The 4th International Conference on Advanced Materials Science and Technology
IOP Conf. Series: Materials Science and Engineering 202 (2017) 012059
doi:10.1088/1757-899X/202/1/012059

Synthesis and Characterization of Microwave Absorber SiO₂ by Sol-Gel Method

S Wardiyati, W A Adi and Deswita
Center for Science and Technology of Advance Materials, National Nuclear Energy Agency. Kawasan Puspiptek Serpong 15314, Tangerang Selatan
Email: siti-war@batan.go.id

Abstract. In recent years, information technology is growing rapidly, such as communication devices. However, there are still many shortcomings, for example, confidential information leaks caused by the leakage of electromagnetic waves used. A coating of electromagnetic materials or formation composite of electromagnetic materials with other materials such as SiO₂ is needed to overcome these problems. For such needs, it is necessary to study the manufacture of SiO₂ which is simple, cheap, and effective. In this research, manufacture of SiO₂ by sol-gel method used a solution of sodium silicate (Na₂SiO₃) as precursors and H₂SO₄ as a catalyst. The parameters tested in this experiment is the effect of sintering temperature on the properties of the resulting SiO₂. The purpose of this study was to obtain an amorphous SiO₂ powder, which is in nanosized and has a high surface area. The characterization of prepared samples were performed by using an X-ray Diffraction (XRD), Fourier Transmission Infra Red (FTIR), Scanning electron microscopy-energy dispersive spectrometer (SEM-EDS), Transmission Electron Microscopy (TEM), and Surface Area Analyzer (SAA). Based on the experimental results, the SiO₂ amorphous structure was obtained with a particle size of 15-20 nm, the surface area of 298 m²/g, and sintering temperature of 100 °C.

Keywords: Microwave absorber, nanomaterial, SiO₂, sol-gel

1. Introduction
In the recent years, the development of information technology gives rise to rocketing growth in the development of microwave electronic systems and telecommunications in high frequency. However, many problems have appeared along with it. It could be originated from the misoperation of precise electronic equipment, and leaks of secret information occurred by leakage of electric waves [1]. To solve above problems, the electromagnetic wave absorbers with wider absorption band and more effective absorption properties constantly become crucial. Electromagnetic wave absorbing materials are being investigated as anti-electromagnetic interference coatings in self-concealing technology, and properties such as dielectric loss, conductivity loss, and magnetic loss. This material includes metal oxides, alloy-epoxy composite, and especially metallic magnetic material [2]. The magnetic composites have attracted intense attention for performance in the various application, such as magnetic resonance imaging, optoelectronic devices, and microwave absorbing [3]. One of promising of composite magnetic materials is silica (SiO₂) and iron (Fe). The use of silica because silica has...
several characteristics such as biocompatibility in a biological system, long suspension in various solvents, surface conductivity modification and improved chemical stability of magnetic composite [3]. The silica for their application, especially for microwave absorbing must be in nano size so that the permeability and permittivity of nano composing ferromagnetic metals (Fe) formed increasing and high electrical resistance ceramics (SiO$_2$) [4]. Therefore, an experiment study of making nanoscale SiO$_2$, which next will be composited with Fe to form the electromagnetic wave absorbers Fe-SiO$_2$ should be conducted.

Over the last decade, there has been rapid progress in research in the field of nanoscience and nanotechnology. Nanoparticles are defined as particles with a diameter of less than 100 nm. Nanomaterials have specific properties, such as small size, large surface area, form a special structure, because of the nature of the unique shape and morphology that the nanomaterial can be manipulated physically and chemically, and is widely used in industrial and biomedical processes [5]. With the development of nanotechnology may increase the economic value of a product.

The nano-sized material has a larger surface area, compared with the bulk material. These factors cause this material has a reaction rate, optical properties, magnetic and catalytic increased [6]. Silicon dioxide (SiO$_2$) nanoparticles can be used as a support material that is ideal for magnetic nanoparticles because it is very easy to experience functionalization; prevent anisotropic dipolar magnetic attraction when given an external magnetic field, and improve the corrosion resistance of the magnetic nanoparticles [7]. Amorphous and dielectric properties of SiO$_2$ are suitable to be used as microwave absorber electric for anti-radar, which in this year is being developed in PSTBM BATAN Indonesia.

