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Preparation of a magnetic aerogel from ferrite-silica nanocomposite

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Abstract : A new kind of magnetic aerogel was prepared from a mixture of ferrite nanoparticles and silica aerogel. The ferrite ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) nanoparticles were prepared by a coprecipitation method and added to tetramethylorthosilicate (TMOS)/ethanol solution in the range of 0 to 20mol%. The mixed ferrite-silica wet gel was dried in the supercritical carbon dioxide fluid. The obtained ferrite-silica aerogel nanocomposite was a ultra-superlight and high-porous material, where the magnetic property of ferrite was held in the aerogel.

Keywords : Sol-gel; Ferrite; Silica aerogel; Nanocomposite; Magnetic property; Supercritical drying.

INTRODUCTION

Aerogel is a porous material derived from a gel, in which the liquid component of the gel has been replaced with a gas. The main properties of aerogel are an extremely low density (<200mg/cm^3), a high porosity (>90%), a high specific surface area (150-1000m^2/g) and a low thermal conductivity (<0.02W/m · K)[1,2]. Thus, aerogel is practically used as carrier and a catalyst[3]. In addition, it is known unique properties such as transparency and a low refractive index, from the characteristic of the structure. By utilizing these properties, some applications such as a transparent low refractive-index material for Cerenkov detectors, a transparent low density material for collecting cosmic dust etc. has been also put into practical use[4].

Usually, an aerogel is prepared by a supercritical drying using carbon dioxide in wet gel obtained by a hydrolysis of metal alkoxide and by a condensation polymerization. As typical aerogels, silica aerogel, alumina aerogel and carbon aerogel are well-known. In addition, some aerogels with functional particles have been studied. For example, an aerogel composed of titania and silica[5] or the composite of metallic nickel and alumina aerogel[6] exhibited superior catalytic performance. However, any functional aerogels consisting

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of a magnetic and dielectric materials have not been prepared due to uncontrollable gelation and lack of variety of their metal alkoxides and their expensive cost etc. We have already reported on the preparation of a ferrite-silica aerogel nanocomposite from a mixture of silica sol and ferrite ($Ni_{0.1}Zn_{0.9}Fe_2O_4$) nanoparticles by a supercritical drying process[7]. In this paper, more magnetic aerogel was prepared by using $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles, and evaluated on a optical and magnetic properties etc.

EXPERIMENTAL PROCEDURE

Preparation of ferrite-silica aerogel nanocomposite

The preparation process was almost the same as the previous report[7] where the report by Tajiri and Tsuchiya et al. was referred[2,8]. Used reagents were as follows : tetramethylorthosilicate (TMOS, Tokyo Chem. Ind. Co., Ltd.); 1,1,1,3,3,3-hexamethyldisilazane (Tokyo Chem. Ind. Co., Ltd.); NH_3 aq. (28mass% aqueous solution, Wako Pure Chem. Ind. Ltd.) and ethanol (Wako Pure Chem. Ind. Ltd.).

Ferrite nanoparticles were prepared by a coprecipitation method[9]. Raw materials of $FeCl_3 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $ZnCl_2$ (Wako Pure Chem. Ind., Ltd.) were weighed to be x=0.5 in $Ni_xZn_{1-x}Fe_2O_4$ and dissolved by adding distilled water. The solution was adjusted to pH13 by adding NaOH, and then refluxed for 24h at 110°C. After cooling, excess NaOH was removed from the precipitation by washing repeatedly with distilled water and ethanol, resulting in ferrite nanoparticles. Synthesized ferrite nanoparticles were identified as $(Ni,Zn)Fe_2O_4$ by the powder X-ray diffraction measurement. And the average particle diameter (d_{50}) of ferrite nanoparticles was 76nm, and d_{90} was 156nm. The obtained ferrite nanoparticles were used as ethanol suspension of about 0.09g/mL without drying.

