Characteristics of Solid State Sintered Silica Ceramic Derived from Rice Husk Ash

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Abstract. Silica xerogel produced from rice husk ash (RHA) taken from South East Sulawesi Indonesia has been successfully sintered by using a microwave oven 2.45 GHz as well as a millimeter waves (MMW) heating system with a 28 GHz gyrotron. The samples were also heated by using an electric furnace where served as a comparison. Physical characterization of the samples before and after sintering were then investigated by using an Archimedes densification measurement method device, a X-ray diffraction (XRD) and a Scanning Electron Microscopy (SEM), respectively. Effect of microwave energy on the characteristics of silica ceramic after processing were analyzed and compared to conventionally sintered results. The effect of frequency to properties of the silica was also revealed and reported previously in separated paper. In this paper, depedency of microwave power and heating rate to grain growth and density of the ceramic are reported. The results suggested that the microwave power affect to grain growth rate of silica xerogel as well as to their density. In other hand, grain growth is also strongly depend on heating rate during fabrication.

1. Introduction
Silica xerogel is one of the useful materials in the world. It is because its properties can be modified to desired properties by special treatment such as heating or doping by another material. Its structure can be shrinks during heating because the aqueous phase in the pores is removed by evaporation, capillary contraction, condensation – polymerization reactions, structural relaxation, or by viscous flow [1,2]. If the material processing by using heat treatment until below melting point, the process known as solid
state sintering [2,3]. Moreover, the silica xerogel ceramic have several industrial applicable characteristics such as high transparency and good chemical durability [3–5]. Its properties can be modified by change its microstructure where can be done by change their chemical composition and physical parameters as well as adjust thermal process parameters during heating [6]. For application to waveguide, it is expected the silica glass ceramic have a high density, good mechanical properties with desired optical properties.

Previous results of processing silica xerogel shows that silica glass-ceramic with maximum density of 2.2 g/cm³ can be obtained at processing temperature 980°C with low heating rate. It is far below its melting point where about 2000°C [2]. However, processing by low heating rates in conventional heating method needs long time which promotes grain growth result in decreasing its optical transparency. In contrast to the conventional heating such as by using electric furnace the heating by using a microwave can be performed in a high heating rate. It is because in microwave heating, the electromagnetic energy is dissipated simultaneously in the whole irradiated volume not only in surface as in conventional heating. Additionally, the microwave radiation offers higher densities of the heating power, selective heating, self heating, etc. Microwave 2.45 GHz up to 1 KW power output available everywhere. But for high frequencies such as millimeter and sub-millimeter waves are rarely available. For a high microwave frequencies, gyrotrons are considered as the most appropriate technology for radiation source up to now.

Applications of the such electromagnetic energy show several unique physical phenomena compared to that conventional method. A significant densification, mechanical properties, and improvement of the reaction rate of several materials have been reported [7-9]. The most materials processed by microwave up to now is alumina. There are reported that shorter processing times and lower sintering temperatures can be achieved compared to the conventional processing. Moreover, in this case the samples were denser and thus stronger than the samples conventionally sintered at the same temperature for the same time duration. For silica xerogel, the time evolution of the density, porosity, and the crystallization of samples observed in the microwave process is similar to the one observed in the conventional process but during the microwave treatment, this evolution occurs at temperatures approximately 200°C lower [9,10]. The materials such as boron carbide and silicon nitride has been also reported recently [11-12]. The effect of microwave frequency are also reported found in these materials [13-15]. The frequency dependency of dielectric loss of materials are indicated as the main factor in this phenomena.

In this paper, we present experimental results of characterization of silica xerogel extracted from local rice husk ash. We study and discuss the influence of the sintering rate and effect of microwave power on the characteristic of the samples after processing.

2. Experimental Method

2.1. Sample preparation

Raw material rice husk was obtained from the rice field taken from South East Sulawesi, Indonesia. Rice husk ashes found by burning rice husk. Rice husk ashes were then washed using 1 M hydrochloric acid (HCl) at 100°C and mixed with 60 ml of 2 M NaOH. After filtered by Whatman No. 41, the silicate was inputted to an ion-exchange resin. The detailed extraction following procedures as described elsewhere [17, 18]. The powder of silica xerogel found from this experiment was characterized by X-ray fluorescence find out its characteristic. The powder was formed to cylindrical shape by applied polyvinyl alcohol as a binder before pressed.

2.2. Sintering experiment

The samples after pressed to cylindrical form were sintered by using a microwave oven 1 KW, 2.45 GHz in Halu Oleo University and a 28 GHz gyrotron heating system in FIR Center University of Fukui, Japan. The sample holder was a hollow cylinder made of thermo-isolating material. Some results of 28 GHz have been reported previously [19]. The power of microwave oven was varied and all
samples heated up to 1200 °C. The heating rates were calculated based on time consumption for each microwave power. The cooling was performed by a natural convection after the microwave off and leaving the samples inside. The temperature profile was measured using an infrared thermometer. Figure 1 shows the 28 GHz gyrotron sintering system.

