IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Synthesis and Characterization of Microwave Absorber SiO_2 by Sol-Gel Methode

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2017 IOP Conf. Ser.: Mater. Sci. Eng. 202 012059

(http://iopscience.iop.org/1757-899X/202/1/012059)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 223.25.97.66
This content was downloaded on 02/06/2017 at 08:50

Please note that terms and conditions apply.

You may also be interested in:

Microwave Dielectric Properties of Lossy Dielectric Composite Materials
Young Joon An, Hirotake Okino, Takashi Yamamoto et al.

Metallugical Analysis of Mix-Phase Y-Ba-Cu Oxides
Kazumasa Takagi, Katsuki Miyauchi, Yukio Ito et al.

Nanoneedles of Lanthanum Oxide (La2O3): A Novel Functional Material for Microwave Absorber Material
W A Adi, S Wardiyati and S H Dewi

Dielectric properties of rubber ferrite composites containing mixed ferrites
M R Anantharaman, S Sindhu, S Jagatheesan et al.

IOP Conf. Series: Materials Science and Engineering **202** (2017) 012059 doi:10.1088/1757-899X/202/1/012059

Synthesis and Characterization of Microwave Absorber SiO_2 by Sol-Gel Methode

S Wardiyati, W A Adi and Deswita

Center for Science and Technolgy 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 material with other materials such as SiO_2 is needed to overcome these problems. For such needs, it is necessary to study the manufacture of SiO_2 which is simple, cheap, and effective. In this research, manufacture of SiO_2 by sol-gel method used a solution of sodium silicate (Na_2SiO_3) as precursors and H_2SO_4 as a catalyst. The parameters tested in this experiment is the effect of sintering temperature on the properties of the resulting SiO_2. The purpose of this study was to obtain an amorphous SiO_2 powder, which is in nano-sized 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 SiO_2 amorphous structure was obtained with a particle size of 15-20 nm, the surface area of 298 m^2/g, and sintering temperature of 100 °C.

Keywords: Microwave absorber, nanomaterial, SiO_2, 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 (SiO_2) and iron (Fe). The use of silica because silica has

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

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 hydroxyl 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].

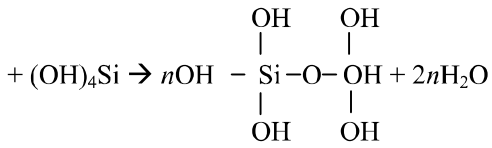
$$\equiv Si-OR + H_2O \rightarrow \equiv Si-OH + ROH \qquad \text{Hydrolisis} \qquad (1)$$

$$\equiv Si-OH + \equiv Si + OR \rightarrow \equiv Si-O-Si \equiv + ROH \qquad (2)$$

$$\equiv Si-OH + \equiv Si-OH \rightarrow \equiv Si-O-Si \equiv + H_2O \qquad \text{Condensation} \qquad (3)$$

