Capoglu & Messer, 2004). The final body of products made from the synthetic material or as a part of formulation should not exhibit anisotropic of shrinkage, be resistant to pyroplastic deformation, have high fracture toughness and strength and allow a glaze to be applied that is resistant to being scratched in service.

The present study focuses on synthesis of anorthite using Malaysia local source materials and its preliminary properties. These properties are quite similar to the properties of natural bone ash, thus the synthetic anorthite can be used as substitution to bone ash material.

MATERIALS AND METHODS

Starting Materials Preparation and Characterization

Starting raw materials for anorthite synthesis consist of commercially local source calcium carbonate (CaCO_3) from Kinta Valley area, Perak, silica (SiO_2) from Bintulu area, Sarawak and aluminium trihydroxide ($\text{Al}(\text{OH})_3$) was imported from Australia. Batch of the starting materials were mixed with a small percentage of MgCO_3 as an additive and wet milled for two hours in porcelain jar with alumina balls. After milling the slurry was dried in oven and then the dried powder cake was ground into powder. Prior to sintering, the starting materials composition was analyzed using Shimadzu XRF Spectrometer and crystalline phases analysis was conducted using Rigaku XRD machine with Cu K α from $5^\circ \leq 2\theta \leq 80^\circ$ at scanning speed of 3°min^{-1} . Particle size distribution (PSD) was conducted using X-ray sedimentation Micromeritics 5100 particle size analyzer. Thermal analysis, TG and DTA were conducted on the mixture of starting materials to indicate the mass loss and their thermal behavior using Rigaku Thermoflex machine at heating rate of $10^\circ \text{Cmin}^{-1}$ up to 1400°C .

Sintering and Samples Evaluation

The loosely packed powder material was placed in alumina crucibles and was sintered at various sintering temperatures of 1000, 1200, 1220, 1240, 1260, 1280, 1300, 1320 and 1350°C to form friable cakes. The heating rate was 5°Cmin^{-1} and

soaked for three hours. Prior to SEM studies, the sintered samples were polished and then etched with 5 % of hydrofluoric acid (HF) for 30 seconds and then rinsed and dried to remove the glassy phase. The specimens were coated before being analyzed for microstructure using Hitachi S2500 Scanning Electron Microscope interfaced with EDX spectrometer. The sintered samples were ground into powder and measurement of the true density was done using Micromeritics AccuPyc 1330 He-Pycnometer machine and their crystalline phases using Rigaku XRD machine.

RESULTS AND DISCUSSION

The chemical composition of the starting materials is shown in Table 1.

Table 1. Chemical composition of starting materials

Composition (%)	Calcium Carbonate (CaCO ₃)	Silica (SiO ₂)	Aluminium Trihydroxide (Al(OH) ₃)
SiO ₂	0.005	98.2	0
Al ₂ O ₃	0.08	0.27	64
CaO	55.8	0.03	0.04
Fe ₂ O ₃	0.003	0	0.01
TiO ₂	0.01	0.02	0.03
MgO	0.2	0.04	0.4
Na ₂ O	0.02	0.01	0.29
K ₂ O	0.02	0	0
LOI	43.7	0.3	36

Particle size distribution of the starting material mixture is shown in Figure 1. After being milled for two hours the mixture of starting material has the median particle size of 13.1 µm and 80 % of particle sizes are less than 25 µm.

