PHASE AND MICROSTRUCTUE INVESTIGATION OF THAI VITREOUS CERAMIC BODIES

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Abstract

Four different vitreous ceramic bodies namely stoneware, bone china, porcelain and porcelain stoneware commercially produced in Thailand have been investigated using XRF, XRD and SEM. Chemical analysis results showed that bone china had relatively lower SiO_2 and Al_2O_3 but higher CaO contents than other bodies. XRD results revealed that the principal phase found in the bone china was β-TCP with anorthite and quartz as the minor phases. However the main phases found in other bodies were quartz and mullite. Minor quantity of corundum and zircon was also found in the porcelain and porcelain stoneware respectively. With the aids of SEM and XRD, it was suggested that β-TCP could possibly be the first phase formed in the bone china while anorthite was formed later from the excess CaO. Mullite crystals were found only in stoneware, porcelain and porcelain stoneware with different features. In the porcelain and the stoneware bodies, both primary and secondary mullite crystals were observed, but with a smaller crystal aspect ratio in the stoneware. In the porcelain stoneware body, however, only small mullite crystals were observed in a large area of glassy phase.

Keywords: bone china, stoneware, porcelain, porcelain stoneware, mullite

Introduction

Traditional ceramic industry in Thailand has played an important role in reinforcement and promotion of Thai economics. It was reported that the annual export value of traditional ceramics is about 400 million USD[1]. However, in an extreme competition particularly with China, Vietnam, and other countries, Thai ceramic production still requires technological development to meet the international standards and demands. To do this, a well insight in the science of ceramics is needed to be developed. One way forward is to understand the role of phase, microstructure and property relationship of the ceramic body.

Ceramic wares can be roughly classified into 4 types, earthen wares, stronewares, porcelain and bone china, in which only the earthen wares are non-vitreous. Around 30 years ago, a new type of vitreous body called porcelain stoneware was introduced. This body is commercially produced for floor tiles due to its excellent mechanical strength[2,3]. These vitreous wares are compounded using different ingredients and thus giving rise to different phases, microstructures and properties. The common ingredients of the vitreous bodies are summarized in Table 1[4-6]. The quantity of each component in commercial wares may be different in some degree according to different recipes.

Table 1 Compositions of various vitreous bodies

Body Type	China clay	Ball clay	Feldspar	Quartz	Other
Porcelain	25	25	25	25	-
Vitreous Sanitary ware	30	20	34	18	
Porcelain stoneware	10	40	40	10	
Bone China	25	-	15	22	38 bone ash

The unfired bodies such as porcelain, stoneware and porcelain stoneware contained quartz and feldspar distributed in the clay particles matrix. Vitrification mechanisms of ceramic bodies have been proposed by many people[7-9.] It was believed that primary mullite which occured by decomposition upon firing of kaolinite crystals was formed around 1100 °C while secondary mullite which appeared as needles occured around 1200 °C from the reaction between feldspar relict and clay relict[8,9] . Both the dispersions of the crystalline phase such as quartz and mullite and their difference in thermal expansion with the matrix glassy phase were proposed to render the superior mechanical strength of the porcelains[10,11]. In the bone china body, however, it was reported that crystalline phases found were mainly beta-tricalcium phosphate (β-TCP), anorthite and a small quantity of quartz[12,13]. The chemical reactions occured upon firing of this body was thus totally different from the above reviews but so far little data had been reported. In porcelain stoneware, which contained less crystalline phase contents after firing, the high strength is due to other factors.

This work was aimed to investigate the underlying characteristics of the commercial vitreous Thai ceramic bodies and to compare and contrast it to the reported literatures.

Experiments

Selected ceramic bodies were porcelain, stoneware, bone china and porcelain stoneware. These bodies were produced in Thailand. The specimens were cut into the desired size then ground and polished to the finest size. Chemical and phase analysis for these specimens were performed using XRF (Mesa-500W, Horiba, Japan) and XRD (X'Pert Pro MPD, Philips, Netherlands) techniques. To examine microstructure, a SEM (1450 VP, LEO, UK) was employed. To reveal the crystalline phases, the polished specimens were etched in 4%HF for 120 seconds prior to the examinations under SEM. Chemical microanalysis was determined using an EDS attached to the SEM (EDAX, USA).

