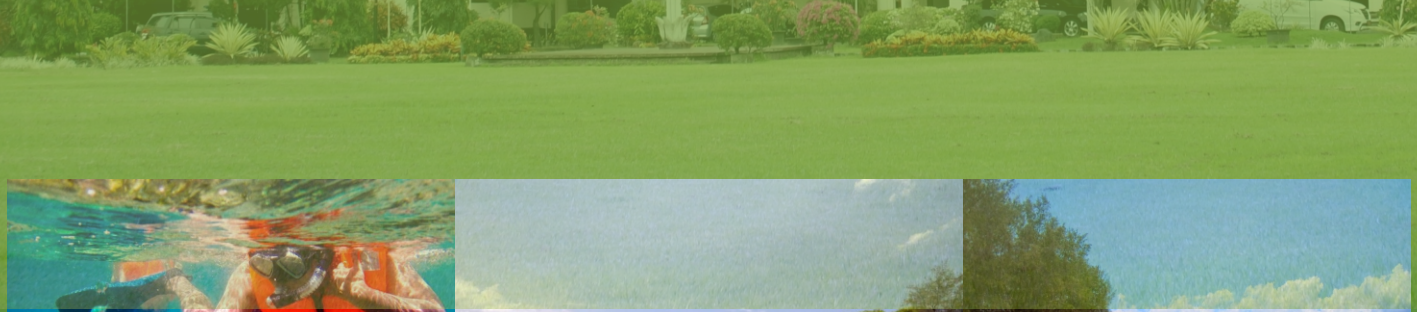
ISBN : 978-979-8911-97-2

PROSIDING
SEMINAR NASIONAL KIMIA (SNK) 2016

"Pengembangan Kimia Berbasis Kearifan dan Sumber Daya Alam Lokal: Integrasi Riset, Pendidikan dan Industri"

Mataram, 10 - 11 Agustus 2016
Puri Indah Hotel & Conventions, Mataram - Lombok



PROGRAM STUDI KIMIA
FAKULTAS MATEMATIKA & ILMU PENGETAHUAN ALAM
UNIVERSITAS MATARAM
Jl. Majapahit No. 62. Mataram - NTB
www.mipa.unram.ac.id
Telp / Fax : (0370) 646506

PROSIDING SEMINAR NASIONAL KIMIA –LOMBOK 2016

"Pengembangan Ilmu Kimia Berbasis Kearifan dan Sumber Daya Alam Lokal: Integrasi Riset, Pendidikan dan Industri"

ISBN: 9-789798-911972

Editor:

Prof. Ir. Surya Hadi, M.Sc, Ph.D
Prof. Dr. Yana Maolana Syah
Prof. Dr. Euis Holisotan Hakim
Prof. Dr. Syamsul Arifin Ahmad
Prof. Dr. A. Bambang Setiaji
Dedy Suhendra, Ph.D
Erin Ryantin Gunawan, Ph.D

Diterbitkan oleh:

Program Studi Kimia
Fakultas Matematika dan Ilmu Pengetahuan Alam
Universitas Mataram

Alamat Penerbit:

Jl.Majapahit No.62 Mataram NTB Telp. (0376) 646506

Kata Pengantar

Bismillahhirrohmanirrohim,

Puji syukur kita panjatkan kehadirat Allah SWT yang telah mencurahkan segala nikmat dan kesempatan yang diberikan sehingga Buku Prosiding Seminar Nasional Kimia – Lombok 2016 dengan tema " Pengembangan Kimia Berbasis Kearifan dan Sumber Daya Alam Lokal: Integrasi Riset, Pendidikan dan Industri" yang dilaksanakan pada tanggal 10-11 Agustus 2016 di Hotel Puri Indah Mataram.

