

## Synthesis and Structural Characterization of BaTiO<sub>3</sub>-SiO<sub>2</sub> Aerogels

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**Abstract:** BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels were prepared by sol-gel route with supercritical drying technique, after silica wet gel was dipped into BaTiO<sub>3</sub> solution. In order to compare with the properties of compounded aerogels, pure BaTiO<sub>3</sub> nanoparticles were also prepared by the sol-gel method. These BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels and BaTiO<sub>3</sub> nanoparticles were characterized by X-ray diffraction (XRD), Raman spectra, transmission electron microscopy (TEM) and photoluminescence (PL) spectra. The size of compounded aerogel nanoparticles distributed from 7 to 20 nm when the BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels were heated at 800 °C. The intensity of PL was obviously increased, comparing with the one of pure BaTiO<sub>3</sub> heated at the same temperature.

**Key words:** BaTiO<sub>3</sub>, compounded aerogels, photoluminescence, supercritical drying method

### 1. INTRODUCTION

It is well known that aerogel is a fractal type of network material with high surface areas, low density and high porosities<sup>[1]</sup>. These materials are extremely interesting and many commercial applications have been found, such as insulators, water purification, optic coating, optics and so on<sup>[2]</sup>. Silica aerogel is one kind of these materials. There are many important attributes about silica aerogel in catalytic, insulating and optical properties<sup>[3,4]</sup>. At the same time, silica aerogel is used as the matrix for other kinds of researches, for example narrow-band-gap semiconductors doped into silica aerogel to improve the optical properties<sup>[5]</sup>, GeO<sub>2</sub> doped silica aerogel in order to raise the refractive index<sup>[6]</sup>.

Due to their wide variety of physical properties such as piezoelectricity, ferroelectricity and electro-optic effect, perovskite-type oxides have seen an explosion of interest over the last few years. Barium titanate (BaTiO<sub>3</sub>) as a typical perovskite material has been attractive for its fundamental research and perspective applications. BaTiO<sub>3</sub> is negative uniaxial crystal when it is tetragonal phase and the nonlinear optical properties of barium titanate were already known 40 years ago<sup>[7]</sup>. Recently the nonlinear optical properties of BaTiO<sub>3</sub> embedded by noble metal nanoparticles were investigated because barium titanate thin films have high dielectric constants, which could strongly influence the local fields around the metal particles<sup>[8]</sup>. But to the best of our knowledge, no work has been reported about the optical properties of BaTiO<sub>3</sub> nanocrystals doped into silica aerogel up to now.

For the sake of BaTiO<sub>3</sub> nanoparticles doped into silica aerogel, ultrafine BaTiO<sub>3</sub> nanoparticles were required to obtain at first. The production and characterization about BaTiO<sub>3</sub> have been performed by many researchers. Nanocrystalline BaTiO<sub>3</sub> powder has been prepared by various methods<sup>[9]</sup>, such as solid phase method and gas phase reaction<sup>[10]</sup>. But the most popular methods for preparing BaTiO<sub>3</sub> nanoparticles are liquid phase processes such as hydrothermal method, sol-gel method,

micro-emulsion method and low temperature direct synthesis<sup>[10]</sup>. It was reported that the ultrafine BaTiO<sub>3</sub> powder with an average size of approximately 7 nm had been produced<sup>[11]</sup>. Nevertheless, Uchino et al.<sup>[12]</sup> reported the disappearance of the tetragonal ferroelectric structure below a critical size of 120 nm at the room temperature. Frey et al.<sup>[13]</sup> observed no electric hysteresis with 25 nm crystals and no anomaly of the dielectric constant at the Curie point.

To keep the tetragonal phase of BaTiO<sub>3</sub>, which has ferroelectricity, a possible strategy is to introduce the BaTiO<sub>3</sub> solution into the silica aerogel matrix. The supercritical drying technique may be a suitable method for preparation of silica aerogel doped with BaTiO<sub>3</sub>. In this paper, with the supercritical drying method, some fractions of BaTiO<sub>3</sub> nanoparticles have been successfully incorporated into silica aerogel, BaTiO<sub>3</sub>-SiO<sub>2</sub> compounded aerogels can be obtained.