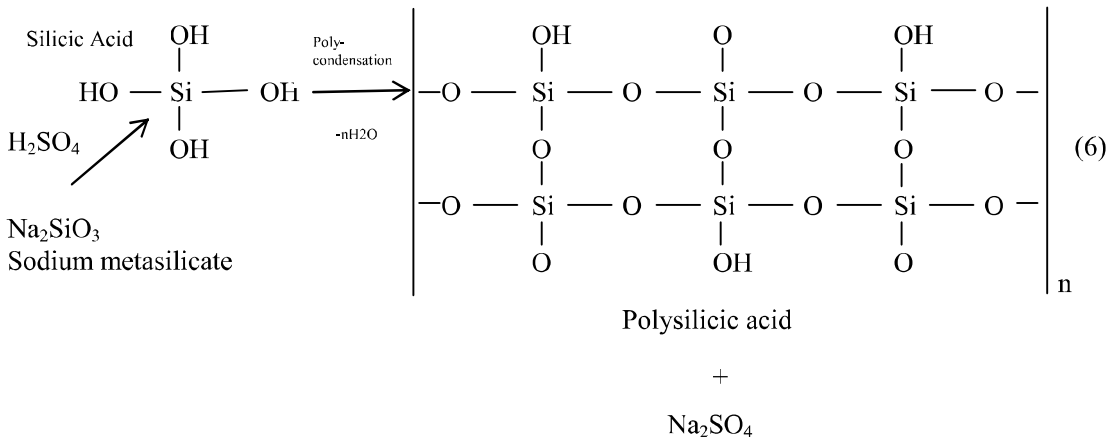
In the process of maturation, the gel network formation is more rigid and stronger; while in the drying process the evaporation of unwanted fluid occurs to obtain SiO_2 having a high surface area. Alkoxide precursor materials are relatively expensive and dangerous. This material can be replaced by other cheaper precursor and soluble in water such as Na_2SiO_3 (sodium silicate or water glass). In the process of hydrolysis, the sodium silicate reacts with water to produce silicic acid (see Equation of reactionof reactionof reaction 4) and then this acid polymerizes to form silica gel as shown in Equation of reactionof reaction of reaction 5 [7].

$$Na_2SiO_3 + H_2O + HCl \rightarrow Si(OH)_4 + 2NaCl \qquad (4)$$



$$n\mathrm{Si(OH)_4} + \mathrm{(OH)_4Si} \rightarrow n\mathrm{OH} - \mathrm{Si(OH)_2O\text{-}Si(OH)_2} - \mathrm{OH} + 2n\mathrm{H_2O} \quad (5)$$

In this study, the synthesis of SiO_2 by sol-gel method using sodium silicate as a precursor and H_2SO_4 as a catalyst according to following reaction was conducted (Equation of reaction 6) [11].



(6)

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_2SiO_3 from Sigma-Aldrich), H_2SO_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_2SiO_3) 25% was heated while stirring with a magnetic stirrer until the temperature of 80-90 °C, then a solution of 10% H_2SO_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_2SO_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 $BaCl_2$ into the washing water. When white precipitate ($BaSO_4$) raised, there was still SO_4^{-2} ion. Furthermore, SiO_2 formed was dried in an oven with different heating temperature of 100, 600, and 700 ^oC for 6 hours, and then the SiO_2 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 SiO_2 is shown in Figure 1.

Figure 1 shows the XRD pattern of SiO_2 synthesized by sol-gel method at 100 °C sintering temperature. This pattern is the same with the XRD pattern of SiO_2 produced by Asmaa Mourhly, et al. where the hump was widened and a strong peak at Bragg angle 22°-23°. This result indicated that SiO_2 product is an amorphous phase. The diffraction pattern in Figure 1 showed only one peak which possibly indicated that SiO_2 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 SiO_2 observed by FTIR is shown in Figure 2.