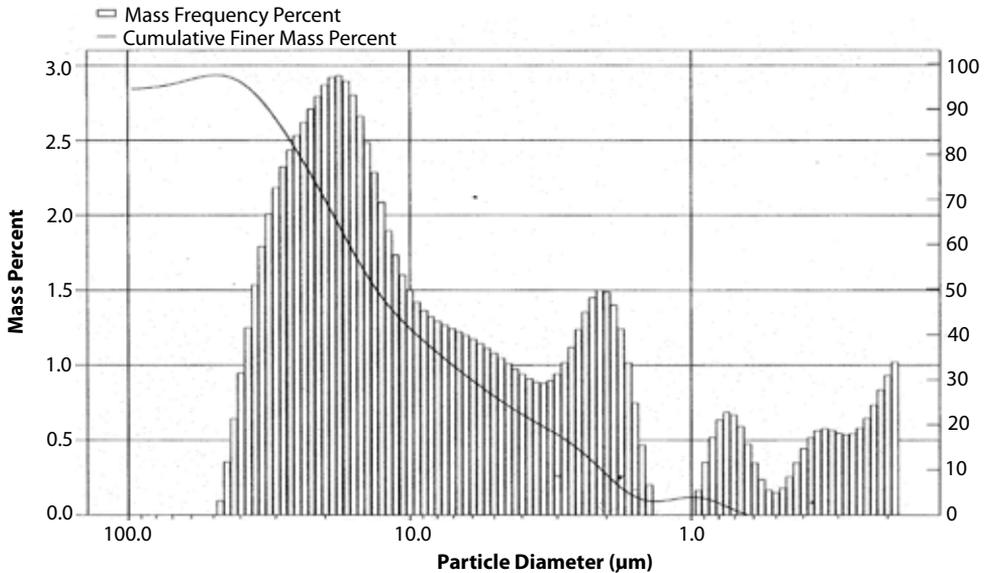


Figure 1. Particle size distribution of starting materials mixture

The mixtures of starting materials (unsintered) contain phases of quartz (SiO_2), gibbsite ($\text{Al}(\text{OH})_3$) and calcite (CaCO_3) as shown in Figure 2.

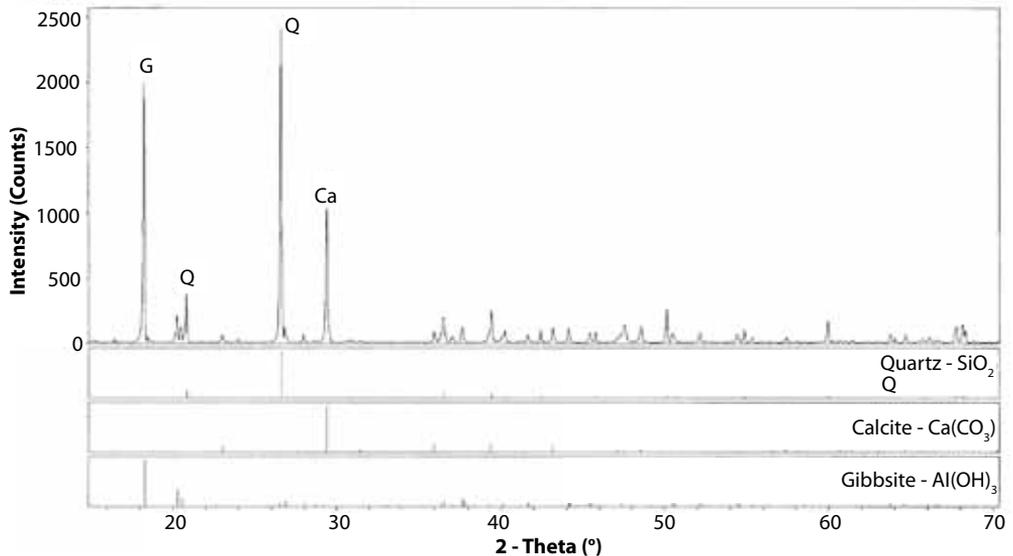


Figure 2. XRD Spectrum of unsintered starting material shows gibbsite, calcite and quartz

TG/DTA analysis as shown in Figure 3 shows that there are two major mass losses due to dehydroxylation of gibbsite at about 250 °C and decomposition of calcite after 700 °C (Okada, 2003). Exothermic reaction due to formation of anorthite phase starts to occur at temperature of about 1150 °C (Wunderlich, 1990).

