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Characteristics of $BaNd_2Ti_5O_{14}$ powders directly prepared by high-temperature spray pyrolysis

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Abstract

$BaNd_2Ti_5O_{14}$ powders were directly prepared by high-temperature spray pyrolysis. The powders prepared at temperatures of 1300 and 1500 °C exhibited a pure $BaNd_2Ti_5O_{14}$ phase. The powders prepared at 1300 °C were spherical in shape. However, the powders prepared at 1500 °C showed non-spherical shapes. The $BaNd_2Ti_5O_{14}$ powders had a composition similar to that of the spray solution. The mean sizes of the $BaNd_2Ti_5O_{14}$ powders increased from 0.23 to 0.60 μm when the concentration of the spray solution was increased from 0.01 to 0.2 M. At a sintering temperature of 1100 °C, bridge-like structures were formed between the powders. Pellets sintered at 1300 °C exhibited a dense structure comprising rod-like crystals.

Keywords: A. Powders: gas phase reaction; A. Powders: chemical preparation

1. Introduction

Spray pyrolysis has several advantages in the preparation of multicomponent ceramic powders containing particles with a fine size and spherical shape [1–3]. For instance, spray pyrolysis enables a high degree of mixing of the constituents of the multicomponent ceramic, thereby decreasing the preparation temperature. However, the residence times of the powders inside the hot wall reactor are short, less than tens of seconds. Therefore, the precursor powders obtained by spray pyrolysis require post-treatment at high temperatures to improve crystallinity and phase purity. The post-treatment process causes deformation of the spherical shape of the particles and leads to particle aggregation. In particular, it is observed that fine powders comprised of particles having sizes in the range of several hundred nanometers possess low thermal stability.

High-temperature spray pyrolysis has been applied to the direct preparation of multicomponent ceramic powders without the post-treatment process [4–7]. The particles of ceramic powders directly prepared by high-temperature spray pyrolysis had a spherical shape, showed high crystallinity, and did not undergo particle aggregation. However, this pyrolysis method will cause composition deviation due to the evaporation of some components of the multicomponent ceramics.

$BaNd_2Ti_5O_{14}$ (BNT), an important compound of the Ba–Nd–Ti–O system, is known to be an important microwave dielectric material because of its high dielectric constant, low dielectric loss, and near-zero temperature coefficient of resonant frequency [8–12]. Fine powders are required to decrease the sintering temperature of BNT. BNT powders prepared by conventional solid-state reaction and liquid solution methods exhibited large particle sizes and irregular morphologies.

In this study, BNT powders were directly prepared by high-temperature spray pyrolysis. The effects of the preparation temperature on the morphologies and crystal structures of the BNT powders were investigated. The effect of the concentration of the spray solution on the mean particle size was also investigated.

2. Experimental

The spray pyrolysis equipment used consisted of six ultrasonic spray generators operating at 1.7 MHz, a tubular

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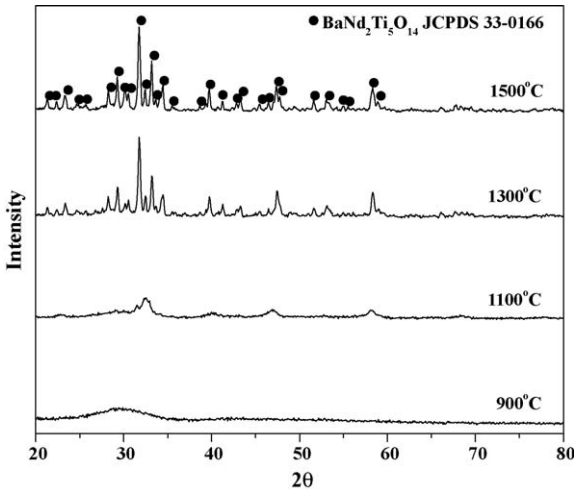


Fig. 1. XRD patterns of the BNT powders directly prepared by spray pyrolysis.

