CHAPTER 4

RESULTS AND DISCUSSION

PART I

0-3 Modified barium titanate-Portland cement composites

This part focuses on electrical, physical and microstructure properties such as dielectric, piezoelectric, acoustic impedance, thermal expansion and microstructure properties of 0-3 Barium zirconate titanate-Portland cement composites (0-3 BZT-PC composites).

4.1 Dielectric properties of 0-3 modified barium titanate-Portland cement composites

4.1.1 Effect of ceramic particle size on the dielectric properties

The dielectric properties of the 0-3 Barium zirconate titanate-Portland cement composites (0-3 BZT-PC composites) were plotted against the BZT particle size at the frequency of 1 kHz at room temperature. The dielectric constant of the composites can be seen to increase with increasing BZT particle size and the dielectric loss was found to decrease with increasing BZT particle size in Fig. 4.1.

For 0-3 BZT-PC composites (for the ceramic particle size range tested), the ceramic of 425 μm particle size can be produced and it gave the highest dielectric constant and lowest dielectric loss. The dielectric constant can be seen to increase with larger particle size of ceramic used perhaps, due to the fact that the contact surface areas between the cement matrix and the particles became smaller with increasing ceramic particle size. These contact surface areas are greatest when ceramic particle is smallest and became less when larger ceramic particle was used for the same volume percentage thus brought out the optimum piezoelectricity in the 0-3 BZT-PC composites. Furthermore, it is believed that due to the greater contact surface area between the ceramic particle size and cement matrix would correspondingly increases thereby leads to the greater loss [3].

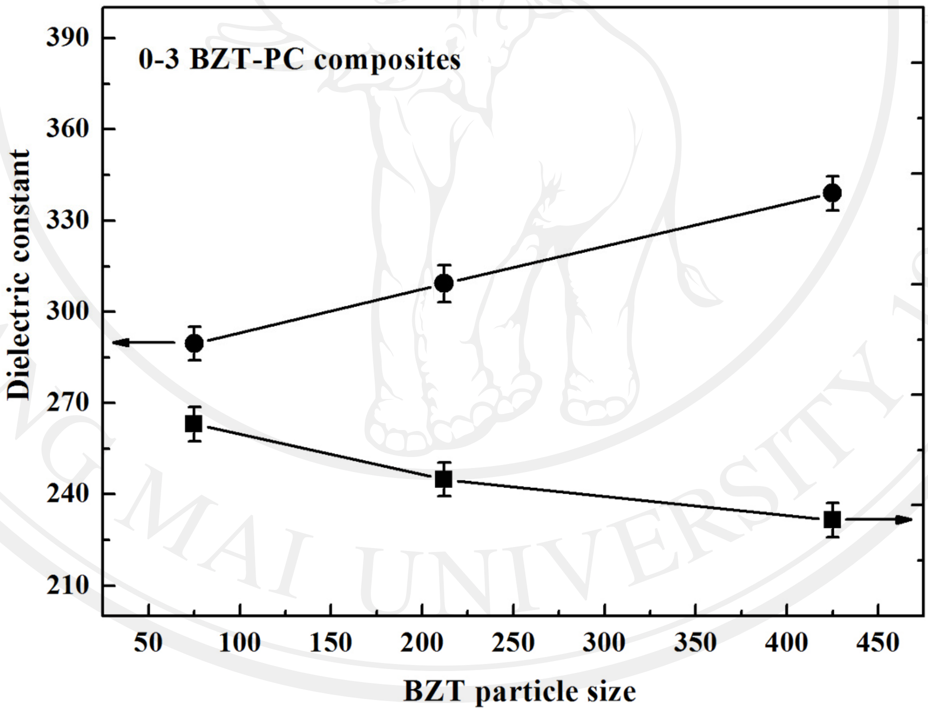

Fig. 4.1 Effect of particle size on dielectric properties results of 0-3 BZT-PC composites.

4.1.2 Effect of ceramic content on the dielectric properties

The dielectric properties of the both composites are measured as a function of content of piezoelectric ceramic (BZT) and were studied at frequency for 1 kHz and at room temperature.

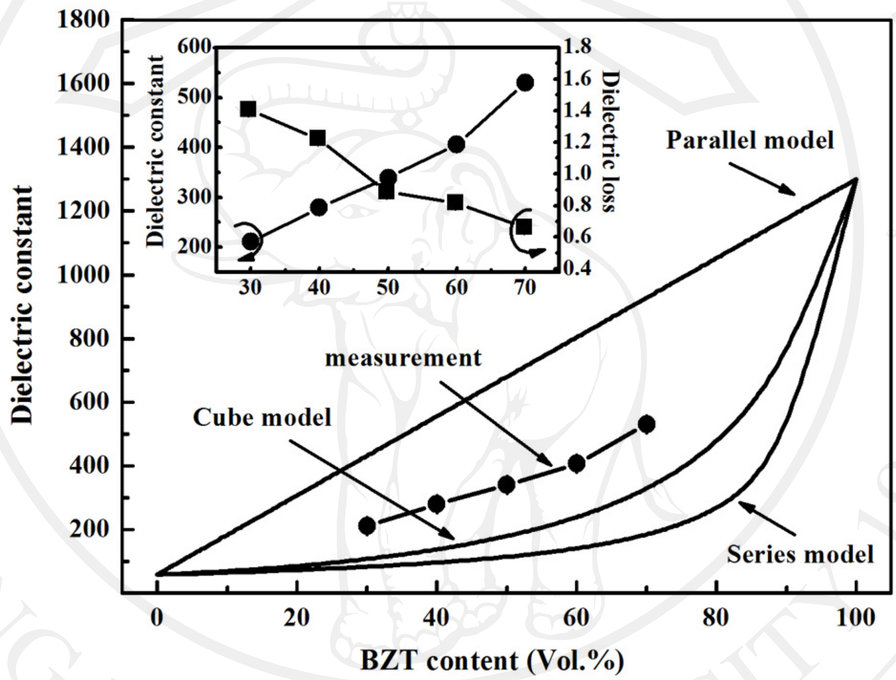

Fig. 4.2 The dielectric properties and comparison of models with dielectric constant of 0-3 BZT-PC composites.

The effect of 0-3 BZT-PC composites on the dielectric constant is plotted against the BZT content in Fig. 4.2. It can be seen that there is a roughly nonlinear increase of the dielectric constant value of the composites as a function of the BZT content and the dielectric loss value was found to decrease with increasing BZT content. This is believed that the BZT ceramic has higher dielectric constant when compared to cement. This leads to the higher dielectric constant of the composites, when there is an increase in the BZT content in the composites. Moreover, the BZT piezoelectric ceramic exists in the composites as tiny grains, just as introduces the more tiny capacitors when more BZT content.

The dielectric loss is found to decrease with increasing BZT content. It is well know that cement is a porous material with a complex microstructure and it is composed of an amorphous phase, crystallites in the micrometer range, bound water [88-89] and conduction ion in the cement matrix would contribute to the loss in the dielectric. The mathematical equations of parallel (Eq. (4.1)), series (Eq. (4.2)), and cube (Eq. (4.3)) models for dielectric constant of composite with different BZT content were used and are shown plotted in Fig. 4.2, respectively. The theoretical values are described as follows:

Parallel model [69] $$\varepsilon_C = {}^1v\,{}^1\varepsilon + {}^2v\,{}^2\varepsilon \qquad (4.1)$$

Series model [69] $$\varepsilon_C = \frac{{}^1\varepsilon \cdot {}^2\varepsilon}{{}^1v\,{}^2\varepsilon + {}^2v\,{}^1\varepsilon} \qquad (4.2)$$

Cube model [69] $$\varepsilon_C = \frac{{}^1\varepsilon \cdot {}^2\varepsilon}{\left({}^2\varepsilon - {}^1\varepsilon\right){}^1v^{-1/3} + {}^1\varepsilon \cdot {}^1v^{-2/3}} + {}^2\varepsilon \cdot \left(1 - {}^1v^{2/3}\right) \qquad (4.3)$$

Where ε_c is the dielectric constant of the composite. The ${}^1\varepsilon$ and ${}^2\varepsilon$ are the dielectric constant of the ceramics and the cement phase, respectively. The ${}^1v$ and ${}^2v$ are the volume percent of the ceramic and the cement phase, respectively.

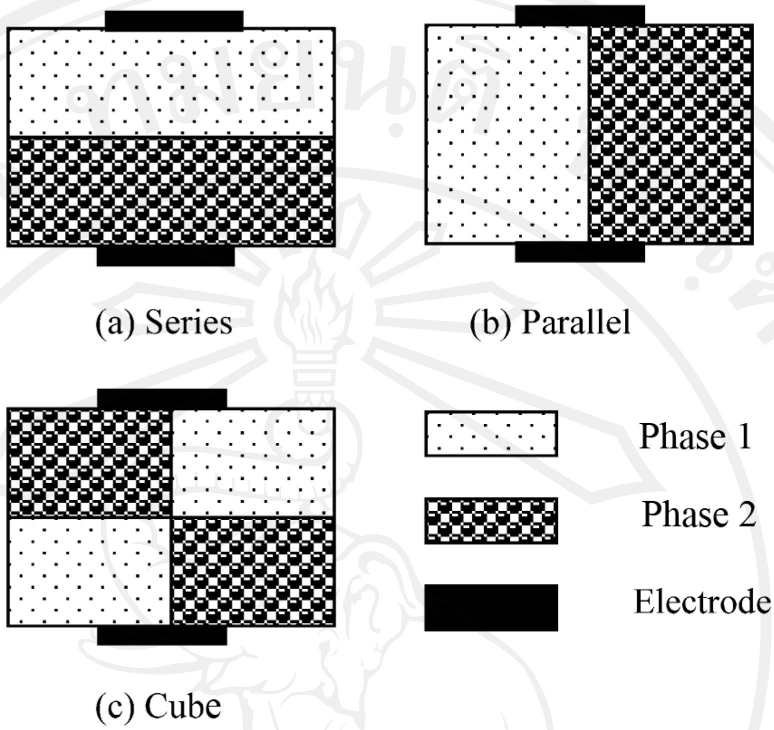

Fig. 4.3 Models of composite; (a) Series model, (b) Parallel model and (c) Cube model [69].

It is clear that parallel model and series model are the upper limit and lower limits for relative dielectric constant, respectively. The dielectric results of 0-3 connectivity BZT-PC composites can be seen to fit closest to that of the cube model. Furthermore, the parallel, series and cube models are shown in Fig. 4.3. For the cube model, it takes into account the anisotropic distribution of cubes in x, y, and z directions, which based on fundamental principal of the physical mixing and it is clear that the experimental results are close to the theoretical value of the cubes models, which means that the ceramic particles in the composites are well-dispersed [77, 90].

4.2 Piezoelectric properties of 0-3 modified barium titanate-Portland cement composites

Piezoelectric properties of 0-3 BZT-PC composites investigated are electromechanical coupling coefficient, piezoelectric coefficient and piezoelectric voltage coefficient. Effects on piezoelectric properties such as effect of BZT particle size, effect of BZT content and the degree of poling (which is critical factor in the piezoelectric properties and is often restricted by character of each component phase of the composites) are reported.

4.2.1 The degree of poling

The effect of the degree of poling on the piezoelectric properties such as piezoelectric coefficient (d_{33}) of 0-3 BZT-PC composites was investigated. The composites were produced using BZT of 50% by volume and the poling temperatures were selected at 40°C, 50°C and 60°C respectively. The effect of poling temperature on the d_{33} value is shown in Fig. 4.4. The d_{33} values were highest at 14 pC/N in composites of the poling temperature at 50°C. It is evident that the d_{33} increases remarkably as the poling temperature increases until 50°C and trends to level off subsequently. In addition, there are ions, such as Ca^{2+}, OH^{-} and Al^{3+} in the Portland cement matrix. As the poling temperature increases ions migration takes place leading to a rise of conductivity and also affected d_{33} because the ions in the cement matrix lead to a rise of leakage current which decrease the piezoelectricity. Therefore, 50°C is chosen as the optimum poling temperature for 0-3 BZT-PC composites.

In our study, poling of the composites was carried out under a poling field E at 1.0 kV/mm and poling time t at 45 min in silicone oil. If the composites were carried out under the poling temperature more than 60°C or the poling field continually increases, the composites have a high chance of breaking down [79]. This is due to the ions, such as Ca^{2+}, OH^- and Al^{3+} in the cement matrix, particle pores and interface pore in the composites. In additional, there is some water in pores, which greatly lowers the resistivity and gives rise to the leakage current in the course of the poling [2, 4] .

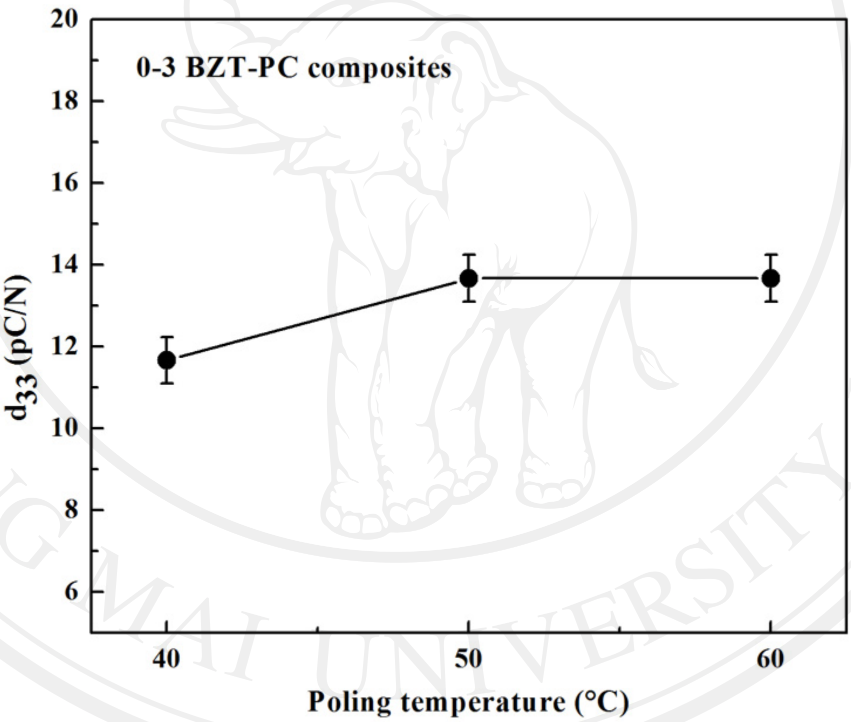

Fig. 4.4 The effect of poling temperature on the piezoelectric coefficient (d_{33}).

4.2.2 Effect of ceramic particle size on the piezoelectric properties

The impedance and phase spectra of the composites with different BZT particle size can be seen in Fig. 4.5. The composites were poled under the same poling field (1kV/mm), poling time (45 min) and poling temperature (50ºC).