The ferrite nanoparticles suspension was added to TMOS/ethanol solution, which was set the ratio of TMOS to ethanol to 1:11, in the range of 0 to 20mol%, mixed for 10min on a magnetic stirrer, and further homogenized for 5min by ultrasonic wave. Then, deionized water and ammonia as a catalyst were added in sequence, and stirred for 5min, respectively. The obtained sol was poured into a resin mold of $\phi 5 \times 5$mm and $\phi 20 \times 3$mm, and it gelled after about 30min. This processing was performed in an ultrasonic wave container in order to avoid a sedimentation of ferrite particles. The obtained wet gel was aged in an ethanol for 2h at 50°C. The ageing treatment was repeated 5times. After that, the wet gel was refluxed for 24h at 110°C in 1.3mol/L hexamethyldisilazane/toluene solution for a hydrophobic treatment. The toluene inside the wet gel was again replaced by an ethanol after cooling. Then, the wet gel was treated by the supercritical drying using carbon dioxide, resulting in ferrite-silica aerogel nanocomposites.

Evaluation of ferrite-silica aerogel nanocomposite

The bulk density and the porosity were calculated from the measurement of size and weight of aerogel. The specific surface area was measured by BET method. The pore size distribution was measured by BJH method using a volumetric nitrogen gas adsorption (Bell Japan, Inc., BELSORP-max) for a mesopore region, and by mercury intrusion porosimeter (Thermo Fisher Scientific Inc., PASCAL140/240) for a macropore region. The optical transmittance was measured by an ultraviolet visible light near-infrared spectrophotometer (UV-Vis-NIR, Hitachi High-Technologies Corp., U-4100). The microstructure was observed by a field emission scanning electron microscope (FE-SEM, JEOL Ltd., JSM-7000F). The composition was analyzed by an energy dispersive X-ray spectrometry (EDS, JEOL Ltd., JED-2300F). The magnetization measurement was performed by a vibrating sample magnetometer (VSM, Toei Ind. Co., Ltd.,VSM-5). The permeability measurement was performed in the range of 10MHz to 1GHz by a RF impedance/material analyzer (Agilent Technologies Ltd., E4991A).

RESULTS AND DISCUSSION

Characterization of ferrite-silica aerogel nanocomposite

Figure 1 shows the bulk density and the porosity of the ferrite- silica aerogel nanocomposites. Since the density of ferrite was larger than that of silica, the bulk density was increased with increasing in the content of ferrite, that is 156mg/cm^3 for 20mol% ferrite-silica aero-

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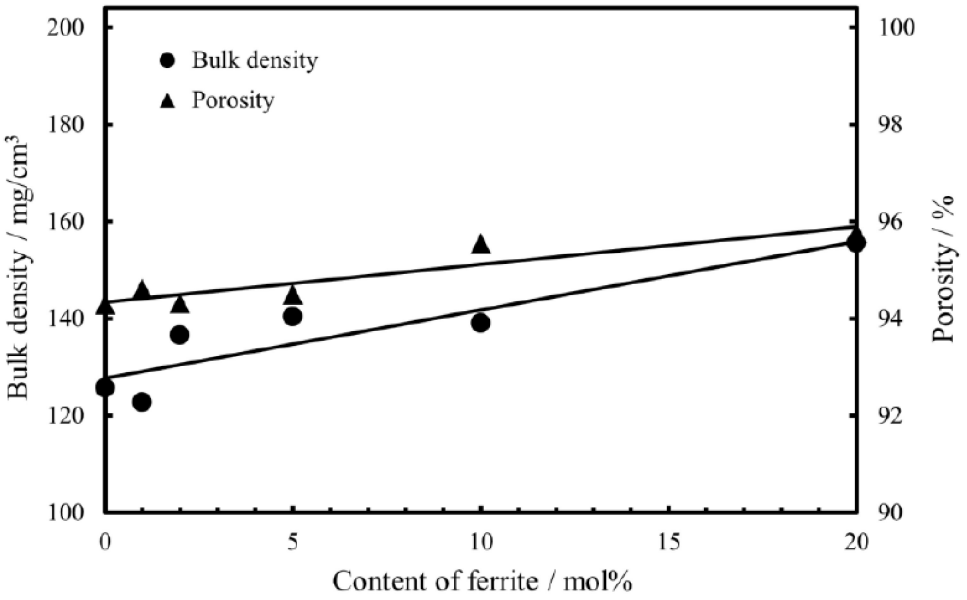

Figure 1 : Bulk density and porosity of ferrite-silica aerogel nanocomposites.