alumina reactor of 1000 mm length and 25 mm ID, and a bag filter. The general flow diagram of the spray pyrolysis process is given elsewhere [13]. The BNT powders were prepared by spray pyrolysis at temperatures between 900 and 1500 °C. The starting materials used in the synthesis of BNT powders were barium carbonate, neodymium nitrate, titanium tetra-*iso*-propoxide (TTIP). A small amount of nitric acid was used to peptize the hydrolyzed TTIP and form a clear solution. The concentrations of metal components were changed from 0.01 to 0.2 M. The flow rate of air used as the carrier gas was 5 L/min. The prepared BNT powders were pelletized under 500 MPa pressure into a 15 mm diameter and thickness of 1 mm. The pellets were then sintered at temperatures between 1000 and 1300 °C for 3 h and cooled naturally to room temperature.

The crystal structures of the BNT powders were investigated using X-ray diffraction (XRD) with Cu Kα radiation (λ 1.5418×10^{-1} nm). The morphological characteristics of the powders were investigated using scanning electron microscopy (SEM). The specific surface areas were measured by Brunauer–Emmet–Teller (BET) method using N_2 adsorption. The pore size distributions of the powders were analyzed by Barrett–Joyner–Halenda (BJH) method.

3. Results and discussion

The crystal structures of powders directly prepared by spray pyrolysis at various temperatures are shown in Fig. 1. The concentration of the spray solution was 0.2 M. The powders prepared at 900 °C had an amorphous phase. XRD patterns of the powders prepared at 1100 °C revealed broad crystalline peaks. BNT powders were not obtained when spray pyrolysis was carried out at temperatures below 1100 °C because of the