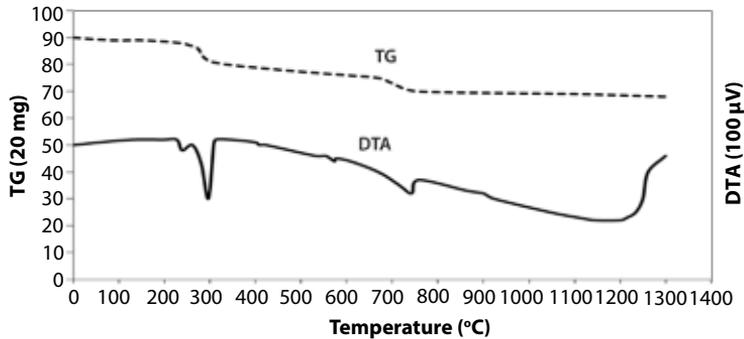


Figure 3. TG/DTA of starting materials

The XRD spectrum of the sintered samples is shown in Figure 4a (for sintering temperature from 1000 °C to 1260 °C) and Figure 4b (for sintering temperature from 1280 °C to 1350 °C). Anorthite was first detected at 1200 °C (Figure 4a). Quartz still prominently appeared at 1000 °C and became lesser and eventually undetected after 1240 °C. Similarly, gibbsite can be detected at 1000 °C and undetected at higher sintering temperature. At 1240 °C and higher the XRD spectrum shows only phases of anorthite and corundum (Figure 4b).

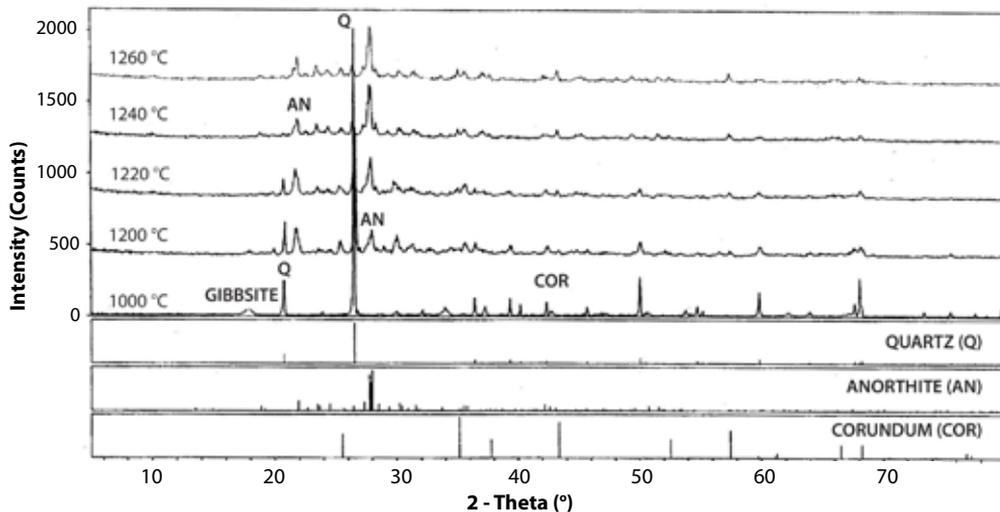


Figure 4a. XRD Spectrum of sintered (at 1000°C to 1260 °C) starting material mixture shows anorthite, quartz and corundum