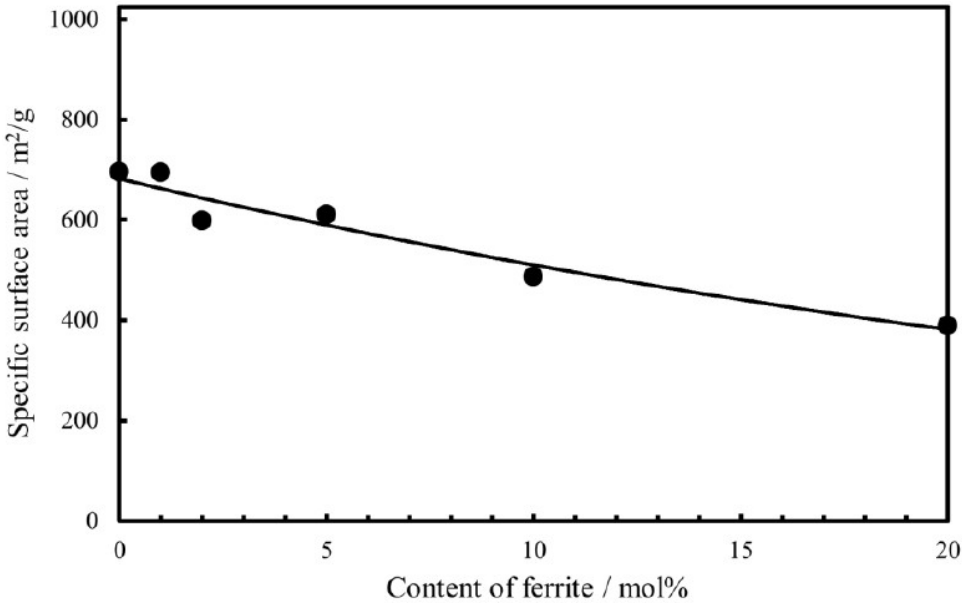

Figure 2 : Specific surface area of ferrite-silica aerogel nanocomposite.

gel nanocomposite. Although the porosity also increased slightly, it was almost around 95%.

Figure 2 shows the specific surface area of the ferrite-silica aerogel nanocomposites. The specific surface area was about 700m^2/g for the silica aerogel. On the other hand, it decreased with increasing in content of ferrite and became to about 400m^2/g for 20mol% ferrite-silica aerogel nanocomposite.

In regard to the pore size distribution, the median size of macropore were around 2μm for all of the ferrite-silica aerogel nanocomposites as shown in Figure 3. The median size of mesopore was 14nm for silica aerogel and shifted to approximately 20nm with increasing in the content of ferrite as shown in Figure 4. Therefore, it was estimated that the porosity was fixed mainly on account of macropores, while the specific surface area was affected mainly by mesopores. Anyway, it was found that the ferrite-silica aerogel nanocomposites held characteristics of aerogel.

Figure 5 shows SEM images of the silica aerogel and 2mol% ferrite-silica aerogel nanocomposite. Both the silica aerogel and the nanocomposite consisted of particles of approximately 50nm, which three-dimensionally connected together to form a skeletal network