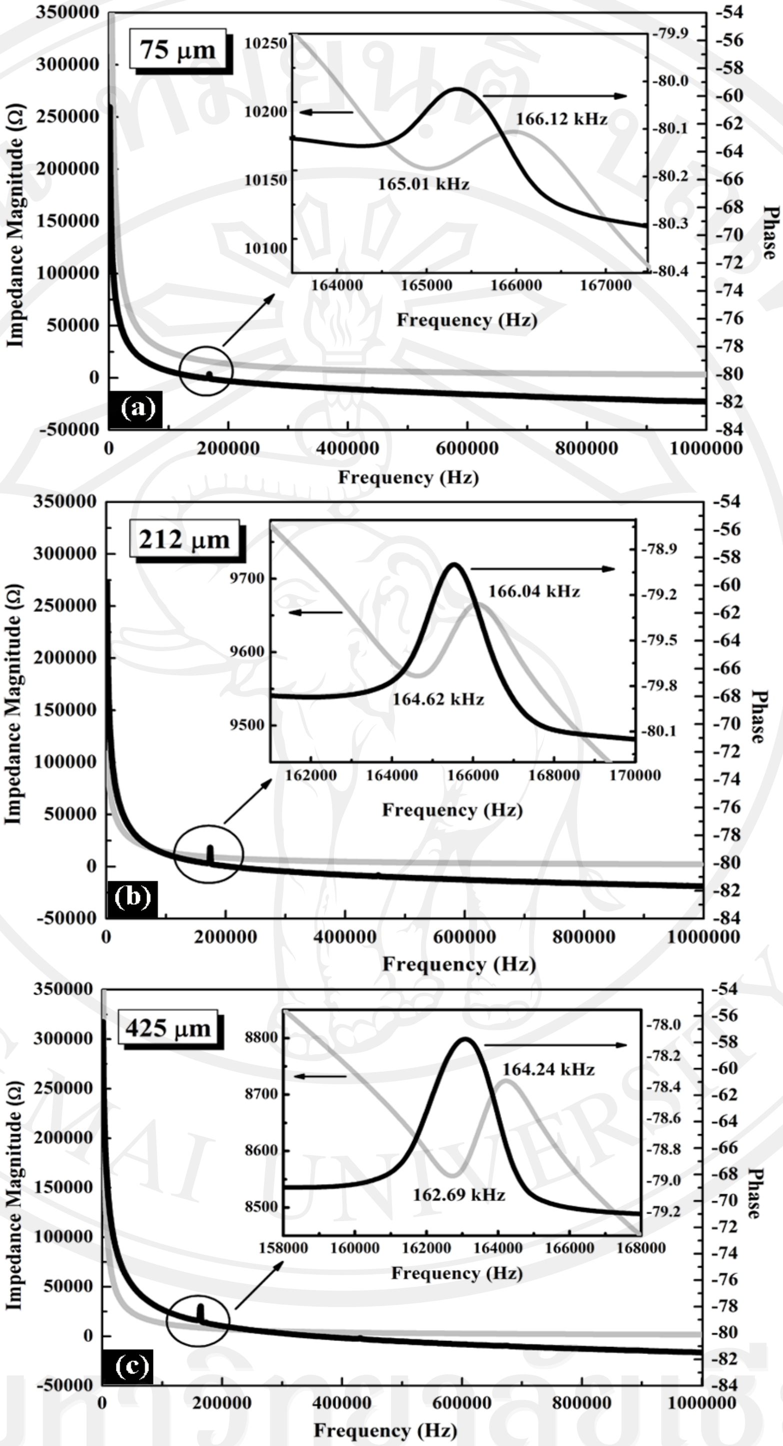

Fig. 4.5 The impedance and the phase spectra results of 0-3 BZT-PC composites with different BZT particle size at (a) 75 μm BZT particle size, (b) 212 μm BZT particle size and (c) 425 μm BZT particle size.

The peaks appear in all impedance and phase curves correspond to the resonance and antiresonance of the piezoelectric-Portland cement based composites [4]. It is clear that the intensity of peaks appears in the impedance and phase curves are found to be greatest when the composites were made using the largest BZT particle size (425 μm) particles (Fig. 4.5(c)) thus the larger particle size brings a higher piezoelectric effect to the composites. The electromechanical coupling coefficient (K_t) was then calculated from the electric impedance graph plotted against the frequency and using the following formula [33]:

$$K_t^2 = \frac{\pi}{2}\frac{f_m}{f_n}\tan\left(\frac{\pi}{2}\frac{f_n - f_m}{f_n}\right) \qquad (4.4)$$

Where f_m and f_n are the frequency at the minimum and maximum electric impedance respectively. Composites with 425 μm BZT particle size and 75 μm BZT particle size have K_t values of 15.2% and 12.8%, respectively (Fig. 4.6). The effect of 0-3 BZT-PC composites on the piezoelectric coefficient (d_{33}) was plotted against the BZT particle size in Fig. 4.6. The d_{33} value was found to increase with increasing BZT particle size. The piezoelectric voltage coefficient (g_{33}) means the sensitivity of a receiving voltage, since g_{33} is calculated as $g_{33} = d_{33}/\varepsilon_0\varepsilon_r$. For the range of particle sizes under 425 μm, the g_{33} increases with increasing particle size of BZT (Fig. 4.6). This behavior can be explained as follows. The phenomenon that the K_t, d_{33} and g_{33} values of the composites can be seen to decrease with the decrease of the BZT particle size could be explained by greater contact surfaces between cement matrix and BZT particles [5].

Moreover, the relationship of particle size with sample thickness is in agreement with the experimental results by model of Newnham *et al* [23]. For the BZT particle size that is significantly smaller than the thickness of samples, when applying an external electric field on the composites the electric field would mainly act on the cement, thus causing the BZT particles not able to reach the saturation condition because BZT particles were enwrapped by the cement matrix. For BZT particle size that is closer to the sample thickness, the connectivity pattern of the BZT particle with cement matrix are more like connectivity of the 1-3 and 2-2 pattern. When an external electric field was applied on the composites, due to BZT particles may contact each other, and some larger particles even run through the whole sample which makes the poling easier [91].

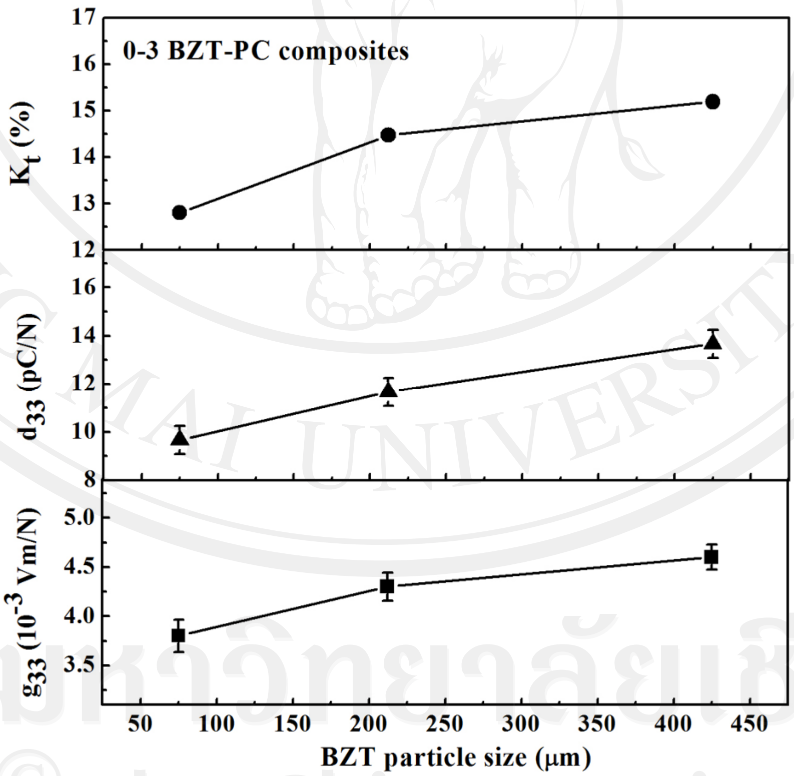

Fig. 4.6 The effect of particle size of 0-3 BZT-PC composites on electromechanical coupling coefficient (K_t), piezoelectric coefficient (d_{33}) and piezoelectric voltage coefficient (g_{33}) results.

Again, this is believed to be due to less contact surfaces and higher connectivity in composites with largest BZT particle size thus would result in better poling efficiency of the composites. Therefore, the BZT ceramic of 425 μm particle size used for the BZT particle size range tested at the same volume led to optimum piezoelectricity in the 0-3 BZT-PC composites.

4.2.3 Effect of ceramic content on the piezoelectric properties

The impedance and phase spectra of the composites were plotted against the frequency and are shown in Fig. 4.7 with different BZT content (40% BZT -70% BZT content). For composites less than 40% BZT content, it should be noted that it would become very difficult to pole samples. Thus at less than 40% BZT content there is higher non-piezoelectric cement matrix volume percent in the composite, their inner water and ions, such as Ca^{2+}, OH^- and Al^{3+} in the Portland cement matrix. So, it should be noted that it would become very difficult to pole samples with composites less than 40% BZT content because of the ions in the cement matrix lead to a rise of leakage current. The variation of piezoelectric coefficient as a function of content of BZT were studied under the same poling field (1kV/mm), poling time (45 min) and poling temperature (50ºC).

An increase in the phase spectra can be seen to be higher in the 70% BZT composite as compared to that of 40% BZT composite due to greater piezoelectric effect when more BZT was added. The K_t values were then calculated from Eq. (4.4). The K_t results of composites are shown in Fig. 4.8. Again, an increase in K_t values can be seen with the increasing BZT content. Under similar poling field of 1 kV/mm and using composite discs of similar size, the K_t result on the 0-3 lead-free piezoelectric-cement composite with 60% BZT composite (K_t =16.3%) is very similar to the reported for 0-3 lead-based piezoelectric ceramic-cement composites at the 60% PZT composite when compared to the recent work ($K_t \approx$ 19.8%) at poling temperature of 130 °C by A. Chaipanich *et al.* [76]. However, not all conditions were the same and that direct comparison is not possible.

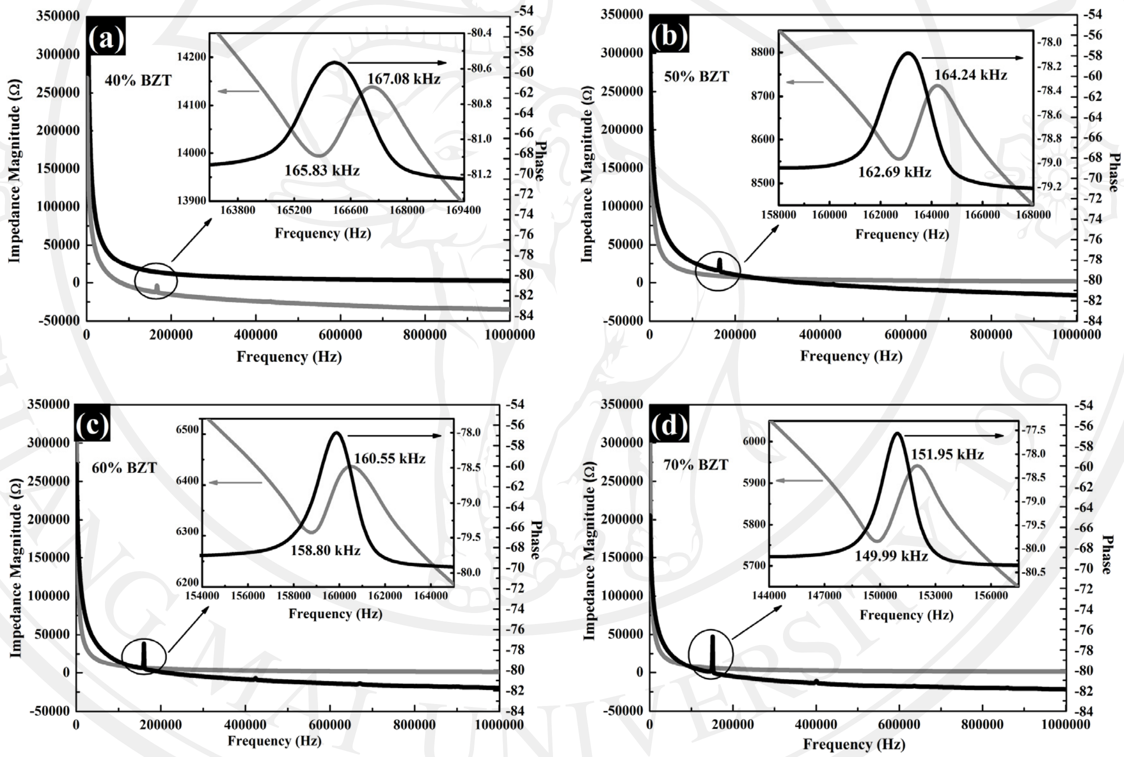

Fig. 4.7 The impedance and the phase spectra results of 0-3 BZT-PC composites with different BZT content at (a) 40% BZT composite, (b) 50% BZT composite, (c) 60% BZT composite and (d) 70% BZT composite.

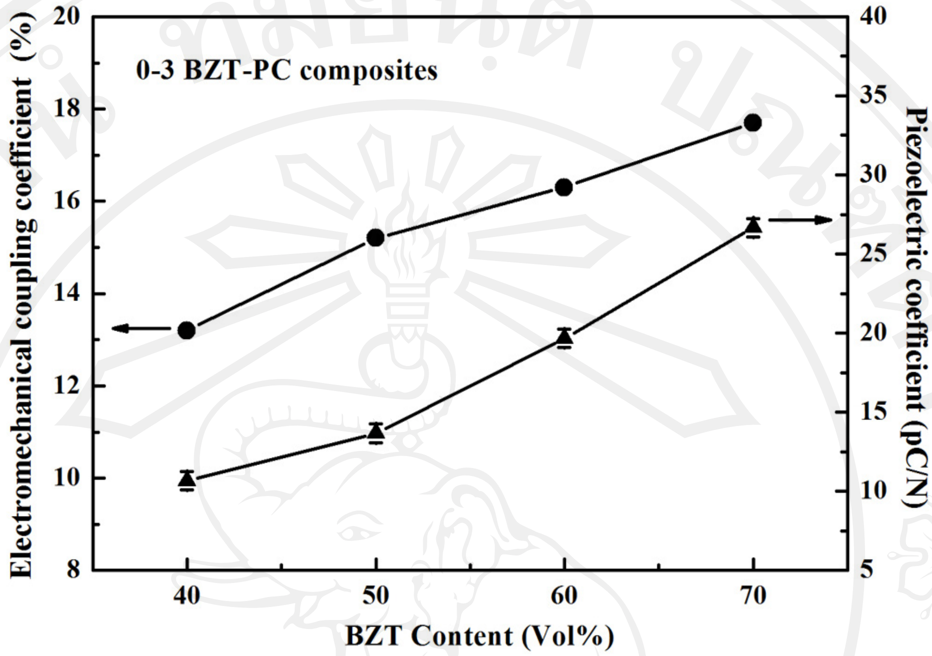

Fig. 4.8 The effect of BZT content of 0-3 BZT-PC composites on electromechanical coupling coefficient (K_t) and piezoelectric coefficient (d_{33}) results.