### 2 EXPERIMENTAL

Ba(OH)<sub>2</sub>·8H<sub>2</sub>O, acetic acid, isopropanol, titanium tetraisopropoxide(TTIP), tetramethyl orthosilicate (TMOS), ethanol and ammonia solution were adopted as starting materials for preparation of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels through sol-gel and the supercritical drying process. The flow chart of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels synthesis used in this study is outlined in Fig.1.

Firstly silica wet gel was produced in a one-step synthesis method by hydrolysis and polycondensation of TMOS diluted in a solvent ethanol using ammonium hydroxide (NH<sub>4</sub>OH at 0.1 mol/l) as a catalyst with aging for 10 hrs. BaTiO<sub>3</sub> precursor solution was prepared from Ba(OH)<sub>2</sub>·8H<sub>2</sub>O, acetic acid, isopropanol and TTIP according to the following method: Ba(OH)<sub>2</sub>·8H<sub>2</sub>O was dissolved by stirring and heating in a 1:1 mixed solution of acetic acid and isopropanol for 30 minutes. Then a stoichiometric amount of TTIP was added dropwise after cooling this solution to room temperature. After stirring a few minutes a clear

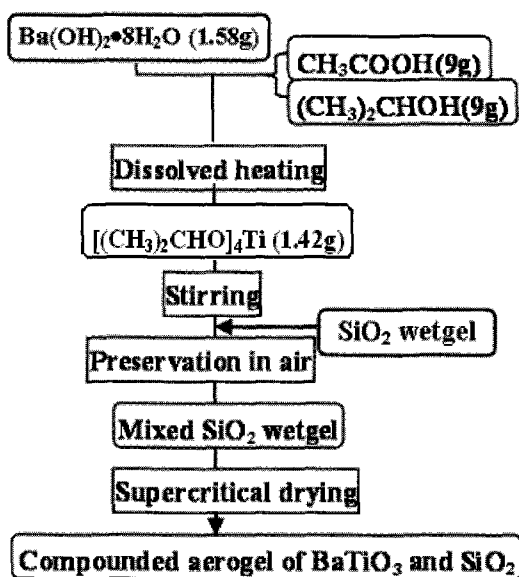


Fig.1 Flow-chart illustrating the procedure for the preparation of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels

solution was obtained. Then silica wet gel was dipped into BaTiO<sub>3</sub> precursor solution for 24 hrs in order to form the compounded wetgels. BaTiO<sub>3</sub>-SiO<sub>2</sub> compounded aerogels were obtained through the supercritical drying process with liquid CO<sub>2</sub> as drying medium. Then the samples were heated at 600°C, 700°C and 800°C and kept for 2~10 hrs for crystal growth respectively. In order to analyze the properties of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels powder, pure BaTiO<sub>3</sub> powder was obtained from BaTiO<sub>3</sub> gels by sol-gel method, which were heated at 600°C, 700°C, 800°C and 900°C respectively.

S1, S2, S3 and S4 were defined the samples of pure BaTiO<sub>3</sub> powder obtained when BaTiO<sub>3</sub> wet gels were heated at 600°C, 700°C, 800°C and 900°C, respectively. S5 and S6 were defined the samples of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels heated at 800°C and unheated at room temperature, respectively. The test and measurement for S1, S2, S3, S4, S5 and S6 were listed in table I.

**Tab. I** The list of test and measurement for the samples

	S1	S2	S3	S4	S5	S6
XRD	O	O	O	O	O	O
Raman		O				
TEM		O			O	
PL		O	O		O	

O showed that the sample was tested in this work.

Identification of synthesized phase and estimation of crystalline size of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogel powder and BaTiO<sub>3</sub> powder were investigated by powder XRD measurement. XRD data was recorded on a diffractometer (Model RINT2000, Rigaku Co., Tokyo, Japan), using CuKα1 radiation, and collected over a 2θ

range of 10°~80° with a scanning step of 0.01° at room temperature. The average size and morphology of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels and BaTiO<sub>3</sub> particles were observed by TEM. The Raman spectroscopy, with the 1064nm lines of the exciting source from an Nd-YAG laser was used for the phase identification. The PL spectrum was taken with 325.0 nm exciting wavelength of an argon ion laser.