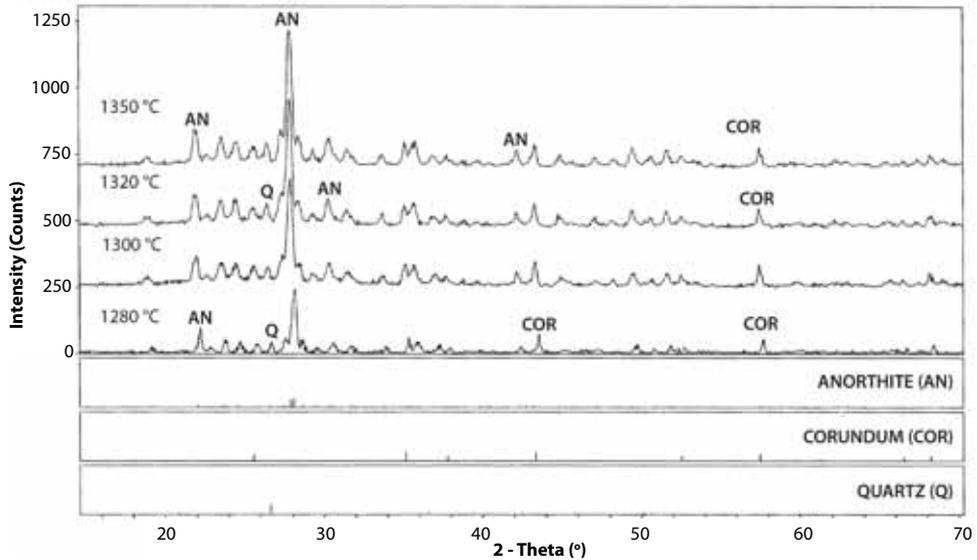


Figure 4b. XRD Spectrum of sintered (at 1280 °C to 1350 °C) starting material mixture sample shows anorthite, quartz and corundum

Maximum XRD intensities of phases were plotted against various sintering temperatures as shown in Figure 5.

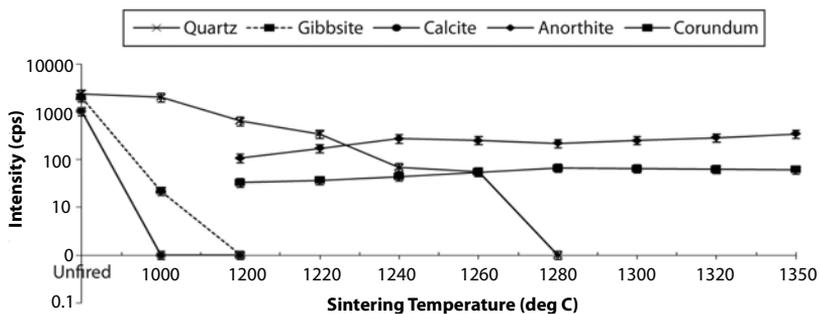


Figure 5. XRD Intensity of phases at different sintering temperature

Calcium carbonate (calcite) was completely decomposed at 1000 °C as shown in the TG analysis (Figure 3). XRD intensity of silica (quartz) gradually decreased until sintering temperature of 1260 °C and undetectable when sintering temperature was increased. This is due to the residual quartz that has probably melted or has been used up in forming anorthite phase that started to appear at 1200 °C together with crystallization of corundum. However the anorthite intensity was rather high and increased with increase of sintering temperature.

Density values of the starting material mixture samples sintered at various temperatures were plotted as shown in Figure 6. The raw starting material mixture sample density was 2.55 g cm^{-3} . The density value drastically increased to about 2.85 g cm^{-3} when sintered up to $1000 \text{ }^\circ\text{C}$ and slightly increased further to 2.87 g cm^{-3} up to $1220 \text{ }^\circ\text{C}$. The increase of density was probably due to the break-up of OH component from gibbsite ($\text{Al}(\text{OH})_3$) through dehydroxylation and decomposition of calcium carbonate or calcite (CaCO_3) to calcium oxide by releasing of CO_2 through calcination that has occurred at temperature below $1000 \text{ }^\circ\text{C}$ (Figure 3 and Figure 5). The density starts decreasing to about 2.79 g cm^{-3} after $1220 \text{ }^\circ\text{C}$ up to $1280 \text{ }^\circ\text{C}$ and further decrease to 2.73 g cm^{-3} at $1300 \text{ }^\circ\text{C}$ before increased again to $>2.82 \text{ g cm}^{-3}$ at $1350 \text{ }^\circ\text{C}$, the highest sintering temperature (Figure 6). The average density was 2.77 g cm^{-3} between $1240 \text{ }^\circ\text{C}$ and $1280 \text{ }^\circ\text{C}$ and it was very close to the theoretical value of natural anorthite density of 2.76 g cm^{-3} .