In this work, three models of series model, parallel model and cubes model were compared to evaluate the results for the piezoelectric coefficient (d_{33}) of the 0-3 BZT-PC composites. The theoretical equations of the series model, parallel model and cubes model for the d_{33} values are as follow:

Parallel model [65] $$^{C}d_{33} = \frac{^{1}\nu.^{1}d_{33}.^{2}S_{33} + ^{2}\nu.^{2}d_{33}.^{1}S_{33}}{^{1}\nu.^{2}S_{33} + ^{2}\nu.^{1}S_{33}} \quad (4.5)$$

Series model [65] $$^{C}d_{33} = \frac{^{1}\nu.^{1}d_{33}.^{2}\varepsilon + ^{2}\nu.^{2}d_{33}.^{1}\varepsilon}{^{1}\nu.^{2}\varepsilon + ^{2}\nu.^{1}\varepsilon} \quad (4.6)$$

Cube model [77] $$ {}^{C}d_{33} = {}^{1}d_{33} \cdot \frac{{}^{1}v}{{}^{1}v^{\frac{1}{3}} + \left(1 - {}^{1}v^{\frac{1}{3}}\right) \cdot \frac{{}^{1}\varepsilon}{{}^{2}\varepsilon}} \cdot \frac{1}{1 - {}^{1}v^{\frac{1}{3}} + {}^{1}v} \qquad (4.7) $$

Where the ${}^{C}d_{33}$ is the piezoelectric coefficient of the composite. The ${}^{1}d_{33}$ and ${}^{2}d_{33}$ are the piezoelectric coefficient of the ceramics and the cement phase. The ${}^{1}\varepsilon$ and ${}^{2}\varepsilon$ are the dielectric constant of the ceramics and the cement phase. The ${}^{1}S_{33}$ and ${}^{2}S_{33}$ are the elastic compliance of the ceramics and the cement phase. The ${}^{1}v$ and ${}^{2}v$ are the volume percent of the ceramic and the cement phase.

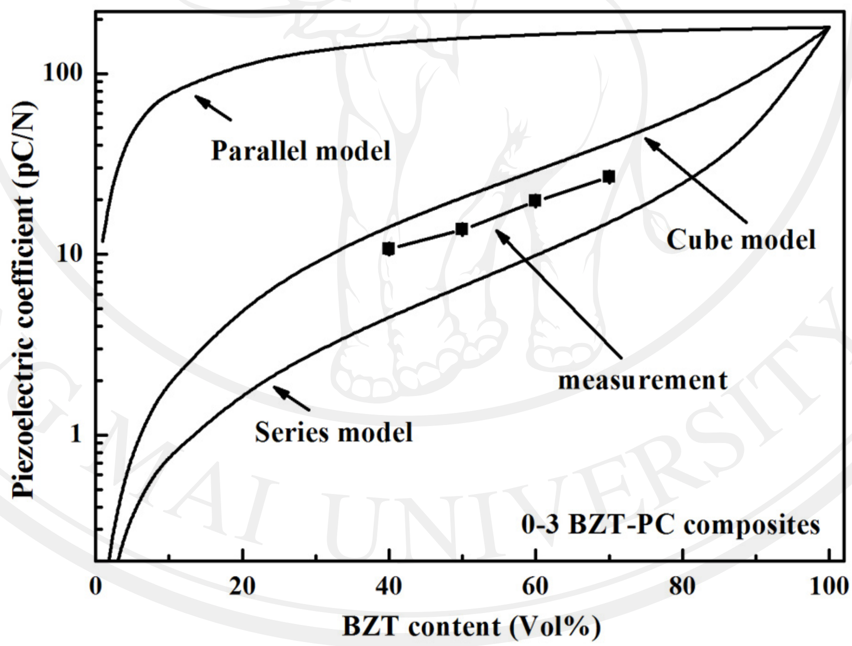

Fig. 4.9 Comparison of models with piezoelectric coefficient of 0-3 BZT-PC composites.

Moreover, the test results of d_{33} values of the composites are plotted against BZT content with prediction curves for different models in Fig. 4.9. It is clear that the parallel model and series model are the upper limit and lower limits for piezoelectric coefficient, respectively. The experimental results can be seen to most closely related to the theoretical value of the cube model, thus agreeing with results by Xin et al. [1] where the d_{33} values of the 0-3 P(LN)ZT-sulphoaluminate cement composites follows the cube model well. The g_{33} values were calculated using the measured values of d_{33} coefficients and the dielectric constants of the composites.

The theoretical equations of series model, parallel model and cubes model for the g_{33} values can be denoted as follows:

Parallel model [65]
$$^{C}g_{33} = \frac{^{1}v.^{1}d_{33}.^{2}S_{33} + ^{2}v.^{2}d_{33}.^{1}S_{33}}{\left(^{1}v.^{2}S_{33} + ^{2}v.^{1}S_{33}\right)\left(^{1}v.^{1}\varepsilon + ^{2}v.^{2}\varepsilon\right)} \tag{4.8}$$

Series model [65]
$$^{C}g_{33} = \frac{^{1}v.^{1}d_{33}}{^{1}\varepsilon} + \frac{^{2}v.^{2}d_{33}}{^{2}\varepsilon} \tag{4.9}$$

Cube model
$$^{C}g_{33} = \frac{^{1}d_{33}\,^{1}v}{\left(^{1}v^{1/3} + \frac{^{1}\varepsilon}{^{2}\varepsilon}(1 - ^{1}v^{1/3})\right)(1 - ^{1}v^{1/3} + ^{1}v)} \times \frac{(^{2}\varepsilon - ^{1}\varepsilon)^{1}v^{-1/3} + ^{1}\varepsilon^{1}v^{-2/3}}{^{1}\varepsilon\,^{2}\varepsilon + \left[^{2}\varepsilon\left(1 - ^{1}v^{2/3}\right)\right]\left[\left(^{2}\varepsilon - ^{1}\varepsilon\right)^{1}v^{-1/3} + ^{1}\varepsilon^{1}v^{-2/3}\right]} \tag{4.10}$$

Where the $^{C}g_{33}$ is the piezoelectric voltage coefficient of the composite. The $^{1}d_{33}$ and $^{2}d_{33}$ are the piezoelectric coefficient of the ceramics and the cement phase. The $^{1}\varepsilon$ and $^{2}\varepsilon$ are the dielectric constant of the ceramics and the cement phase. The $^{1}S_{33}$ and $^{2}S_{33}$ are the elastic compliance of the ceramics and the cement phase. The ^{1}v and ^{2}v are the volume percent of the ceramic and the cement phase.

The results of g_{33} values of the 0-3 BZT-PC composites are plotted against BZT content with series model, parallel model and cubes models and the experimental results can be seen to be most closely related to the theoretical value of the series model in Fig. 4.10. However, the 0-3 connectivity piezoelectric-cement based composites is still difficult to obtain a high piezoelectric properties due to the difficulty in poling ceramic particles in such composite because of the high dielectric loss and pores, their inner water and ions from the cement matrix in the composites. This results in lower piezoelectric voltage constant of 0-3 connectivity piezoelectric-cement based composites. The connectivity types, such as 1-3 and 2-2 connectivity composites can effectively improve the material performance in piezoelectric-cement based composites (the results of 1-3 and 2-2 connectivity piezoelectric-cement based composites show in part II and III).

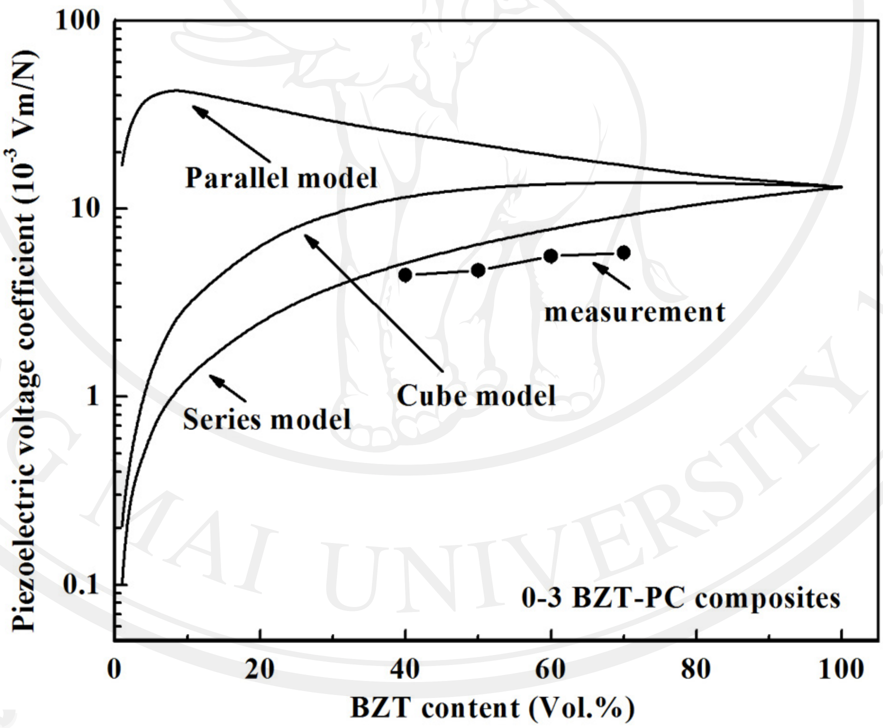

Fig. 4.10 Comparison of models with piezoelectric voltage coefficient of 0-3 BZT-PC composites.

4.3 Acoustic impedance properties of 0-3 modified barium titanate-Portland cement composites

4.3.1 Effect of ceramic particle size on the acoustic impedance properties

The acoustic impedance (Z_c) of the composite can be calculated using the following formula [3, 77]:

$$\rho_c = v_1\rho_1 + v_2\rho_2 \quad (4.11)$$

$$Z_c = V_c\rho_c \quad (4.12)$$

Where ρ_1, ρ_2 and ρ_c are the densities of the ceramics phase, the cement phase and composites, respectively. The v_1 and v_2 are the volume percent of the ceramics phase and the cement phase, respectively and V_c is the acoustic velocity in composites. The ρ_c, porosity and Z_c values of 0-3 BZT-PC composites are plotted against the BZT particle size in Fig. 4.11 where it can be seen that the Z_c values results were found to be slightly different in values with different BZT particle size. The ρ_c values can be seen to decrease with the decreasing BZT particle size which corresponds to decreasing Z_c values by the following Eq. (4.12). It is believed that the lower ρ_c values of composite with smaller BZT particle may be related to defects such as porosity in the composite due to greater contact surfaces between cement matrix and ceramic particles. Furthermore, it is clear that the 0-3 BZT-PC composite in the range tested can be close to that of concrete (acoustic impedance of the concrete ≈ 6.90-11.23 x 10^6 kg/m^{2}s) [13-14].

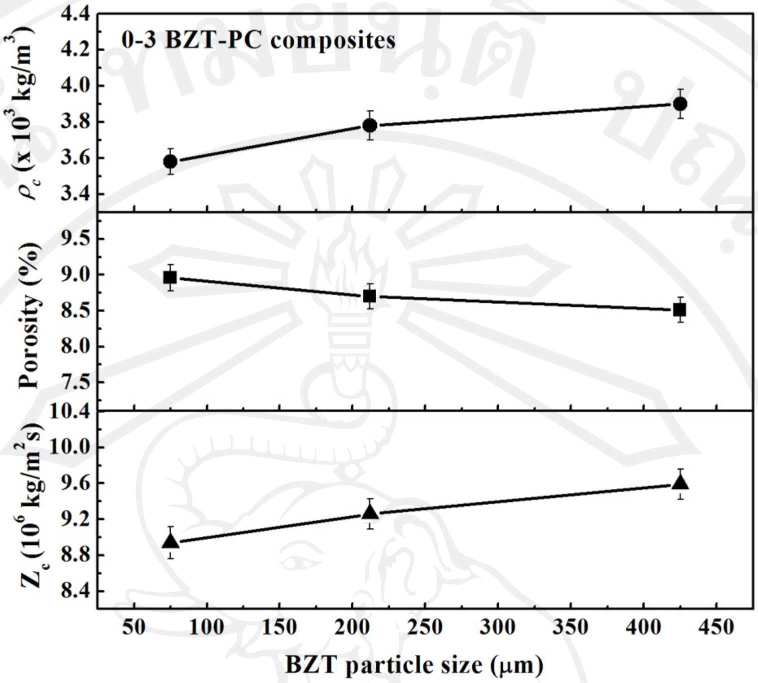

Fig. 4.11 The effect of particle size of 0-3 BZT-PC composites on density, porosity and acoustic impedance results.

4.3.2 Effect of ceramic content on the acoustic impedance properties

The dependences of density are shown in Fig. 4.12. It can be seen that with increasing BZT content, the porosity was found to slightly increase with increasing the BZT content. This is mainly because the higher the BZT volume percent is, these is less binder (cement) to bind the ceramics together, resulting in an increase of porosity. Fig. 4.13 shows the acoustic impedance of the composites (Z_c) calculated using the formula Eq. (4.12) with different BZT contents. The Z_c values of composites are found to be increasing with increasing BZT content.