Buku Prosiding ini memuat sejumlah artikel hasil penelitian pada berbagai aspek bidang kimia yang dilakukan oleh peneliti, akademisi dan praktisi industri serta mahasiswa dari berbagai daerah di seluruh indonesia yang dikumpulkan dan ditata oleh tim kepanitiaan dari Program Studi Kimia Fakultas MIPA Universitas Mataram. Dengan disusunnya Buku Prosiding ini, diharapkan dapat bermanfaat bagi kita semua dalam mengembangkan ilmu pengetahuan demi kemajuan bangsa dan negara.

Sebagai Panitia yang berkhidmat dalam memberi pelayanan sebaik-baiknya kepada seluruh peserta untuk kelancaran dan keberhasilan Seminar Nasional Kimia ini, kami mohon maaf yang sebesar-besarnya, jika terdapat kekurangan dalam persiapan, selama penyelenggaraan seminar berlangsung maupun kekurangan dalam isi Buku Prosiding ini. Kepada segenap pihak yang membantu hingga suksesnya penyelenggaraan seminar ini, kami menyampaikan banyak terimakasih dan penghargaan setinggi-tingginya, semoga kerjasama yang baik ini dapat terus terbina di masa mendatang.

Mataram, 1 Agustus 2016
Panitia SNK-Lombok 2016
Ketua,

PANITIA SNK - FMIPA UNRAM 2016

Dr. Maria Ulfa

SNK02-03

EFEK PENAMBAHAN ALUMINA PADA KARAKTERISTIK MIKROSTRUKTUR DAN FISIS CORDIERITE DARI SILIKA AMORPH SEKAM PADI

EFFECT OF ALUMINA ADDITION ON THE MICROSRUCTURE AND PHYSICAL PROPERTIES OF CORDIERITE FROM AMORPHOUS RICE HUSK SILICA

Simon Sembiring[1]*, Agus Riyanto[1], Wasinton Simanjuntak[2], Rudy Situmeang[2]

Kerista Sebayang[3]

[1]Department of Physics, Faculty of Mathematics and Natural Sciences, University of Lampung,

Jl. Prof. Soemantri Brojonegoro No.1 Bandar Lampung, 35145, Indonesia

[2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Lampung,

JL. Prof. Soemantri Brojonegoro, No 1 Bandar Lampung, 35145, Indonesia

[3]Department of Physics, Faculty of Mathematics and Natural Sciences, University of North Sumatera,

Jl. Bioteknologi No.1, Kampus Padang Bulan, Medan 20155, Indonesia

**Corresponding author: simonsembiring2@gmail.com*

Abstrak

Penelitian ini bertujuan untuk menyelidiki pengaruh penambahan alumina terhadap karakteristik mikrostruktur dan fisis cordierite yang dipersiapkan dari bubuk silika sekam padi, alumina dan periclase. Sampel yang diperoleh disintering pada suhu 1230 ^oC dengan penambahan alumina, 0, 5, 10, 15 dan 20 %, selanjutnya struktur dikarakterisasi menggunakan XRD dan SEM. Hasil yang diperoleh menunjukkan bahwa secara significant dengan penambahan alumina cordierite mengalami dekomposisi menjadi alumina, spinel, cristobalit dan periclase, dan cordierite praktis tidak terdeteksi dengan penambahan alumina dari 10 ke 20 %, sementara alumina, spinel dan cristobalit sebagai phase yang dominan. Formasi alumina dan spinel diikuti dengan peningkatan densitas, porositas dan konduktivitas termal, sementara konduktivitas listrik kebalikannya.

Kata Kunci: Cordierite, sekam padi alumina, struktur, listrik

Abstract

This study aims to investigate the effect of alumina addition on the microstructure and physical characteristics of cordierite prepared from rice husk silica, Al_2O_3, and MgO powders. The samples without and with alumina addition of 5, 10, 15 and 20% were prepared and subjected to sintering temperature of 1230 ^oC and the structures were characterised using X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results obtained indicated the significant role of alumina addition on the phase decomposition of cordierite into alumina, spinel, crystoballite and periclase, in which at alumina addition of 10-20% the cordierite is practically disappeared, while alumina, spinel and crystoballite emerged as dominant phases. Formation of alumina and spinel was followed by increase in density, porosity, and thermal conductivity, while for electrical conductivity the opposite was true.

