CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the results are presented of the investigation of ZrO_2 reinforced dental porcelain systems. Chemical composition, microstructure properties relationships are brought out and discussed in terms of phase formation and densification.

In order to determine the crystalline phase development in each porcelain-based samples with different amount of ZrO_2 additives (detailed in Table 4.1), they were examined by using XRD technique. The X-ray diffraction pattern of dental porcelain ceramics in this study is given in Fig. 4.1(D0), indicating a background of amorphous glassy phase and evidence of the formation of only leucite crystalline phase, which could be matched with JCPDS file no. 15-47, in agreement with other works [72, 146]. To a first approximation, this crystalline phase has a tetragonal leucite-type structure in space group $I4_1/a$ (no. 88) with cell parameters a = 1306 pm and c = 1375 pm [147]. As demonstrated in Fig. 4.1(D1-D9), it can be seen that all samples showed almost identical XRD patterns. The strongest reflection in the majority of XRD traces derived from all ZrO_2-modified porcelain groups indicated a combination of monoclinic-zirconia which could be match with JCPDS file no. 36-420 [148] and tetragonal-leucite phase. In addition, it should be noted that XRD peaks of leucite (323) and zirconia ($\bar{1}11$) at $2\theta \sim 28.5^{\circ}$ are superimposed. In this study, no phase transformation of leucite can be detected at 1040°C and the XRD patterns of the samples did not reveal the formation of any additional crystalline phases, which is in agreement with the results of others [3, 4]. This is probably indicating the effectiveness of ZrO_2 as the leucite stabilizer, in analogous with those found for another similar system [72].

From Table 4.1, it can be seen that some relationship was found between the amount of ZrO_2 additive and the concentration of leucite phase in the samples. In general, it has been observed that with increasing amount of ZrO_2 additive, some diffraction lines e.g. (004) and (400) peaks (see Fig. 4.2) indicated of a continuous

Table 4.1 Physical properties of dental porcelain ceramics containing varies amount of ZrO_2 additives.

Materials	**ZrO_2 Content (wt%)**	**XRD**			**Density ($\pm$ 0.1 g/cm^3)**	**SEM**
		Relative intensity $(I_{(400)}/I_{(\bar{1}11)})$	Leucite content (± 1 wt%)	Leucite crystallite size (± 2 nm)		Mean leucite particle size (nm) /standard deviation
D0	0	204/308	39.82	20.35	2.39	275.83 / 103.05^{a}
D1	5	211/247	45.99	18.19	2.51	124.50 / 46.09^{b}
D2	10	299/256	53.83	22.89	2.59	157.68 / 42.93^{a,b}
D3	15	179/304	37.06	16.90	2.65	119.17 / 38.97^{b}
D4	20	175/365	32.41	15.45	2.68	105.50 / 22.33^{b}
Ref. 7	20	-	30.00	19.90	2.71	-
Ref. 149	20	-	26.14	15.76	2.43	-
D5	25	170/473	26.44	13.11	2.78	102.83 / 39.93^{b}
D6	35	127/402	14.35	13.03	1.86	-
D7	45	112/539	7.62	10.64	1.79	-
D8	55	98/602	2.74	11.01	1.54	-
D9	65	89/657	0.83	10.47	1.41	-

[a-b] There is no significant statistical different ($p > 0.05$) between materials with the same superscript letters.