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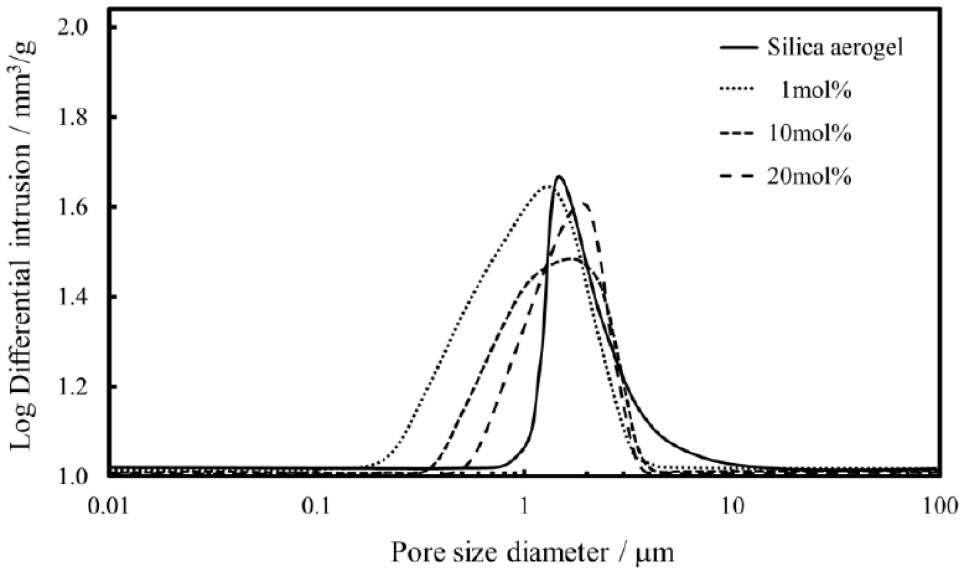

Figure 3 : Pore size distribution of ferrite-silica aerogel nanocomposites in the macropore region.

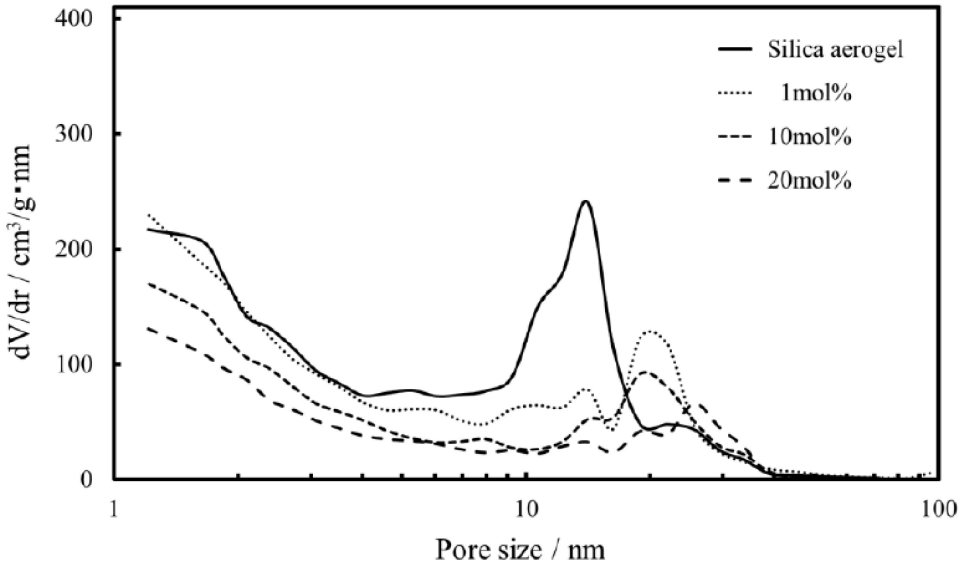

Figure 4 : Pore size distribution of ferrite-silica aerogel nanocomposites in the mesopore region.

structure. It looked just as if chains of particles surrounded the bubbles of air. Then, the size of bubble, that is a macropore, was measured by using the intercept method[10]. As a result, the pore size was estimated to be from 1 to 2μm. This size almost accorded with around 2μm of the pore size shown in Figure 3. In addition, the ferrite particles could not detect by EDS analysis as shown in Figures 5(e) and 5(f). Therefore, it was thought that the ferrite particles existed homogeneously in the nanocomposite in the scale of SEM.

These results were almost identical to the results reported on the $Ni_{0.1}Zn_{0.9}Fe_2O_4$-silica aerogel nanocomposites[7].