Keywords: Cordierite, rice husk, alumina, structure, electrical

INTRODUCTION

Related to raw materials for preparation of ceramics, rice husk is a very attractive source of reactive silica, primarily since this agriculture residue is abundantly high silica content, which makes this agroindustrial residu as an excellent source of high-grade amorphous silica. In addition, many researchers [1,2] have shown that rice husk silica can be produced by simple acid-leaching process of the husk. 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, [3], and silicon carbide [4]. 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, aluminosilicates [5], mullite [6] and cordierite [7]. Cordierite ($2MgO.3Al_2O_3.5SiO_2$) is a material having a low thermal expansion coeficient and dielectric constant, high thermal and mechanical stability. These characteristics make its an interesting candidate for many industrial application, such as refractory products, microelectronics, and thermal shock-resistance [8], catalyst carriers for exhaust gas purification, heat exchanger for gas turbine engines [9], electrical and thermal insulation [10].

There are many routes to prepare cordierite ceramics, the most popular way still solid-state reaction. At temperatures of 1200-1400 °C, a reaction occurs between MgO, Al_2O_3 and SiO_2 to form cordierite, which is stoichiometrically mixed, but a significant amount of silica was still present in the finalised product [11]. In previous studies [8], solid-state reaction was applied to synthesize cordierite from Al_2O_3, MgO, and rice husk silica. The results obtained indicate that crystallization of μ-cordierite occurred at temperature of 1050 °C, and transformed into α-cordierite at temperatures in the range of 1050 to 1350 °C. It was also reported that thermal expansion of cordierite is 2.2 x 10^{-6}/ºC [12], while the others reported the value of around 3.3 x 10^{-6}/ºC [7], 1- 4 x 10^{-6}/ºC [13], and 0.8-2 x10^{-6}/ºC [14].

To take advantage of its availability and excellent properties, this present study is aimed to evaluate the potential of rice husk silica for production of cordierite, with the specific purpose to study the effect of Al_2O_3 (alumina) additions on the microstructure and physical properties of the cordierite produced.

EXPERIMENTAL METHODS

Materials

Raw husk used as a source of silica was from local rice milling industry in Bandar Lampung Province, Indonesia. The chemicals, Al_2O_3, MgO powders, KOH, HCl, and absolute alcohol (C_2H_5OH) were purchased from Merck (kGaA, Damstadt, Germany).

Procedures

Preparation of silica powder from rice husk

Rice husk silica was obtained using alkali extraction method following the procedure reported in previous study [6]. 50 g dried husk was mixed with 500 ml of 5% KOH solution, folowed by boiling of the mixture for 30 minutes in a beaker glass. The mixture was allowed to cool to room temperature and left for 24 hours, followed by filtration using Millipore filter to separate the silica sol from the residual husk. The sol was acidified by dropwise addition of 5% HCl solution until conversion of the sol into gel was completed. The gel was oven dried at 110 ºC for eight hours and then ground into powder.

Preparation of cordierite-alumina

Preparation of cordierite was carried out by mixing raw materials with the composition of MgO: Al_2O_3:SiO_2 of 2:2:5 by mass, in accordance with the composition of cordierite as reported in previous studies [7]. The raw materials were mixed with alcohol under magnetic stirring for 6 hours. Then, the mixture was filterred and the solid was oven dried at 110 ºC for eight hours to remove the adsorbed alcohol. The solid was ground into powder by mortar and sieved to obtain the powder with the size of 200 meshes. After that, alumina was added to the cordierite powder in different content (5, 10, 15 and 20 % by mass). The powder was pressed in a metal die with the pressure of 2 x 10^4 N/m^2 to produce cylindrical pellet and the pellets were sintered at temperature of 1230 ºC, using temperature programmed with a heating rate of 3 ºC /min and holding time of 4 hours at peak temperatures.