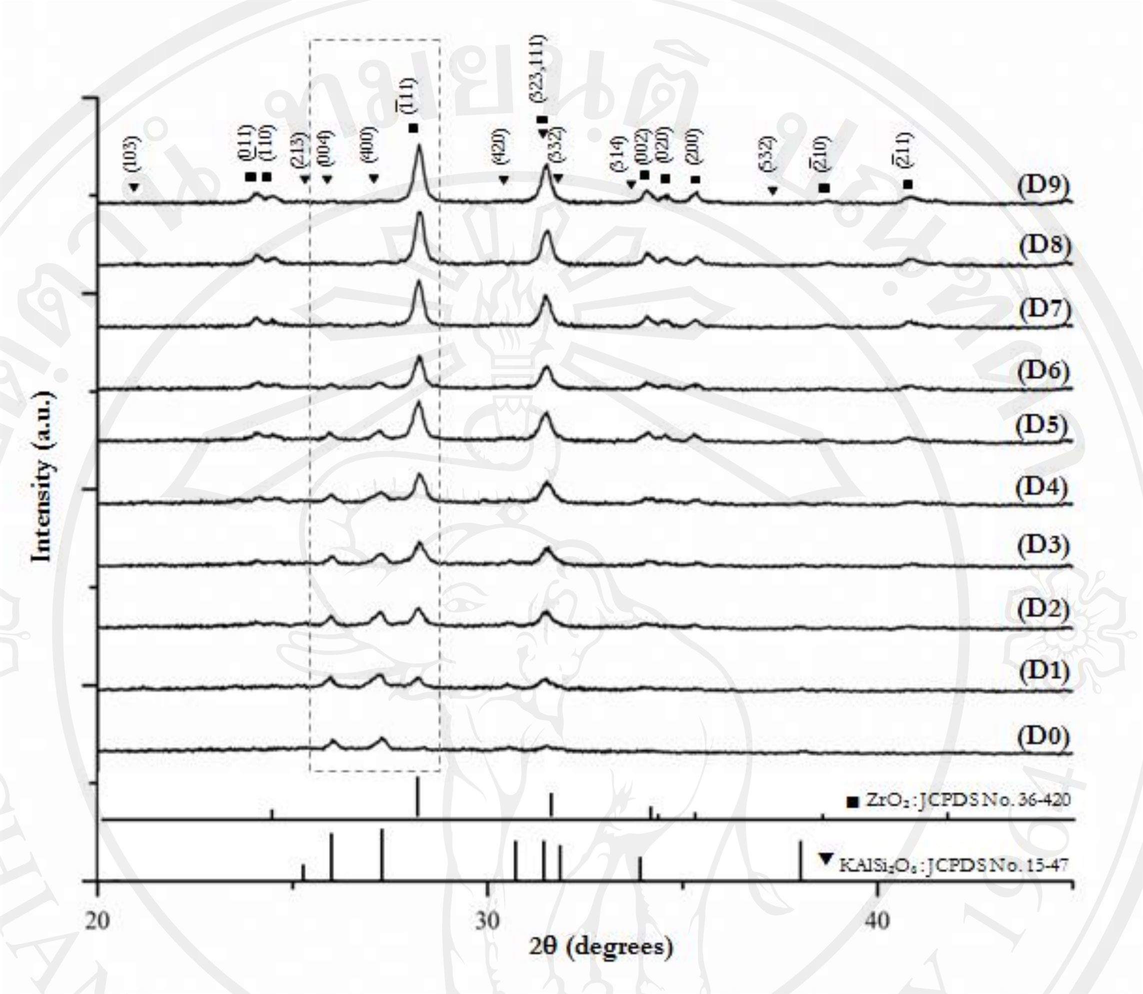

Fig. 4.1 X-ray diffraction patterns of dental porcelain doped with various amount of ZrO_2 additive.

decrease in amount of leucite content, crystalline size and of the reduction of lattice strain, in agreement with earlier work reported by Sanitnapapong et al. [7] In their work, the maximum leucite content of ~ 30 wt% was achieved after sintering the porcelain with 20 wt% ZrO_2 additive at 1040˚C for 5 min then tempering at 940˚C for 90 min. However, in this study, the highest amount of leucite content (~ 54 wt%) was found in the samples containing only 10 wt% ZrO_2 additive after experienced the same heat treatment schedule. As predicted by our previous work [7], it is believed that leucite crystallization in porcelain ceramics can be effectively suppressed by addition of ZrO_2