### 3 RESULTS and DISCUSSION

#### 3. 1 Structural characterization

Fig. 2 shows the XRD patterns of pure BaTiO<sub>3</sub> powder heat treated at different temperature ranging from 600 to 900°C. Yong-I. Kim et al<sup>[14]</sup> reported that the tetragonal phase has two peaks, (002) and (200), which are clearly separated near 2θ=45°, while only (200) peak of the cubic phase lies between tetragonal peaks, however, if the size of crystallite decreases, the separated two peaks of tetragonal phase may be overlapped because of the broadening of diffraction peaks. Fig. 2 shows that the peak shapes of pure BaTiO<sub>3</sub> powder are not obviously changed except for the peaks intensities when the heat treatment temperature is increased. In order to prove whether the tetragonal phase exists in pure BaTiO<sub>3</sub> powder or not, the measurement of Raman spectrum had been done.

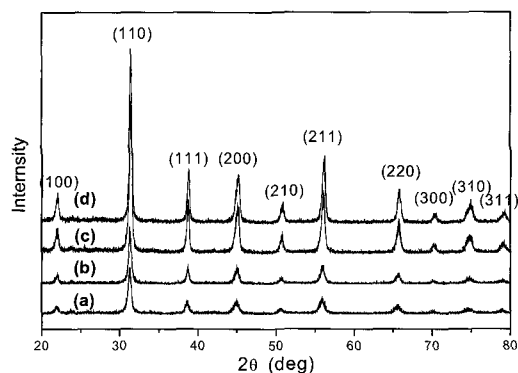


Fig.2 the XRD patterns of pure BaTiO<sub>3</sub> powder heat treated at 600°C (a), 700°C (b), 800°C (c) and 900°C (d) respectively.

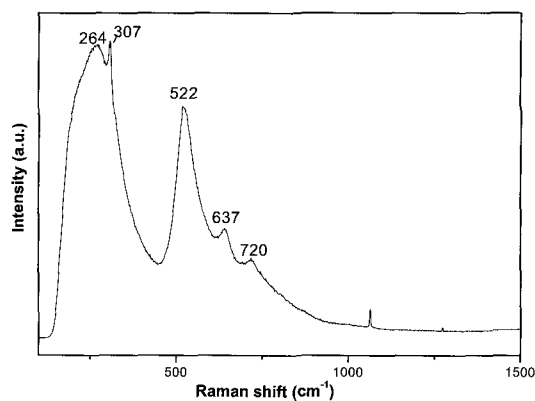


Fig.3 Raman spectra of BaTiO<sub>3</sub> powder heat treated at 700°C

Fig.3 shows the Raman spectrum of BaTiO<sub>3</sub> powder heat treated at 700°C. From the Raman spectrum, it could be found that Raman spectrum of the powder contains the Raman peaks corresponding to the cubic and tetragonal phases. The peak around 307cm<sup>-1</sup>[14,15] is a typical one for the tetragonal BaTiO<sub>3</sub>, while the peak at 522cm<sup>-1</sup>[14,15] is characterized as one of the cubic phase in BaTiO<sub>3</sub>. The result of Raman spectrum supports that pure BaTiO<sub>3</sub> powder in this work contains both cubic and tetragonal phases.

The XRD patterns of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels at room temperature and heated at 800°C are shown in Fig.4. There is only peak in the XRD pattern of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels (a) at room temperature, because it comes from the amorphous SiO<sub>2</sub>. It shows that the BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels at room temperature are amorphous. The BaTiO<sub>3</sub> nanocrystals were obtained in compounded aerogels when BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels were heated at 800°C, which can be concluded from the sharpness of the diffraction peaks (b). Fig.5 shows the electron diffraction pattern of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels heat treated at 800°C. Polycrystalline structures of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels can be identified from the rings clearly seen in Fig.5. Fig. 4 shows that the peak positions of XRD patterns in BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels were different from the ones in pure BaTiO<sub>3</sub> powder. It was speculated that the BaTiO<sub>3</sub> nanocrystals were obtained, simultaneously new compound generated when the BaTiO<sub>3</sub>-SiO<sub>2</sub> compounded aerogels were heated at 800°C.