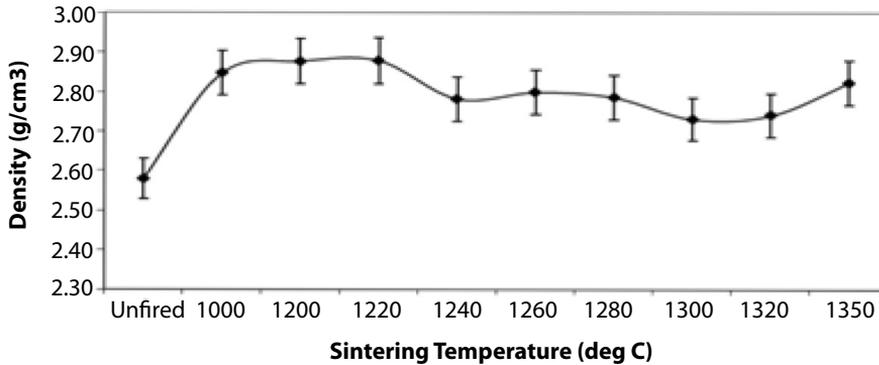


Figure 6. Densities of samples at different sintering temperature

After $1280 \text{ }^\circ\text{C}$ up to $1320 \text{ }^\circ\text{C}$ the density decreased as bubbles or pores formed by evolving gases from calcite decomposition. After $1320 \text{ }^\circ\text{C}$ more phases had melted and most of the pores were filled with liquid leading to increase in density (Iqbal *et al.*, 2000).

SEM micrographs for etched sample sintered at $1260 \text{ }^\circ\text{C}$ for one hour is shown in Figure 7. Anorthite crystals grew in the form of nodules. By increasing and prolong sintering temperature to $1300 \text{ }^\circ\text{C}$ for 3 hours, the anorthite crystal grew closer and can be visible as chained-up nodules (Figure 8).

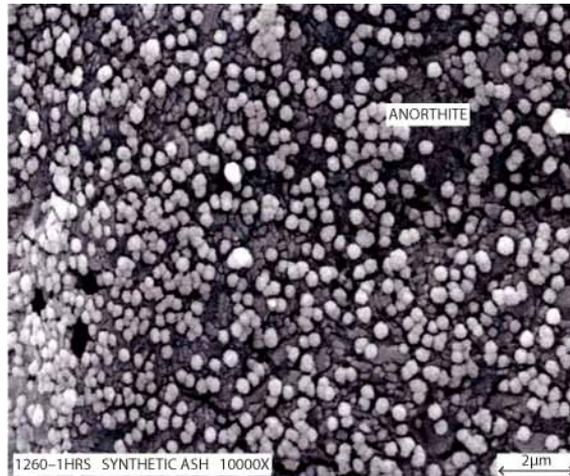


Figure 7. Etched sample sintered at 1260 °C shows anorthite in nodule form (mag 10,000x)

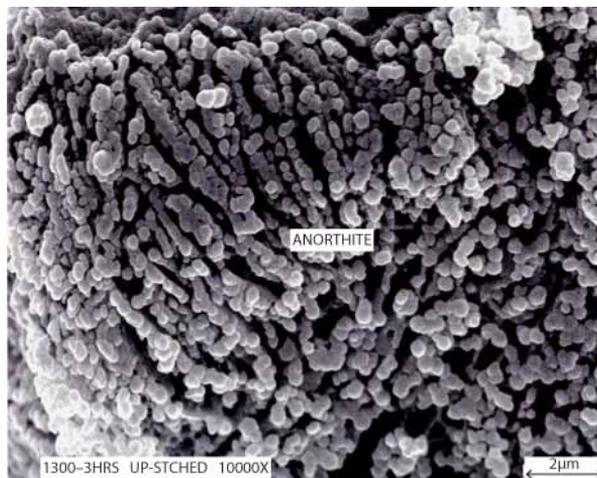


Figure 8. Etched sample sintered at 1300 °C shows chained (nodule) anorthite (mag 10000X)