Optical property of ferrite-silica aerogel nanocomposite

Figure 6 shows the appearance of silica aerogel and ferrite-silica aerogel nanocomposites. The silica aerogel was transparent, while the ferrite-silica aerogel nanocomposites became opaque with increasing in the content of ferrite.

Figure 7 shows the optical transmittance of ferrite-silica aerogel nanocomposites. Even in the near-infrared region, the silica aerogel showed the very high optical transmittance of 90% or more. However, as approaching the ultraviolet region, the optical transmittance of silica aerogel decreased for Rayleigh scatter-

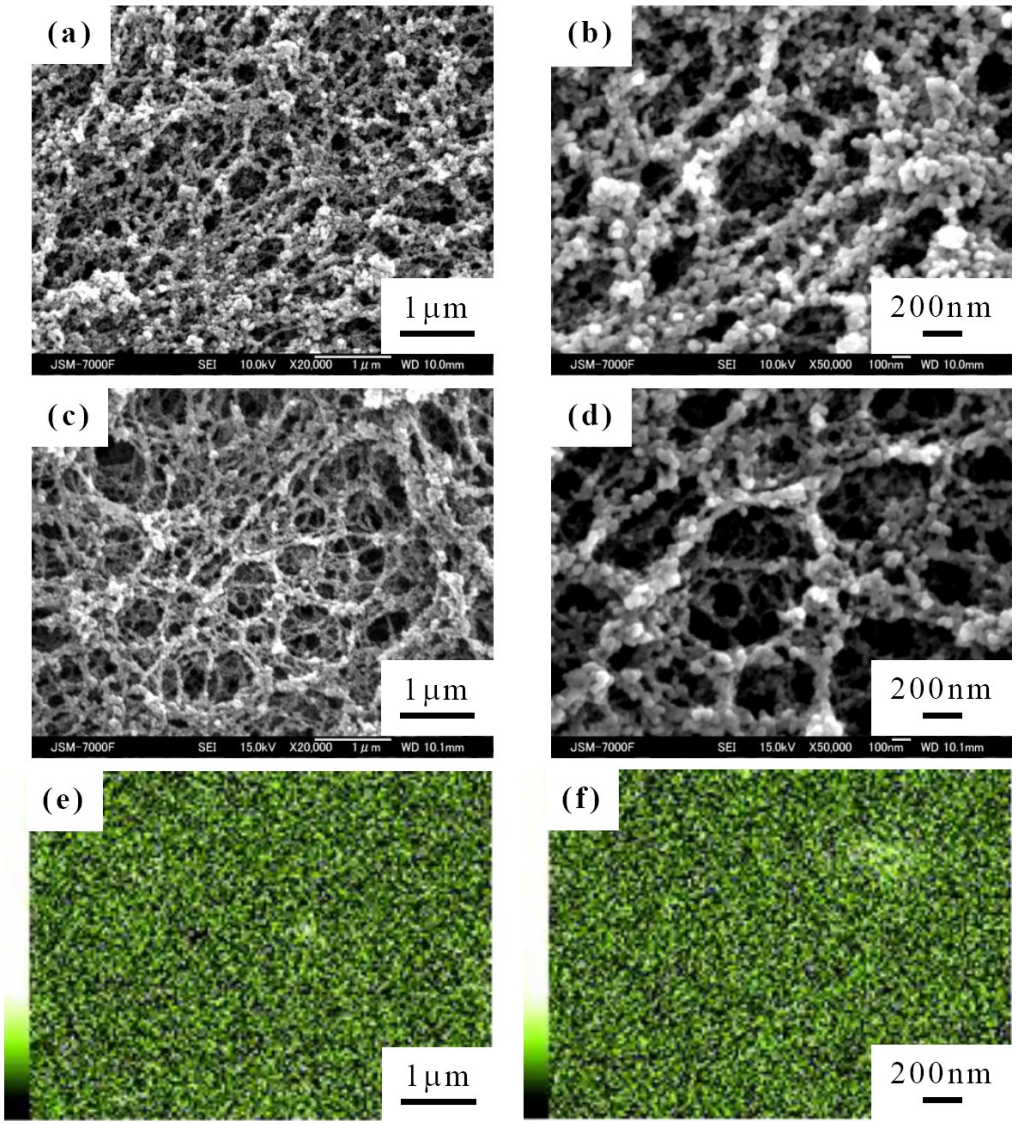

Figure 5 : SEM images of silica aerogel ((a) and (b)) and 2mol% ferrite-silica aerogel nanocomposite ((c) and (d)), and Fe mapping of nanocomposite ((e) and (f)).