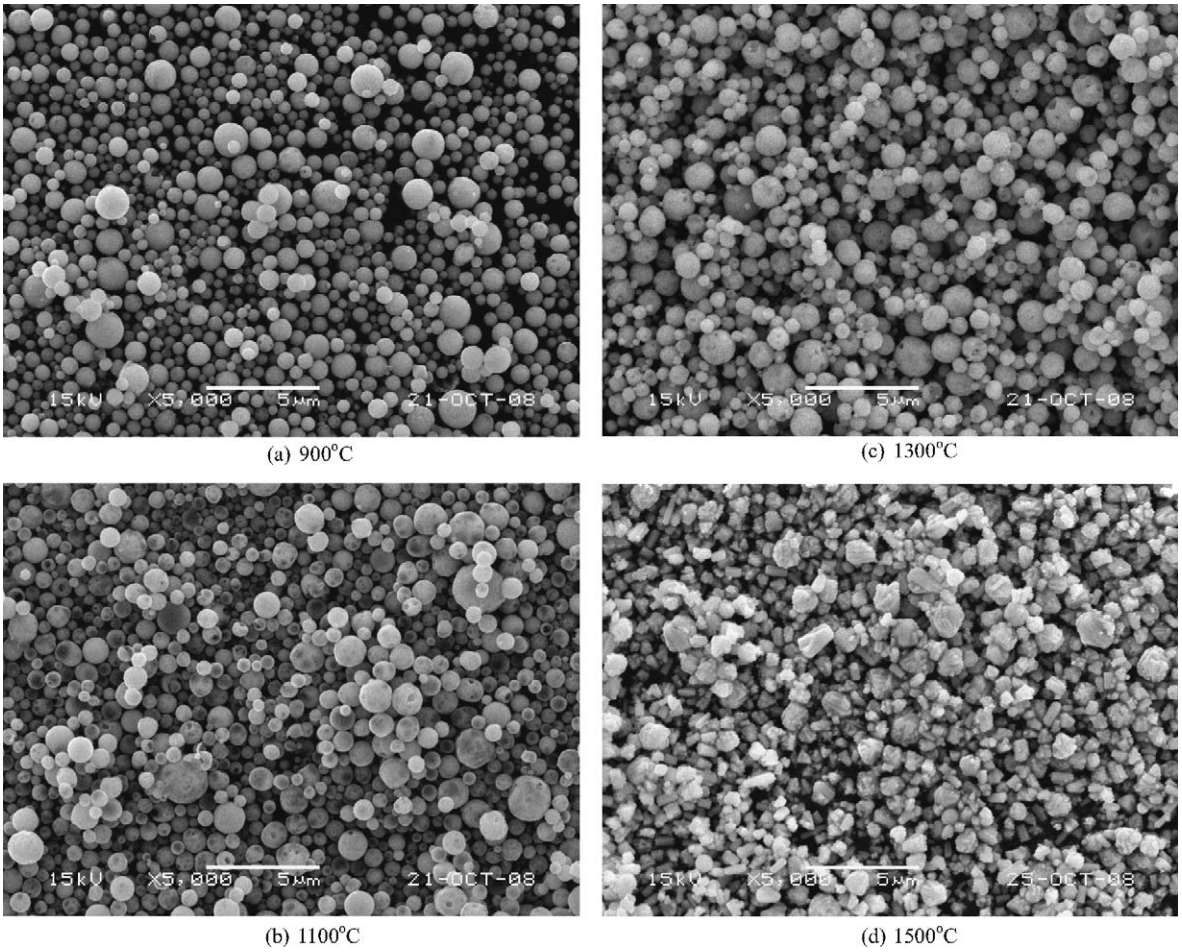


Fig. 2. SEM images of the BNT powders directly prepared by spray pyrolysis.

