**Structure and Microstructure Properties of Refractory Cordierite Prepared from Amorphous Rice Husk Silica by Periclace Addition**

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Abstract. Refractory cordierite ceramic using amorphous rice husk silica was modified by addition of periclase from 5 to 20% by weight, followed by sintering treatment at temperature of 1230 oC. The phases, structural changes and microstructure characteristics of samples were investigated by x-ray diffraction (XRD), scanning electron microscopy (SEM). The results obtained indicated the significant role of periclace addition on the phase decomposition of cordierite into spinel and forsterite. Addition of periclace was found to increase forsterite and decrease spinel. Formation of spinel and forsterite was followed by decrease in electrical resistivity, porosity and by increase density.

Keywords: Cordierite, periclace, silica, rice husk, structure

1. **Introduction**

At present, rice husk is a very attractive source of reactive silica as raw materials for preparation of ceramics, since this agriculture residue is abundantly high silica content. This kind of silica has been shown to be a good material for the synthesis many types of materials such as pure silicon, silica nitride, [1], and silicon carbide [2]. In our previous investigations, reactive silica from rice husk was obtained by simple acid leaching, and the silica has been used to produce several ceramics materials include, borosilicate [3], carbosil [4], aluminosilicates [5], mullite [6,7] and cordierite [8,9,10].

Cordierite (2MgO.3Al2O3.5SiO2) is a material having a low thermal expansion coeficient and dielectric constant, high thermal and mechanical stability. It was reported that thermal expansion of cordierite is 2.2 x 10-6/oC [11], while the others reported the value of around 3.3 x 10-6/ºC [8], 1- 4 x 10-6/ºC [12], and 0.8-2 x10-6/ºC [13]. Therefore, cordierite based materials are extensively used in a broad range of applications, including catalysts, microelectronic, integrated circuit boards, membranes and refractories [14-17], electrical and thermal insulation [18,19].

Several researchers studied the feasibility of fabricating dense cordierite ceramic by reduce or add one of the three oxides (MgO, Al2O3 and SiO2). It is necessary to consider in a number of applications where change in crystalline phase can affect physical, termal, and mechanical properties of cordierite. For example, Ye, et al, 2014 [19] evaluated the synthesis of cordierite by reducing the Al2O3 mole ratio from 2 to 1.4, they found bulk density to reach the maximum value of 2.5 kg/m3, which is close to the value for dense cordierite ceramic. Meanwhile, alumina addition to cordierite leads to production of spinel, crystoballite and periclase phases [20], and with increasing the addition of alumina from 10 to 20 wt% both the density and thermal conductivity of cordierite are effectively increased, while for electrical conductivity the opposite was true.

The purpose of study is concerned on the effect of MgO (periclace) addition on the microstructure and physical characteristics of cordierite prepared from amorphous rice husk silica. To gain insight on several basic characteristics, the structure and mictrostruture crystallisation of cordierite with periclace addition were studied by means of x-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

1. **Experimental Methods**

Sol silica was obtained by mixing 50 g dried husk with 500 ml of 5% KOH solution, folowed by boiling of the mixture for 30 minutes in a beaker glass as reported in previous study [**7**]. The sol was acidified by dropwise addition of 5% HCl until conversion of the sol into gel was completed. The gel was oven dried at 110ºC for eight hours and then ground into powder. Preparation of cordierite was carried out by mixing raw materials with the composition of MgO: Al2O3:SiO2 of 2:2:5 by mass as reported in previous studies [8]. The solid was ground into powder by mortar and sieved to obtain the powder with the size of 200 meshes. After that, periclace was added to the cordierite powder in different content (0, 5, 10, 15 and 20% by mass). The powder was pressed in a metal die with the pressure of 2 x 104 N/m2 to produce cylindrical pellet and the pellets were sintered at temperature of 1230ºC with a heating rate of 3ºC /min. The examination of density and porosity was done according to Archimedes method [21]. The structure analysis was carried out using an automated Shimadzu XD-610 X-ray diffractometer and microstructural analysis was conducted with SEM Philips-XL. The electrical resistivity (ρ) was measured using the four-probe method.

1. **Results and Disccusion**

Fig 1 shows the XRD patterns of the samples at sintering temperature of 1230ºC with different periclace addition.