Characterisation

The examination of porosity and density was done according to Archimedes method [15]. 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 conductivity was measured using the LCR programmable automatic, and thermal conductivity of the samples was measured by laser flash analyzer (Type, TC-7000H).

RESULTS AND DISCUSSION

Fig. 1a displayed the XRD patterns of the samples without alumina addition sintered at different sintering temperatures and Fig 1b shows the XRD patterns of the samples at sintering temperature of 1230ºC with different alumina addition.

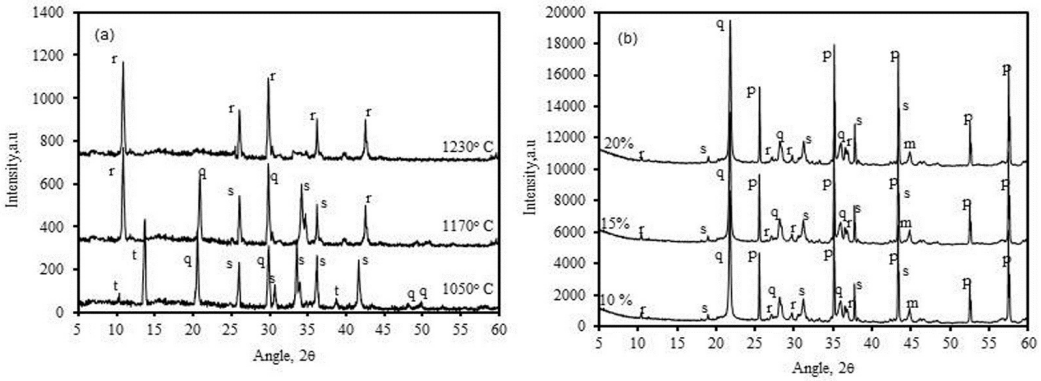


Figure. 1. The x-ray diffraction patterns of the samples, (a) different temperatures of sintering, (b) different alumina content relative to cordierite.p= alumina, q= cristobalite, r= α-cordierite, s= spinel, m= periclase, t= μ-cordierite

The phases identified with the PDF diffraction lines using search-match method [16], clearly show the presence of alumina (PDF-46-1212), α-cordierite (PDF-13-0294), μ-cordierite (PDF-14-0249), spinel (PDF-21-11520), cristobalite (PDF-39-1425), and periclase (PDF-45-0946. At 1050ºC (Fig 1a) several phases with a noticeable amount of μ-cordierite, spinel and cristobalite are clearly detected while α-cordierite is practically undetected. At 1170°C, the μ-cordierite was changed into α-cordierite, and followed by the formation spinel and cristobalite phases (Fig. 1a). Further increase of sintering temperature to 1230 ºC caused the spinel and cristobalite phases disappeared almost completely, leading to formation of α-cordierite. This finding is in agreement with the result of previous study [17], in which it was suggested that the formation of α-cordierite is most likely as a result of inter-diffusion between cristobalite and spinel.

Fig 1b shows the XRD patterns of each samples after alumina addition at sintering temperature of 1230ºC and Fig 2 presents the high peak intensity of each phases. As shown in Figs 1 and 2, cordierite drastically decrease, while crystobalite and alumina increase as alumina was added from 0 to 10 %. From 10 to 20 % alumina addition (Fig. 1b and Fig 2), the α-cordierite slightly decreased and followed by the formation alumina and cristobalite, while spinel and periclase increase. A further decrease in the α-cordierite phase following the increases in alumina content reflects the more intensive augmentation of periclase phase formation as well as spinel.