![Figure 1. (a) 2.45 GHz Microwave and (b) Gyrotron 28 GHz heating system](image1)

Figure 2. Silica samples after sintering

2.3. Characterization
All silica samples after sintering were then characterized by using Archimedes’s method to calculate their density, open and closed pores. The procedure is followed a standard test method of the American Society for Testing and Material Specification (ASTM) C373-88 [20]. To determine their grain growth, the SEM photos of fracture surface of samples were performed by using a scanning electron microscope (SEM) at different magnification and at accelerating voltage of 10-15 kV in Halu Oleo University. SEM photos were processing by using image processing to calculate average grain size, and pores. Another experiments were performed to investigated effect of microwave energy to samples such as XRD, FTIR, and Vicker Hardness testing. They will reported in separated papers.

3. Results and Discussion
Figure 3 shows the grain size of silica with various heating rates in microwave (2.45 GHz). All samples wer sintered at 1200 °C. The conventional sintering result served as a comparison. The quantitative analysis of microstructure from SEM photos for determining grain size for each samples shows that grain growth of silica strongly depend on heating rate. Furthermore, Fig. 3 also shows that grain growth can be depressed by using fast heating. This is may because of the grain growth depend more strongly to time than to temperature. The conventional sintering samples was also calculated at same temperature i.e. 1200°C.
Figure 3  Grain size of silica xerogel as a function of the heating rate at 1200 °C

It indicates that increasing the heating rate will affect to mass transport which contribute to grain growth during sintering. From theory of sintering, there are several atomic diffusion paths may occurs during sintering. Some paths contribute to grain growth and the others are not [21]. The change in diffusion path from surface to grain boundaries and vice versa will change grain growth rate. The atomic diffusion $D$ follow the equation,

$$D = D_0 \exp \left( -\frac{Q}{RT} \right)$$

[1]

where $D_0$ is pre-exponential of $D$ which represents number of atomic jump per time, $Q$ is activation energy, $R$ is constant, and $T$ is temperature. From this equation we can see that heating rate s one of the main parameter of atomic diffusion.

The atomic diffusion rate and path are also depend on microwave power applied for heating source during sintering. It can be seen in Fig 4. However, changing the microwave power also changes the heating rate byself. It indicates that the changes in grain growth rates affected by both parameters i.e. microwave power and heating rate.

Figure 4  Grain size of silica xerogel as a function of the microwave power at 1200 °C

Figure 5 shows the density dependency to heating rate for samples sintered at 1200 °C. The Archimedes method applied for each sample to determine the density resulted that not only grain growth but also densification also depend on the heating rate. For densification ($\rho$) of material which processing by a thermally activated process such as in solid state sintering of ceramics, the densification is follows the equation [21],

$$\frac{d\rho}{dt} = C \exp(-Q/RT)$$

[2]

where $C$ is function of grain size and density and $Q$ is apparent activation energy.
However densification rate is not only depend on atomic diffusion only. There are several mechanisms during sintering may affect to this physical property. The appearance of pores is ascribed to the empty sites of the evaporated water and to some residues of alcohol binder as well as to combusted residual organics when the sintering process is one factor to change density. In the temperature range up to 800°C, the increase in density is because of the condensation reactions occurs on the surface of the silanols groups (Si-O-H) [1]. It cause the silica xerogel structure tends to shrink due to the loss of the hydroxide (OH) groups and densification rate increase. In the temperature range more than 1200°C, cannot be achieved by using microwave oven used in this experiment. However for 28 GHz sintering results have been reported in previous paper [19]. Moreover a crystallization of silica glass that affects the grain growth where was also observed in 28 GHz of silica xerogel ceramic will reported in separated paper. The increase in the densification explained by atomic diffusion where also can applied In the case of effect of microwave power to densification as shown in Fig. 6.

For isothermal sintering methods, where the desired temperature keep during heating, we strongly can applied the Equation 2 to estimated the activation energy, Q. The Q describes atomic diffusion rate itself. we estimate the time required to reach a target density at a specific temperature. The rate of densification is recorded at each individual temperature. The experiment commonly is using a dilatometer. In the absence of a dilatometer, sintering runs are performed at regular intervals of time and the resulting densities are recorded. It will be performed in future experiments.

4. Conclusion
A series of experiments to investigate effects of heating rate and microwave power to silica xerogel were successfully performed. The experiments were performed by using a 2.45 GHz microwave sintering system. The different grain growth rate as well as densification rate were found for variation of heating rate and microwave power. It has been found that the high sintering rate depressed the grain growth of silica. But the sintering rate also decreasing densification. It may be because of change the path of atomic
diffusion. As a whole, the experimental results obtained in this study demonstrate that the microwave sintering of silica glass-ceramics using a 2.45 GHz shows a microwave power and heating rate. It can be considered as an appropriate technology for control industrial production of silica ceramics to desired properties for applications.

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