Several methods can be employed for the manufacture of SiO$_2$, including precipitation [8-10], and sol-gel [11-13]. The sol-gel method is widely used because the process takes place at low temperature, the simple and the resulting product has a high purity and nanoscale. This method is one of the wet method because the process involves the solution as a medium. In the sol-gel method, the change in the phase of the solution becomes sol (colloid has suspended solids in the solution) and then it turns into a gel (colloidal but has a solid fraction larger than the sol). Basically, the synthesis of materials by the sol-gel method is through 4 (four) stages of the process, i.e. (1) hydrolysis, (2) condensation, (3) maturation (aging), and (4) drying [7].

In general, the synthesis of SiO$_2$ by sol-gel method is by using a precursor containing alkoxy ligands, such as TEOS (Triethyl orthosilicate) and TMOS (Tetraethoxysilane) [14]. On the use of precursors containing ligand alkoxy, in the hydrolysis reaction happen of replacement ligand alkoxy (-OR) with a hydroxyl group (-OH). Whereas, at this stage of the hydroxy groups condensation will react with ligands alkoxy and the hydroxyl group to another, forming Si-O-Si as shown in Equations of reaction 1,2 and 3 [13].

\[
\begin{align*}
Si - OR + H_2O & \rightarrow Si - OH + ROH \quad \text{Hydrolysis} \\
Si - OH + Si + OR & \rightarrow Si - O - Si + ROH \quad \text{(2)} \\
Si - OH + Si - OH & \rightarrow Si - O - Si + H_2O \quad \text{Condensation} \quad \text{(3)}
\end{align*}
\]

In the process of maturation, the gel network formation is more rigid and stronger; while in the drying process the evaporation of unwanted fluid occurs to obtain SiO$_2$ having a high surface area. Alkoxide precursor materials are relatively expensive and dangerous. This material can be replaced by other cheaper precursor and soluble in water such as Na$_2$SiO$_3$ (sodium silicate or water glass). In the process of hydrolysis, the sodium silicate reacts with water to produce silicic acid (see Equation of reaction of reaction of reaction 4) and then this acid polymerizes to form silica gel as shown in Equation of reaction of reaction of reaction 5 [7].

\[
Na_2SiO_3 + H_2O + HCl \rightarrow Si (OH)_4 + 2NaCl \quad \text{(4)}
\]
In this study, the synthesis of SiO$_2$ by sol-gel method using sodium silicate as a precursor and H$_2$SO$_4$ as a catalyst according to following reaction was conducted (Equation of reaction 6) [11].

$$n\text{Si(OH)}_4 + (\text{OH})_4\text{Si} \rightarrow n\text{OH} - \text{Si} - \text{O} - \text{OH} + 2n\text{H}_2\text{O}$$

(5)

The purpose of this study is to obtain an amorphous SiO$_2$ powder which is in nano-sized, has a high surface area, and is ready to be composited with Fe to form Fe-SiO$_2$ microwave absorber. To achieve these objectives, in this experiment was carried out the variation of sintering temperature was carried out, which has not been done in the previous studies. The interest in sintering temperature variations is to determine the effect of heating to the physical structure of SiO$_2$ that occurs, such as surface area and particle size.

2. Experimental Method

2.1 Materials and equipment

The chemicals used were sodium silicate (Na$_2$SiO$_3$ from Sigma-Aldrich), H$_2$SO$_4$ (Merck), NaCl (Merck), BaCl$_2$ (Sigma-Aldrich), demineralized water. All materials were used in the pure analysis grade.

For the characterization we used X-ray diffractometer (XRD) to determine the structure, FTIR (Fourier Transformation Infra Red) to determine the functional bonds, scanning electron microscopy - energy dispersive spectrometer (SEM-EDS) to analyze microstructural and determine the chemical composition of the microstructural features that are formed, transmission electron microscopy (TEM) to determine the morphology and particle size, and surface area analyzer (SAA) to determine of surface area of the particles.

2.2 Preparation of Silica oxide from Sodium silicate

250 mL of sodium silicate solution (Na$_2$SiO$_3$) 25% was heated while stirring with a magnetic stirrer until the temperature of 80-90 °C, then a solution of 10% H$_2$SO$_4$ was added dropwise by using a peristaltic pump until a pH of 9.5 - 10. After that, the solution was cooled to room temperature and neutralized with H$_2$SO$_4$ 10% followed by stirring for 30 minutes [8]. If the reaction has been completed, a solution of NaCl was added as much as 1-5 g/L and stirred for 30 minutes to bind the sulfate ions. After that, the precipitates formed were washed with water until free from SO$_4^{2-}$ ion. SO$_4$
ion test was done by adding BaCl₂ into the washing water. When white precipitate (BaSO₄) raised, there was still SO₄²⁻ ion. Furthermore, SiO₂ formed was dried in an oven with different heating temperature of 100, 600, and 700 °C for 6 hours, and then the SiO₂ product was ready to be characterized.