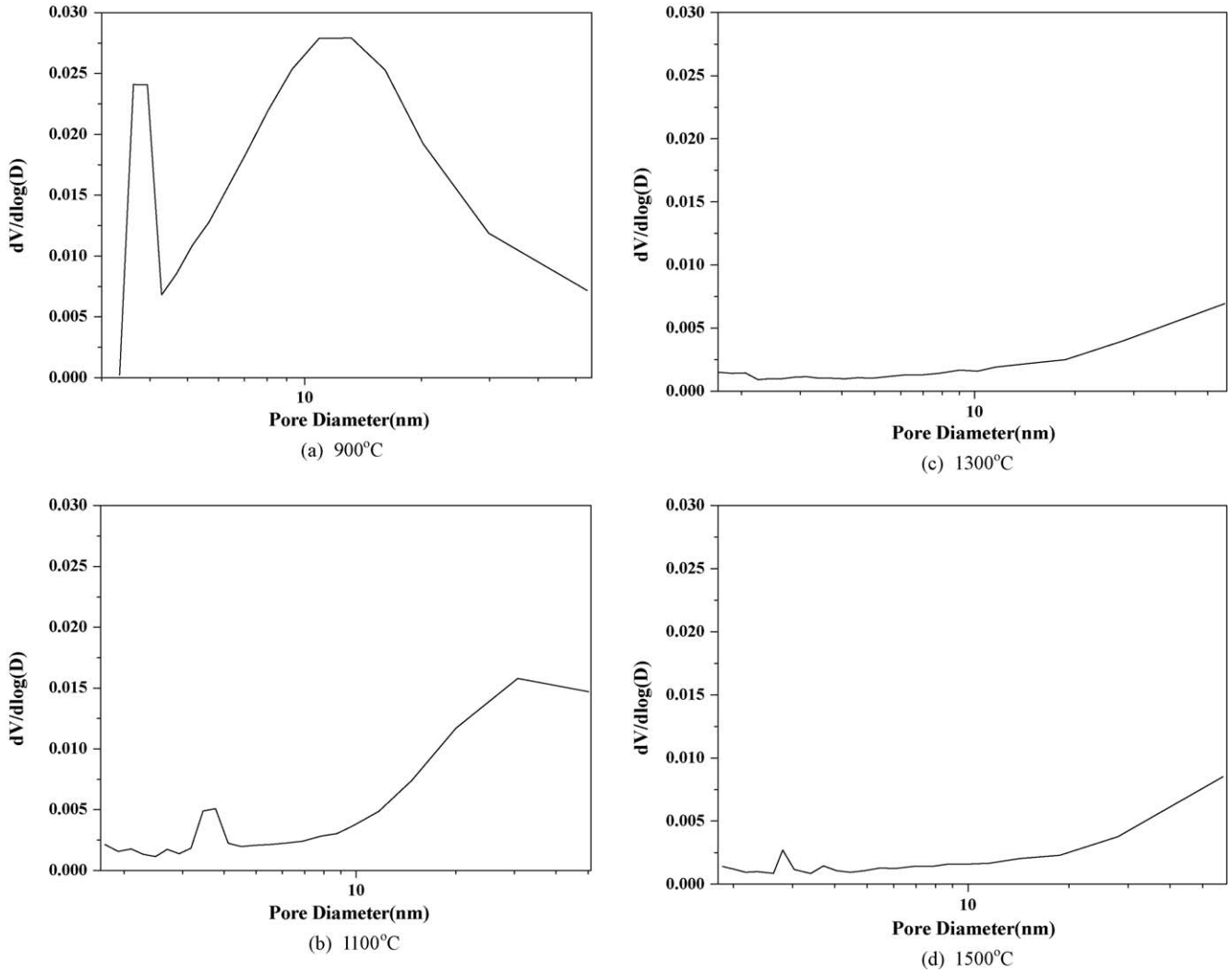


Fig. 3. Pore size distributions of the BNT powders directly prepared by spray pyrolysis.

short residence time of the powders inside the hot wall reactor. However, powders prepared at 1300 and 1500 °C exhibited a pure BNT phase. The high degree of mixing of the Ba, Nd, and Ti components produced BNT powders without impurity phases, even when the powders had short residence times inside the hot wall reactor. The residence times of the powders inside the hot wall reactor maintained at 1300 and 1500 °C were 3 and 2.8 s, respectively.

The morphologies of the powders prepared by spray pyrolysis at various temperatures are shown in Fig. 2. The concentration of the spray solution was 0.2 M. The powders prepared at temperatures below 1300 °C comprised particles with spherical shapes. However, the powders prepared at 1500 °C comprised non-spherical particles. Crystallization of the BNT phase destroyed the spherical shape of the particles. The BNT powders crystallized at high temperatures to form rod-like crystals. The pore structures of the spherical powders were affected by the preparation temperature. The pore size distributions of the powders prepared at various temperatures are shown in Fig. 3. The powders prepared at 900 °C contained mesopores with pore sizes between 3 and 50 nm. Mesopores smaller than 10 nm disappeared at preparation temperatures above 1100 °C. The pore volumes of the powders decreased with an increase in the preparation temperature up to 1300 °C. The pore volumes of the powders, as shown in Fig. 2(a)–(d), were 0.026, 0.020, 0.008, and 1.74 cm^3/g, respectively. A high pore volume was observed in case of BNT powders made of rod-like crystals prepared at 1500 °C. The BET surface areas of

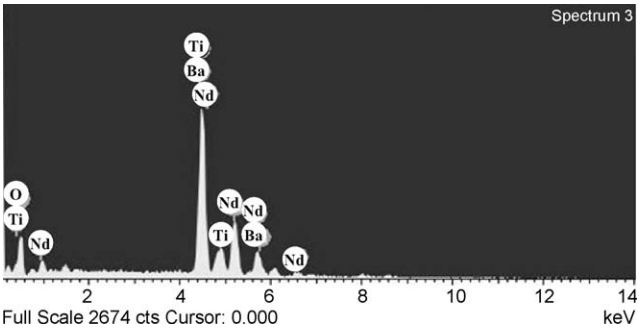


Fig. 4. EDX spectrum of the BNT powders directly prepared by spray pyrolysis.

Table 1
Compositions of the BNT powders prepared by spray pyrolysis.