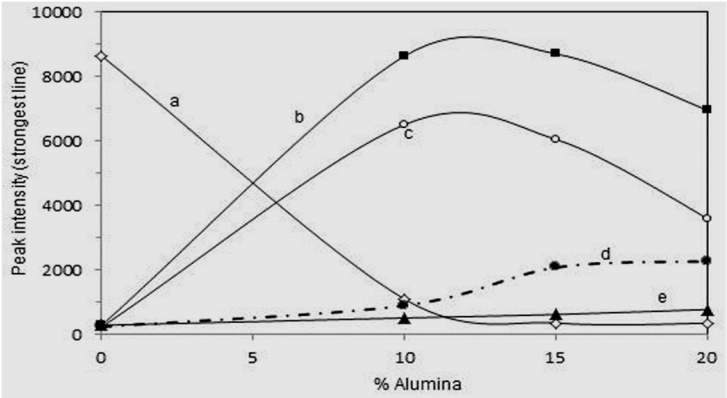


Figure. 2. The variation of XRD strongest peak of the samples depending on the alumina content (a) cordierite, (b) crystobalite, (c) alumina, (d) spinel and (e) periclase

The surface morphologies of the sintered samples at temperature 1230°C with different alumina contents were characterized using SEM. The results show quite significant effect of alumina addition on the surface morphology, most likely a result of crystallisation. The micrographs presented in Fig. 3(a-d) present significant effect of alumina on the size and distribution of the particles on the surface.

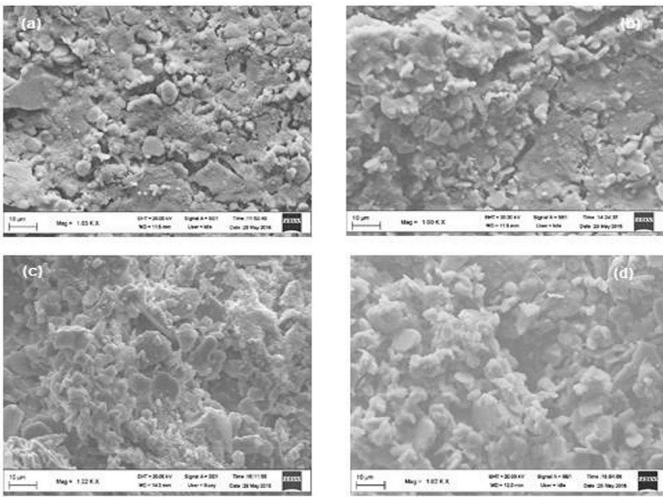


Figure. 3. The scanning electron microscopy (SEM) images of the samples sintered at 1230 ºC with different alumina content (a) 0 % (b) 10%., (c) 15 %., and (d) 20 %.

As displayed by the images in Fig. 3(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 % alumina (Fig. 3a) shows large grains without grain boundaries, while for the samples with 10 and 15% alumina addition, grain boundaries were evidently observed (Fig. 3b-c). In addition, it is obvious that the large grains in the sintered sample with 0 % alumina is most likely composed of α-cordierite. 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 alumina content (10 - 15%) as presented in Fig. 3 (b-c) is dominated by some fine grains of cristobalite, alumina, spinel and periclase and covered some large grains of α-cordierite. Both samples are marked by initiated coalescence of spinel as a result of α-cordierite crystallization. This feature suggests that with 10 and 15 % alumina addition, α-cordierite phase continue to change, leading to the formation of spinel, alumina, cristobalite and periclase. This change is supported by the result of XRD analysis for the sintered samples with 10-15% alumina (Fig 1b), in which small α-cordierite was detected. The formation of spinel, alumina, cristobalite and periclase can be seen more clearly by inspecting the SEM micrographs of the sintered sample with 20% alumina content (Fig. 3d), which display intensified agglomeration on the entire surface as the alumina increased.

The physical properties of the sintered samples at different alumina addition are shown in Fig. 4a-b and Fig 5a-.b.