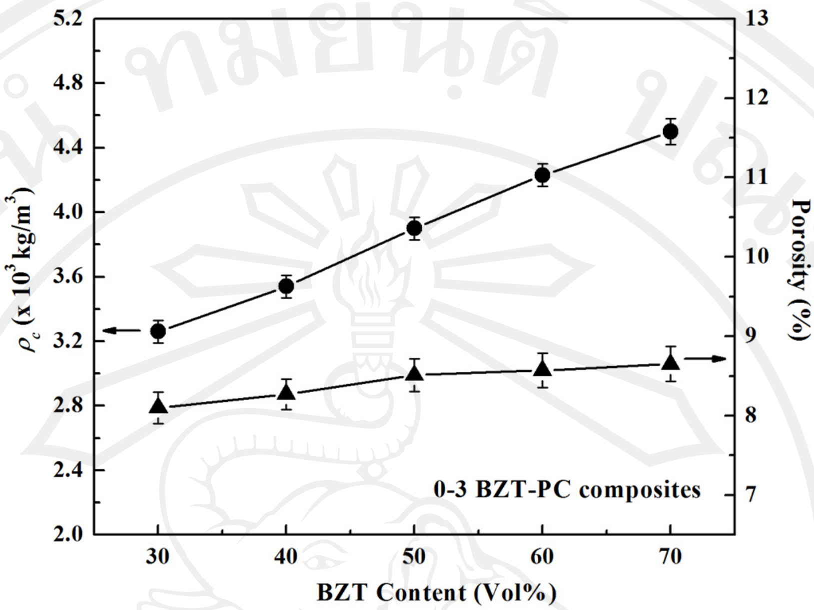

Fig. 4.12 The density and porosity results of 0-3 BZT-PC composites with different BZT content

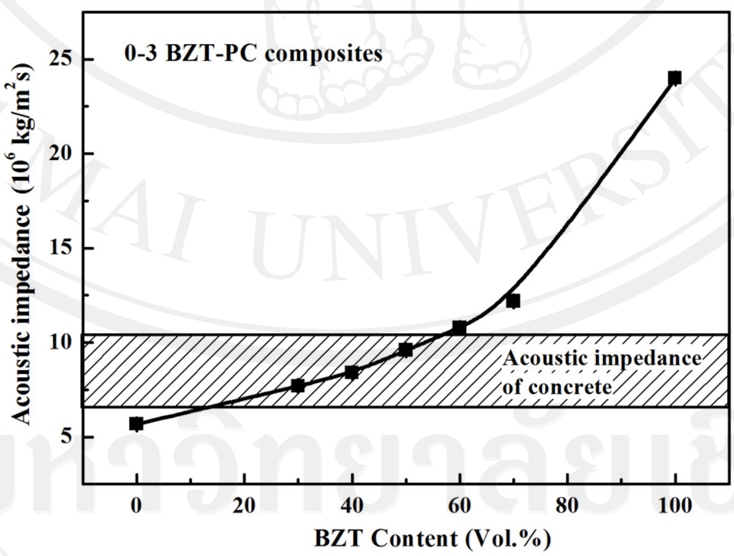

Fig. 4.13 The acoustic impedance results of 0-3 BZT-PC composites with different BZT content.

Moreover, it is clear that the Z_c values of 0-3 BZT-PC composite with ≈ 30-60% BZT composites are closer to that the acoustic impedance of concrete and the Z_c value of composite can be tuned to a compatible value to match the requirement of structure materials, i.e. concrete (acoustic impedance of concrete ≈ 6.90-11.23 x 10^6 kg/m^2s) [13-14].

4.4 Thermal expansion of 0-3 modified barium titanate-Portland cement composites

The thermal strain dependences of temperature of 0-3 BZT-PC composites with different BZT content are presented in Fig. 4.14. The result shows measurement of composites as temperature was increased from -100 °C to 250 °C at a rate of 2 °C/min. For the heating first run, note that from -100 °C to ≈ 100 °C the composite expansion. It contracted for the remainder of the temperature range (≈ 100 °C to 250 °C). The shrinkage at elevated temperatures has been attributed to a loss of moisture from cement matrix.

Near room temperature water resides in cement matrix in several forms. It is present in pores and voids in a free state, and also chemically bound to hydration products constituting the solid material that gives cement its strength. Increasing temperatures first drive out the free pore water and, if severe enough, also dehydrate the solid paste matrix [92]. Moreover, the most important products of the hydration reactions are the calcium silicate hydrate (C-S-H) and the portlandite, also called calcium hydroxyde, (CH) [60].

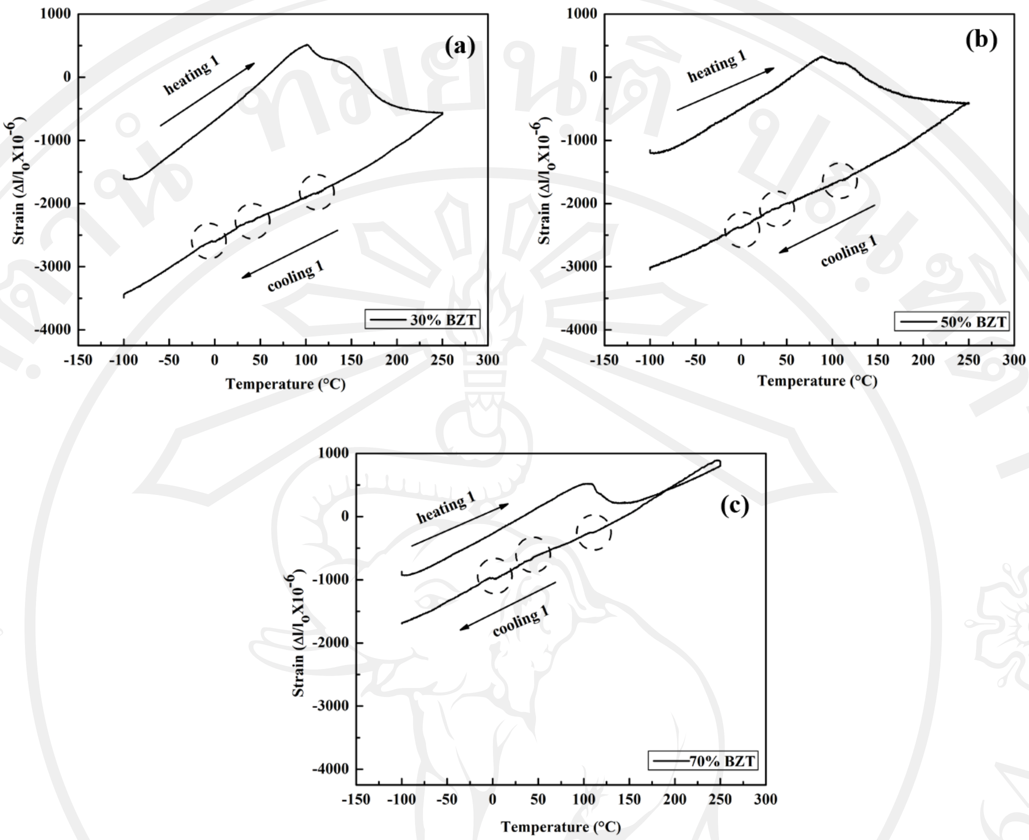

Fig. 4.14 Thermal expansion as a function of temperature for 0-3 BZT-PC composites for first run; (a) 30% BZT composite, (b) 50% BZT composite and (c) 70% BZT composite.

The reactions that occur with an increase of temperature in cement matrix [57]: the evaporable water and a part of the bound water escapes at 30-105 °C. It is generally considered that the evaporable water is completely eliminated at 120 °C [60]. The high temperature tends to change the mechanism of ettringite formation; a marked reduction in stability of ettringite between 60 and 80 ◦C is observed. Ettringite hydrates begin to dehydrate within this temperature range [60]. At 180-300 °C, the loss of bound water from the decomposition of the C-S-H undergoes [62].

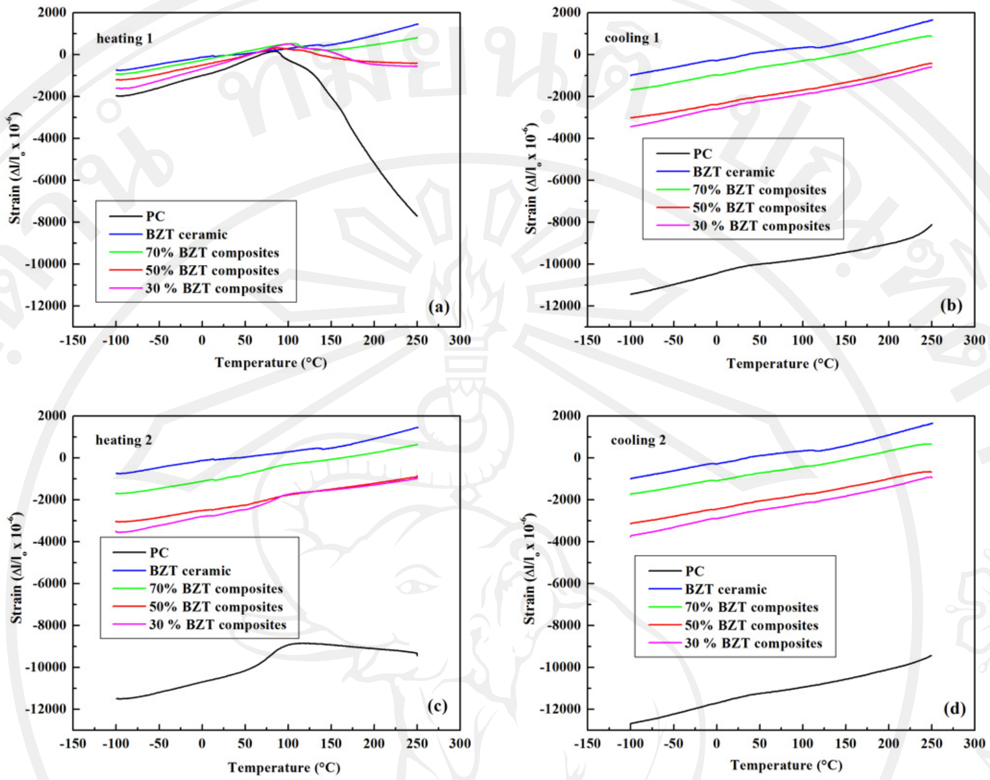

Fig. 4.15 Thermal expansion as a function of temperature for 0-3 BZT-PC composites, Portland cement and BZT ceramic; (a) heating (first run), (b) cooling (first run), (c) heating (second run) and (d) cooling (second run).

For the cooling first run, Fig. 4.15 shows the three phase transition of barium zirconate titanate; BZT and the transitions of rhombohedral-to-orthorhombic, orthorhombic-to-tetragonal and tetragonal-to-cubic occur at ≈ 0, ≈ 47 and ≈ 110 ºC, respectively of all composition in the range tested. When compare 0-3 BZT-PC composites with BZT ceramic and Portland cement, the 30% BZT content can be seen clearly the trend of heating (Fig. 4.15(a)) was similar behavior with Portland cement. However, the second run (Fig. 4.15(c)) shows smooth curve of the thermal strain more than first run because the first run already resulted in the loss of some moisture and water from cement matrix. Besides, it can be seen the three phase transition of BZT ceramic in cooling both first run (Fig. 4.15(b)) and second run (Fig. 4.15(d)) of all 0-3 BZT-PC composite.

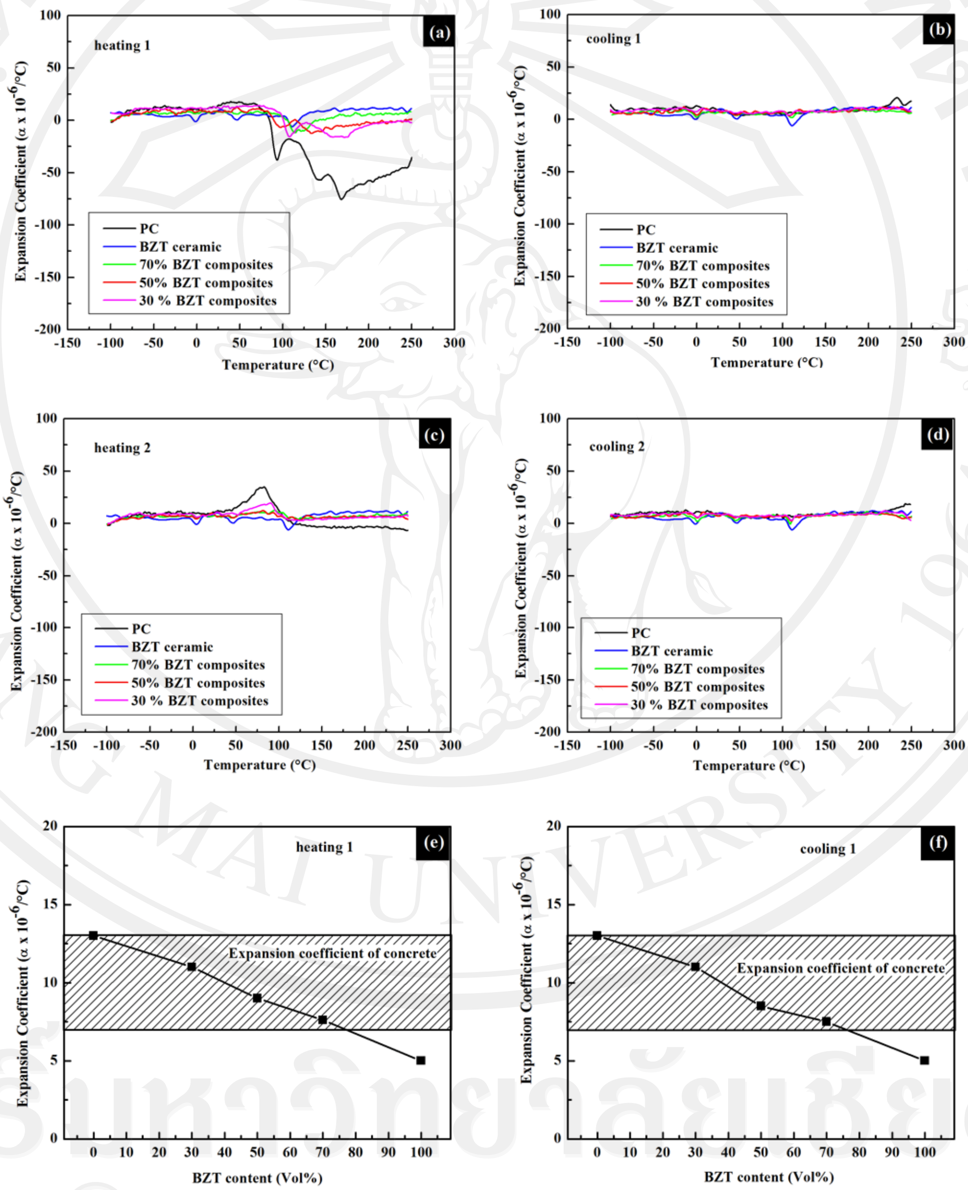

Fig. 4.16 Thermal expansion coefficient for 0-3 BZT-PC composites, Portland cement and BZT ceramic; (a) heating (first run), (b) cooling (first run), (c) heating (second

run), (d) cooling (second run), (e) effect of BZT content (heating and first run) and (f) effect of BZT content (cooling and first run).

