Addition of BaTiO$_3$ and carbon nanoparticles to silica aerogel and its dielectric properties

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A tetramethylorthosilicate(TMOS)/ethanol solution was gelled together with BaTiO$_3$ nanoparticles or carbon nanoparticles. The wet gel was dried in supercritical carbon dioxide, resulting in aerogel nanocomposites with compositions in the range of BaTiO$_3$/SiO$_2 = 1/100$ to $20/100$ and $C/SiO_2 = 20/100$ to $80/100$. The bulk density of the aerogel obtained was in the range of 0.1 to 0.2 g/cm$^3$, the porosity was about 95%, and the specific surface area was in the range of 400 to 700 m$^2$/g. These values represent the characteristics of the aerogel. The relative permittivity and dielectric loss were respectively approximately 2 and 5 x $10^{-3}$ for the BaTiO$_3$-silica aerogel nanocomposite, and in the range of 5 to 10 and 0.012 to 0.4 for the carbon-silica aerogel nanocomposite.

Key-words : Dielectric properties, BaTiO$_3$, Carbon, Silica aerogel, Nanocomposite, Sol–gel, Supercritical drying

1. Introduction

An aerogel is a ultra-porous material derived from a gel, in which the liquid component of the gel has been replaced with a gas. The main properties of an aerogel are an extremely low density (<0.2 g/cm$^3$), high porosity (>90%), high specific surface area (150 to 1000 m$^2$/g), and low thermal conductivity (<0.02 W/m·K). Thus, for practical applications, an aerogel can be used as a carrier and a catalyst. In addition, since an aerogel typically shows a low permittivity of about 1.1 to 1.5, approximately equal to that of air, it is also expected to be utilized as a super low permittivity material.

Usually, an aerogel is prepared by supercritical drying after introducing carbon dioxide into a wet gel, which is obtained by hydrolysis of a metal alkoxide and condensation polymerization. Silica aerogel, alumina aerogel and carbon aerogel are well known as typical representative aerogels. Other aerogels composed of functional materials have also been studied. However, there are many problems such as uncontrollable gelation and lack of variety in the metal alkoxides used, as well as high cost. Therefore, a composite of a functional material and a silica or alumina aerogel have been examined. Example include an aerogel composed of titania and silica and a composite of metallic nickel and an alumina aerogel, which exhibited superior catalytic performance. In addition, we have prepared a ferrite-silica aerogel nanocomposite from a mixture of silica sol and ferrite nanoparticles using a supercritical drying process. This magnetic aerogel could be applied to a radiowave absorber and for drug delivery.

Although a silica aerogel is characterized as having almost the same low permittivity as air, we attempted to prepare a new dielectric aerogel with relatively high permittivity and/or high dielectric loss. Such a material could be applied as an ultra-light dielectric and as a radiowave absorber due to the high dielectric loss. An approach commonly used to enhance the permittivity of a composite is to load high-permittivity ceramic particles randomly into the matrix.

In the case of BaTiO$_3$-SiO$_2$, Nuzhnyy et al. reported enhancement of the permittivity by the addition of BaTiO$_3$ (30 to 45 wt %) in a porous silica matrix such as Vycor glass or opal silica, where the porosity was 30 to 40 vol %. In addition, there have been some reports on the enhancement of permittivity by constructing a BaTiO$_3$ core-silica shell nanostucture, where silica was coated on the surface of BaTiO$_3$ particles, and used for Multi-Layer Ceramic Capacitor, high-frequency dielectric applications, and supercapacitors. However, these were not porous materials. Thus, we first tried to prepare a new dielectric aerogel by loading BaTiO$_3$ nanoparticles into a silica aerogel with high porosity over 90%.

Another common approach for enhancing the permittivity of a composite is to load conductive filler particles randomly into the matrix. It is well known that such a composite exhibits a space charge polarization arising from a difference in the conductivity between the filler and matrix under an electric field, where motion of charge carriers occurs readily through the filler particles but is interrupted when the carriers reach the boundary between the filler particles and matrix; this then causes a build-up of charge at the interface corresponding to large polarization and high permittivity. This phenomenon has been widely applied for the preparation of semiconducting BaTiO$_3$ polycrystalline ceramics, wherein the grain boundaries have high resistance, to be used as grain-boundary barrier layer (BL) capacitors with high apparent permittivity.