**Figure. 1.** The x-ray diffraction patterns of the samples sintered at 1230 ºC different periclace content (a) 0%, (b) 5%, (c) 10%, (d)15% and (e) 20%, r= α-cordierite, s= spinel, t= forsterite

The phases identified with the PDF diffraction lines using search-match method [22], clearly show the presence of α-cordierite (PDF-13-0294) with the high peak intensity, 2θ = 10,5º, forsterite PDF-34-0189) 2θ = 36.55º, and spinel (PDF-21-11520), 2θ = 36.91º. The sample without addition of periclase (Fig. 1a), α-cordierite as the dominant phase is clearly detected. Spinel phase was strongly observed, and α-cordierite drastically decreased in the sample with 5% periclace addition (Fig. 1b). The presence of high spinel peak is an indication that with 5% periclace addition led to more intensive diffusive reaction between MgO and Al2O3, to produce more spinel and decrease α-cordierite. At 10% periclace addition (Fig. 1c), the α-cordierite was totally changed into spinel and forsterite, and followed by the decrease of spinel phase. This presumption is in accordance with the results observed for the sample with 15% periclace addition (Fig. 1d), in which the spinel and forsterite were detected, but, the phase of forsterite was evidently increased. These phases remained practically the same up to 20% periclace addition (Fig. 1e). The spinel was formed through interaction of AlO6 and MgO6 octahedral [23], while the presence of forterite is most likely as a result of interaction beween SiO4 and MgO4 [24].

The surface morphologies of the sintered samples at temperature 1230oC with different periclace contents were characterized using SEM. The results show quite significant effect of periclace addition on the surface morphology, most likely a result of crystallisation. The micrographs presented in Fig. 2(a-e) show significant effect of periclace on the size and distribution of the particles on the surface. As displayed by the images in Fig. 2(a-b), the surfaces morphologies of the samples are marked by the existence of particles with different grain sizes and distributions. The microstructure of the sintered sample with 0% periclace (Fig. 2a) shows large grains with grain boundaries, while for the samples with 5 and 10% periclace addition without grain boundaries were evidently observed (Fig. 2b-c). In addition, it is obvious that the large grains in the sintered sample with 0% periclace is most likely composed of α-cordierite.



b

a



d

c



e

**Figure. 2.** The scaning electron microscopy (SEM) images of the samples sintered at 1230 ºC different periclace content (a) 0%, (b) 5%, (c) 10%, (d)15% and (e) 20%, r= α-cordierite, s= spinel, t= forsterite

This is supported by the result of XRD analysis for the sample sintered at 1230ºC presented in Fig. 1a, in which α-cordierite was detected. The surface of samples sintered samples with higher periclace content (15-20%) as presented in Fig. 2 (d-e) is dominated by some large grains of spinel and forsterite. Both samples are marked by initiated coalescence of spinel as a result of α-cordierite crystallization. This feature suggests that with 15 and 20 % periclace addition, α-cordierite phase continue to change, leading to the formation of spinel and forsterite as supported by the result of XRD in Figs 1d and e). The formation of spinel and forsterite can be seen more clearly by inspecting the SEM micrographs of the sintered sample with 20% periclace content (Fig. 2e). The physical properties of the sintered samples at different periclace addition are shown in Fig. 3 and Fig 4.



**Figure.3.** Density (a) and Porosity (b) as a function of periclace content.

Fig. 3a-b shows the changes in density and porosity of the samples as a function of periclace content. As can be observed, density of sample with 0% periclace (Fig 3a) increases drastically as periclace content increase up to 5%, and beyond this content of periclace, slow decrease were observed up to 20% periclace. As shown in Fig 3a, the densities of the samples increase from 2.36 to 3.45 g/cm3 as the periclace content increased from 0 to 5%, and decreased slowly and reached the value of 3.25 g/cm3 at the periclace content of 20%. The change in density was most likely due to conversion of cordierite into spinel and forsterite, as observed by the XRD results (Fig. 1). These results are in accordance with the results of others [25-27], the density of spinel, and forsterite phases are higher than that of cordierite. In those previous studies, it was reported that the density of spinel, forsterite and cordierite are 3.54 and 2.96 and 2.3 g/cm3 respectively. The slow decrease of porosity (Fig 3b) with increasing periclace content up to 5 % was attributed to decrease formation of cordierite phase, leading to decreased porosity. Beyond this periclace content, porosity is continually decreased, probably indicating the domination of spinel, and forsterite, smaller particles distances and also smaller sizes in the samples as a result of higher periclace content applied, which is in accordance with the surface morphologies of the samples as seen in SEM results (Fig 2a-e).

Fig. 4 shows the change in electrical resistivity of the samples as a function of periclace addition. As shown in Fig. 4, the higher the periclace content, the lower the electrical resistivity, which implies that the samples became resistance to electricity as a result of increased amount of spinel and forsterite as supported by XRD results in Fig 1. This profile demonstrates that the electrical resistivity of the samples can be controlled by controlling the formation of the spinel and periclace phases, which is very useful for adjusting the suitability of the material for specified applications, such as insulator and conducting element in electronic devices.



**Figure. 4.** Variations of electrical resistivity as a function of periclace content.

1. **Conclusions**

This study demonsrated the effet of periclace addition on the microstructure and physical properties of cordierite prepared from rice husk silica. The addition of periclace from 5 to 20% revealed that the formation of cordierite was practically undetected, while spinel and forsterite are dominant phases. Phase transformation was found to result in the change of the characatersitics of the samples, including increased density is related to conversion of cordierite into spinel and forsterite, followed by decreased porosity and electrical resistivity. Based on these characteristics, the samples are considered as insulator.

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