Figure 9 shows anorthite phase that can be visible as lath shaped of 1 µm. Anorthite grew and showed morphological change from nodule to chained type and then to lath shape. Anorthite and corundum crystals that were detected by XRD can be clearly visible in SEM micrographs as shown in Figure 10 and detected by EDS as shown in Figure 11. Corundum has bigger size up to 10 µm and has a brighter tone that can be distinguished from anorthite (Figure 10).

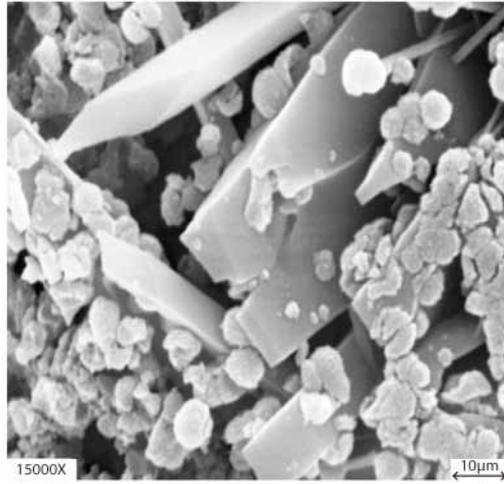


Figure 9. Etched sample sintered at 1300 °C shows well formed anorthite crystal (mag 15,000X)

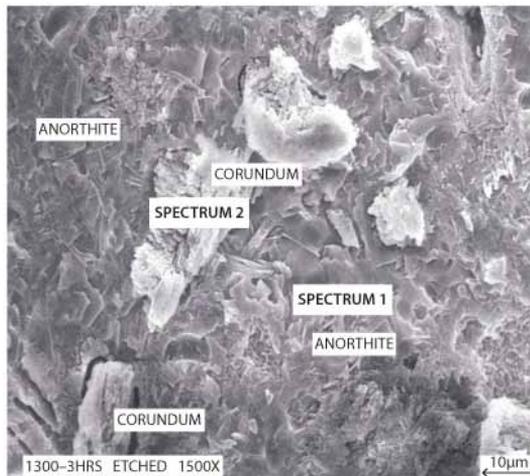


Figure 10. Etched sample sintered at 1300 °C shows anorthite (Spectrum 1) and corundum (Spectrum 2) (mag 1,500X)

Energy Dispersive X-ray (EDX) analysis (Figure 11) shows the presence of the elements Ca, Al, Si and O which are associated with the occurrence of anorthite (Spectrum 1) and corundum (Spectrum 2) as shown in Figure 10 and as detected by XRD (Figure 4a and 4b). Mg appeared in EDX Spectrum 1 (Figure 11) as a little additive in the mixture.