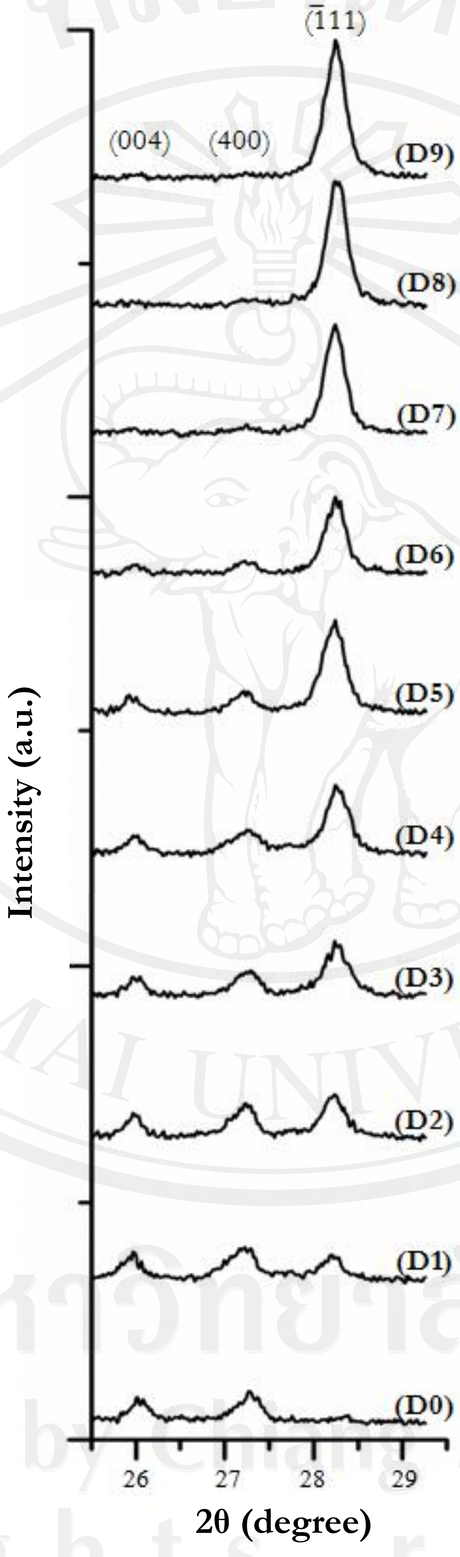

Fig. 4.2 Enlarged X-ray diffraction patterns of dashed box in Fig. 4.1.

To further study the influence of ZrO_2 additive on the leucite crystallite size, their XRD data were manipulated, as results given in Table 4.1. As seen for low ZrO_2 content (i.e. 5-10 wt%), the calculated crystallite size value of the leucite was found to increase with increasing the amount of ZrO_2. By contrast, ZrO_2 addition larger than 10 wt% greatly decrease the leucite crystallite size. This observation suggests that zirconia influences an increase in the viscosity, or strengthening the glass network, which results in hampering the crystal growth, consistent with work reported by Apel et al. [8]. As seen in Table 4.1, Sanitnapapong et al. [7] and Pisitanusorn et al. [149] have reported leucite crystallite size values of 19.90 nm and 15.76 nm for porcelain with 20 wt% ZrO_2 addition, respectively. This work has shown this value is 15.45 mm which can be compared with earlier work [149]. Though, the relative intensities of the Bragg peaks exhibit independent of ZrO_2 additive, it is well documented that, as Scherer's analysis provides only a measurement of the extension of the coherently diffracting domains, the crystallite sizes determined by this method can be significantly under estimated [144]. In addition to strain, factors such as defects, homogeneity of materials, the complex nature of the background due to amorphous matrix, processing variables and instrument effect can attribute to peak shape, making it almost impossible to extract a reliable leucite crystallite size solely from XRD patterns [102]. In this connection, SEM was also employed for the leucite particle size measurement (Table 4.1 and Fig. 4.3).