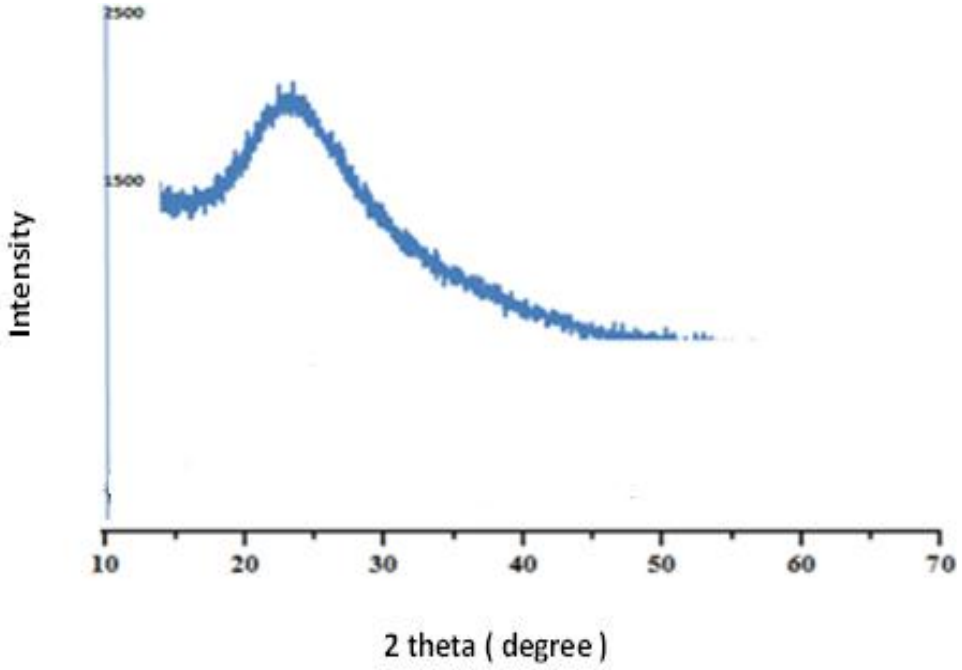


Figure 1. XRD patterns of SiO_2 synthesized by sol-gel method at 100 °C sintering temperature.

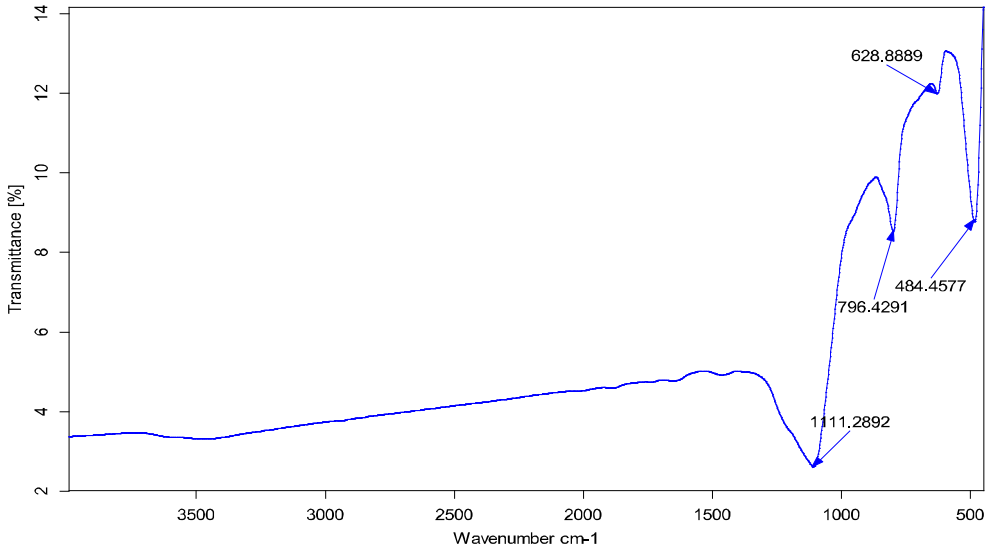


Figure 2. Infra Red Spectrum of SiO_2 by sol-gel method by using Na_2SiO_3 precursor.

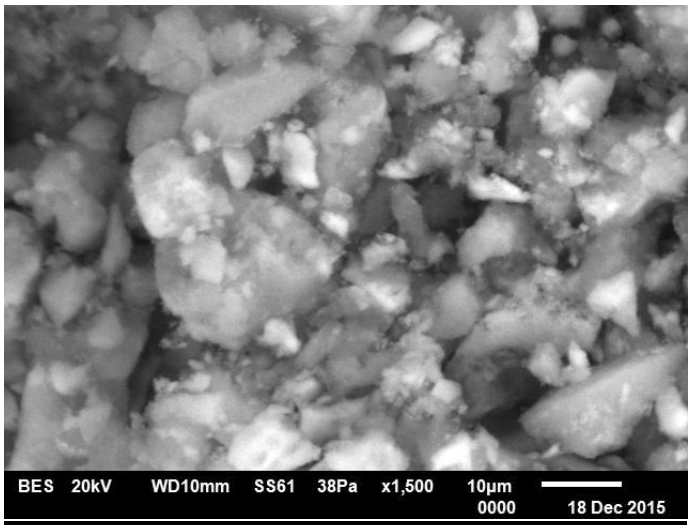


Figure 3. SEM image of SiO_2 synthesized by sol-gel method.