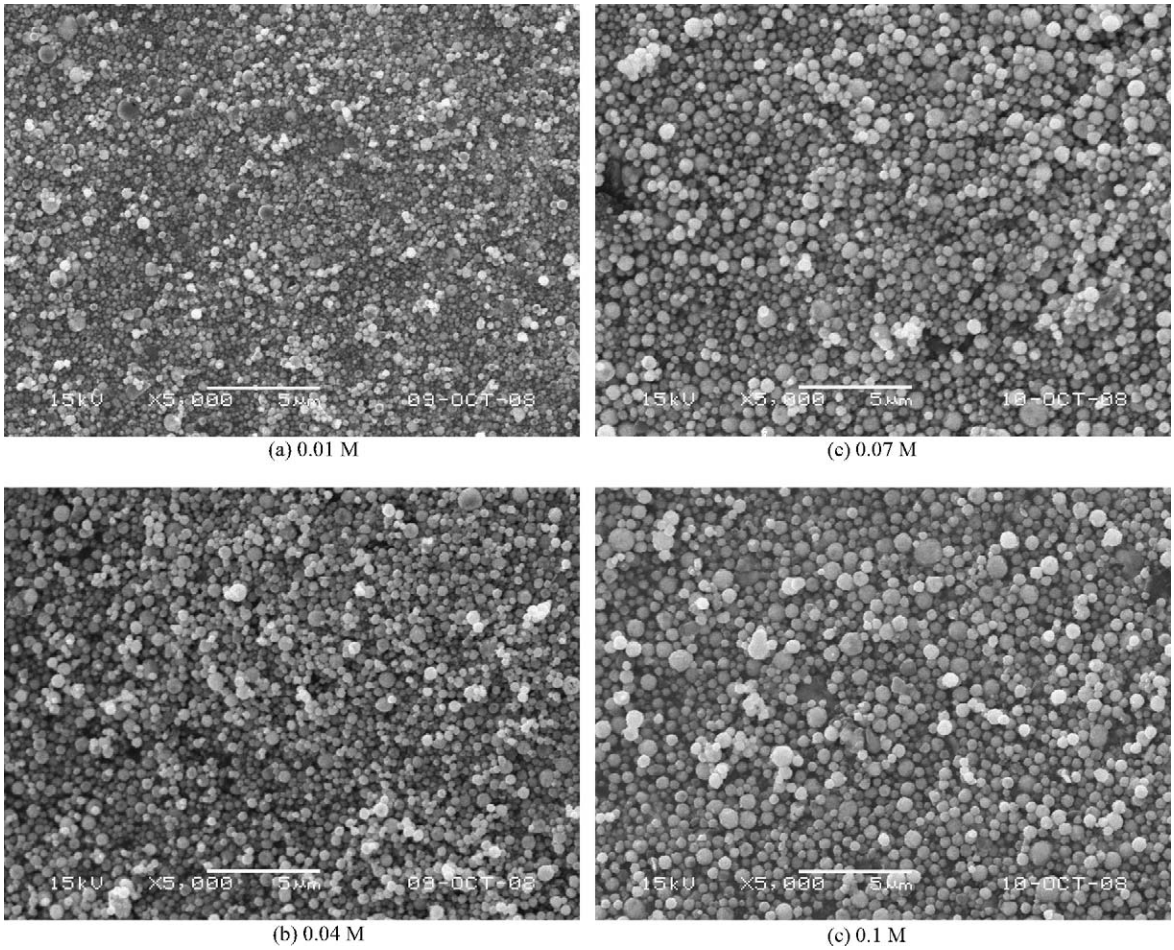
Element	Prepared powders (at.%)	Spray solution (at.%)
Ba	12.77	10
Nd	24.95	20
Ti	62.27	50
Ba/Nd/Ti	1.02/2/4.99	1/2/5

the powders, as shown in Fig. 2(a)–(d), were 7.6, 4.6, 2.4, and 2.5 m^2/g, respectively. Therefore, it was found that to obtain BNT powders with spherical shape, fine size, non-hollow structure, and low porosity by spray pyrolysis, the optimum preparation temperature was 1300 °C.

Fig. 4 shows the EDX spectrum of the BNT powders prepared at 1300 °C. The composition of the powders, as measured by the EDX spectrum, is shown in Table 1. The BNT powders had a composition similar to that of the spray solution. There was no compositional deviation of the BNT powders due to evaporation of some of the components of the powder at 1300 °C.