Fig. 4.3(D0) is a SEM micrograph of dental porcelain ceramics experienced the two-step sintering with no ZrO_2 additive showing leucite particulates which vary between 180 and 500 nm in size and are clustered together along the smooth surface of typical porcelain glass-ceramics. On the basis of this, the surface crystallization is believed to be the key mechanism responsible for the appearance of leucite phase in the glassy matrix [3, 150]. Furthermore, there is no evidence of crack formation in the matrix or within the leucite crystals. The microstructural features of all ZrO_2-modified porcelain samples were also examined, as shown in Fig. 4.3(D1-D9). On the contrary, these samples showed two (or more) distinct phase structures with a glassy matrix phase reinforcing crystalline phase dispersed in the glassy matrix. In general, they have a very fine microstructure with agglomerates. As shown in Fig. 4.3(D1-D5) for the case of 5-25 wt% ZrO_2-modified porcelain ceramics, it can be seen that some leucite particle sizes in the range ~ 70-200 nm (closer observation of Fig. 4.3(D2) as inserted) were initiated from the surface of zirconia grains, leading to the evolution of ceramic-nanocomposite structure, consistent with those reported earlier [3, 149, 151]. It is interesting to noted that dendritic leucite morphology previously reported by several researchers [66, 152] are also found here. These observations may be attributed to the influence of ZrO_2 additives as nucleating agents for leucite crystallization behavior, similar to those found in another similar glass-ceramic system [66]. Interestingly, for the case of 15-25 wt% Zr modified porcelain ceramics, it can be seen that large particle of ZrO_2 (~ 5 µm) and some leucite particles (~ 70-200 nm) were initiated from the surface of zirconia grains. In both 5 and 10 wt% ZrO_2-modified samples, the additives are observable in two forms: 1) the agglomerates (as also found in 15, 20 and 25 wt% ZrO_2-modified samples) and 2) the nanocomposite formations in reticulate sheets (~ 100 nm thickness), in agreement with earlier work reported by Sanitnapapong et al. [7]. Such a difference in morphology may be described on the basis of difference in crystallization and growth mechanisms. The early stages of bulk leucite growth have been observed as dendrites growing in their preferred crystallographic directions. A diffusion controlled growth process that evolved at the smooth atomic-scale faceted crystal-glass interface was suggested. In the work of Sanitnapapong et al. [7], with longer tempering times applied, a significant change in dendrite shape due to the growth of secondary and tertiary fibrils and their ripening resulted in a highly organized tetragonal leucite structure, consistent with those observed in other similar systems [142, 150, 153]. In agreement with this, in this study, small amount of ZrO_2 ($\leq$ 10 wt%) can control the growth of leucite crystal with the same growth process. Signs of leucite particle coalescence were also visible in all ZrO_2-modified porcelain samples which may have been driven by a reduction in interfacial energy when larger particles grow at the expense of smaller ones (Ostwald ripening) [154].

At the higher content of ZrO_2 additives (i.e. > 25 wt%), however, different microstructural evolution with more homogeneous grain arrangement were observed (Fig. 4.3(D6-D9)). As it has been reported in many studies [102, 155, 156], the higher the ZrO_2 content is, the higher the firing temperature is required due to relatively high