The thermal expansion coefficient dependences of temperature of 0-3 BZT-PC composites are presented in Fig. 4.16(a-d). It is found that, the results of the thermal expansion coefficient was confirm a loss of moisture and water from Portland cement and all of 0-3 BZT-PC composites (for the BZT content range tested; heating) $\approx$ 100 ºC. The coefficient of thermal expansion, in range below ≈ 100 °C, is not a unique value but depends on the moisture content of the cement matrix. There is an unusual moisture dependency, in which the coefficient increases considerably at intermediate relative humidities. This has been explained by considering that internal rearrangement of water take place between capillary pores and gel pores without a change in the total water content the paste [37]. If a moist in cement matrix is heated, loss of moisture should be accompanied by shrinkage. The amount of shrinkage that can occur will depend on the duration of heating, the permittivity of cement paste, and the thickness of the sample. Much greater shrinkage is observed for given amount of moisture loss above $\approx$100 °C than for the same loss below $\approx$100 °C, because structural breakdown of the hydration products is occurring [37]. For thermal expansion coefficient of cooling are presented three phase transition of BZT ceramic and the transitions are the same temperature with the thermal strain.

The thermal expansion coefficient at room temperature of 0-3 BZT-PC composites varies with different BZT content are shown in Fig. 4.16(e-f). The results show heating and cooling of first run are observed. All of curve of the thermal expansion coefficient exhibits the trend of decrease with increasing BZT content. The thermal expansion coefficient value of the 0-3 BZT-PC composites is close to the Portland cement more than BZT ceramic. Moreover, it is seen that the 0-3 BZT-PC composite in the range tested can be matched with concrete (thermal expansion coefficient of the concrete = 7.4-13 x 10^{-6}/°C [37]).

4.5 Microstructure properties of 0-3 modified barium titanate-Portland cement composites

Fig. 4.17(a) shows the SEM micrographs of 0-3 BZT-PC composite (50% BZT composite and 425 μm BZT particle size). On closer investigation using greater magnification (x5,000), the SEM micrographs of composite show a typical microstructure at the interfacial zone between the BZT ceramic particles and the cement matrix where BZT ceramic particles can be seen next to hydration products of Portland cement such as calcium silicate hydrates (CSH) and calcium sulfoaluminate hydrate (ettringite). Furthermore, the CSH gel (the main hydration products of Portland cement) acts as the binder which binds the composites together. The BZT ceramic particles can be seen clearly surrounded by the cement matrix, suggesting good bonding between the two materials.

From Fig. 4.17(b), energy dispersive X-ray spectrometry (EDX) analysis of the composite shows the elements of CSH, ettringite and BZT ceramic. EDX analysis shows the presence of barium, titanium, zirconium and oxygen as the main elements of BZT ceramic (apart from gold which was used to coat the samples). Elements of CSH (Ca, Si, O) and ettringite (Ca, Al, S, O) were detected (hydrogen cannot be detected) in the cement grains.

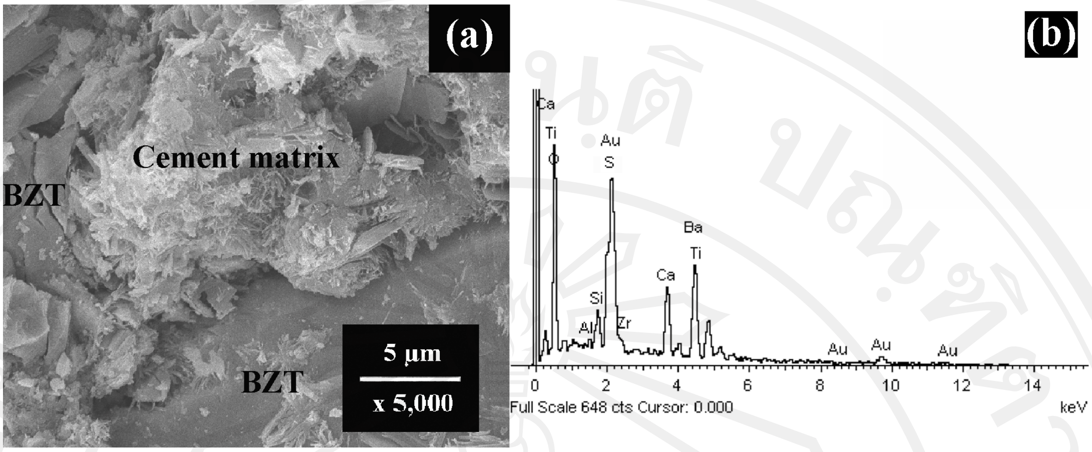

Fig. 4.17 Microstructure of 0-3 BZT-PC composite; (a) SEM micrograph and (b) EDX analysis.

4.6 Summary

In this part, the 0-3 connectivity modified barium titanate-Portland cement composites were investigated. The following conclusions can be drawn from the experiments;

1. The 0-3 Barium zirconate titanate-Portland cement composites (0-3 BZT-PC composites) were fabricated by normal mixing, pressing and curing method. It is more easily fabricated in complicated shapes than other forms of composites.

2. Effect of particle size show that the dielectric constant, electromechanical coupling coefficient, piezoelectric coefficient and piezoelectric voltage coefficient of 0-3 composites were found to increase with increasing ceramic particle size. Therefore, the BZT ceramic of 425 μm particle size used for the ceramic particle size range tested at the same volume content led to optimum piezoelectricity in the 0-3 composites. This result could be explained by the contact surfaces between cement

matrix and ceramic particles, porosity and relationship of particle size with connectivity patterns.

3. For the 0-3 BZT-PC composites, the optimum poling conditions are that the poling field *E* is 1.0 kV/mm, the poling time *t* is 45 min and the poling temperature is 50 °C.

4. Effect of BZT content as the dielectric constant, piezoelectric coefficient and piezoelectric voltage coefficient of 0-3 BZT-PC composites obtained from experiment are close to the predictions of the cubes and series model, suggestions that the ceramic particles in the composites are uniformly dispersed and closely relate to the experiment results. The dielectric constant, electromechanical coupling coefficient, piezoelectric coefficient and piezoelectric voltage coefficient of the 0-3 composites were found to increase as a function of the ceramic content. For the dielectric loss of 0-3 composites were found to decrease with an increase of ceramic content.

5. The ≈ 30-60% BZT composites is the optimal ceramic content for an acoustic impedance match between 0-3 BZT-PC composites and concrete and the acoustic impedance of the 0-3 composites was much lower than that of pure ceramics.

6. For the thermal expansion, the 0-3 composites contracted for the temperature range (≈ 100 °C to 250 °C). The elevated temperatures induced shrinkage in composites due to a loss of some moisture and water from cement matrix and the physical and mechanical properties of hydration product in cement matrix was change at elevated temperatures. For the cooling of 0-3 BZT-PC composites are found the three phase transition of BZT. The thermal expansion coefficient value of the 0-3

composites in the range tested can be match with concrete and the results were confirm no chemical reaction between ceramic and Portland cement in composites.

7. From SEM micrographs, calcium silicate hydrates (the main hydration products of Portland cement) acts as the binder which binds the composites together.

However, the 0-3 connectivity composite is still difficult to obtain a great piezoelectric properties due to the difficulty in poling ceramic particles in composite because of the high dielectric loss. The effective ways to improve piezoelectric value was the connectivity types such as 1-3 and 2-2 connectivity composites. This was investigated and reported in the part II&III.

PART II

1-3 Modified barium titanate-Portland cement composites

The connectivity types, such as 1-3 connectivity composites are effective way to improve the material performance in piezoelectric-cement based composites. So, this part focuses on electrical, physical and microstructure properties such as dielectric, piezoelectric, acoustic impedance and microstructure properties of 1-3 barium zirconate titanate-Portland cement composites (1-3 BZT-PC composites). The properties of 1-3 BZT-PC composites are discussed in details.

4.7 Dielectric properties of 1-3 modified barium titanate-Portland cement composites

The dielectric constant and dielectric loss on the BZT content are shown in Fig. 4.18. The dielectric constant of the composites can be seen to increase with increasing BZT volume content and the dielectric constant is highest at 795 for 70±2% BZT composites at 1 kHz. The reason is probably that the higher the volume content of piezoelectric ceramic and higher is the contribution of the piezoelectric ceramic, which leads to an increase of the dielectric constant of the composite [9-10]. In addition, the dielectric loss is found to decrease with increasing BZT content and the loss of 70±2% BZT composite is lowest at ≈ 0.09 (f = 1 kHz). Furthermore, the parallel, series and cube models were compared to evaluate the experimental results for dielectric constant of the 1-3 BZTPC composites.

The series and parallel mixing models represent the extreme cases where the model is alternating layers of each phase, perpendicular and parallel to the applied field, respectively [70]. For the cube model, Banno [67-70] proposed a ‘‘modified cube model,’’ which took into account the anisotropic distribution of cubes in x, y, and z directions, which based on fundamental principal of the physical mixing. The mathematical equations of parallel, series and cube models for dielectric constant are calculated using the formula ((Eq. (4.1)), (Eq. (4.2)) and (Eq. (4.3)) respectively.

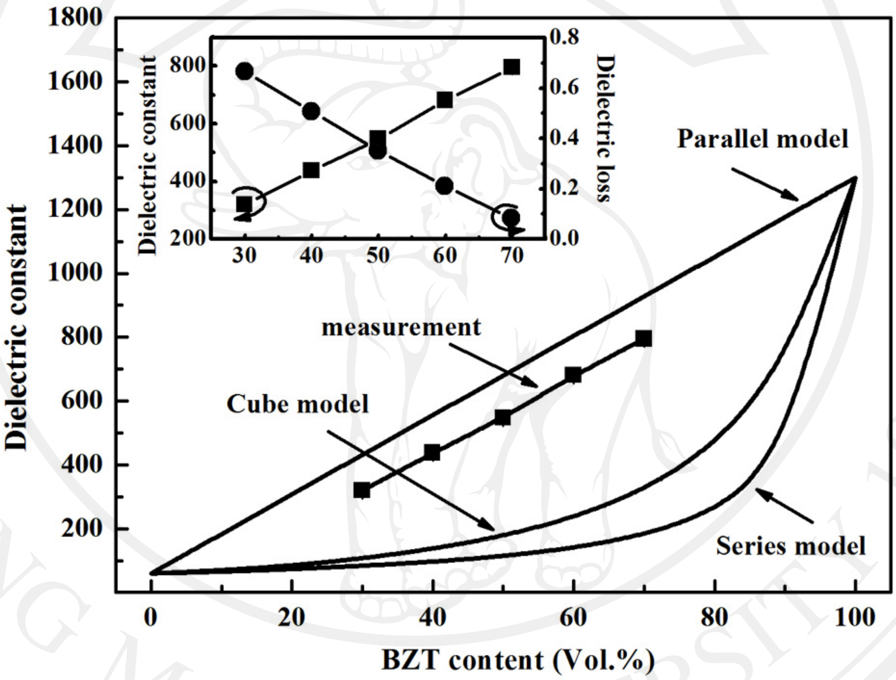

Fig. 4.18 The dielectric properties and comparison of models with dielectric constant of 1-3 BZT-PC composites.

Fig. 4.18 shows that the dielectric constant of the 1-3 BZT-PC composites is close to the prediction by the parallel models and the results are shown to be higher than 0-3 connectivity composites. This is because the 1-3 connectivity essentially contains the piezoelectric ceramic fully aligned in one direction (1 connectivity prism) which allows the ceramic to possess greater dielectric constant and less loss that would otherwise occur in the 0-3 composites. Moreover, the piezoelectric ceramic of 0-3 composites existed as random particles surrounded by cement matrix and thus the 0-3 composites are more closely related to the series or cube models [9].

4.8 Piezoelectric properties of 1-3 modified barium titanate-Portland cement composites

The impedance and phase spectra of 1-3 connectivity BZT-PC composites with different BZT contents are shown in Fig. 4.19. The impedance and phase spectra of the composites were plotted against the frequency and the phase spectra of the composites can be seen increase as the BZT content increasing. The poling condition was poled under that the poling field *E* of 1.5 kV/mm, the poling time *t* of 30 min and the poling temperature of 50 °C.

It is clear that addition of BZT in composite brings the electromechanical coupling behavior to the composites, which is caused by the piezoelectric effect (resonance and antiresonance peaks) [4]. The electromechanical coupling coefficient (K_t) of composites is calculated using the formula in Eq. (4.4). The plot of K_t value against BZT particle size of the composites can be seen in Fig. 4.20. It is seen that K_t value increased with increasing BZT content which means that an efficient conversion between electrical and mechanical energy is influenced by BZT contents.

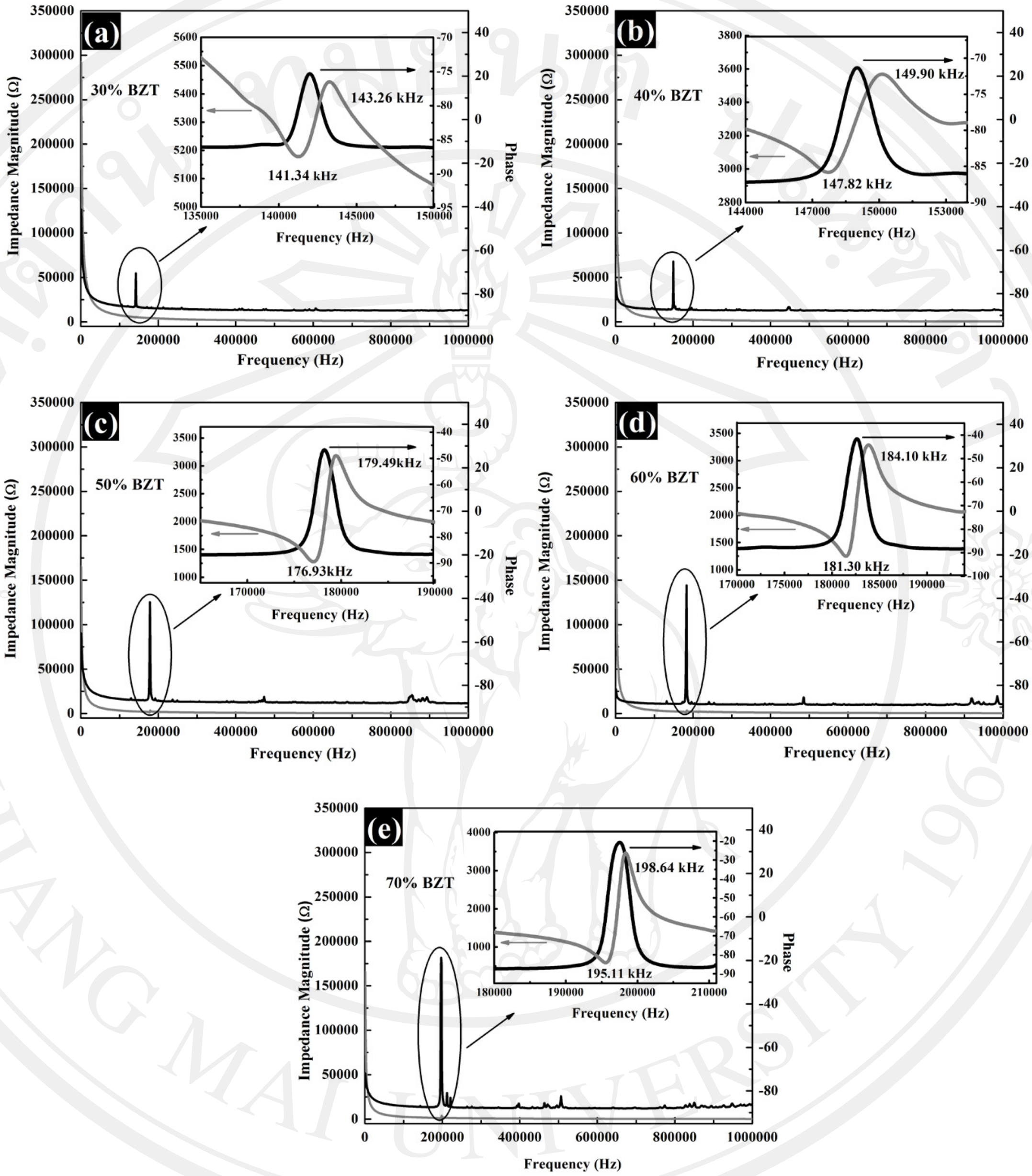

Fig. 4.19 The impedance and the phase spectra results of 1-3 BZT-PC composites with different BZT content at (a) 30±2% BZT composite, (b) 40±2% BZT composite, (c) 50±2% BZT composite, (d) 60±2% BZT composite and (e) 70±2% BZT composite.