Further, conductor-insulator composites have been studied as dielectrics for developing the percolation theory. Recently, enhancement in permittivity below the percolation threshold and/or a drastic increase in permittivity at the percolation threshold were observed in polymeric composites filled with conductive particles, such as metal or carbon, and in ceramic-metal composites. For conductor-silica porous nanocomposites, Ryan et al. prepared conductive porous nanocomposites with metallic percolation networks by loading conductive RuO$_2$ nanoparticles into a silica aerogel. Liu et al. reported the preparation...
and surface area measurements of a carbon-silica aerogel and aerogel composites. Si et al. and Hubert et al. reported the preparation and the electrical conductivity of carbon-silica porous nanocomposites. However, none of these previous studies reported dielectric properties. Thus, we attempted to enhance the permittivity of a silica aerogel by loading carbon nanoparticles.

2. Experimental procedure

The preparation process used is the same as in previous reports. The following reagents were used: tetramethyldisiloxane (TMOS, Tokyo Chem. Ind. Co., Ltd.); 1,1,1,3,3,3-hexamethyldisilazane (Tokyo Chem. Ind. Co., Ltd.); NH3 aq. (28 mass % aqueous solution, Wako Pure Chem. Ind. Ltd.); and ethanol (Wako Pure Chem. Ind. Ltd.).

BaTiO3 nanoparticles was a commercial Sigma-Aldrich reagent, with a relative permittivity of 150, a particle size of <100 nm, and a purity of ≥99%. These were ball-milled with ethanol and zirconia balls in a resin pot for 48 h for dispersion treatment. After the obtained suspension was sampled in an ultrasonic wave container for 20 min, it was again ball-milled for 48 h. Finally, BaTiO3 nanoparticles were used for an ethanol suspension of about 0.2 g/mL without drying. The BaTiO3 nanoparticles were identified to be cubic phase by powder X-ray diffraction measurements. The average particle diameter (d50) was 76 nm by particle size distribution measurements, and the particle size was estimated to be around 50 nm from TEM images. Carbon nanoparticles were prepared from conductive carbon paste (DOTITE XC-12, FujiKura Kasei Co., Ltd.), where an acrylic resin included in the paste was removed with acetone, and used as an ethanol suspension of about 0.03 g/mL.

The BaTiO3 nanoparticles suspension or the carbon nanoparticles suspension was added to a TMOS/ethanol solution, where the TMOS/ethanol molar ratio was 1/11. The molar ratio of BaTiO3/SiO2 (hereinafter referred to as BT/S) was in the range of 1/100 to 20/100, and the molar ratio of C/SiO2 (hereinafter referred to as C/S) was in the range of 20/100 to 80/100. The mixed solution was treated for 10 min on a magnetic stirrer, and further homogenized for 5 min by an ultrasonic wave treatment. Deionized water and ammonia were then added as a catalyst, and the solution was stirred for 5 min. The obtained sol was poured into a resin mold of φ5 mm × 5 mm and φ20 mm × 3 mm, and it gelled after about 30 min. This process was performed in an ultrasonic wave container in order to avoid a sedimentation of BaTiO3 and carbon particles.

The obtained wet gel was aged in ethanol for 2 h at 50°C. The aging treatment was repeated 5 times, where fresh ethanol was used each time. After that, the wet gel was refluxed for 24 h at 110°C in 1.3 mol/L hexamethyldisilazane/toluene solution for a hydrophobic treatment. After cooling, the toluene in the wet gel was again replaced by ethanol. The wet gel was subjected to supercritical drying using carbon dioxide, resulting in BaTiO3-silica aerogel nanocomposites and carbon-silica aerogel nanocomposites.

