Structural characterization of mixed local material for a ceramic porcelain insulator

H Aripin¹,*, I Usrah¹, N Busaeri¹, R Priyadi², Y Hermawan³, I N Sudiana⁴, I M Joni⁵ and S Sabchevski⁶

¹Department of Electrical Engineering, Faculty of Engineering, Siliwangi University, Jl. Siliwangi 24, Tasikmalaya 46115, Indonesia.
²Department of Agrotechnology, Faculty of Agriculture, Siliwangi University, Jl. Siliwangi 24, Tasikmalaya 46115, Indonesia.
³Faculty of Education, Siliwangi University, Jl. Siliwangi 24, Tasikmalaya 46115, Indonesia.
⁴Department of Physics, Faculty of Mathematics and Natural Sciences, University of Haluoleo, Kendari, Southeast Sulawesi 93132, Indonesia
⁵Nano Technology and Graphene Research Center (NTGRC), Padjadjaran University, Bandung, West Java 45363, Indonesia
⁶Lab. Plasma Physics and Engineering, Institute of Electronics of the Bulgarian Academy of Sciences, 72 Tzarigradsko Shose Blvd., Sofia 1784, Bulgaria.

*Email: aripin@unsil.ac.id

Abstract. A novel type of ceramic porcelain insulator material was produced by mixing kaolin with zeolite. The composition was prepared by adding a controllable amount of kaolin ranging from 30 wt% to 100 wt% into the zeolite. Then a series of samples were sintered at 1200°C. The influence of the composition on the structural properties was studied in detail using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM). The results show that the microstructure of porcelain body is characterized by the presence of elongated mullite grains. It was found also that the decrease of the kaolin content in the porcelain body leads to a decrease in the crystalline phase of mullite. The analysis of the structural properties of such ceramics indicates that zeolite could not be recommended as an appropriate material for manufacturing of high-voltage ceramic porcelain insulators by mixing it with kaolin.

1. Introduction
Porcelain is being considered as a ceramic material, which has vitreous characteristics, i.e a high degree of melting on firing, porosity lower than 0.5%, and glass content greater than 40% [1]. Additionally, the porcelain possesses high hardness, low electrical and thermal conductivities, and brittle fracture [2]. It is known as a primary material for high-quality vases [3], tableware [4], decorative objects [5] and electrical insulators [6]. A promising and actively studied variety of the latter is the insulator material used in electrical power transmission systems due to the high stability of its electrical, mechanical and thermal properties in the presence of harsh environments.

Many studies have been carried out in order to investigate the properties of different porcelain materials used for electrical insulators and their dependence on the technological parameters, such as
the temperature and time of the thermal treatment, chemical composition, and starting materials. Ezenwabude and Madueme [7] have prepared porcelain insulators with clay, feldspar, and quartz as starting materials. It has been found that the composition of 50% clay, 20% feldspar and 30% quartz with an appreciable insulation breakdown voltage of 45 V is appropriate for the manufacturing of electrical porcelain insulators. Ecé and Nakagawa [8] have investigated the influence of various factors on the strength of porcelain insulators. Among them are the acicular mullite interlocking as well as mullite amount and size. Such observation is supported by the results of Arman Sedghi et al [9]. They have reported that the increase in the alumina content in porcelain material increases the mullite phase which, in turn, increases the bending strength. In the research carried out by Dunia and Al-Nasrawy [6], the acceptable electrical performance of the porcelain bodies has been achieved decreasing the glassy phase. These studies have demonstrated that the formation of the mullite and limitation of the glassy phase and unresolved quartz particles could effectively increase the strength and reliability as well as the electrical performance of the porcelain insulators.

The intention to use kaolin as a raw material for ceramic porcelain insulators is motivated not only by its abundance and low price but also by its plasticity during firing, which provides adequate mechanical strength for both the green and the dried body pieces. At the same time, a blend of clay and quartz still has some technical issues when it is used for fabricating ceramic porcelain insulators. The detailed analysis [10-11] of the experimental data shows that excessive plasticity can cause problems at the forming stage and make it difficult to achieve the required body permeability. Therefore, the proper selection of the raw material is very important for the further improvement of the technology for production of high-quality ceramic insulators. In this paper, we present the results of our study on the structural properties of a ceramic porcelain insulator derived from locally available materials (kaolin and zeolite). The purpose of this study was to investigate the effects of the replacement of quartz by zeolite on the properties of kaolin ceramic and on the underlying structural changes.