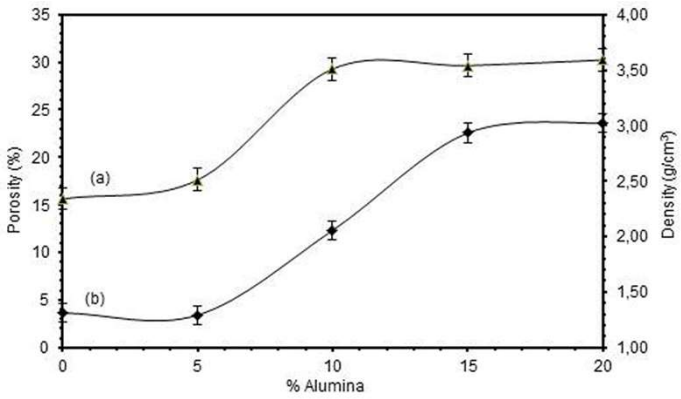


Figure.4. Density (a) and Porosity (b) as a function of alumina content relative to cordierite

Fig. 4a-b shows the changes in density and porosity of the samples as a function of alumina content. As can be observed, the density and porosity of the sintered sample at 1230ºC with 0 % alumina (Fig 4a-b) increase slowly as alumina content increase up to 5 % alumina, and beyond this content of alumina, sharp increase were observed up to 20 % alumina. As shown in Fig 4a, the densities of the samples increase from 2.34 to 2.51 g/cm^3 as the alumina content increased from 0 to 5 %, and increased sharply and reached the value of 3.59 g/cm^3 at the alumina content of 20 %. The slow increase of the density with increasing alumina content up to 5 % was attributed to the small increased of the amount of spinel, cristobalite, alumina phases, followed by sharp increase with increasing alumina content up to 15 %. The change in density was most likely due to conversion of cordierite into spinel, cristoballite, alumina and periclase at 20 % alumina, as displayed by the XRD

results presented in Fig 1b and Fig 2. These results are in accordance with the results of others [18,19,20], in which it was reported that the density of spinel, critobalite, alumina and periclase phases is higher than that of cordierite. In those previous studies, it was reported that the density of spinel, cristobalite alumina and periclase are 3.58, 2.6, 3.97, and 3.58 g/cm^3 respectively, while for cordierite, the value is 2.3 g/cm^3 was reported.

The slow decrease of porosity (Fig 4b) with increasing alumina content up to 5 % was attributed to decrease formation of cordierite phase, leading to decreased porosity. Beyond this alumina content, density and porosity are increased shaply, probably indicating the domination of spinel, cristobalite alumina and periclase, larger particles distances and also larger pore in the samples as a result of higher alumina content applied, which is in accordance with the surface morphologies of the samples as seen in SEM results (Fig 3a-d). Moreover, the porosity was found to increase as the alumina content increased (Fig 4b), which is in agreement with the increase in the amount of spinel, and periclase (See Fig 1b and Fig 2).

Fig. 5a and 5b show the change in electrical conductivity and thermal conductivity of the samples as a function of alumina addition, respectively. As shown in Fig. 5a, the higher the alumina contents, the lower the electrical conductivity, which implies that the samples became resistance to electricity as a result of increased amount of spinel and periclase as supported by XRD results in Fig 1b and Fig 2. This profile demonstrates that the electrical conductivity of the samples can be controlled by controlling the formation of the spinel and alumina phases, which is very useful for adjusting the suitability of the material for specified applications, such as insulator and conducting element in electronic devices.