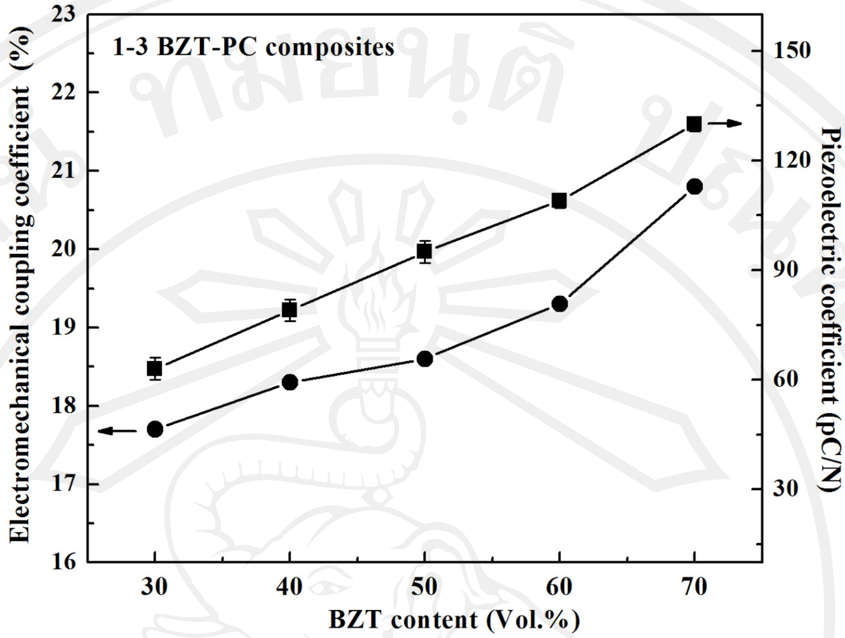

Fig. 4.20 The effect of BZT content of 1-3 BZT-PC composites on electromechanical coupling coefficient (K_t) and piezoelectric coefficient (d_{33}) results.

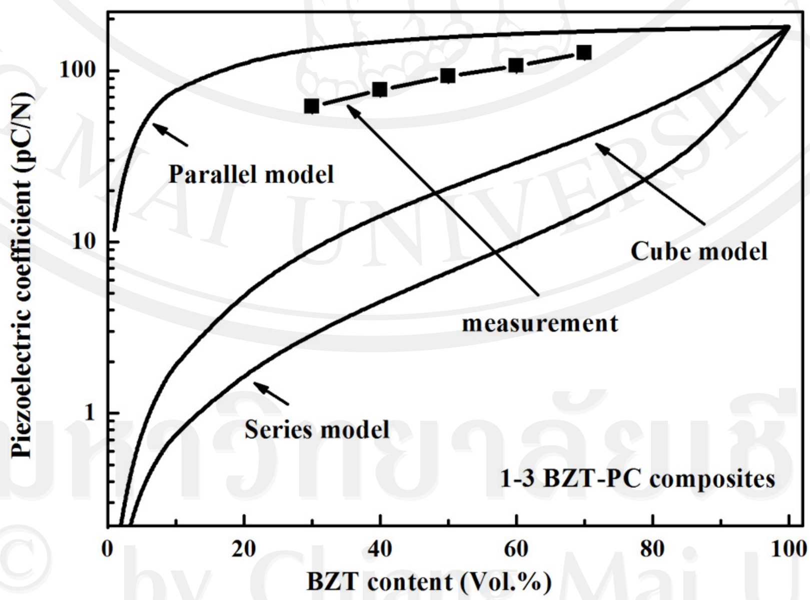

Fig. 4.21 Comparison of models with piezoelectric coefficient of 1-3 BZT-PC composites.

The effect of BZT on piezoelectric coefficient (d_{33}) can be seen in Fig. 4.20. The d_{33} value was higher at 130 pC/N for composite with 70±2% BZT composite as compared to that of 30±2% BZT composite (63 pC/N). Moreover, the test results of d_{33} values of the composites were plotted against BZT content with prediction curves for different models in Fig. 4.21. The theoretical equations of parallel, series and cube model for the d_{33} values are calculated using the formula ((Eq. (4.5)), (Eq. (4.6)) and (Eq. (4.7)) respectively. The d_{33} values of the 1-3 BZT-PC composites are close to the parallel models and this is in good agreement with the results of the dielectric constant measurement. The experimental results are far from the series model throughout the entire range and it is clear that the cube model gives the lower limit compared to the measured results for d_{33} values of 1-3 BZT-PC composites. This is because the 1-3 connectivity is more closely related to the 2-2 parallel models with the complete phase of BZT ceramic in the Y direction [9].

The piezoelectric voltage coefficient (g_{33}) means the sensitivity of a receiving voltage and the theoretical equations of parallel model, series model and cube model for the g_{33} values are calculated using the formula ((Eq. (4.8)), (Eq. (4.9)) and (Eq. (4.10)) respectively. The results of g_{33} values of the composites were plotted against BZT content with several mathematical models and the experimental results can be seen to be most closely related to the theoretical value of the parallel model in Fig. 4.22. The g_{33} values were found to decrease slowly trend with increasing BZT content because of the greater increase trend of the dielectric constant of the composites when compare with d_{33} value. Furthermore, the results show that g_{33} values of 1-3 BZT-PC composites in this work at 50±2% BZT by volume ($g_{33} \approx 19.6 \times 10^{-3}$ Vm/N) were found to be close to the previous work of 1-3 lead-based piezoelectric cement composites at 54.9% PZT by volume (g_{33} = 24.5 x 10^{-3} Vm/N) by Xu et al. [12]. However, these results were more likely to be affected by the technique used and cannot be compared directly.

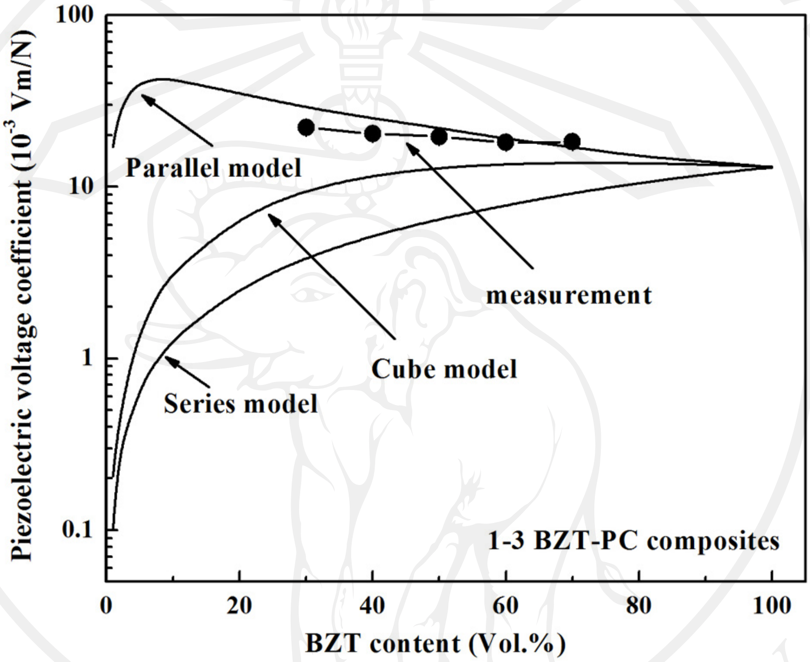

Fig. 4.22 Comparison of models with piezoelectric voltage coefficient of 1-3 BZT-PC composites.

4.9 Acoustic impedance properties of 1-3 modified barium titanate-Portland cement composites

The density and porosity of the composites were measured using a method based on the Archimedes principle. The results of 1-3 BZT-PC composites are presented in Fig. 4.23. It can be seen that the porosity slightly decreases with the increase of BZT content. In addition, the density of the composites can be seen to increase as the BZT content increases due to BZT being a denser material (density of BZT ceramic ≈ 5.80 x 10^3 kg/m^3) when compared to the pure cement disk. The densities were found in the region of 3.29 x 10^3 to 4.59 x 10^3 kg/m^3 when BZT content increases from 30±2% to 70±2%, respectively. The acoustic impedance (Z_c) of composites can be obtained by the following Eq. 4.12. Fig. 4.24 shows the acoustic impedance of the composites with the different BZT content. This further demonstrated that, by adjusting volume content of piezoelectric ceramic (≈ 30-50% BZT composites), the Z_c value of 1-3 BZT-PC composite can be seen to be close to that of concrete and match that of concrete structure.

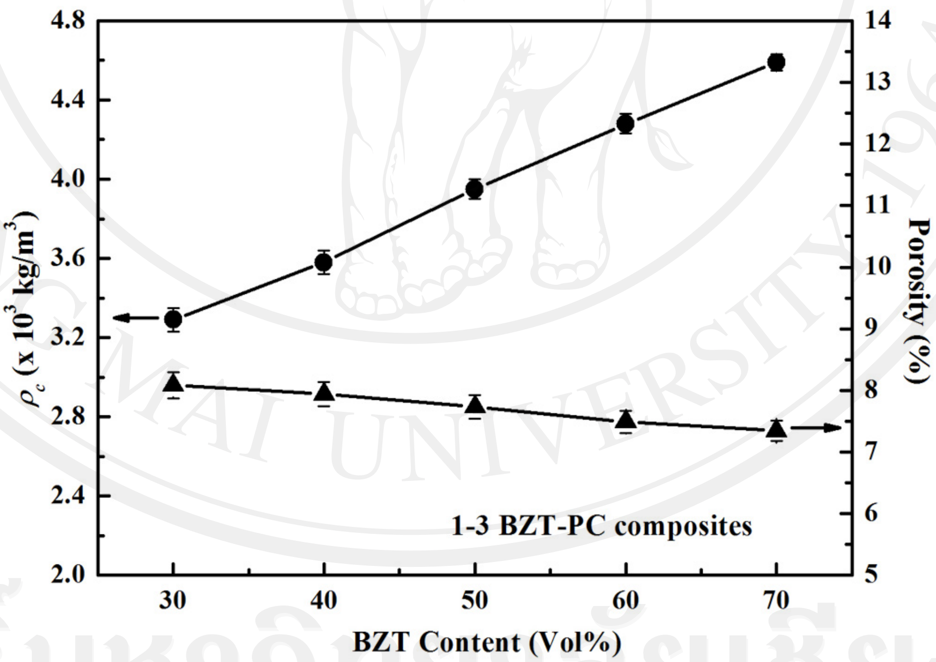

Fig. 4.23 The density and porosity results of 1-3 BZT-PC composites with different BZT content.

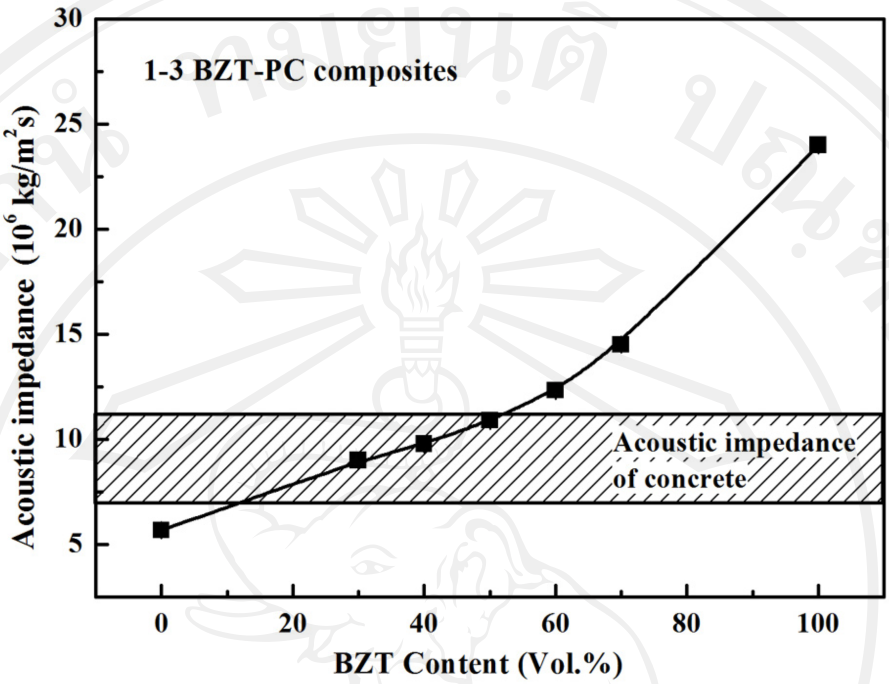

Fig. 4.24 The acoustic impedance (Z_c) results of 1-3 BZT-PC composites with different BZT content.

4.10 Microstructure properties of 1-3 modified barium titanate-Portland cement composites

The SEM micrographs of composites (60±2% BZT composite) shows a typical microstructure at the interfacial zone between the BZT ceramic and the cement matrix where BZT ceramic can be seen next to hydration products of Portland cement. Fig. 4.25(a) shows the 1-3 connectivity essentially contains the piezoelectric ceramic fully aligned in one direction, with a clear separation between part of BZT piezoelectric ceramic and Portland cement phase. Furthermore, The hydration products of Portland cement such as calcium sulfoaluminate hydrate (ettringite) and calcium silicate hydrates (CSH; the main hydration products of Portland cement) acts as the binder which binds the composites together, suggesting good bonding between the BZT ceramic and the cement matrix. Energy dispersive X-ray spectrometry (EDX) analysis of the composite can be seen in Fig. 4.25(b). EDX analysis of the composite shows the elements of BZT ceramic, CSH and ettringite where apart from gold which was used to coat the samples (hydrogen cannot be detected).