2. Experimental Procedure

2.1 Raw material preparation.

The raw materials used to prepare electric porcelain are kaolin and zeolite. They were obtained from Tasikmalaya (Indonesia) and selected manually. Then the raw materials were cleaned by washing with water, dried in the sun and grinded using a jar mill to pass through a 100 μm sieve. The samples were prepared according to the porcelain body formulations presented in Table 1. For example, the porcelain body sample K30Z was prepared by mixing 30 wt.% of kaolin in 100 mL deionized water, and then stirring at 80 °C for one hour. Next, 70 wt.% of the zeolite powder was added gradually into the mixture under continuous stirring at 50 °C for 6 hours. The resultant porcelain body powder was dried in an oven at a temperature of 120 °C for 2 hours and then stored in a desiccator for further treatment. The samples K50Z, K70Z, and K100Z were prepared following the same procedure.

| Sample       | Mass percentages (wt.%) |
|--------------|-------------------------|
|              | Kaolin  | Zeolite  |
| 30 wt% K (K30Z) | 30      | 70       |
| 50 wt% K (K50Z) | 50      | 50       |
| 70 wt% K (K70Z) | 70      | 30       |
| 100 wt% K (K100Z) | 100   | 0        |
2.2 **Sintering the synthesized porcelain body**
The powder samples were placed into a porcelain crucible and then inserted into a horizontal furnace, where they were sintered at a controlled heating rate of 10°C/min up to the temperature of 1200°C in air. Then the temperature was kept constant at 1200 °C for 2 hours. The cooling was performed by natural convection after turning off the electric furnace and leaving the samples inside.

2.3 **Method for characterization of the synthesized porcelain body**
The XRF measurements were carried out on a Philips PW2400 wavelength-dispersive spectrometer. The calibration was performed following the prescribed standard procedure. In addition, some correction factors for determining the influences of other elements were calculated. The measurement conditions were 24 kV – 100 mA, collimator mask 27 mm and Rh-X ray tube as an excitation source. A gas flow detector was used for controlling the rate of the gas flow. Furthermore, the experiments on the X-ray diffraction (XRD) of the samples have been carried out using a Smartlab X-ray diffractometer with filtered Cu Kα radiation at a wavelength of 0.15418 nm. The accelerating voltage and the applied currents were 40 kV and 30 mA, respectively. The diffraction patterns were registered over the range from 10° to 90° at a scan rate of 0.01 º/s. Fourier transform infrared (FTIR) spectra were obtained using a Varian 800 FTIR spectrometer (Scimitar Series model) in the wavenumber range of 400–4000 cm⁻¹ with a spectral resolution of 4 cm⁻¹. All FTIR measurements were carried out at room temperature in a specular reflectance mode using the KBr pellet technique. The SEM photos of fracture surface of the samples were taken by using a scanning electron microscope (SEM) at a magnification of 10,000 times and at accelerating voltage of 15 kV. The detailed electrical strength test procedures are described elsewhere [12]. It was measured using a spherical and a plat brass electrode in liquid dielectric in the isolated chamber.

3. **Results and Discussion**
Table 2 shows the chemical composition of oxide contents for kaolin and zeolite from Karangnunngal. Both of the kaolin and zeolite contain SiO₂ as the main constituents at about 42.20 wt.% and 59.30 wt.%, respectively. It is also accompanied by a significant amount of Al₂O₃ and Na₂O for kaolin and ZrO₂, Al₂O₃, Fe₂O₃, K₂O and CaO for zeolite. It can also be seen that kaolin and zeolite contain a small amount of TiO₂. The loss on ignition is associated with the presence of hydroxides, organic matter, and volatile components.

| Chemical composition | Kaolin (%) | Zeolite (%) |
|----------------------|------------|-------------|
| SiO₂                 | 42.20      | 59.30       |
| TiO₂                 | 1.10       | 0.70        |
| ZrO₂                 | 0.46       | 5.02        |
| MgO                  | -          | 0.12        |
| Al₂O₃                | 24.80      | 5.02        |
| Na₂O                 | 30.10      | -           |
| Fe₂O₃                | 1.11       | 8.47        |
| K₂O                  | -          | 12.30       |
| CaO                  | -          | 7.81        |
| LOI                  | 0.23       | 1.27        |