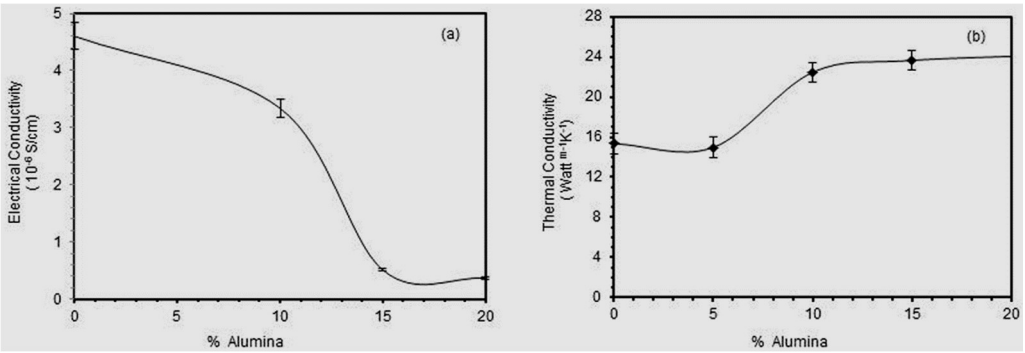


Figure. 5. (a) Electrical conductivity at 100 Hz, (b) Thermal conductivity as a function of alumina content relative to cordierite

Figure 5b shows the characteristics of thermal conductivity of the samples as a function of alumina content relative to cordierite. The result reveals the thermal conductivity increased

as the alumina content increased. The results show that the thermal conductivity of the samples increased slowly as the alumina content increase from 0 to 5% and increased sharply from 5 to 10 % and practically plat up to 20 % as shown in Fig 5b.

Table 1. Thermal and electrical conductity values of the materials

Material	Thermal Conductivity (watt.$m^{-1}K^{-1}$)		lelectrical Conductivity (Siemens/cm)	
Cordierite	18	[21]	(0.3-1.4)x10^{-6}	[20]
Alumina	27.2	[22]	7.8 x10^{-6}	[24]
Spinel	1.2	[23]	4.9 x10^{-13}	[25]
Periclace	42	[19]	4.2x10^{-7}	[26]
Silica/cristobalite	-		10^{-12}	[20]

It can be summarised that, as the alumina content increased, the thermal conductivity increased, most probably due to the decrease in the amount of cordierite, spinel and cristobalite, as supported in the XRD results in Fig 1b. It is also found that thermal conductivity of cordierite; spinel and cristobalite are smaller than those of alumina and periclace as shown in Table 1. In accordance with the above values reported by others, it is then clear that increased thermal conductivity of the samples investigated in this study is most likely associated with the increased amount of alumina and periclace, as confirmed by XRD results.

CONCLUSIONS

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

ACKNOWLEDGMENTS

The authors wish to thank and appreciate the Directorate General of Higher Education Republic of Indonesia (DIKTI) for research funding provided through the Competency Research Grant Batch II Program 2016, with contract number: 040/SP2H/LT/DRPM/II/2016 and 79/UN26/8/LPPM/2016.

REFFERENCES

[1] Daifullah, A.A.M., Awwad, N.S., and El-Reefy, S.A., 2004. Purification of phosphoric acid from ferric ion using modified rice husk, J. Chem. Eng. Proc. **43**, 193-201.

[2] Della, V.P., Kuhn, I., and Hotza, D., 2002. Rice husk ash an alternate source for active silica production, Mater. Lett. **57,** 818-821.

[3] Sun, L., and Gong, K., 2001. Silicon-based materials from rice husks and their applications. Ind. Eng. Chem. Res. **40**, 5861.

[4] Singh, S.K., Mohanty, B.C. and Basu, S., 2002. Synthesis of SiC from rice husk in a plasma reactor, Bull.Mater. Sci. **25**, **(**6), 561-563.

[5] Simanjuntak, W., Sembiring, S., Manurung, P., Situmeang, R and Low, I.M., 2013. Characteristics of aluminosilicates prepared from rice husk silica and aluminum metal, Ceram. Int. **39**, (8), 9369-9375.

[6] Sembiring, S., Simanjuntak, W., Manurung, P., Asmi, D and Low, I.M., 2014. Synthesis and characterisation of gel-derived mullite precursors from rice husk silica, Ceram. Int. **40**, (5), 7067-7072.

[7] Sembiring, S., Simanjuntak, W., Situmeang, R., Riyanto, A and Sebayang, K., 2016. Preparation of Refractory Cordieirite Using Amorphous Rice Husk Silica for Thermal Insulation Purposes Ceram. Int. **42,** (7), 8431-8437.