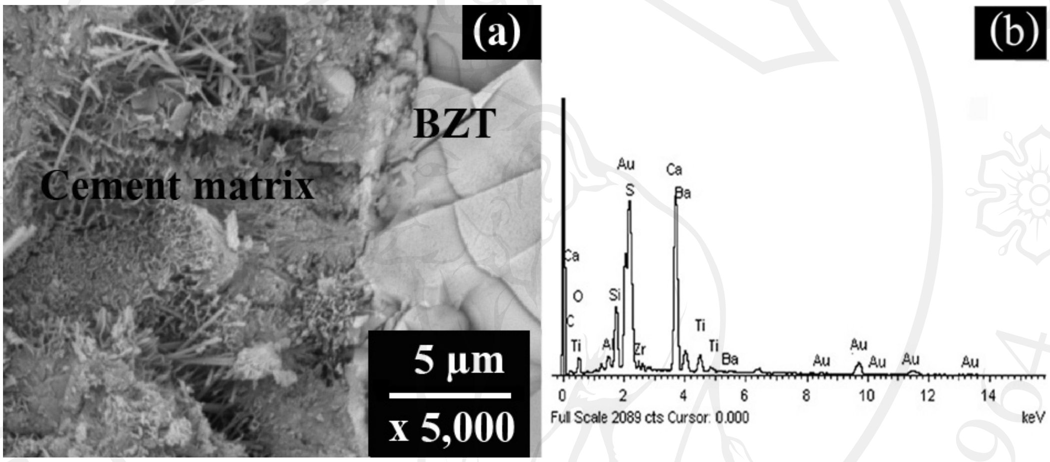

Fig. 4.25 Microstructure of 1-3 BZT-PC composite; (a) SEM micrograph and (b) EDX analysis.

4.11 Summary

In this part, the 1-3 connectivity modified barium titanate-Portland cement composites were investigated. The following conclusions can be drawn from the experiments;

1. The 1-3 barium zirconate titanate-Portland cement composites (1-3 BZT-PC composites) were successfully fabricated using dice-and-fill method.

2. The dielectric constant, piezoelectric coefficient and piezoelectric voltage coefficient of 1-3 BZT-PC composites obtained from experiment are close to the

predictions of the parallel models and the results are shown to be higher than 0-3 connectivity composites.

3. The dielectric constant, electromechanical coupling coefficient and piezoelectric coefficient of the 1-3 BZT-PC composites were found increase as a function of the ceramic content. For the dielectric loss of 1-3 composites were found to decrease with increased of ceramic content and the results are shown to be lower than 0-3 connectivity composites.

4. The piezoelectric voltage coefficient of 1-3 BZT-PC composites was found to decrease slowly with increasing ceramic content. The g_{33} value of the 1-3 composites (for the range tested) was higher than that of pure ceramics and 0-3 composites.

5. Composites at ≈ 30-50% BZT gave the optimal ceramic content for an acoustic impedance match close to concrete.

6. SEM micrographs, ceramic can be seen next to hydration products of Portland cement matrix where a dense microstructure can be observed in the interfacial zone.

PART III

2-2 Modified barium titanate-Portland cement composites

This third part focuses on improving the material performance in piezoelectric-cement based composite by the 2-2 type connectivity composites. The dielectric, piezoelectric, acoustic impedance and microstructure properties of 2-2 barium zirconate titanate-Portland cement composites (2-2 BZT-PC composites) are also discussed in details.

4.12 Dielectric properties of 2-2 modified barium titanate-Portland cement composites

The dielectric properties of the both composites are measured as a function of content of ceramic piezoelectric (BZT) has been studied at frequency for 1 kHz at room temperatures in Fig. 4.26. It can also be explained that with increasing the BZT content, the dielectric constant of the composite increased gradually. On the other hand, the dielectric loss was found to decrease with increasing BZT content and the lower $tan\delta$ value was obtained for the composite with BZT of 70±2 vol% ($tan\delta \approx$ 0.07). It is well know that cement is a porous material with a complex microstructure and it is composed of an amorphous phase, bound water [19] and conduction ion in the cement matrix would contribute to the loss in the dielectric.

The mathematical equations of parallel, series and cube models for dielectric constant are calculated using the formula ((Eq. (4.1)), (Eq. (4.2)) and (Eq. (4.3)) respectively. The test results of dielectric constant of the composites were plotted against BZT content with prediction curves for different models in Fig. 4.26 and the results values confirm close to the theoretical values of the parallel model. The experimental results are far from the series model throughout the entire range and it is clear that the cube model gives the lower limit compared to the measured results for dielectric constant of 2-2 BZT-PC composites. Moreover, the 2-2 connectivity composites are shown to be higher dielectric constant and less loss that would otherwise occur in the 0-3 connectivity composites, while the dielectric constant of 2-2 connectivity composites are shown to be slightly higher than the 1-3 connectivity composites.

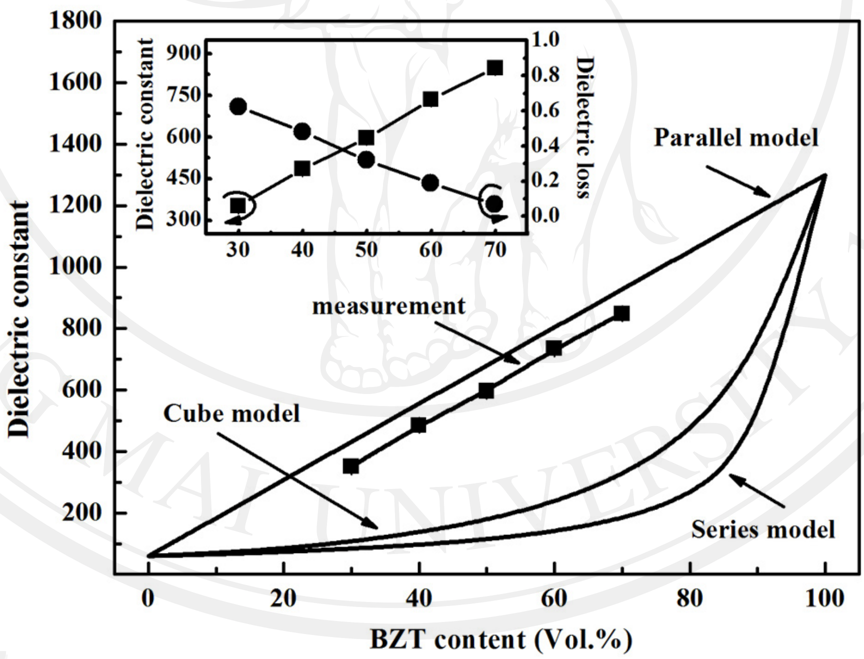

Fig. 4.26 The dielectric properties and comparison of models with dielectric constant of 2-2 BZT-PC composites.

4.13 Piezoelectric properties of 2-2 modified barium titanate-Portland cement composites

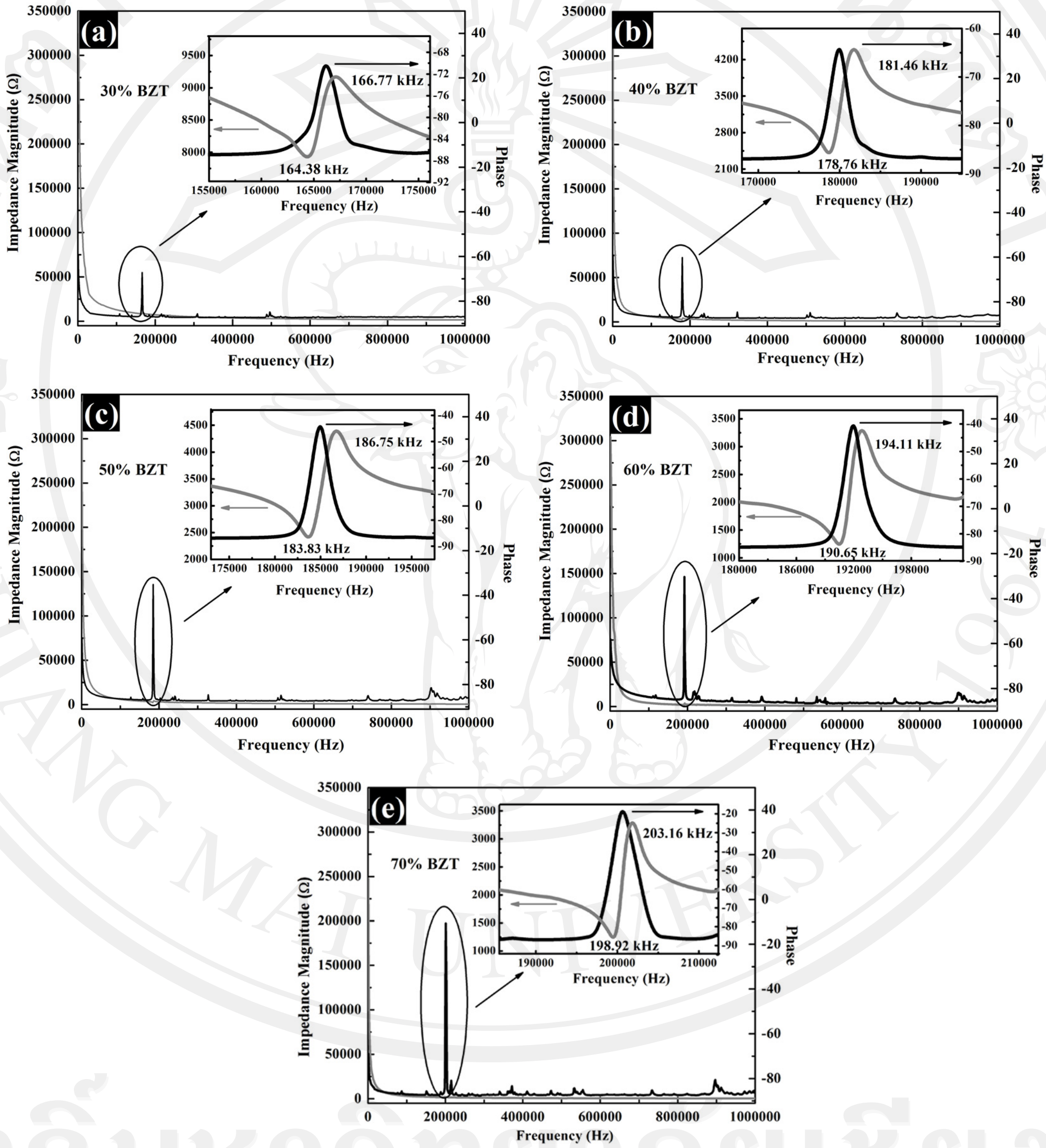

Fig. 4.27 The impedance and the phase spectra results of 2-2 BZT-PC composites with different BZT content at (a) 30±2% BZT composite, (b) 40±2% BZT composite, (c) 50±2% BZT composite, (d) 60±2% BZT composite and (e) 70±2% BZT composite.

Fig. 4.27 shows the impedance and phase spectra of the composite with BZT content, where they can be seen to represent a strong peak at ≈203.16-164.38 kHz for both composites. The poling condition was poled under that the poling field *E* of 1.5 kV/mm, the poling time *t* of 30 min and the poling temperature of 50 °C. In addition, an increase in the phase spectra can be seen to be higher in the 70±2% BZT composite as compared to that of the 30±2% BZT composite because of the piezoelectric effect (resonance and antiresonance peaks) and the thickness electromechanical coupling coefficient (K_t) is calculated using the formula in Eq. (4.4).

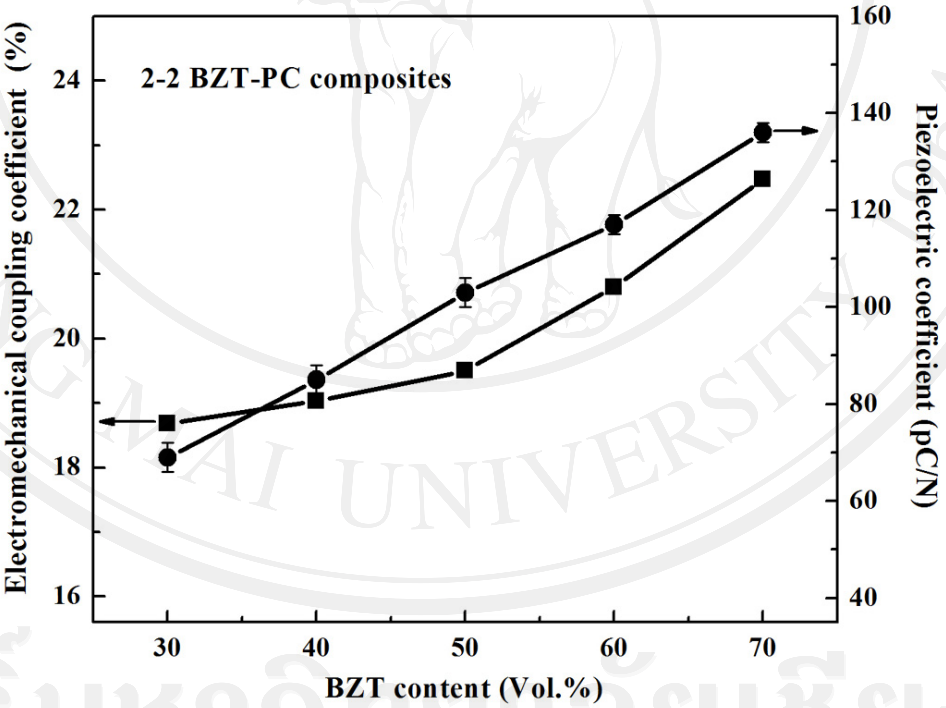

Fig. 4.28 The effect of BZT content of 2-2 BZT-PC composites on electromechanical coupling coefficient (K_t) and piezoelectric coefficient (d_{33}) results.

It can be seen that there is an increase in the K_t values with increasing BZT content which corresponds to the piezoelectric and reverse piezoelectric effects of the piezoelectric-cement based composite influenced by BZT contents in Fig. 4.28. At ≈ 60-70% of BZT content, the K_t value is > 20% and adequate for sensor application [2]. With the increase of BZT content, the piezoelectric coefficient (d_{33}) increases gradually and the 2-2 BZT-PC composites with high d_{33} value could be tailored by varying volume content of functional phase in Fig. 4.28. The theoretical equations of parallel, series and cube model for the d_{33} values are calculated using the formula ((Eq. (4.5)), (Eq. (4.6)) and (Eq. (4.7)) respectively. The d_{33} values of 2-2 BZT-PC composites are presented in Fig. 4.29 and comparison with several mathematical models. The experimental results confirm that the d_{33} value of the 2-2 BZT-PC composites can well be described by the parallel model.