3. Results and Discussion

3.1 X-ray diffraction

X-Ray diffractometer (XRD) analysis was carried out in the 2θ range of 10°-70° by using PANanalytical diffractometer employing CuKα radiation (0.154060 nm) source operated at 40 kV and 40 mA. The result of X-Ray diffraction pattern of SiO₂ is shown in Figure 1.

Figure 1 shows the XRD pattern of SiO₂ synthesized by sol-gel method at 100 °C sintering temperature. This pattern is the same with the XRD pattern of SiO₂ produced by Asmaa Mourhly, et al. where the hump was widened and a strong peak at Bragg angle 22°-23°. This result indicated that SiO₂ product is an amorphous phase. The diffraction pattern in Figure 1 showed only one peak which possibly indicated that SiO₂ product has a high degree of purity.

3.2 Fourier transform infrared spectroscopy

Observation of Fourier transforms infrared spectroscopy (FTIR) study was carried out by using Brucker, Germany with KBr as a reference in the wave number range of 500 – 4000 cm⁻¹. This observation needs to be done for determining the type bonding of compound formed. Spectrogram of SiO₂ observed by FTIR is shown in Figure 2.

![Figure 1. XRD patterns of SiO₂ synthesized by sol-gel method at 100 °C sintering temperature.](image-url)
In Figure 2, the three IR spectra were found, i.e. spectrum at a wavenumber of 484.4577 cm\(^{-1}\) which is bending vibrations of O-Si-O; IR spectrum at 800 cm\(^{-1}\) which is symmetric stretching vibration of Si-O-Si and IR spectrum 1111 which is the asymmetric stretching vibration of Si-O-Si. If these spectra are compared to experiment of Music et al. [8] on the synthesis of SiO\(_2\) by by using precipitation method, there are some differences. The SiO\(_2\) results of the experiment conducted by Music showed the presence of stretching vibration of H\(_2\)O molecules in the IR band ± 3485 cm\(^{-1}\) and vibrational bending H\(_2\)O molecules in the IR band ± 1632 cm\(^{-1}\). Meanwhile, in this experiment, they were not found. This phenomenon shows that the sol-gel method is better to be used for synthesizing SiO\(_2\) because the water content is lower, so it is more stable.

**Figure 2.** Infra Red Spectrum of SiO\(_2\) by sol-gel method by using Na\(_2\)SiO\(_3\) precursor.

**Figure 3.** SEM image of SiO\(_2\) synthesized by sol-gel method.
Figure 4. EDS spectrum and chemical composition ( % atom) of SiO$_2$ synthesized by sol-gel method.

| Element | Atom % |
|---------|--------|
| C       | 12.17  |
| O       | 39.62  |
| Na      | 2.86   |
| Si      | 25.00  |
| S       | 0.34   |

Figure 5. TEM image of (a) SiO$_2$ synthesized by sol-gel method and (b) SO$_2$ commercial product

3.3 Scanning electron microscopy - energy dispersive spectrometer (SEM-EDS)

Scanning electron microscopy - energy dispersive spectrometer (SEM-EDS) used in this experiment was JEOL from Japan. The SEM-EDS was used for observation of microstructural and analysis of chemical composition of ions formed. Figure 3 shows the microstructural of SiO$_2$ observed by SEM and analysis result of the chemical composition of SiO$_2$ by using EDS presented in Figure 4. Amorphous SiO$_2$ from irregular shape and aggregate of SiO$_2$ particle is detected in Figure 3.

Figure 4 shows the presence of Si atoms with relatively high counts ± 6200 at 1.6 keV and O ions at an energy value of 0.525 keV with counts of ± 2850. It shows that Si and O atoms exist. Besides Si (25%) and O (59.62%) atoms, the presence of Na, S and C atoms are also shown although they are very small. Na atom was derived from reactants of Na$_2$SiO$_3$ with a value of 2.86%; S atom came from H$_2$SO$_4$ used to neutralize the silicate of 0.34%, and the C atom came from the tape used for preparation sample on measurement by SEM-EDS with a value of 12.17%. The existence of Na and S ions on SiO$_2$ was possible because the washing process was less than perfect.
3.4 Transmission electron microscope (TEM)
The electron microscopy (TEM) instrument used in this experiment was JEOL from Japan. TEM was used to analyze the microstructural, and determine the size particle of SiO₂ formed. The observation results of microstructural and size particle of SiO₂ by TEM are presented in Figure 5.