Results and Discussion

Chemical and phase analysis

It was found that SiO_2 and Al_2O_3 contents in the bone china were relatively low when compared with those observed in other ceramic bodies (Table 2). However, the CaO found in this body was much higher than those found in other bodies due to the added bone ash.

Table 2 Chemical analysis results of the vitreous bodies

Oxides	Stoneware	Porcelain	Bone China	Porcelain Stoneware
SiO_2	70.243	64.407	35.184	73.639
Al_2O_3	22.576	31.640	15.494	16.534
K_2O	2.388	1.763	2.395	4.367
Na_2O	2.444	1.416	1.847	2.054
Fe_2O_3	1.067	0.237	0.321	0.517
CaO	0.209	0.537	21.767	-
MgO	0.536	-	0.890	0.617
TiO_2	0.374	-	0.115	0.369
BaO	0.162	-	-	-
ZrO_2	-	-	-	0.517

In the bone china, there existed 3 crystalline phase, β-tricalcium phosphate (β-TCP), anorthite and quartz, in which the dominant phase was β-TCP (Fig. 1). Two hypotheses on the formation of the anorthite and β-TCP in bone china were proposed and were reviewed by Alpagut Kara and Ron Stevens[12,13]. The first hypothesis stated that anorthite was formed solely from the excess calcium oxide in the bone ash surplus to the amount required to form tricalcium phosphate. In the second hypothesis, all the calcium oxide in the bone ash was combined with the alumina and silica present in the china clay to form anorthite. The remaining calcium oxide was assumed to form tricalcium phosphate (TCP) and all the other constituents including excess P_2O_5 from the bone ash reacted to form the glassy phase. From our XRD result, it was noted that no mullite phase was found in this body type which suggested that the densification of the bone china took place through the route where mullite formation was suppressed.

The crystalline phases found in porcelain were mainly quartz, mullite and corundum. Formation of mullite had been reported by many research groups. Corundum was sometimes incorporated in the porcelain to enhance its strength and whiteness. Corundum contributes very little in the chemical reaction upon firing; it was therefore still survived after firing as observed in the XRD patterns in Fig. 1. In the stoneware body, the crystalline phases present were similar to the porcelain body but without the presence of corundum. The content of the mullite phase observed in this body type was, however, lower than that observed in the porcelain. The crystalline phases presented in the porcelain stoneware body were quartz, mullite and zircon in which zircon was added to increase whiteness of the body. It was noted that the quantity of mullite formed in this body was relatively lower than that formed in the porcelain and stoneware.

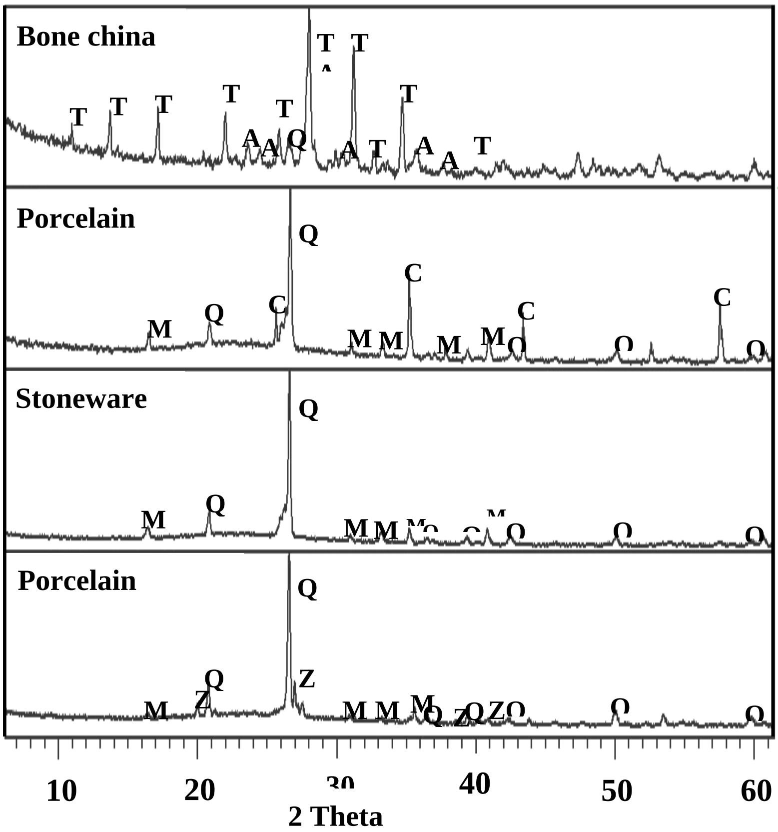

Figure 1 XRD spectrum for different ceramic bodies. (Q): quartz, (M):mullite, (Z): zircon, (C) corundum or alumina, (T): β-TCP and (A): anorthite