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 spectrums 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_2O molecules in the IR band ± 3485 cm^{-1} and vibrational bending H_2O 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.

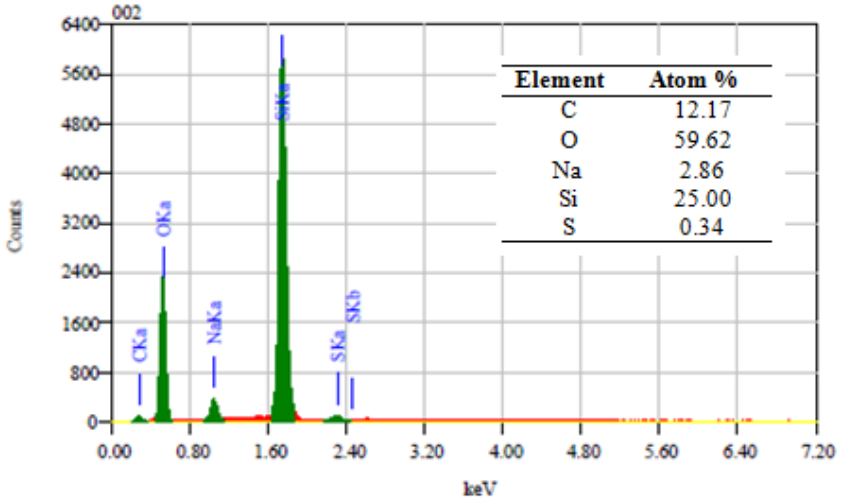


Figure 4. EDS spectrum and chemical composition (% atom) of SiO_2 synthesized by sol-gel method.

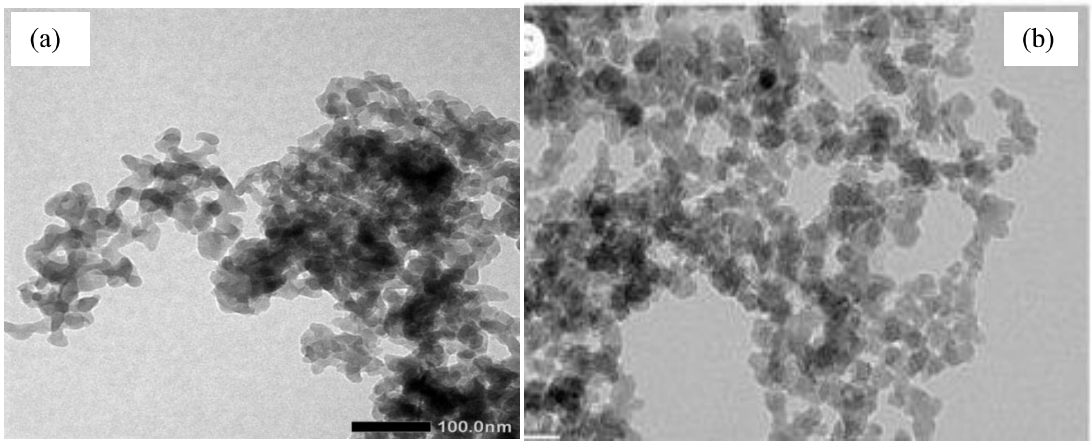


Figure 5. TEM image of (a) SiO_2 synthesized by sol-gel method and (b) SO_2 commercial product

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_2SiO_3 with a value of 2.86%; S atom came from H_2SO_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 SiO_2 formed. The observation results of microstructural and size particle of SiO_2 by TEM are presented in Figure 5.