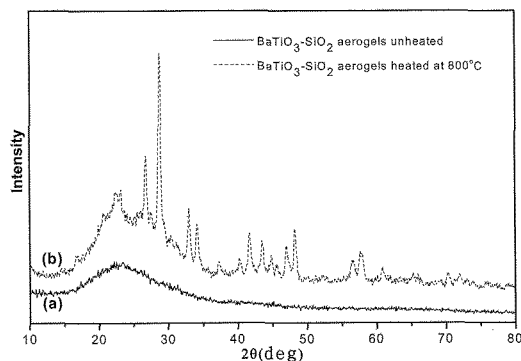


Fig.4 XRD patterns of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels (b) heated at 800°C and (a) unheated at room temperature

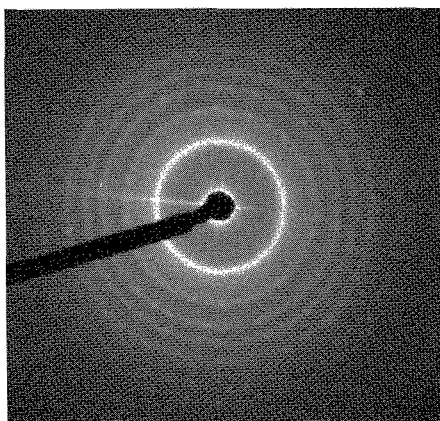


Fig.5 Electron diffraction pattern of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels heated at 800°C

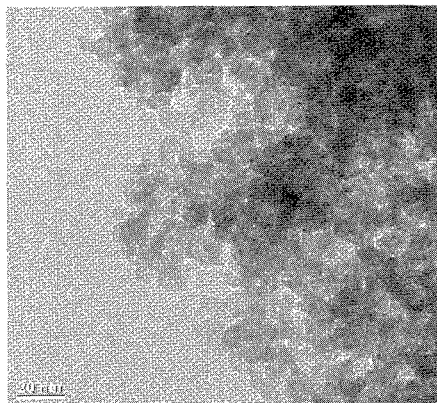


Fig. 6 TEM image of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels heated at 800°C

The TEM image of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels heated at 800°C is shown in Fig. 6. The size distribution of the particles ranges from 7 to 20 nm. The size and shape of BaTiO<sub>3</sub> particles can be affected by the silica aerogels. The structural styles of BaTiO<sub>3</sub> particles in silica aerogels were extracted that some BaTiO<sub>3</sub> particles loaded in pores of silica aerogel and others entered into the lattices of silica aerogel. The growth mechanics of BaTiO<sub>3</sub> particles in aerogels was that BaTiO<sub>3</sub> particles were adsorbed by silica aerogel at the beginning, however, the growth of BaTiO<sub>3</sub> particles was limited when BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels were heated at 800°C. The silica aerogel played a model role to limit the growth of BaTiO<sub>3</sub> crystals. So the particle sizes of BaTiO<sub>3</sub> in BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels were less than ones of pure BaTiO<sub>3</sub> powder.

### 3.2 Optical characterization

Fig.7 shows PL spectra of the BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels heat treated for 2 hrs at 800°C in the air and the BaTiO<sub>3</sub> powder heat treated at 700°C and 800°C in the air. According to the PL spectra of Fig.7, the intensity of the PL was not obviously changed when the heat treatment temperature of pure BaTiO<sub>3</sub> powder was increased. However, the intensity of BaTiO<sub>3</sub>-SiO<sub>2</sub> compounded aerogels increased when they were heated at 800°C. Fig.7 shows that the shapes of curves are not changed. This finding indicated strongly that the room-temperature PL stemmed from the BaTiO<sub>3</sub> nanoparticles. A comparison of the different samples revealed that the PL behavior of the BaTiO<sub>3</sub>-SiO<sub>2</sub> compounded aerogels was stronger than the ones of pure BaTiO<sub>3</sub> powder. It was possible because the BaTiO<sub>3</sub> nanoparticles of BaTiO<sub>3</sub>-SiO<sub>2</sub> compounded aerogels were less than the ones of pure BaTiO<sub>3</sub> powder.