The sintering characteristics of the BNT powders were affected by the mean particle sizes of the powders. Therefore, controlling the mean particle size of the BNT powders is important to decrease the sintering temperature. One particle was formed from one droplet by conventional spray pyrolysis. Therefore, the mean size of the powders could be controlled by changing the concentration of the spray solution. Fig. 5 shows the morphologies of the BNT powders prepared at 1300 °C from spray solutions of various concentrations. An SEM image of the BNT powders prepared from a spray solution of 0.2 M is shown in Fig. 2(c). Irrespective of the concentration of the spray solution, the BNT powders had a spherical shape and did not aggregate characteristics. The mean size of the BNT powders increased with the concentration of the spray solution. Fig. 6 shows the size distributions of the BNT powders prepared from 0.01 and 0.2 M spray solutions. In this study, the maximum concentration of the spray solution was 0.2 M because of the low solubility of Ba. The mean size and geometric standard deviation of the BNT powder particles prepared from the 0.01 M spray solution were 0.23 μm and 1.26, respectively. However, for the 0.2 M spray solution, the corresponding values were 0.60 μm and 1.33.

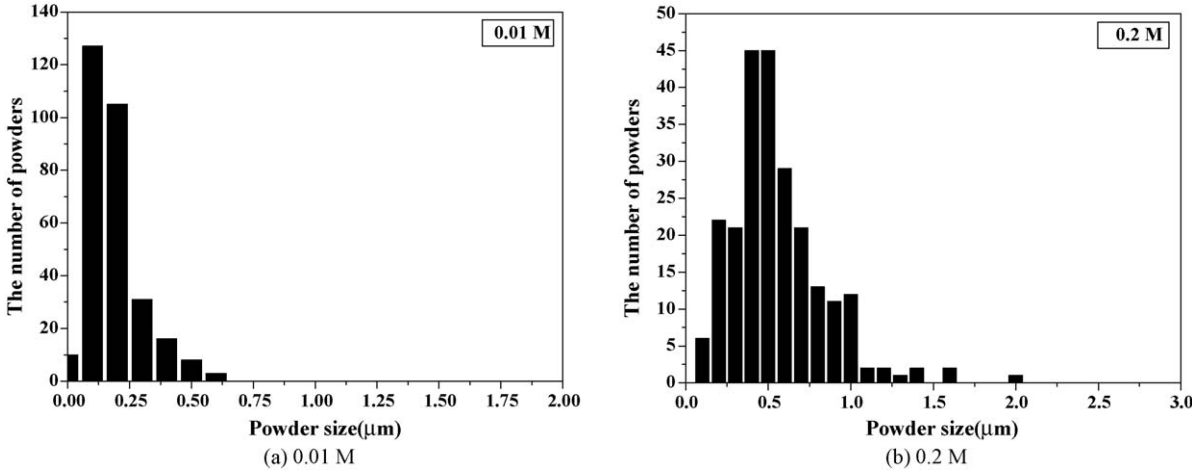
The sintering characteristics of the BNT powders directly prepared by spray pyrolysis at 1300 °C are shown in Fig. 7. The concentration of the spray solution was 0.2 M. Fig. 7 shows SEM images of the surfaces of pellets sintered at temperatures between 1000 and 1300 °C. The spherical shape of the powders