The bulk density and porosity were calculated from measurements of the size and weight of the sample. The specific surface area was measured by the Brunauer-Emmet-Teller (BET) method. The pore size distribution was measured by the Barrett-Joyner-Halenda (BJH) method using volumetric nitrogen gas adsorption (Bell Japan, Inc., BELSORP-max) for the mesopore region, and by a mercury intrusion porosimeter (Thermo Fisher Scientific Inc., PASCAL 140/240) for the macropore region. The microstructure was observed in a field emission scanning electron microscope (FE-SEM, JEOL Ltd., JSM-7000F) and a transmission electron microscope (TEM, JEOL Ltd., JEM-2100). The composition was analyzed by energy dispersive X-ray spectrometry (EDS, JEOL Ltd., JED-2300F and JED-2300). The dielectric properties were measured in the range of 10 MHz to 1 GHz by an RF impedance/material analyzer (Agilent Technologies Ltd., E4991A) at room temperature. Each sample was 20 mm in diameter and about 3 mm thick, and was held between two electrodes of 20 mm diameter forming a kind of capacitor. The measurement was repeated 3 times for 2 identical samples. For testing purposes, the relative permittivity and dielectric loss of air and Teflon were checked using identical geometrical shapes and electrodes, and good agreement with literature values was obtained.

3. Results and discussion

3.1 Preparation of BaTiO3-silica aerogel nanocomposites

Figure 1 shows the bulk density, porosity, and specific surface area of the BaTiO3-silica aerogel nanocomposites. Since the density of BaTiO3 (6.02 g/cm3) was larger than that of silica (2.2 g/cm3), the bulk density increased with increasing BaTiO3 content. For example, the bulk density was 0.126 g/cm3 for the silica aerogel, while it was 0.17 g/cm3 for the sample with BT/S = 20/100. On the other hand, the porosity hardly changed and remained substantially constant at around 95%. In addition,
although the specific surface area of the silica aerogel was about 700 m$^2$/g, this value decreased with increasing BaTiO$_3$ content, and was about 400 m$^2$/g for the sample with BT/S = 20/100.

With regard to the pore size distribution, the median size of macropore was around 2 $\mu$m for both the silica aerogel and for all the BaTiO$_3$-silica aerogel nanocomposites, where the peaks showed almost the same height as in Fig. 2(a). This means that the quantity of the macropores was almost the same for all the samples. Therefore, it was thought that the porosity of the samples became constant. On the other hand, the median size of the mesopores was about 14 nm for the silica aerogel and it shifted to 20 to 30 nm with increasing BaTiO$_3$ content, as shown in Fig. 2(b). Furthermore, the peaks became smaller with increasing BaTiO$_3$ content. It was thought that this decrease in pores in the mesopore region should be responsible for the decrease in specific surface area. Therefore, it was thought that the BaTiO$_3$-silica aerogel nanocomposites retained the characteristics of the aerogel.

Figure 3 shows SEM images of the silica aerogel and the BT/S = 20/100 sample. Both consist of nanoparticles of approximately 50 nm, where the nanoparticles were three-dimensionally connected to form a skeletal network structure. As shown in Figs. 3(c) and 3(d), several BaTiO$_3$ nanoparticles of about 50 nm size aggregated to form clusters, and the clusters were uniformly dispersed all over the nanocomposites. As seen from comparison of Figs. 3(d) and 3(e), the crystal surface of BaTiO$_3$ was covered with silica nanoparticles, where the skeletal network structure was somewhat broken. Therefore, it was considered that such heterogeneity of the skeletal network structure caused a decrease of pores in the mesopore region, resulting in a decrease in the specific surface area.

3.2 Preparation of carbon-silica aerogel nanocomposites

Figure 5 shows the bulk density, porosity and specific surface area of the carbon-silica aerogel nanocomposites. Since the density of carbon was almost the same as that of silica, the bulk density hardly changed, even when the carbon content increased. Similarly, the porosity hardly changed from around 94%. As for the specific surface area, compared to a value of about 700 m$^2$/g for silica aerogel, the value of the carbon-silica aerogel
The specific surface area of the nanocomposite was about 600 m$^2$/g for the C/S = 80/100 sample.