Figure 5(a) shows the image of SiO_2 structure synthesized by sol-gel method with precursor of Na_2SiO_3, H_2SO_4 catalyst, and sintering temperature of 100 °C. Meanwhile, Figure 5(b) is TEM image of commercial SiO_2 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 SiO_2 product of this experiment was good because the products have the same shape and size with the commercial SiO_2.

3.5 Surface Area Analyzer (SAA)

Determination of surface area of SO_2 product was carried out by using Surface area analyzer (SAA). From the observation, the surface area of SiO_2 was 298.3 m^2/g. These results were lower than the surface area of SiO_2 generated from Pumice Rock by Asmaa Mourhly et al. which reached 422 m^2/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 SiO_2 having high porosity values so that the resulted SiO_2 was higher as well.

3.6 The Effect of sintering temperature on the characteristic of SiO_2 synthesized

The sintering temperature is one of the factors that affects the properties of the resulting SiO_2 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 SiO_2 product observed by using SAA with the variations of sintering temperature.

Table 1. shows that the surface area of the resulting SiO_2 was getting smaller with the increase of the sintering temperature. This phenomenon is similar to the statement Wenbo Liu et.al. [16] stating that the higher the sintering temperature, the possibility of joining crystal lattice with another crystal is getting bigger so that the crystal size becomes large and the surface area decreases. Besides surface area, sintering temperature differences also affect against the diffraction pattern of obtained SiO_2. Effect of sintering temperature SiO_2 at temperatures of 100, 600, and 700 °C are shown in Figure 6.

Table 1. Surface area of SiO2 on different sintering temperatures

Sintering temperature [°C]	Surface area of SiO_2 [m^2/g]
100	298.31
600	236.99
700	85.60

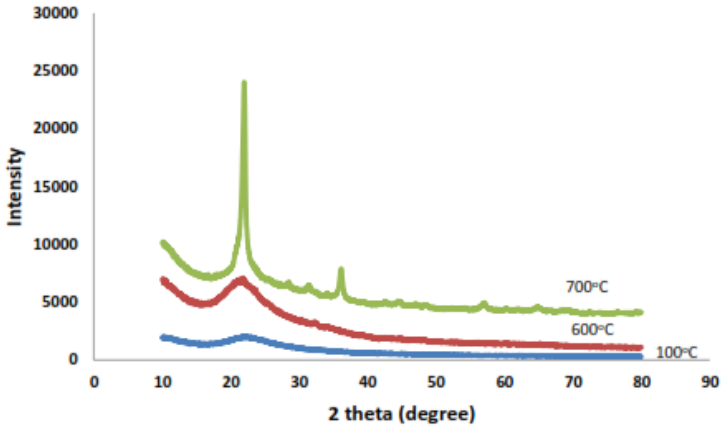


Figure 6. XRD patterns of SiO_2 synthesized at different sintering temperatures.

Table 2. Size crystalline of SiO_2 on different sintering temperatures.

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

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 this will affect the size of SiO_2 particles produced, where the peak is getting cone, size particle increasing, this can be proved by using Debey-Scherrer Equation 7 [17].

$$D = \frac{0.89\lambda}{B\cos\theta} \tag{7}$$

where D is the size of the crystals, a factor of 0.89 is characteristic of round object, λ is the wavelength of X-ray, *B* is the FWHM (full width at half maximum), and θ is the diffraction angles. Equation of reactionof reaction1 shows the relationship between the crystal diameter (*D*) with FWHM, where *D* is inversely proportional to the FWHM. The smaller the FWHM, the diameter (*D*) particles formed increase. Table 2 shows the size crystalline of SiO_2 on the different sintering temperatures.

Based on the results of SiO_2 characterization by using SAA and XRD, we can see that at a high-temperature sintering, the particle size became large and another phase appeared. However, from Tables 1 and 2, we can see that the temperature sintered up to ≤ 600 °C, the particle size was still in the nanoscale, i.e., about 20 nm and a surface area of over 237 m^2/g, this phenomenon indicated that SiO_2 produced was quite stable.