Microstructure

SEM micrographs in Fig. 2-5 revealed the difference in microstructure of the body. In bone china body, the round shaped crystals of β-TCP were largely found (Fig. 2c). Some quartz grains were also present but with much smaller quantity. Although the body was vitreous, the true porosity of this body was about 8-10%[9,10] which could be seen by the presence of large quantity of closed pores in Fig. 2a. This body contains high glassy phase proportion which was etched away in Fig. 2b. Although three crystalline phases, β-TCP, anorthite and quartz were detected by XRD, the major phase was β-TCP. A study by Alpagut Kara and Ron Stevens on the fired bone china indicated that it was difficult to locate anorthite crystal using SE-SEM possibly it was formed from very fine grain clay which might be distributed uniformly[12,13]. Besides, anorthite crystal could be slightly etched away by HF. The β-TCP crystals of small grain size observed in their study were sintered together to form a crystal pocket. Since our SEM micrographs showed the majority of one crystal type and the XRD result showed that the major phase found in this body was β-TCP, our finding thus supported the first hypothesis on the formation of the anorthite and β-TCP in bone china which stated that anorthite was formed from the excess calcium oxide surplus from the amount required form the formation of β-TCP.

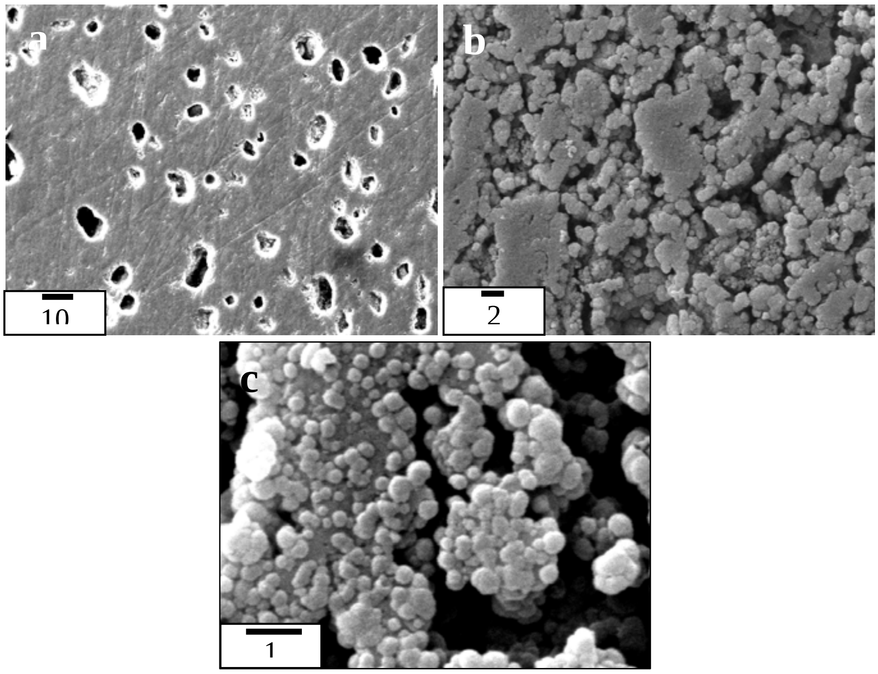

Figure 2 SEM micrographs for the fired bone china taken at different magnifications

In porcelain body, more densification was generally observed (Fig. 3a). The body contained a high quantity of mullite crystals with very small amount of quartz grains (Fig 3b). In Fig 3c, two types of mullite crystals were observed. Elongated needle-shaped crystals (marked as M_{II}) interlocking with each others were the secondary mullite while the cuboidal shaped crystals (marked as M_I) were primary mullite[8,9].