With regard to pore size distribution, the macropore showed almost the same peak at a median size of around 2 µm for all of the carbon-silica aerogel nanocomposites, as shown in Fig. 6(a). In addition, the median size of the mesopores was about 14 nm for the silica aerogel, and it shifted to approximately 20 nm with increasing carbon content as shown in Fig. 6(b). The peaks became smaller with increasing carbon content. This was regarded to be the cause for the slight decrease in the specific surface area. From the above, it can be concluded that all of the prepared samples showed the characteristics of an aerogel.

Figure 7 shows SEM images of the C/S = 20/100 sample. There was no difference between the silica aerogel, the BaTiO$_3$-silica aerogel nanocomposites, and the carbon-silica aerogel nanocomposite. The size of the macropores measured by the intercept method was estimated to be in the range of 1 to 2 µm for all of the carbon-silica aerogel nanocomposites, as shown in Fig. 6(a). As seen from Figs. 7(c) and 7(d), there was a lack of uniformity in the C (carbon) mapping. Apparently, it was observed that the C concentration in the particles in front was high, while the C concentration of the particles at the back was low. Since the energy of the characteristic X-rays of carbon was low, the characteristic X-rays emitted by the back particles was absorbed by collision with the front particles. Therefore, the mapping image lighted up the shape of the network structure formed by the front particle chains. However, there was no significant difference between the front particles. Therefore, it was concluded that carbon nanoparticles also existed homogeneously in the skeletal network structure on the scale of the SEM.

Figure 8 shows TEM images of carbon nanoparticles and the C/S = 80/100 sample. The carbon particles with size of about 20 to 50 nm formed a small number of clusters by aggregation. They were surrounded by silica nanoparticles, where the skeletal network structure was somewhat broken.

### 3.3 Dielectric properties of BaTiO$_3$-silica aerogel nanocomposites and carbon-silica aerogel nanocomposites

Figures 9 and 10 show changes in the relative permittivity and dielectric loss for the silica aerogel, the BaTiO$_3$-silica aerogel nanocomposites, and the carbon-silica aerogel nanocomposites as a function of frequency. The relative permittivity of the silica aerogel was about 1.3 which is very low, similar to that of air, and it slightly decreased with increasing frequency. The dielectric loss also had a low value of about $1 \times 10^{-3}$. Its frequency dependence was not clear due to a large fluctuation of $\pm 1 \times 10^{-3}$ in measured values. As a conclusion, it was thought that the relative permittivity of 1.3 and dielectric loss of $1 \times 10^{-3}$ were in accordance with literature values, e.g., relative permittivity of 1.1 at 1 MHz for an aerogel with porosity of 95% prepared by Kawakami and Uehara, and the relative permittivity of 1.25 and dielectric loss of $5 \times 10^{-4}$ at 1 kHz for an aerogel with porosity of 92% prepared by Brüesch et al.

As shown in Fig. 9, the relative permittivity of the BaTiO$_3$-silica aerogel nanocomposites increased slowly with increasing BaTiO$_3$ loading, reach about 2.1 for the BT/S = 20/100 sample,
showing no frequency dependence in the range of 10 MHz to 1 GHz. The values varied somewhat in repeated measurements for 2 samples. For example, the relative permittivity was in the range of 1.79 to 1.81 for \(\text{BT/S} = 1/10\), 1.89 to 1.96 for \(\text{BT/S} = 5/10\), and 2.10 to 2.19 for \(\text{BT/S} = 20/10\) at 100 MHz. The dielectric loss yielded a low value of about \(1 \times 10^{-3}\) in a manner similar to the silica aerogel. Its frequency dependence was not clear since the values of the dielectric loss scattered in the range of about \(\pm 1 \times 10^{-3}\) by variation in \(\text{BaTiO}_3\) loading and/or by individual differences between samples.