Figure 1a shows the XRD pattern of porcelain with a varying amount of kaolin and zeolite and sintered at 1200°C. In accordance with XRD data from Figure 1a, the sample of 100 wt.% consists of...
kaolin (Al$_2$Si$_2$O$_5$(OH)$_4$) at 2θ = 20.9° and 24.9° [13-14], cristobalite (SiO$_2$) at 2θ = 22.9° [15] and mullite (3Al$_2$O$_3$2SiO$_2$) at 2θ = 27.9° [16]. The peak intensity of the kaolin and the mullite for the sample with a kaolin content 70 wt.% and below decreases gradually with the decrease of the kaolin content. The decrease of the peak is attributed to the formation of crystalline zeolite (Mx/n[(AlO$_2$)$_x$(SiO$_2$)$_y$]mH$_2$O) at 2θ = 27.2° and 30°, according to data from other studies [17]. The intensities of the zeolite peaks in the pattern increase with decreasing the kaolin content. From the above-mentioned data, we can conclude that the bending strength of porcelain decreases with decreasing the kaolin content since the latter correlates with a decreased amount of mullite formation and an increase of the cristobalite phase.

Figure 1. (a) XRD patterns and (b) FTIR spectra for porcelain with a varying kaolin content and sintered at 1200°C.

Figure 2. SEM images for porcelain with (a) 100wt%, (b) 70wt%, (c) 50wt%, and (d) 30 wt% kaolin and sintered at 1200°C.
Figure 1b shows the FTIR spectra for porcelain with varying kaolin content and sintered at 1200°C. For all samples, the band (peak 1) located at 464 cm\(^{-1}\) is assigned to tetrahedral T–O (T= Si or Al) bending vibrations, is common to the starting metakaolin [18]. Its intensity does not change substantially in the course of the zeolitization. The peak 2 that appears at 626 cm\(^{-1}\) corresponds to crystalline cristobalite [19]. The peak 3 at 800 cm\(^{-1}\) and the peak 4 at 1100 cm\(^{-1}\) can be assigned to the symmetric stretching vibrations of Si–O–Si and the anti-symmetric stretching vibrations of Si–O–Si [20], respectively. The absorption bands (peak 5) observed at about 1645 cm\(^{-1}\) was attributed to the bending H–O–H bond groups of adsorbed water molecules. The broadband (peak 6), at 3452 cm\(^{-1}\), is attributed to the O–H stretching of hydroxyl groups that are present on the surface of the material [21].

It has been found that the integrated intensity of the symmetric stretching vibrations of Si–O–Si increases with decreasing the amount of kaolin. The big quantity of Si–O–Si bonds in the samples with smaller amounts of kaolin indicates that more zeolite particles facilitate the elimination of the SiO\(_2\)-rich phase so that the zeolite decreases the mullite grain growth in the porcelain body.

Figure 2 shows SEM images of porcelain with varying content of kaolin and sintered at 1200°C. The SEM image for the sample with 100 wt% kaolin illustrates that the micrographs are characterized by more elongated mullite grains surrounded by unsolvable cristobalite particles. In this sample, the elongated mullite grains are seen as major crystalline phases that are formed by using kaolin as the starting material. It may be due to the presence of a large amount of liquid phase during sintering. At 70 wt% kaolin, it can be seen that the addition of zeolite provided the formation of a smaller amount of mullite grains in the sample. At 50 wt% kaolin, the elongated mullite grains gradually appeared. At 30 wt% kaolin, a compact microstructure with glassy phase was seen to be uniformly distributed in the sample. Then, the excess zeolite eliminated the SiO\(_2\)-rich phase then retarded the mullite grain growth at 1200°C. The results are supported by the detected results of the XRD patterns and FTIR spectrum.