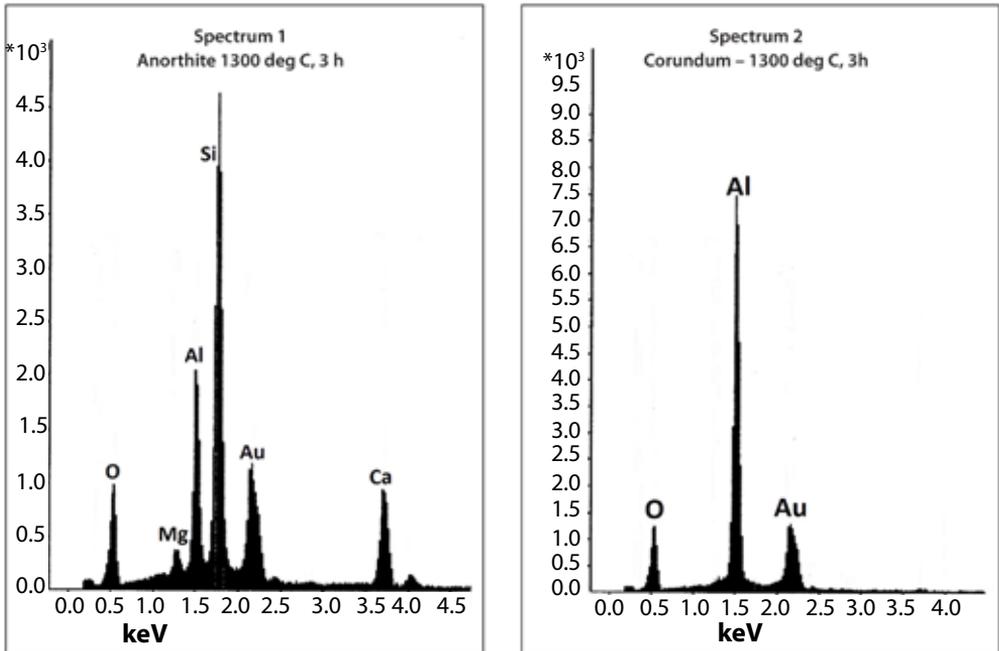


Figure 11. EDX Spectrum represents anorthite (Spectrum 1) and corundum (Spectrum 2)

Quantitative phase analysis using XRD Rietveld method shows that the synthetic anorthite materials contained 90.4 % anorthite and 9.6 % corundum.

CONCLUSION

Local raw materials such as limestone and silica together with aluminium trihydroxide had been successfully synthesized into anorthite material that contained about 90 % anorthite and 10 % corundum phases. The sintered temperature between 1240 °C and 1280 °C produces the synthetic anorthite with an average density of 2.77 gcm⁻³ that was very close to the theoretical value of natural anorthite density of 2.76 gcm⁻³. The ground synthetic anorthite can be used as precursor material for ceramic products such as synthetic bone china.

ACKNOWLEDGEMENT

The author would like to acknowledge MOSTI for the support grant through IRPA Project No. 09-01-01-0028EA001. The author also thanks En. Saidin for review and comments; En. Zaini, En. Hanaffi, Pn Zalena, Pn Afzan and Pn Azura of SIRIM Berhad for their help in experimental works.

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.

Gautron, L, Kesson S.E., and Hibberson (1996). Phase relations for $\text{CaAl}_2\text{Si}_2\text{O}_8$ in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ at 14 GPA. *Physics of the earth and planetary interiors 97 Elsevier Science*, pp 71-81.

Hong S.H. (1999). Synthesis of anorthite by Pechini process and structural investigation of the hexagonal phase. *J. Material Research*, 14(5), pp 1828-1833.

Iqbal, Y., Messer P. F. and Lee, W.E.(2000). Microstructural evolution in bone china. *British Ceramic Transaction*, 99 (5), pp 193-199.

Kobayashi Y. and Kato E. (1994). Low temperature fabrication of anorthite ceramics *Journal American Ceramic Society*, 77(3), pp. 833-834.

Okada, K.(2003). Effect of grinding and firing condition on $\text{CaAl}_2\text{Si}_2\text{O}_8$ phase formation by solid-state reaction of kaolinite with CaCO_3 . *Applied Clay Science*, 23, pp. 329-336.

Wunderlich, B. (1990). Differential Thermal Analysis. In: *Thermal Analysis*, Academic Press, Inc. San Diego, pp 166-171.

Yunfa, C., Yusheng X. and Yuming S. (1997). Crystallization behavior of sol-gel derived anorthite powders. *Engineering Chemistry and Metallurgy China*, 8, pp. 117-123.