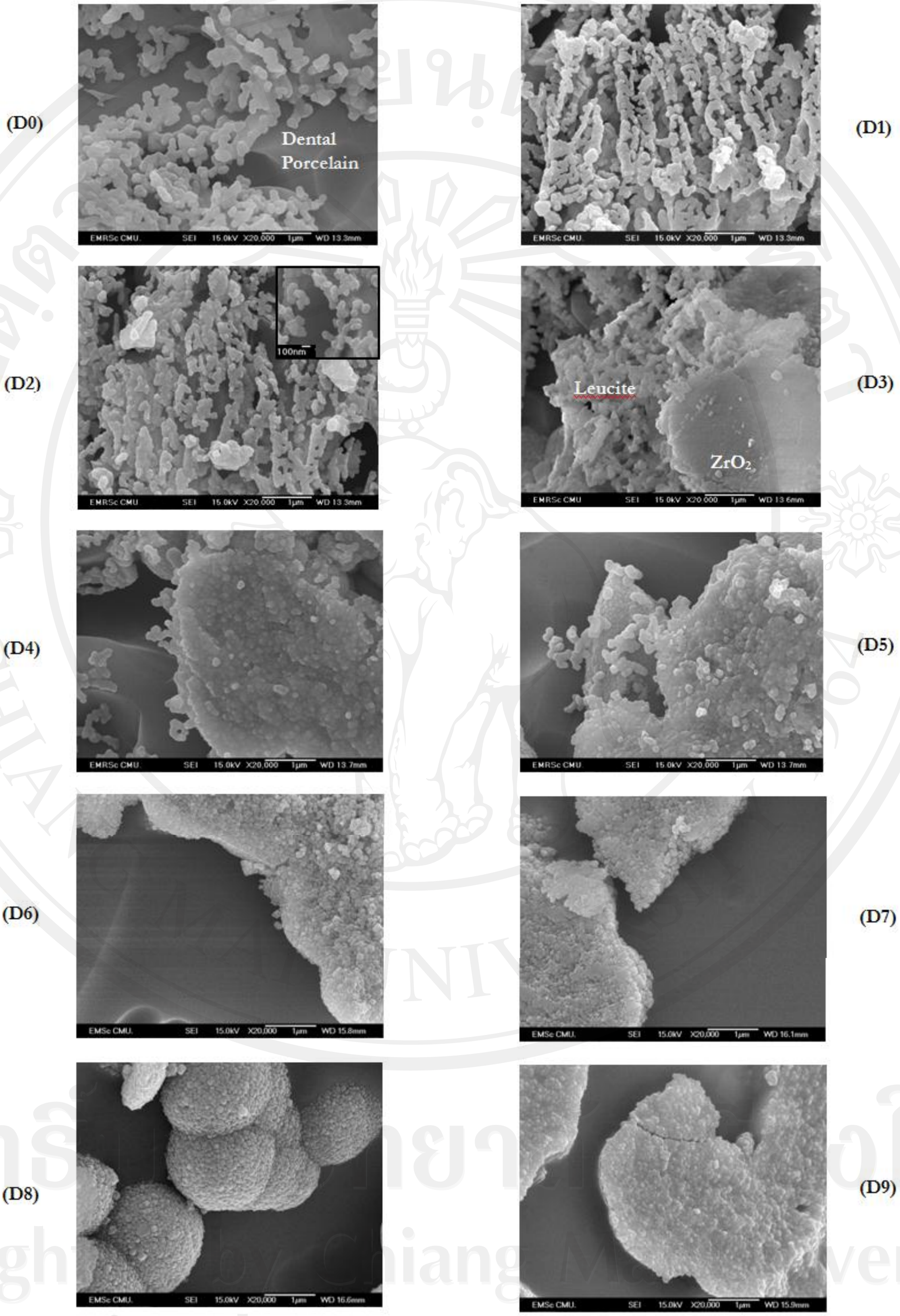

Fig. 4.3 SEM micrographs of dental porcelain ceramics with various amount of ZrO_2 additive.

melting point of ZrO_2 (~ 2,700˚C [102]). For better understanding and verifying the proper firing temperature of leucite crystallization further, a study on the firing condition on crystallization of leucite in dental porcelain nanocomposite with high ZrO_2 content is required.

Additionally, it was found that the leucite particle size of the samples with 5-10 wt% ZrO_2 increases with increasing amount of ZrO_2 additives and might be attributed to the influence of ZrO_2 additives acting as nucleating agents for leucite crystallization behavior, similar to those found in other similar glass-ceramic systems [66, 157]. On the contrary, above 10 wt% of ZrO_2 additive, it appears that the nucleating agent capability of ZrO_2 for the crystallization of leucite is suppressed. Meanwhile, it is of interest to point out that by increasing the amount of ZrO_2 additive further up to 65 wt%, both amount and size of leucite particles in the sintered porcelain ceramics were found to decrease, consistent with work of Apel et al. [8]. From the above observations, we conclude that the ZrO_2 additive especially its content is one of the key factor controlling leucite crystallization behavior in dental porcelain ceramics.

SEM-EDX analysis of the dental porcelain ceramics (Table 4.2 and Fig. 4.4) marked as “(1)” reveals the strong presence of silica and oxygen indicating the compositional of glass matrix (Fig. 4(b)). It can be seen that the glass matrix are composed of mullite ($3Al_2O_3{\cdot}2SiO_2$), silica (SiO_2), potassium oxide (K_2O) and sodium oxide (Na_2O). In general, dental porcelains derived from the basic silicon-oxygen networks acting as the glass-forming matrices but additional properties, such as low fusing temperature, high viscosity, and resistance to devitrification, are built-in by the addition of other oxides to the glass-forming lattice SiO_4. These oxides generally consist of potassium, sodium, calcium, aluminium and boric oxides [9]. As shown in Table 4.2, Fig. 4.4(a) and (c), EDX spectra obtained from area “(2)” confirms the existence of all key elements related to the composition of leucite ($KAlSi_2O_6$) [147]. The combination of X-ray and SEM/EDX results strongly support that, in this study, leucite phase was formed. However other chemical compositions from area “(2)”, Al_2O_3, SiO_2 and Na_2O, missed by XRD diffraction method could be the small compositions from the glass-forming matrices. Whilst EDX analysis of the large grain

Table 4.2 EDX chemical analysis of dental porcelain ceramics containing various amount of ZrO_2 additives.