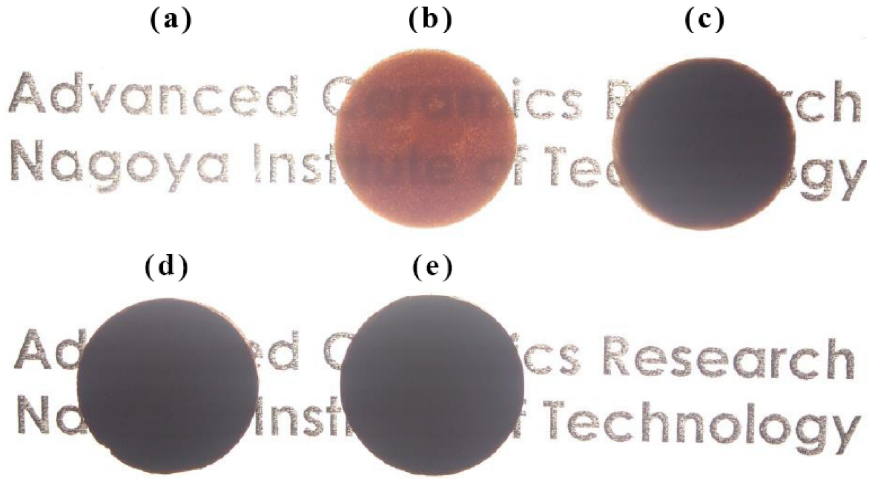

Figure 6 : Appearance of silica aerogel (a) and ferrite-silica aerogel nanocomposites (b):1mol%, (c):2mol%, (d):5mol%, (e):10mol%.

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ing by minute particles[11]. On the other hand, the transmittance of the ferrite-silica aerogel nanocomposite drascally decreased with increasing in content of ferrite to be less than 10% in the entire wavelength for 20mol% ferrite-silica aerogel nanocomposite. However, 1-2mol% ferrite-silica aerogel nanocomposites demonstrated some transmittance in the near-infrared region.

Magnetic property of ferrite-silica aerogel nanocomposite

Figure 8 shows the magnetization curves of the ferrite powder and the ferrite-silica aerogel nanocomposites measured by VSM. As a matter of course, the magnetic susceptibility of the ferrite-silica aerogel nanocomposites increased with increasing in content of ferrite. In addition, the magnetic susceptibility became much larger than that in the case of $Ni_{0.1}Zn_{0.9}Fe_2O_4$[7].

Figure 9 shows the permeability of the ferrite-silica aerogel nanocomposites. Although it was low because the majority of aerogel was air (c.a.95%), it increased with increasing in content of ferrite. In addition, it slightly decreased with increasing in frequency. Anyway, it was considered that the magnetic property of ferrite was