However, these dielectric properties were considered to be proper in comparison with a report by Nuzhny et al. They confined \(\text{BaTiO}_3\) in a nanoporous artificial opal silica with 35 to 40 vol % porosity, where the \(\text{BaTiO}_3\) content was 45 wt % and filled about 50 vol % of the pores. The relative permittivity and dielectric loss in this case decreased with increasing frequency to become almost constant, where the relative permittivity was 5 to 10 in the range of 10 MHz to 1 GHz. To obtained another point of view, the relative permittivity of the \(\text{BaTiO}_3\)-silica aerogel nanocomposites was roughly estimated by Eq. (1), which is used

![Fig. 6. Pore size distribution in the carbon-silica aerogel nanocomposites.](image.png)

![Fig. 7. SEM images of the C/S = 20/100 carbon-silica aerogel nanocomposite [(a) and (b)] and C mapping of the nanocomposite [(c) and (d)]. The color in the C mapping indicates the concentration of C, increasing with the change from black to white according to the color bar on the left.](image.png)

![Fig. 8. TEM images and elemental analysis of the C/S = 80/100 carbon-silica aerogel nanocomposite [(a) and (b)] and carbon nanoparticles (c).](image.png)

![Fig. 9. Frequency dependence of the relative permittivity and dielectric loss of the silica aerogel and \(\text{BaTiO}_3\)-silica aerogel nanocomposites.](image.png)
to determine the influence of the porosity on the dielectric constant of TiO$_2$-polycrystalline.\textsuperscript{36)}

$$\kappa' = \nu_1\kappa'_1 + \nu_2\kappa'_2$$  \hspace{1cm} (1)

Here, $\kappa'_1$ and $\kappa'_2$ are the dielectric constant of each phase and $\nu_1$ and $\nu_2$ are the volume fraction of each phase. The volume fractions of air, silica, and BaTiO$_3$ were 95, 4, and 1%, respectively, in the BT/S = 20/100 sample. The relative permittivity is 1 for air, 4 for silica, and 150 for BaTiO$_3$. As a result, the calculated value of 2.6 agreed well with the measured value of 2.1. Consequently, it was concluded that the relative permittivity of the aerogel could be enhanced in this way. However, since it was difficult to prepare silica aerogel nanocomposites with higher BaTiO$_3$ loadings in this experimental procedure, it would be necessary to add nanoparticles with much larger relative permittivity in order to obtain a larger overall relative permittivity. For example, an aerogel having a relative permittivity of 10 could be prepared by adding nanoparticles having a relative permittivity of 1000.

The resistivity of the carbon-silica aerogel nanocomposites showed comparatively high values in the range of $10^2$ to $10^4$ $\Omega \cdot$cm. This was because the conductive carbon nanoparticles did not form a conductive network structure, and were surrounded by insulating silica nanoparticles as shown in the TEM images. Therefore, it was expected that many electric charges could be accumulated in the interface between carbon and silica by space charge polarization as in carbon-polymer composites. According to some reports on carbon-polymer composites,\textsuperscript{20,21,26} the relative permittivity increased with increasing carbon loading until the percolation threshold owing to space charge polarization and decreased increasing frequency since the polarization could not be maintained at higher frequencies. The dielectric loss also exhibited frequency dependence, which was particularly significant at low frequencies. In this study, similarly, the relative permittivity and dielectric loss of carbon-silica aerogel nanocomposites increased with increasing carbon loading and decreased with increasing frequency as shown in Figs. 10 and 11. The C/S = 20/100 sample with low carbon loading showed a relative permittivity of about 6 and dielectric loss of about 0.02, which were almost not frequency dependent. On the other hand, the C/S = 80/100 sample with higher carbon loading showed a higher relative permittivity of about 10 and higher dielectric loss of 0.4 at 10 MHz, while the respective values were about 6 and 0.05 at 1 GHz. The carbon-silica aerogel nanocomposites thus possess higher relative permittivity and higher dielectric loss at a lower filler loading compared to the BaTiO$_3$-silica aerogel nanocomposites.