EDX positions	Compositions (at%)					Possible phase (s)
	K (K)	Al (K)	Si (K)	Na (K)	Zr (L)	
(1)	1.62	2.30	10.15	1.25	-	$3Al_2O_3 \cdot 2SiO_2$, SiO_2, K_2O, Na_2O
Ref. 149	1.54	2.43	8.22	1.84	-	-
(2)	1.10	1.92	6.42	1.14	-	$KAlSi_2O_6$, Al_2O_3, SiO_2, Na_2O
Ref. 149	0.97	1.91	6.86	1.81	-	-
(3)	-	1.21	-	-	10.27	ZrO_2, Al_2O_3
Ref. 149	-	-	-	-	9.58	-

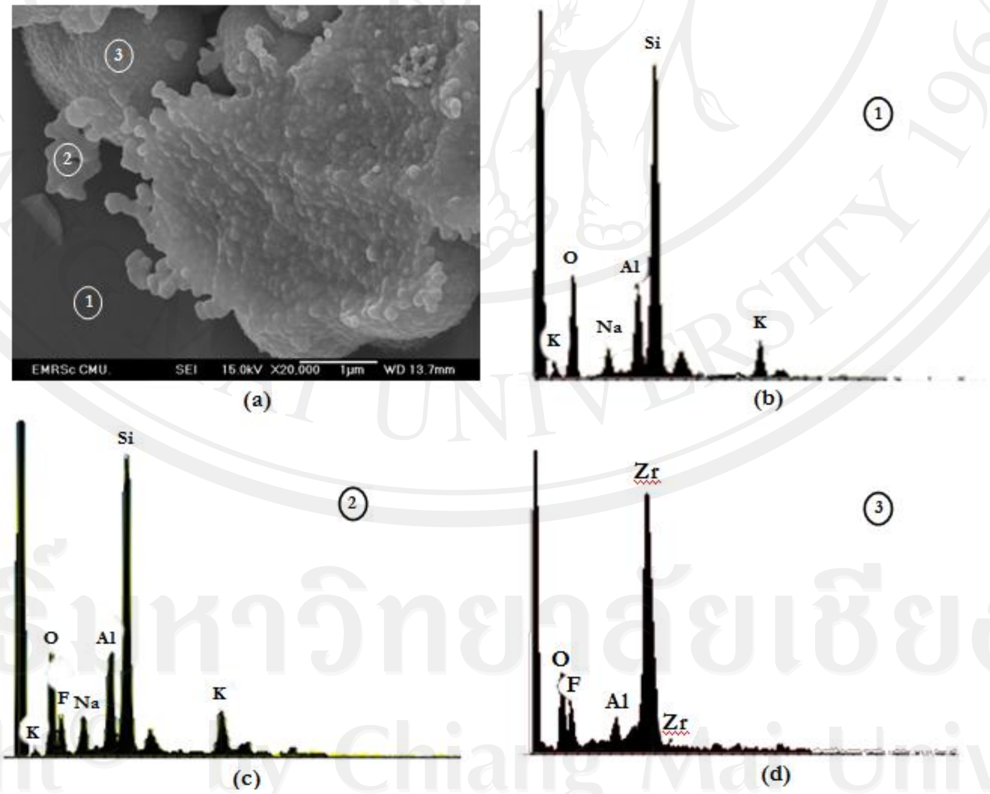

Fig. 4.4 Representative (a) SEM micrograph of 20 wt% ZrO_2 modified sample and their corresponding EDX analysis, indicating the chemical compositions of (b) glassy matrix, (c) leucite and (d) ZrO_2 phases, respectively.

marked as “(3)” show zirconia rich phase together with spectra of oxygen, indicating the existence of ZrO_2 additive. Besides ZrO_2 phase, some Al_2O_3 phase also existed in the large grains. The results of SEM-EDX measurement supported the XRD observation discussed earlier (Fig. 4.1). From the SEM images shown in Fig. 4.3, the results of the statistical analysis of the leucite particle size are extended for comparison, as given in Table 4.1. There was a significant different of leucite particle size between the dental porcelain and the ZrO_2-modified porcelain groups significantly but not significant different among ZrO_2-modified porcelain groups. This observation is important because literature [102] have shown the difficulty in sintering of such microstructure to full density at low temperature due to hard ZrO_2 particles.