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_2SiO_3 and catalyst of H_2SO_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_2O 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

[1] Chen L *et al.* 2010 Influence of SiO_2 fillers on microwave absorption of carbonyl iron/carbon black double-layer coatings *Material & Design* **08** 021

[2] Jin F *et al.* 2006 Structure and microwave absorbing properties of Fe-particle containing alumina prepared by micro-arc discharge oxidation *Surface & Coating Technology* **201** 292-295

[3] Yang Y 2013 Synthesis and microwave absorbing properties of Fe/SiO_2 particles with core/shell structure

[4] Fujieda F 2002 Microwave absorption properties of Fe-SiO_2 nanocomposite powder *Journal of the Japan Institute of Metals* **66**(3)135-138

[5] Fibroblasts L, Qiang Z X, Hong Y L, Meng T and Pu P Y 2011 ZnO, TiO_2, SiO_2, and Al_2O_3 nanoparticles-induced toxic effects on human fetal *Biomed Environ Sci* **24**(6) 661-669

[6] Xi-gui W, Xia Q I, Su-ling B O, Mi-la N A 2011 Preparation and luminescence properties of nanomaterials TiO_2-SiO_2 doped with eu^{3+}, spectroscopy and spectral analysis **31**(5) 1193-96

[7] Yamahata C et al. 2012 Influence of the precursor concentration on the characteristics of silica powder obtained from Na_2SiO_3 by a facile low-temperature synthesis process *Journal of Materials Science and Engineering B* **2**(8) 429-436
[8] Musić S, Filipović-Vinceković N and Sekovanić L 2011 Precipitation of amorphous SiO_2 particles and their properties *Brazilian Journal of Chemical Engineering* **28**(01) 89 - 94
[9] Mohanraj K et al. 2012 Preparation and characterization of nano SiO_2 from corn cob ash by precipitation method *Optoelectronics and Advanced Materials-Rapid Communications* **6**(3-4) 394-397
[10] Cui J, Sun H, Luo Z, Sun J and Wen Z 2015 Preparation of low surface area SiO_2 microsphere from wheat husk ash with a facile precipitation process *Materials Today Proceedings* **2**(4–5) 3575–3579
[11] Essien E R, Olaniyi O A, Adams L A and Shaibu R O 2012 Sol-gel-derived porous silica: economic synthesis and characterization *Journal of Minerals and Materials Characterization and Engineering*c **11** 976-981
[12] Dubey R S, Rajesh Y B R D and More M A 2015 Synthesis and characterization of SiO_2 nanoparticles via sol-gel method for industrial applications *Materials Today Proceedings* **2** 3575-79
[13] Rahman I A and Padavettan V 2012 Synthesis of silica nanoparticles by sol-gel: size-dependent properties, surface modification, and application in silica-polymer nanocomposites-a review *Journal of Nanomaterial* **2012** article ID 132424
[14] Zhang H, Hong C and Qiao Y 2011 Synthesis, structural and thermal properties of nano-porous SiO_2-based aerogel, advances in nanocomposites-synthesis, characterization and industrial aplications, Dr. Boreddy Reddy (ed), ISBN: 978-953-307-165-7
[15] Mourhly A, Khachani M, El Hamidi A, Kacimi M, Halim M and Arsalane S 2015 The synthesis and characterization of low-cost mesoporous silica SiO_2 from Local Pumice Rock *Nanotechnology and Nanomaterial* ISSN 1847-9804
[16] Liu W, JiY, Tan P, Zang H, He C, Yun D, Zhang C and Yang Z 2016 Irradiation induced microstructure evolution *Nanostructured Materials* **9** 105
[17] Monshi A, Foroughi M R and Monsh M R 2012 Modified Scherrer Equation of reactionof reactionto estimate more accurately nano-crystallite size using XRD *World Journal of Nano Science and Engineering* **2** 154-160

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.