4. Conclusion

A new type of dielectric aerogel was prepared by supercritical drying of a silica sol containing BaTiO$_3$ nanoparticles or carbon nanoparticles. Both the BaTiO$_3$-silica aerogel nanocomposites and carbon-silica aerogel nanocomposites showed a three-dimensional skeletal network structure with macropores of about 2 $\mu$m and mesopores of 10 to 30 nm size. In this structure, several of the BaTiO$_3$ nanoparticles (about 50 nm) or the carbon particles (about 20 to 50 nm) were aggregated, and these aggregates were homogeneously dispersed in the silica aerogel matrix. The density of the dielectric aerogel was 0.1 to 0.2 g/cm$^3$, the porosity was about 95%, and the specific surface area was in a range from 400 to 700 m$^2$/g. For the BaTiO$_3$-silica aerogel nanocomposites, the relative permittivity increased slightly with increasing BaTiO$_3$ content. In addition, by adding the conductive carbon nanoparticles into the silica aerogel, both the relative permittivity and
dielectric loss became much larger. These aerogels are anticipated to be used as ultra-light dielectrics.

References
1) H. D. Gesser and P. C. Goswami, Chem. Rev., 89, 765–788 (1989).
2) K. Tajiri, Hyomen Kagaku, 14, 546–549 (1993).
3) “Nano Technology with Supercritical Fluids”, Ed. by M. Ajiri, CMC Publishing, Tokyo (2010) pp. 189–191.
4) N. Kawakami and K. Uchida, Kobe Steel Works Engineering reports, 52, 39–44 (2002).
5) P. Brüesh, F. Stucki, Th. Baumann, P. Kluge-Weiss, B. Brühl, L. Niemeyer, R. Strümpler, B. Ziegler and M. Mielke, Processing and Application to Ceramics, Second Edition, John Wiley & Sons, New York (1976) p. 953.
6) H. Izumi, “Denshi Seramikkusu” [Electronic ceramics], Seibundo Shinkosha, Tokyo (2002) pp. 27–30.
7) S. H. Jasem and W. A. Hussain, Journal of Basrah Researches (Sciences), 38, 1, A, 60–71 (2012).
8) G. Sui, S. Jana, W. H. Zhong, M. A. Fuqua and C. A. Ulven, Acta Mater., 56, 2381–2388 (2008).
9) J. Xu, K.-S. Moon, C. Tison and C. P. Wong, IEEE Trans. Adv. Packag., 29, 295–306 (2006).
10) D. Nuzhnyy, P. Vanek, J. Petzelt, V. Bovtun, M. Kempa, I. Gregora, M. Savinov, R. Krupková, V. Studnicka, J. Bursík, M. I. Samoylovich and W. Schranz, Processing and Application to Ceramics, 4, 215–223 (2010).
11) N. Hadik, A. Outzourhit, A. Elmansouri, A. Abouelaoualim, A. Ouerciagl and E. L. Mameziane, Active and Passive Electronic Components, Vol. 2009, Article ID 437130, 6 pages.
12) M. E. Hossain, S. Y. Liu, S. O’Brien and J. Li, Acta Mech., 225, 1197–1209 (2014).
13) T. Hu, J. Juuti, H. Jantunen and T. Vilkan, J. Eur. Ceram. Soc., 27, 3997–4001 (2007).
14) D. Nuzhnyy, J. Petzelt, V. Bovtun, M. Kempa, M. Savinov, C. Elissalde, U.-C. Chung, D. Michau, C. Estournès and M. Maglione, Journal of Advanced Dielectrics, 1, 309–317 (2011).
15) U.-C. Chung, C. Elissalde, S. Mornet, M. Maglione and C. Estournès, Appl. Phys. Lett., 94, 072903 (2009).
16) U.-C. Chung, C. Elissalde, F. Mompiou, J. Majmud, S. Gomez, C. Estournès, S. Marinol, A. Klein, F. Weil, D. Michau, S. Mornet and M. Maglione, J. Am. Ceram. Soc., 93, 865–874 (2010).
17) R.-Z. Chen, A.-L. Cui, X.-H. Wang, Z.-L. Gui and L.-T. Li, Mater. Lett., 54, 314–317 (2002).
18) W. D. Kingery, H. K. Bowen and D. R. Uhlmann, “Introduction to Ceramics, Second Edition”, John Wiley & Sons, New York (1976) pp. 947–950.