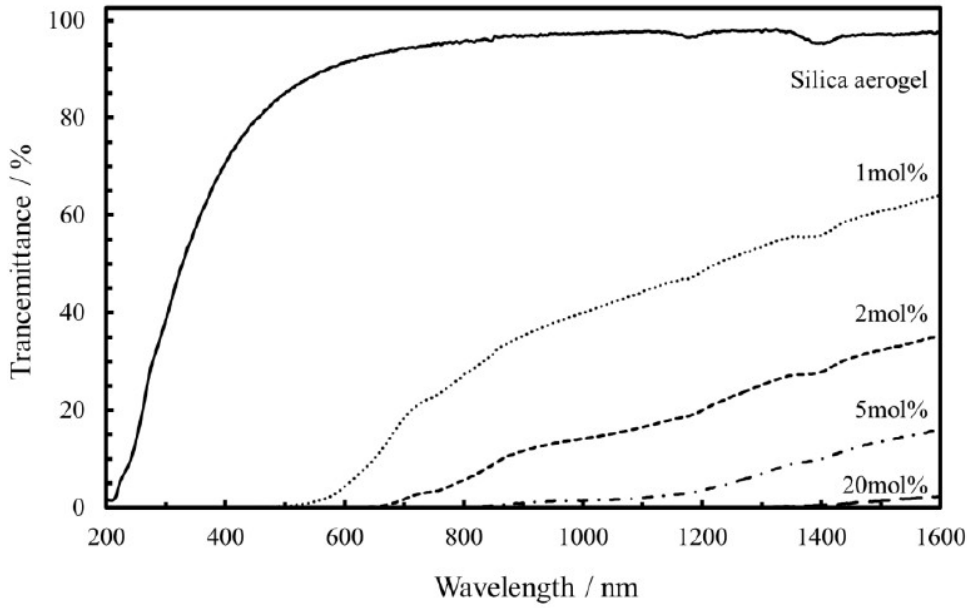

Figure 7 : Optical trancemittance of ferrite-silica aerogel nanocomposites.

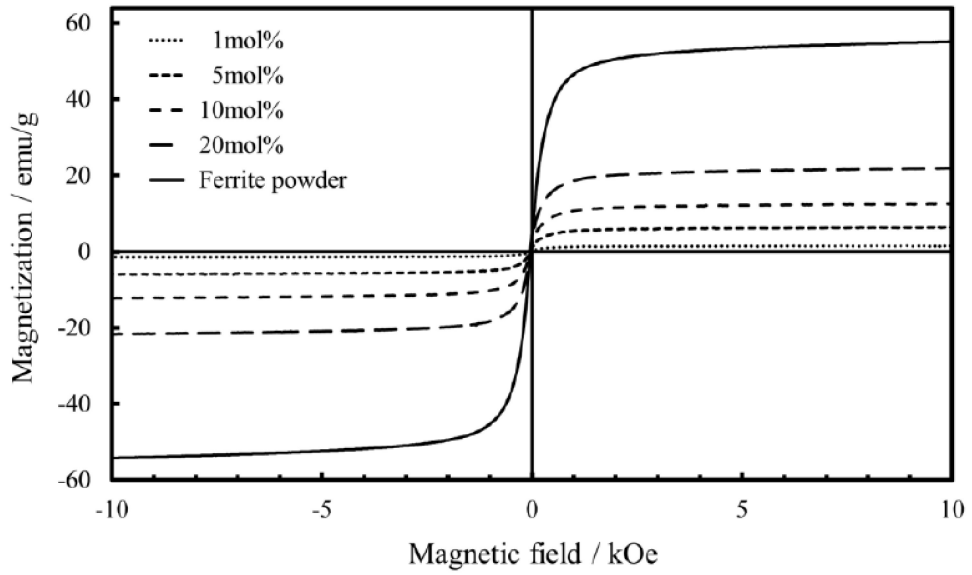

Figure 8 : Magnetization curve of ferrite-silica aerogel nanocomposites and ferrite powder.