![Electrical strength for porcelain with varying kaolin content and sintered at 1200°C.](image)

**Figure 3.** Electrical strength for porcelain with a varying kaolin content and sintered at 1200°C.

Figure 3 shows electrical strength for porcelain with varying kaolin content and sintered at 1200°C. Base on this figure, electrical strength increases with increasing kaolin content. There are at least two occurrences that result in increasing the electrical strength. The first one arises from an open pores reduction when the kaolin content increases in the sample. This behavior was attributed to the presence of calcium oxide (CaO) in zeolite. In this case, under sintering conditions it takes place the
decomposition reaction between CaO and CO$_2$ gas from CaCO$_3$ [22] and then the open pores are ascribed to the empty sites left the released CO$_2$ gas. The amount of liquid phase produced by sintering SiO$_2$ does not fully fill the open pores, then it is responsible for decrease of electrical strength in the sample for higher content of zeolite. Another one stems from a decrease of the mullite phase and an increase of the cristobalite phase as detected by the XRD pattern. In the case, the presence of larger amount of cristobalite and smaller amount of mullite lead to a low electrical strength [6, 9].

4. Conclusion
A novel ceramic material for porcelain electric insulators has been produced successfully from kaolin and zeolite by controlling the amount of kaolin at 1200°C. The results presented in this paper show that incorporation of zeolite into the kaolin gives an appreciable effect on the microstructure of porcelain body. An interesting phenomenon has been observed analyzing the XRD pattern of samples. It has been found that the crystalline phase of mullite decreases as the zeolite content in the sample increased from 30 wt.% to 70 wt.%. Such interpretation is supported by the observed microstructure of the elongated mullite in the sample. Nonetheless, the overall results suggest that the replacement of kaolin by zeolite as a raw material could not be considered as a prospective route for the production of an appropriate material for high-voltage ceramic porcelain insulators.

References
[1] Perez J, Rincon, J and Romero M 2012 Ceram. Int. 38 317.
[2] Callister D and Rethwisch D 2008 Fundamentals of Materials Science and Engineering (Singapore: John Wiley & Sons, Inc.,)
[3] Jeoung-Ah K 2006 J. Eur. Ceram. Soc. 26 1023.
[4] Boussak H, Chemani H and Serier A 2015 Int. J. Phys. Sci. 10 38.
[5] Colomban P 2013 Arts 2 77.
[6] Dunia K, and Al-Nasrawy M 2016 Iraqi J. Sci. 57 404.
[7] Ezenwabude E and Madueme T 2015 Int. J. Mult. Sci. Eng. 6 28.
[8] Ece O, and Nakagawa Z 2002 Ceram. Int. 28 131.
[9] Sedghi A, Riahi-Noori N, Hamidinezhad M and Reza Salmani M, 2014 Bull. Mater. Sci. 37 321.
[10] Ajakor E, Anih L, and Ogwata C, 2015 Int. J. Sci. Res. Publ. 5 1.
[11] Al-Araji N, Aal Dhabi L, and Alshammari W, 2014 Int. J. Sci. Eng. Res. 5 1348.
[12] Sedghi A, Riahi-Noori N, Hamidinezhad N, and Reza Salmani M 2014 Bull. Mater. Sci. 37 321.
[13] Gougazeh M, and Buhl J 2010 Clay Miner. Mineral. Soc. 45 281.
[14] Zhao H, Deng Y, Harsh J, Flury M, Boyle J 2004 Clay Clay Miner. 52 1.
[15] Aripin A, Mitsudo S, Sudiana I, Tani S, Sako K, Fujii Y, Saito T, Idehara T, Sabchevski S 2011 J. Infrared Milli. Terahz Waves 32 867.
[16] Aripin H, Mitsudo S, Prima E, Sudiana I, Kikuchi H, Sano S, Sabchevski S 2015 Ceram. Int. 41 6488.
[17] Rodrigues M, Souza A, and Santos I 2016 Am. Chem. Sci. J. 12 1.
[18] Gougazeh M, and Buhl J 2014 J. Assoc. Arab Univ. Basic Appl. Sci. 15 35.
[19] Aripin H, Mitsudo S, Sudiana I, Saito T, and Sabchevski S 2015 T. Indian Ceram. Soc. 74 1.
[20] Shinoohara Y and Kohyama N 2004 Ind. Health 42 277.
[21] Yang S, and Gao L 2006 J Am. Ceram. Soc. 89 1742.
[22] Kaur H, Kumar Bulasara V, and Kumar Gupta R 2015 Desal. Water Treat. 57 15154.

Acknowledgments
This research was supported by a fund of the Siliwangi University through the Project of Research for Dosen Pembina in 2017 with contract number: 1140/D3/PL/2017.