[8] Chowdhury, A., Mitra, S., Das, S., Sen, A., Samanta, G.K., Datta, P., 2007. Synthesis properties and application of cordierite ceramics, Part 1. Int.Ceram., **56**, 18-22

[9] Oliveira, F.A.C and Fernandez, J.C., (2002), Mechanical and thermal behavior of cordierite zirconia composites, Ceram. Int**. 28** 79-91.

[10] Evans, D.L., Fischer, G.R., Geiger, J.E., Martin, F.W., 1980. Thermal expansions and chemical modifications of cordierite, J. Am. Ceram. Soc. **63**, 629-634.

[11] Ghitulica, C., Andronescu, E., Nicola, O., Dicea, A and Birsan, M., 2007. “Preparation and characterization of cordierite powders,” J. Eur. Ceram. Soc. **27**, 711–713.

[12] Kobayashi, Y., Sumi, K and Kato, E., (2000), Preparation of dense cordierite ceramics from magnesium compounds and kaolinite without additives, Ceram. Int. **26** 739-743.

[13] Yamuna, A., Jhonson, R., Mayajan, Y.R and Lalithambika, M., 2004. Kaolin-Based cordierite for pollution control, J. Eur. Ceram. Soc. **24** 65-73.

[14] Kurama S and Kurama, H., 2008. The reaction kinetics of rice husk based cordierite ceramics, Ceram. Int. **34**, 269-272.

[15] Australian Standard, 1989. Refractories and refractory material physical test methods: The determination of density, porosity and water adsorption, 1-4, 1774.

[16] Powder Diffraction File (Type PDF-2), 1997. Diffraction Data for XRD Identification. International Centre for Diffraction data, PA USA.

[17] Naskar, M.K and Chatterjee, M., 2004. A novel process for the synthesis of cordierite ($Mg_2M_4Si_5O_{18}$) powder from rice husk ash and other sources of silica and their comparative study, J. Eur. Ceram.Soc. **24**, (13) 3499-3508.

[18] Aluminium oxide (alumina) ceramics and properties- Marketch International Inc. 2002.

[19] Kinniburgh, C.G., 1976. Grain size dependence of fracture energy in MgO, J. Phys. C: Solid State Phys. **9**, 2692-2715.

[20] Charles, A.H., 2001. *Handbook of ceramic glasses and* diamonds, Mc Graw Hills, Company Inc, USA.

[21] Zhang, L., Ferreira, J.M.F., Olhero, S., Curtois, L., Zhang, T., Maire E and Ranhe, J.C., 2012. Modeling the mechanical properties of optimally processed cordierite-mullite-alumina ceramic foams by x-ray computed tomography and finite element analysis, Acta Materialia ,**60**, 4235-4246.

[22] Schneider, H., Osaka, K and Pask, J.A., 1994. Mullite and Mullite

Ceramics, , Wiley Chichester, 1-251

[23] Lee, M., 1990, Ionic conductivity measurement in $MgAl_2O_4$ spinel and solid state galvanic cell with $MgAl_2O_4$ electrolyte. Korea Advanced Institute of Science and Technology, Republic of Korea.

[24] Lux, F., 1993, Models proposed to explain the electrical conductivity of mixtures made of conductive and insulating materials, J. Material Science **28**, 285-301.

[25] Padmaraj, O., Venkateswarlu, M., and Satyanarayana, N., 2015 Structural, electrical and dielectric properties of spinel type $MgAl_2O_4$ nanocrystalline ceramic particles synthesized by sol gel-combution method, Ceramic International, **41**, 3178-3185

[26] Mbarki, R., Mnif, A., and Hamzaoui, A.H., 2014, Structural, dielectric relaxation and electrical conductivity behavior in MgO powders synthesized by sol-gel, J. Materials Science in Semiconductor Processing ,1-6