To elucidate the densification characteristics of the ZrO_2-modified porcelain ceramics in detailed, the bulk density measurements were performed via Archimedes principle. The change in density versus the amount of ZrO_2 additives is shown in Table 4.1. Density values increase with increasing of ZrO_2 additives up until at 25 wt%. Then the density value was found to decrease with the higher ZrO_2 content. This feature creates a density value of about 2.68 g/cm^3 at 20 wt% ZrO_2 additives which is comparable to the values reported by Pisitanusorn et al. [149] (~ 2.43 g/cm^3) where 20 wt% ZrO_2 was used as additive. Furthermore, density value at the same amount of ZrO_2 additives and firing condition with study of Sanitnapapong et al. [7] (20 wt% ZrO_2, firing at 1040°C for 5 min and tempering at 940°C for 90 min) is comparable (2.71 g/cm^3). The increasing density with rising amount of ZrO_2 additives up to 25 wt% may be explained by the enhanced densification related to the effect of ZrO_2 and the more reactive two-step sintering used [88, 102, 113]. It was proved to be difficult in obtaining highly dense samples with ZrO_2 additive $\geq$ 25 wt% because they couldn’t be densified by the employed sintering condition and had many pores.

To highlight the effect of ZrO_2 additive, the variation of leucite content and density of the products fabricated using different amount of ZrO_2 additives are shown in Fig. 4.5. As it is appeared in Fig. 4.5, there are some kinds of relationships between ZrO_2 content, leucite content and density. At small amount of ZrO_2 content, the variation of both the leucite content and the density versus the amount of ZrO_2 additives indicates significant effect of the ZrO_2 concentration. The higher the ZrO_2

is, the higher values of both the leucite content and the density are. By adding 10 wt% of ZrO_2, the leucite content approached maximum whilst the samples with highest density require ZrO_2 additive of 25 wt%. On the contrary, increasing the ZrO_2 additive higher than 20 wt% resulted in significant reduction of both values. In general, these graphs show some relationship between the leucite content and the density of the products. Besides the leucite content, we found that leucite morphology also relate to the density of samples. From Fig. 4.3(D2, D3), it is found leucite morphology in reticulate sheet in the high density samples. In some samples that there are very rare leucite content and leucite disperse in agglomerate form (Fig. 4.3(D6-D9)) indicate reducing in density. It can be predicted further that when the porcelain based-ceramics could be densified completely, the addition of ZrO_2 could improve the mechanical properties of the products greatly. In connection with this, further studies have been carried out to investigate the effect of ZrO_2 content on the change of the suitable heat treatment schedules. This would extend an understanding on the processing-composition-microstructure relationships in dental porcelain ceramics.

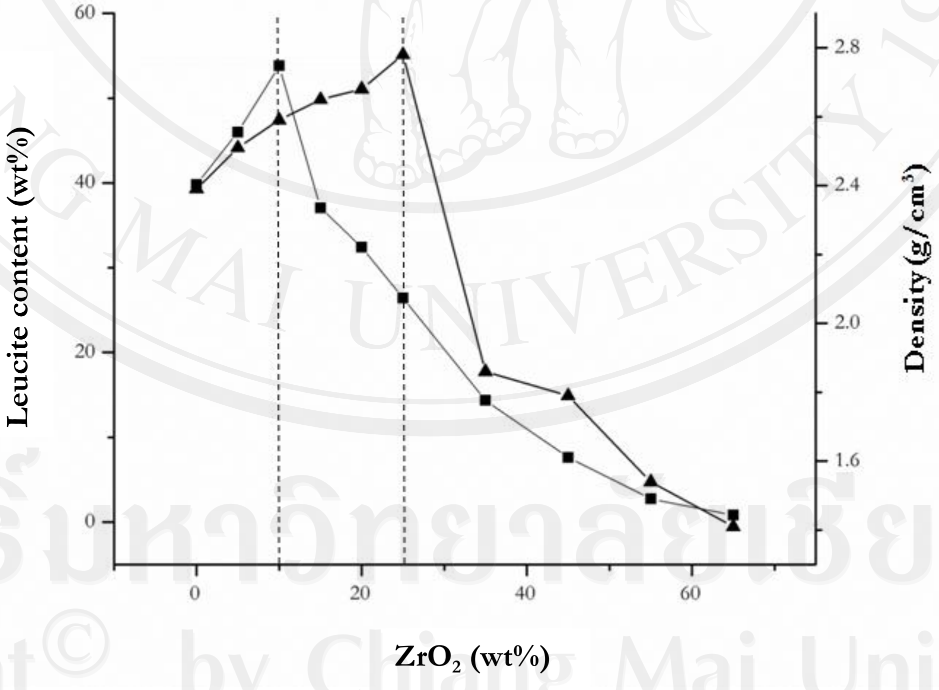

Fig. 4.5 The variation of leucite content (■) and density (▲) of the porcelain based samples as a function of the amount of ZrO_2 additive.