Moreover, the d_{33} result on the 2-2 connectivity composites are the highest reported so far for 0-3 connectivity composites at the same BZT content. This is because the piezoelectric ceramic of 0-3 composites existed as random particles surrounded by cement matrix and thus the 0-3 composites are more closely related to the series or cube models. However, the d_{33} value of 2-2 BZT-PC composites are shown to be slightly higher than the 1-3 BZT-PC composites. For composites with 1-3 connectivity, the piezoelectric ceramic is continuously connected in one dimension and the more closely related to the 2-2 parallel models.

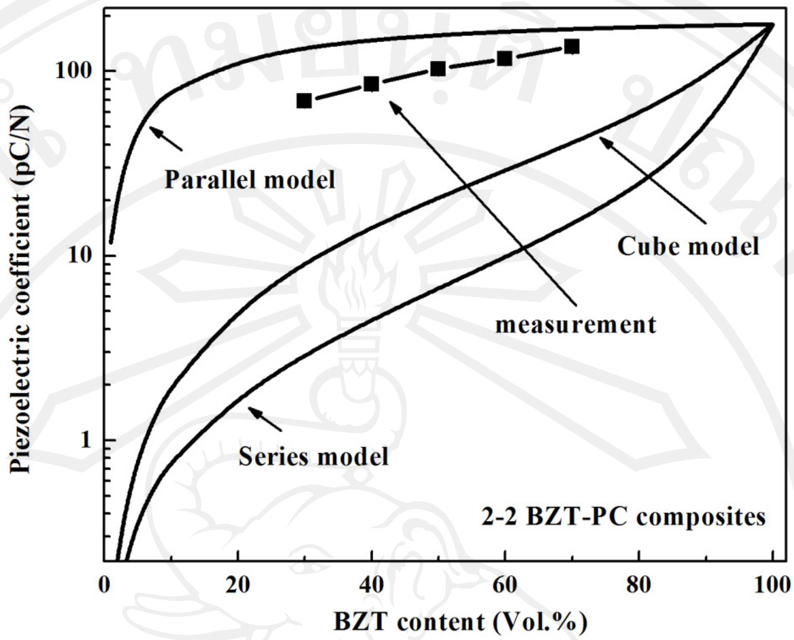

Fig. 4.29 Comparison of models with piezoelectric coefficient of 2-2 BZT-PC composites.

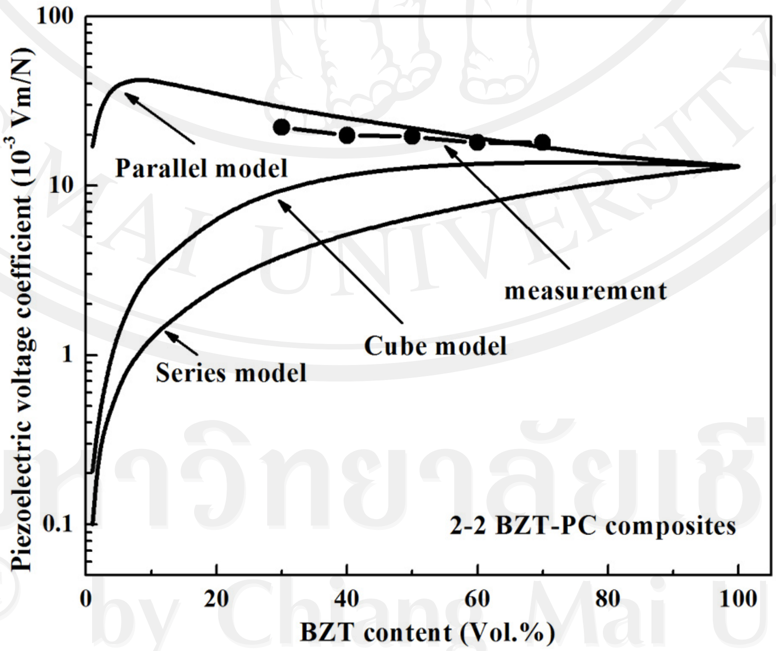

Fig. 4.30 Comparison of models with piezoelectric voltage coefficient of 2-2 BZT-PC composites.

The effect of BZT content on the piezoelectric voltage coefficient (g_{33}) of 2-2 BZT-PC composites and comparison with parallel models can be seen in Fig. 4.30. The theoretical equations of parallel model, series model and cube model for the g_{33} values are calculated using the formula ((Eq. (4.8), (Eq. (4.9)) and (Eq. (4.10)) respectively. The g_{33} values of the composites are close to the parallel models and the g_{33} value was found to decrease slowly with increasing BZT content. This is due to the greater increase trend of the dielectric constant of the composites when compare with d_{33} value. Moreover, the g_{33} value on the 2-2 lead-free piezoelectric-cement composite with 50±2% BZT composite ($g_{33} \approx 19.5 \times 10^{-3}$ Vm/N) is very similar to the reported for 2-2 lead piezoelectric-cement composites at the 53.9% PZT composite when compared to the recent work ($g_{33} = 24.4 \times 10^{-3}$ Vm/N) by Xu et al. [8]. However, these results were more likely to be affected by the technique used and cannot be compared directly. Besides, comparing this result with the pure piezoelectric ceramic, the g_{33} value of the composites increases significantly, which indicates that the piezoelectric composites have good receiving sensitivity.

4.14 Acoustic impedance properties of 2-2 modified barium titanate-Portland cement composites

The effect of BZT content on density and porosity of 2-2 BZT-PC composites can be seen in Fig. 4.31. The ρ_c values can be seen to increase with the increase in of BZT content. But the porosity presents the opposite trend, that is, the porosity slightly decreases as the BZT content increases. The porosities of composites were found to slightly decrease with increased of BZT content in the range from 8.11% to 7.36% when BZT content used was 30±2% and 70±2% respectively. The acoustic impedance

(Z_c) of composites can be obtained by the following Eq. 4.12. Furthermore, comparing with the phase BZT ceramic (acoustic impedance ≈ 24 x 10^6 kg/m^{2}s), the acoustic impedance of the composite decreases obviously, which makes it easier to match with that of concrete in civil engineering fields. The acoustic impedance of composites (≈ 30-50% BZT composites) can be seen to be close to that of concrete (acoustic impedance ≈ 6.90-11.23 x 10^6 kg/m^{2}s [13-14]) and good acoustic impedance matching ability with concrete (Fig. 4.32). Therefore, the 2-2 BZT-PC composites can easily be tailored to meet kinds of requirement by adjusting the proportion of piezoelectric ceramic and cement matrix

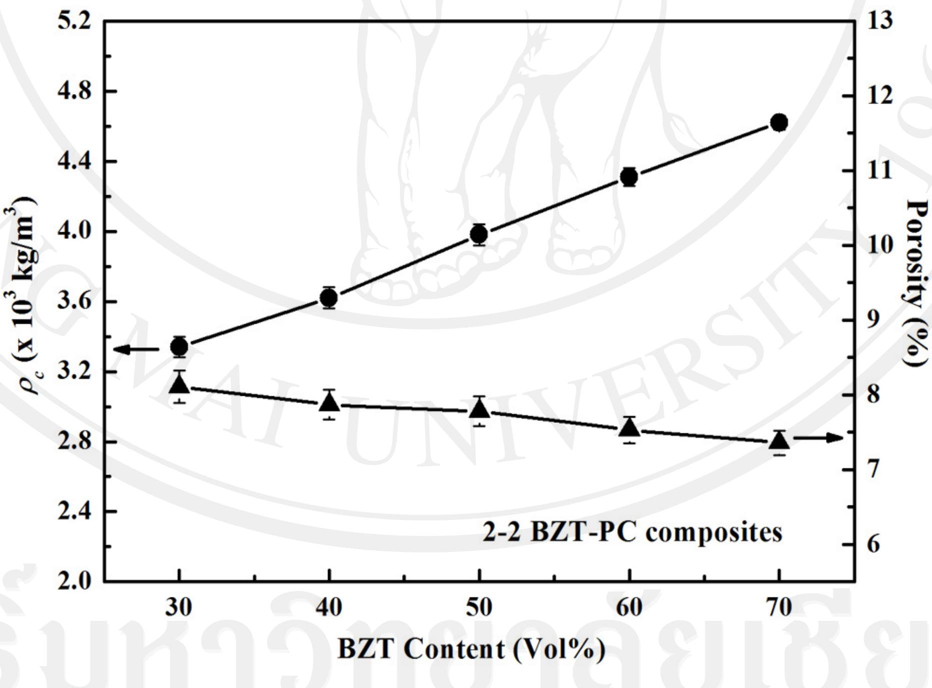

Fig. 4.31 The density and porosity results 2-2 BZT-PC composites with different BZT content.

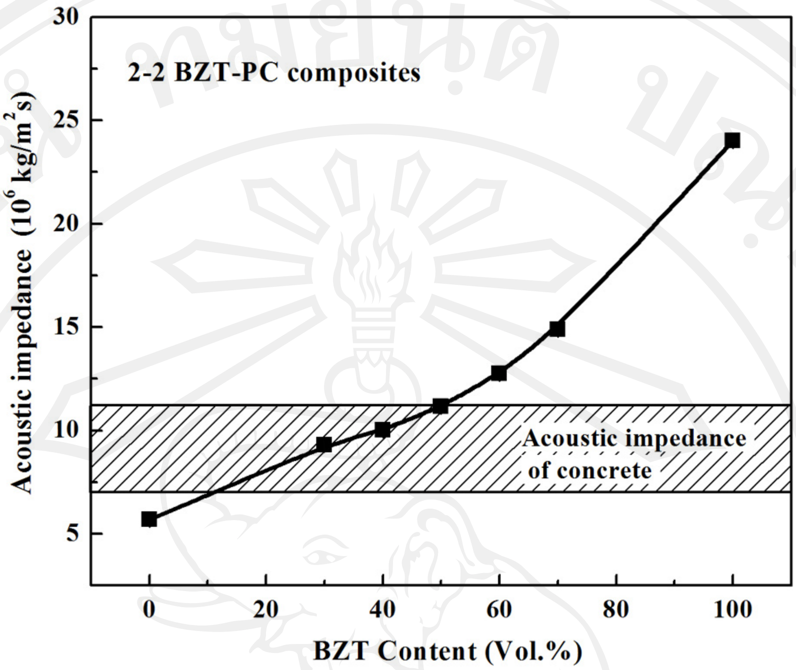

Fig. 4.32 The acoustic impedance (Z_c) results of 2-2 BZT-PC composites with different BZT content.

4.15 Microstructure properties of 2-2 modified barium titanate-Portland cement composites

Scanning electron microscope (SEM) was used to investigate the morphology of 2-2 BZT-PC composites (50±2% BZT composite) at the interfacial zone. The interface combination of ceramic and cement are shown in Fig. 4.33(a) and the BZT ceramic was found to bind well with the cement matrix. No new phases were seen between ceramic and cement matrix phase. The BZT ceramic can be seen to bind firmly with the cement matrix that comprises of cement hydration products such as calcium sulfoaluminate hydrate (ettringite) and calcium silicate hydrates (CSH). The CSH gel (the main hydration product of Portland cement) acts as the binder which binds the composites together. Furthermore, energy dispersive X-ray spectrometry (EDX) analysis of the composite is shown in Fig. 4.33(b), where the elements of BZT ceramic, CSH and ettringite (hydrogen cannot be detected) were detected in both composites. EDX analysis shows the presence of barium, titanium, zirconium and oxygen as the main elements of BZT ceramic. Apart from gold, which was used to coat the samples, calcium, silicon and oxygen were detected as the main elements, thus confirming that the bond provided between BZT ceramic is indeed by calcium silicate hydrate.

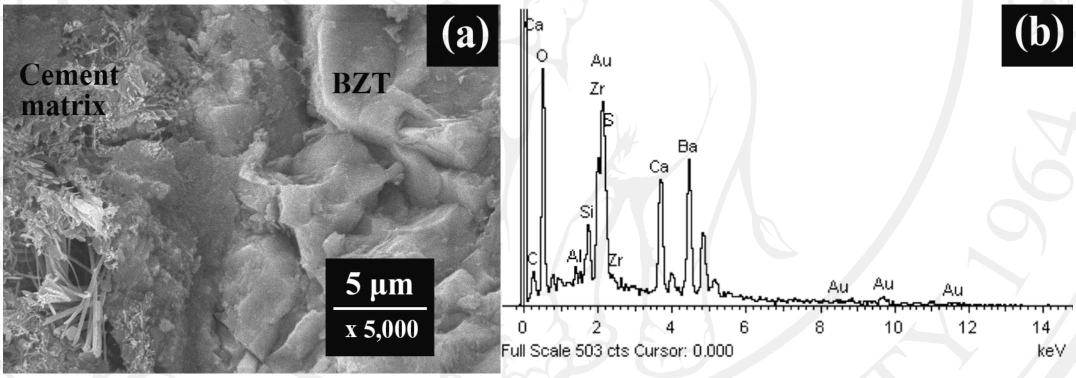

Fig. 4.33 Microstructure of 2-2 BZT-PC composite; (a) SEM micrograph and (b) EDX analysis.

4.16 Summary

In this part, the 2-2 modified barium titanate-Portland cement composites were investigated. The following conclusions can be drawn from the experiments;

1. The 2-2 barium zirconate titanate-Portland cement composites (2-2 BZT-PC composites) were fabricated using Portland cement as matrix and BZT ceramic as the active component by a dice-and-fill technique.

2. The dielectric constant, piezoelectric coefficient and piezoelectric voltage coefficient of 2-2 BZT-PC composites were found to fit closest to that of the parallel model. The g_{33} value of the 2-2 composites (for the range tested) was higher than that of pure ceramic.

3. The 2-2 BZT-PC composites were found to have the higher dielectric constant, electromechanical coupling coefficient, piezoelectric coefficient, piezoelectric voltage coefficient and acoustic impedance value when compared to the 0-3 BZT-PC composites

4. 2-2 BZT-PC composites had the higher dielectric constant, electromechanical coupling coefficient, piezoelectric coefficient, acoustic impedance than 1-3 composites, while 1-3 BZT-PC composites had higher dielectric loss and piezoelectric voltage coefficient value than 2-2 composites.

5. The 2-2 composites were found to give higher piezoelectric voltage coefficient and lower acoustic impedance value than pure ceramic. Composites at ≈ 30-50% BZT composites gave the optimal BZT content for an acoustic impedance match close to concrete.

6. SEM micrographs, The BZT ceramic was found to bind well with the cement matrix and clear separation between part of BZT piezoelectric ceramic and Portland cement phase.