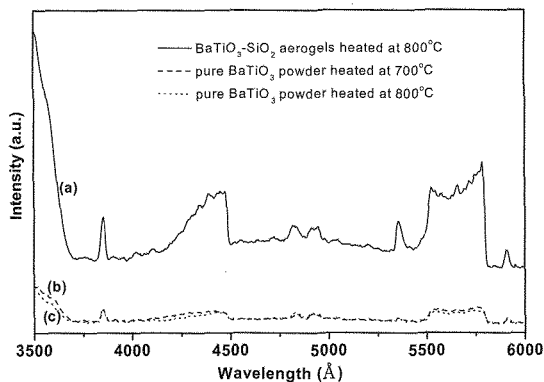


Fig.7 PL spectra of BaTiO<sub>3</sub>-SiO<sub>2</sub> compounded aerogels heated at 800°C (a) and pure BaTiO<sub>3</sub> powder heated at 700°C (b) and 800°C(c)

#### 4 CONCLUSIONS

BaTiO<sub>3</sub> nanoparticles dispersed silica aerogel were prepared by a sol-gel route combined with supercritical drying method. There was good crystallinity when the BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels were heated at 800°C. BaTiO<sub>3</sub> nanoparticles were loaded in the silica aerogel matrix with the sizes from 7 to 20 nm. Silica aerogel played a model role to limit the growth of BaTiO<sub>3</sub> nanoparticles in compounded aerogels when BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels were heated at 800°C, so the particles of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels were less than the ones of pure BaTiO<sub>3</sub> powder. The PL intensity of BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels heated at 800°C was stronger than the ones of pure BaTiO<sub>3</sub> powder heated at 700°C and 800°C. The properties and components of compounded aerogels will be investigated further in future work when BaTiO<sub>3</sub>-SiO<sub>2</sub> aerogels are heated at different temperatures.

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#### REFERENCE

- [1]C.J. Brinker, G.W. Scherer, Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing, Academic Press, New York, 1989, ISBN 0-12-134970-5.
- [2]L.W. Hrubesh, *Chem. Industry* 24 (1989) 824.
- [3]C.J. Brinker, R.J. Kirkpatrick, D.R. Tallant, B.C. Bunker, *J. Non-Cryst. Solids* 99(1988) 418
- [4]L.C. Klein (Ed.), Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty shapes, Noyes, Park Ridge, NJ, 1987.
- [5]L.Z. Yao, C.H. Ye, C.M. Mo, W.L. Cai, L.D. Zhang, *J. Cryst. Growth* 216, 147-151(2000).
- [6]S. Grandi, P. Mustarelli, A. Magistris, M. Gallorini, E. Rizzio. *J. Non-Cryst. Solids* 303, 208-217 (2002).
- [7]C. Miller, D.A. Kleinman, A. Savage, *Phys. Rev. Lett.* 11(4), 146-149 (1963).
- [8]Yong Yang, Jianlin Shi, Weiming Huang,

Shugang Dai, Lin Wang, *Mater. Lett.* 56 1048-1052(2002).

[9]Weiling Luan, Lian Gao, *Cera. Intel.* 27 645-648 (2001).

[10]Keigo Suzuki, Kazunori Kijima, *J. Ceram. Soc. Jpn.* Supplement 112-1, Pacrim5 Special Issue, 112 (5) S916-S923 (2004).

[11]Keigo Suzuki and Kazunori Kijima, *Jpn. J. Appl. Phys.*, 44(4A) 2081-2082 (2005).

[12]Uchino, K., Sadamaga, E., Oonish, T., Morohashi, T., Yamamura, H., *Ceram. Transactions.* 8, 107 (1980).

[13]Frey, M. H., Payne D. A., *Appl. Phys. Lett.* 63(20) 2753 (1993).

[14]Yong-I. Kim, Jae Kap Jung, Kwon Sang Ryu, *Mater. Res. Bull.*, 39 1045-1053 (2004).

[15]Song Wei Lu, Burtrand I. Lee, Zhong Lin Wang, Willian D. Samuels, *J. Cryst. Growth* 219 269-276 (2000).

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