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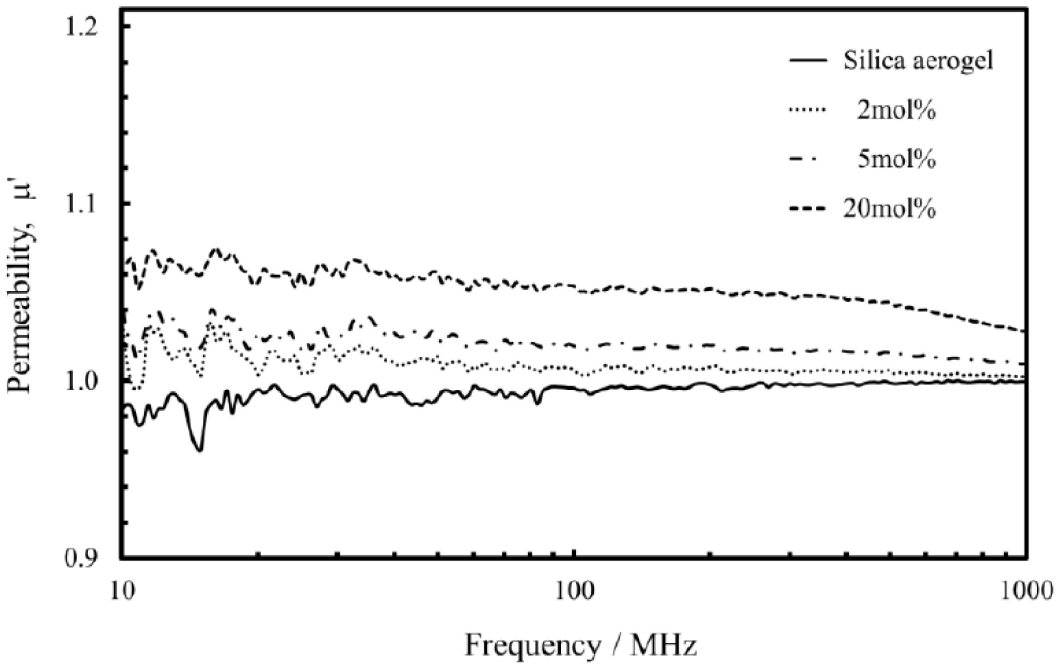

Figure 9 : Permeability of ferrite-silica aerogel nanocomposites.

also entirely held in the ferrite-silica aerogel nanocomposites.

CONCLUSION

An aerogel with a magnetic property was prepared by a supercritical drying process from a mixture of ferrite ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) nanoparticles and silica sol. The obtained ferrite-silica aerogel nanocomposites had three-dimensional skeletal network structure with macropores of about 2μm and mesopores of about 20nm. The porosity was about 95%. The specific surface area changed from 700 to 400m^2/g with increasing in content of ferrite. The characteristics as a so-called aerogel was held in the ferrite-silica aerogel nanocomposites, and moreover a magnetic property of the ferrite remained unchanged in the aerogel nanocomposites. Consequently, it was expected that this ultra-superlight magnetic aerogel could be applied to many kinds of new functional materials such as electromagnetic wave absorber, hyperthermia and drug delivery system etc.

REFERENCES

[1] Aerogel-Wikipedia; http//ja.wikipedia.org/wiki/, accessed 2009-12-18, **(2009)**.
[2] K.Tajiri; Doctor Thesis, Nagoya Institute of Technology, **(2002)**.
[3] C.T.Wang, R.J.Willey; J.Non-Cryst.Solids, **225**, 173-177 **(1998)**.
[4] M.Tabata; Master Thesis, The University of Chiba (2006), http://www.ppl.phys.chiba-u.jp/~makoto/publication/master-thesis_M.Tabata.pdf, accessed 2013-10-7, **(2013)**.
[5] L.Luo, A.T.Cooper, M.Fan; J.Hazard.Mater., **161**, 175-182 **(2009)**.
[6] T.Ozaki, T.Horiuchi, T.Sugiyama, K.Suzuki, T.Mori; National Industrial Research Institute of Nagoya, Japan Patent, P3136336, **(2000)**.
[7] N.Katagiri, N.Adachi, T.Ota; J.Ceram.Soc.Japan, (In press).
[8] T.Tuchiya, K.Nishio; Synthesis of the ceramics by a sol gel process, http://www.hst.titech.ac.jp/~meb/Ceramics/hybrid/hybrid.htm, accessed 2010-9-17, **(2010)**.
[9] Y.Harada; Master Thesis, The University of Mie (2007), http://miuse.mie-u.ac.jp/bitstream/10076/8987/1/2006T038.pdf, accessed 2012-2-14, **(2012)**.
[10] J.C.Wurst, J.A.Nelson; J.Am.Ceram.Soc., Discussions and Notes, **2**, 109 **(1972)**.
[11] S.Sakka et al.; 'New Development of Application in Sol-Gel Processing', CMC Publishing, 110-111 **(2008)**.