Figure 5(a) shows the image of SiO₂ structure synthesized by sol-gel method with precursor of Na₂SiO₃, H₂SO₄ catalyst, and sintering temperature of 100 °C. Meanwhile, Figure 5(b) is TEM image of commercial SiO₂ from Nano Nanjing High Technology Co. Ltd. product. Both Figures have the similarities, namely the shape and size of the particles, the shape is amorphous, and particle size is about 20 nm. These result proved that the SiO₂ product of this experiment was good because the products have the same shape and size with the commercial SiO₂.

3.5 Surface Area Analyzer (SAA)
Determination of surface area of SO₂ product was carried out by using Surface area analyzer (SAA). From the observation, the surface area of SiO₂ was 298.3 m²/g. These results were lower than the surface area of SiO₂ generated from Pumice Rock by Asmaa Mourhly et al. which reached 422 m²/g [15]. This difference is possibly due to the differences in the raw materials used. Pumice Rock was used as raw materials in the formation of SiO₂ having high porosity values so that the resulted SiO₂ was higher as well.

3.6 The Effect of sintering temperature on the characteristic of SiO₂ synthesized
The sintering temperature is one of the factors that affect the properties of the resulting SiO₂ characteristics, especially the surface area and particle size. The Changes of surface area can be observed by using SAA. Table 1 shows the surface area value of SiO₂ product observed by using SAA with the variations of sintering temperature.

Table 1. Surface area of SiO₂ on different sintering temperatures

| Sintering temperature [°C] | Surface area of SiO₂ [m²/g] |
|---------------------------|----------------------------|
| 100                       | 298.31                     |
| 600                       | 236.99                     |
| 700                       | 85.60                      |

Figure 6. XRD patterns of SiO₂ synthesized at different sintering temperatures.
5. Equation of reaction No reaction 1 shows the relationship between the crystal diameter (D) with FWHM, where D is inversely proportional to the FWHM. The smaller the FWHM, the crystal diameter (D) particles formed increase. Table 2 shows the size crystalline of SiO\(_2\) on the different sintering temperatures.

\[
D = \frac{0.89\lambda}{B \cos \theta}
\]

Figure 6 shows that the sintering temperature affects the shape of the SiO\(_2\) peaks. The shape peak of SiO\(_2\) was initially widened. The peak became more cone as the increase of the sintering temperature. The change in peak form will affect the size of SiO\(_2\) particles produced, where the peak is getting cone, size particle increasing, this can be proved by using Debye-Scherrer Equation 7 [17].

| Compound | Temperature of calcination (°C) |  \(B\) observed (FWHM) |  \(B\) standard (FWHM) | Crystallite Size (nm) |
|----------|-------------------------------|-------------------------|------------------------|-----------------------|
| SiO\(_2\) | 100                           | 4.9108                  | 0.0923                 | 16.19                 |
| SiO\(_2\) | 600                           | 4.0216                  | 0.0923                 | 20.23                 |
| SiO\(_2\) | 700                           | 0.5777                  | 0.0923                 | 167.16                |

4. Conclusion

The potential of microwave absorber of SiO\(_2\) amorphous materials with nanoscale was successfully synthesized by Sol-gel method using a precursor of Na\(_2\)SiO\(_3\) and catalyst of H\(_2\)SO\(_4\) at a sintering temperature of ≤ 600 °C. It was obtained that the size of the particle was around 20 nm. Meanwhile, the surface area was 298.31 m\(^2\)/g. Spectroscopic studies showed that functional bond of O-Si-O exists at wavenumbers of 484.4577 cm\(^{-1}\), Si-O-Si at 800 cm\(^{-1}\), and 1111 cm\(^{-1}\) which indicated the existing of SiO\(_2\). The vibrations bending and stretching of H\(_2\)O from observation by FTIR were not visible. It means that the synthesis of SiO\(_2\) by using sol-gel method at a sintering temperature ≤ 600 °C produced SiO\(_2\) with low water contents, so it was more stable as compared with the previous research.

5. References

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Acknowledgements
The authors would like to thank all those who have helped the experiment. This research was funded from DIPA funds in 2014 and 2015 with the title of The Optimization of waste treatment with photocatalytic method and advanced smart magnetic materials and magnetic oxide, Center for Science and Technolgy of Advance Materials, National Nuclear Energy Agency.