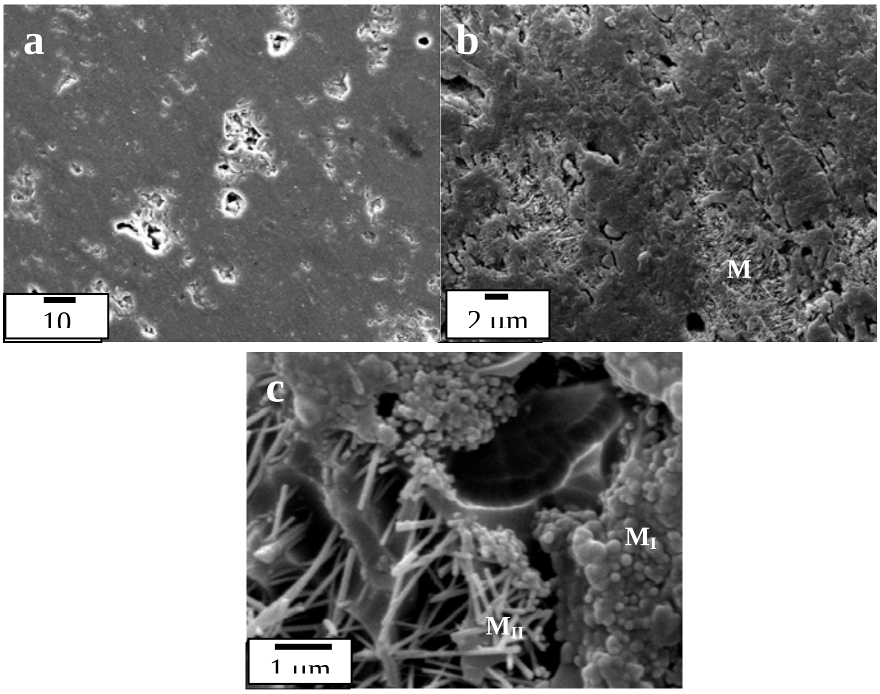

Figure 3 SEM micrographs for the fired porcelain taken at different magnifications

The stoneware body principally contained three types of crystals, large quartz grains and two types of mullite; primary and secondary (Fig. 4c). It is noted that the aspect ratio (length to diameter) of the secondary mullite found in this body was smaller in size than that found in the porcelain body. Normally the growth of crystals required a pool of liquid to grow. This could be achieved by the melting of feldspar in the composition. It was thus possible that feldspar content in the initial mix of the porcelain body was higher than that of the stoneware body. However, the chemical analysis result in Table 2 showed that both K_2O and Na_2O contents in stoneware body were higher than those in the porcelain body, so this hypothesis thus ddid not fit to our finding. Another possibility was that the elongated needle shape mullite crystals could be formed by precipitation of alumina-rich liquid obtained by dissolution of alumina filler and is called tertiary mullite[6]. However, this type of mullite was not common and thus not usually found in a high quantity. Besides, the corundum left in the vitrified body was still in a high quantity while this type of mullite was found in a high multitude in this porcelain body. So the possibility was that this mullite could be only secondary mullite which is formed from reaction of feldspar relicts and clay relicts. The firing cycle of this body could be more suitable for mullite crystal to grow in size. Cracks were due to the presence of large quartz grains (Figure 4a). Quartz grains over about 10µm give microcracks on cooling through 573ºC, and these were the principal source of Griffith flaws which could reduce MOR of the body[14].