(a) 0.01 M (c) 0.07 M

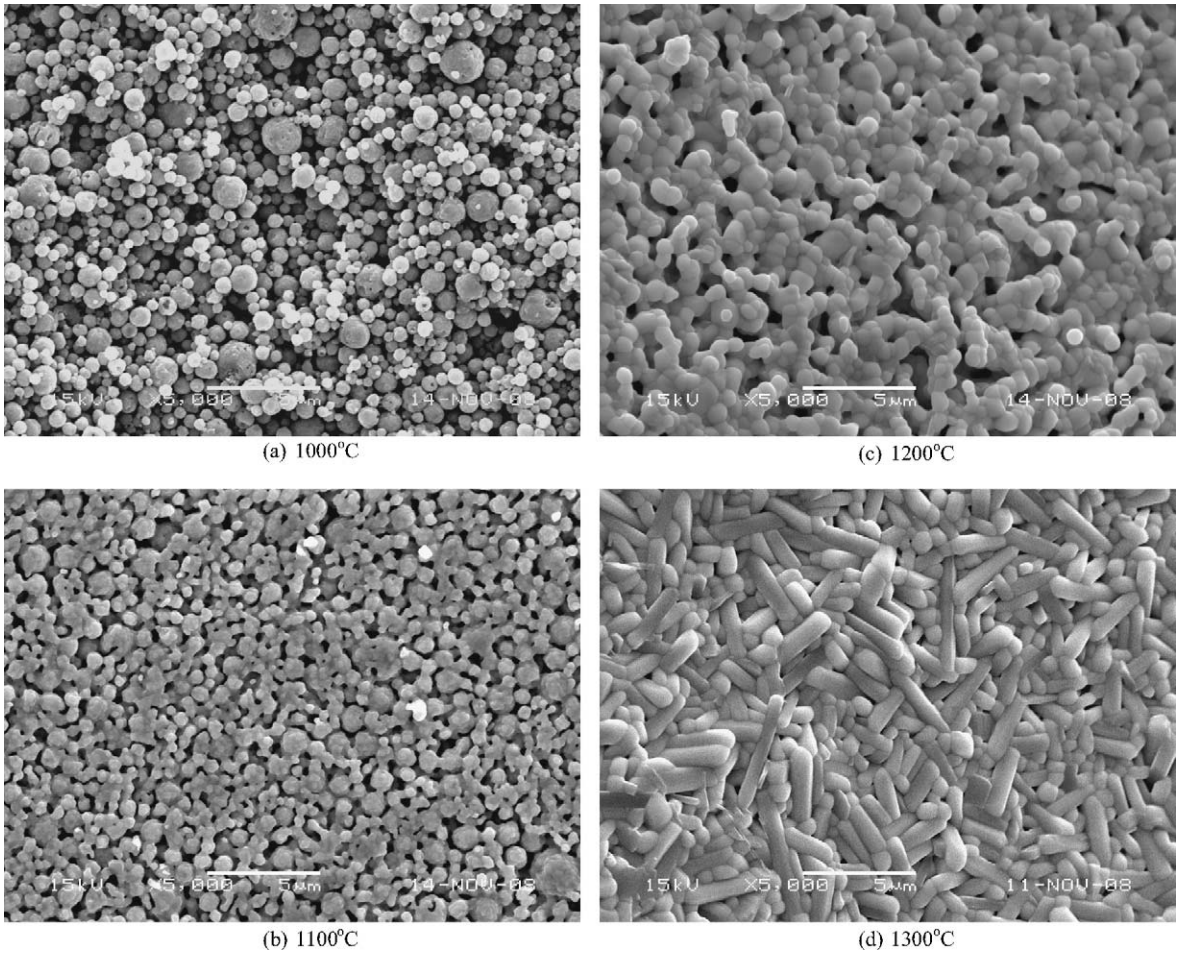
(b) 0.04 M (c) 0.1 M

Fig. 5. SEM images of the BNT powders directly prepared by spray pyrolysis from the spray solutions with various concentrations.



(a) 0.01 M (b) 0.2 M

Fig. 6. Size distributions of the BNT powders directly prepared by spray pyrolysis.



(a) 1000°C (c) 1200°C

(b) 1100°C (d) 1300°C

Fig. 7. SEM images of surfaces of the sintered BNT pellets.

was maintained after sintering at 1000 °C. At 1100 °C, bridge-like structures were formed between the powder particles. Crystal growth of the pellets occurred in accordance with the sintering temperatures. Pellets sintered at a temperature of 1300 °C exhibited a dense structure comprising rod-like crystals. The sample densities were measured by Archimedes' method. The relative densities of the pellets sintered at 1200 and 1300 °C were 97 and 94%, respectively.

4. Conclusions

The crystal structures and morphologies of $BaNd_2Ti_5O_{14}$ powders directly prepared by spray pyrolysis were investigated. To prepare $BaNd_2Ti_5O_{14}$ powders with a spherical shape, filled structure, and non-aggregation characteristics, the optimum preparation temperature was found to be 1300 °C. Sintering of fine $BaNd_2Ti_5O_{14}$ powders occurred at low temperatures.

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