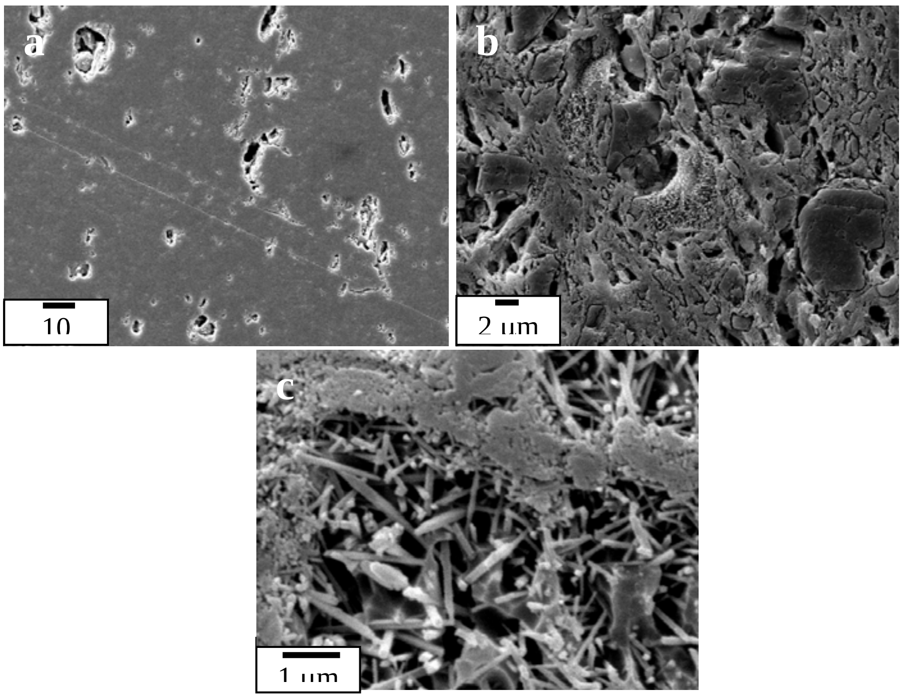

Figure 4 SEM micrographs for the fired stoneware body taken at different magnifications

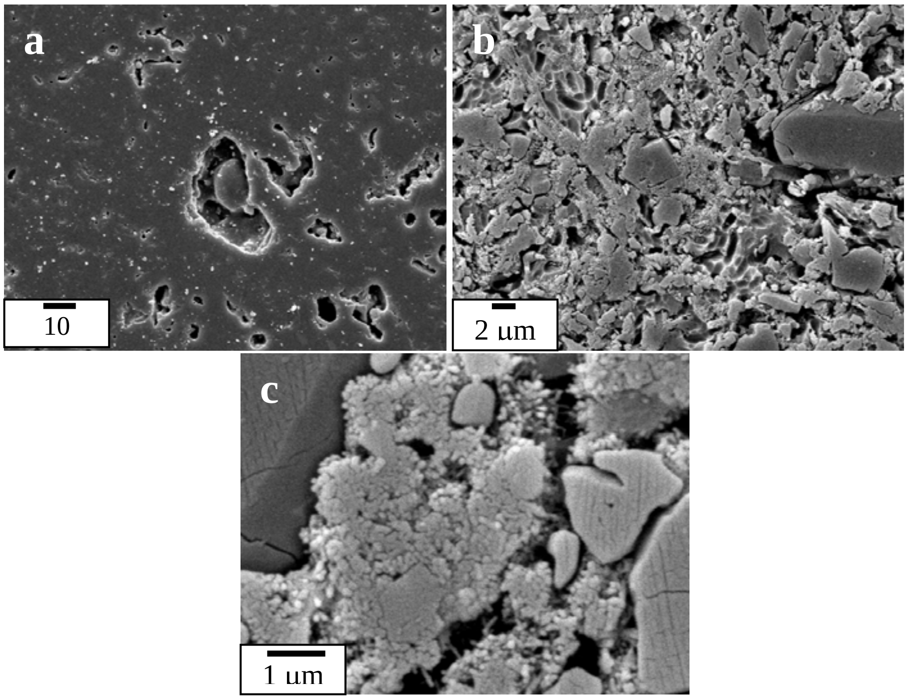

Figure 5 SEM micrographs for the fired porcelain stoneware body taken at different magnifications

The porcelain stoneware tile contained some big pores which were quartz grain relict. Figure 5(b) showed that this body type contains a large quantity of glass which was etched away by the acid. The etched sample showed the presence of quartz and small mullite crystals (Fig. 5c). Firing cycle of this body type was only 60 minutes and the top temperature was 1200 °C, possibly too short for mullite to grow.

Conclusions

This investigation has following conclusions:

1. In the bone china, the main phases observed were β-TCP with minor amount of anorthite and quartz in the glassy matrix indicating that β-TCP was the first phase form. No mullite crystal was observed in this body.
2. Porcelain, stoneware and porcelain stoneware mainly contained similar phases of quartz and mullite in the glassy matrix. While mullite crystals found in porcelain has the largest aspect ratio (length to diameter) and the highest distribution, those found in porcelain stoneware were rather small in size and less in content due to the short firing cycle of this body.

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