Fabrication and characterization of fine-grained barium strontium titanate ceramics by the heterogeneous precipitation method

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Abstract The heterogeneous precipitation method has been successfully used to prepare $SrCO_3$ nanoparticle-coated BTO ($BaCO_3$ or TiO_2) powders by using PAA (polyacrylic acid) and NH_4HCO_3 as the dispersant and precipitator, respectively. Compared to the mixture obtained by the direct ball milling of the $BaCO_3$, $SrCO_3$ and TiO_2 powders during the conventional solid-state process, this coated structure is effective for the low temperature synthesis of barium strontium titanate (BST) powders. Sintering study of the powder synthesized by this method showed the dense and fine-grained BST ceramics could be obtained at a low sintering temperature. The grain size effect on the sensitivity of the dielectric constant vs. frequencies was discussed for the first time. Compared to the coarse-grained material, the fine-grained sample exhibits the better sensitivity of dielectric constant vs. frequency at ferroelectric state. It was shown that as the grain size decreased, the transition became diffuse, transition temperature (T_c) decreased and the dielectric constant increased.

Introduction

Ferroelectric BST ($Ba_{1-x}Sr_xTiO_3$, $0 < x < 1$) is a kind of favorable electronic materials for its high dielectric constant and alterable Curie temperature with composition [1]. It has been found that BST have many applications in electric devices such as piezoelectric sensors, dynamic random access memories (DRAM), microwave phase shifters and uncooled infrared detectors due to their high dielectric, ferroelectric, and pyroelectric properties [2–5]. Since all these properties are strongly related to the microstructure of the ceramics, high chemical purity and uniform microstructure are the most important features for BST ceramics. Furthermore, the outstanding dielectric property observed on $BaTiO_3$-based ceramics possessing small grains has motivated the interest for the synthesis of the fine-grained BST ceramics [6]. Conventional solid-state reaction including the direct ball milling of the $BaCO_3$, $SrCO_3$ and TiO_2 is not suitable for preparing BST materials with high performance as the calcinating and sintering temperatures are too high. Recently, in order to synthesize the fine-grained and high dense BST ceramics, lots of studies have focused on decreasing the two temperatures such as chemical fabrication of the nanoscaled BST powders [7–9] and liquid-phase sintering by adding sintering aids [10]. However, to our best of knowledge, there has not been an available chemical method on the synthesis of the fine-grained BST ceramics without the external drives such as hot-pressing sintering, microwave sintering and spark plasma sintering. The reason is that the nano-powders fabricated by the chemical methods, in general, are agglomerated which would lead to abnormal grain growth during sintering process. In order to decrease the grain size, some researchers synthesized the nanoscaled, low-density and fragile BST samples by sintering these nano-powders at a very low temperature. This is not proper because the mechanical and electrical properties of these quasi-ceramics are very poor. On the other hand, liquid-phase sintering by adding the sintering aids into the original powders may probably introduce the impurity and decrease the electrical properties of the materials.

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In recent years, the coating process with nanoparticles through the heterogeneous precipitation method has been widely used for the synthesis of the composite materials [11]. This process improves not only the sintering activity and densification, but also the different phase uniformity and mechanical properties of the sintered body [12, 13]. The heterogeneous precipitation method is based on the precipitation of the un-coexistent ions in a slurry on the surface of the heterogeneous particles serving as the cores, which forms the coated structure. The coated structure is very effective in decreasing the calcination temperature as the coated structure can make the reactants contact more closely and increase the reaction activity because the precipitates serving as the coating layer are generally nanoscaled. As the calcination temperature decreased, the powders obtained will be more homogeneous and fine-grained BST ceramics can be synthesized in a decreased sintering temperature. However, there is no report on the fabrication of BST ceramics using this method.

The purpose of present work is to synthesize the fine-grained BST ceramics with a relatively high density by a simple and innovative method. In the present paper, BTO powders coated with the $SrCO_3$ nanoparticles were successfully fabricated by the heterogeneous precipitation method. The forming process and microstructure of the coated structure are investigated in detail. In particular, the comparison of the heterogeneous precipitation method and conventional solid-state reaction in the synthesis of BST ceramics are studied. The grain size effects on the dielectric properties of the ceramics are also discussed. The final goal is to develop the fabrication science and technology of materials.

Experimental

The flowchart for the preparation of the $Ba_{0.70}Sr_{0.30}TiO_3$ powders by the heterogeneous precipitation method was shown in Fig. 1. $BaCO_3$ (99.0%), TiO_2 (99.44%), $Sr(NO_3)_2$ solution (1.0 M) in stoichiometric proportion and PAA (50%, 0.5–1.0 wt.% of the sum of the $BaCO_3$ and TiO_2 weight) as the dispersant were mixed in a polyethylene pot for 24 h using the agate balls as the grinding medium. After milling, the slurry was diluted with appropriate distilled water. Then, NH_4HCO_3 solution of 1.0 M in a same quantity to Sr^{2+} ions was slowly added to the homogeneous slurry with continuous stirring when a white precipitate was obtained. To ensure the completed precipitation, the pH value of the mixture was adjusted high enough by the NH_3H_2O solution. The reaction is shown in the following equation:

$$Sr(NO_3)_2 + NH_4HCO_3 + NH_3H_2O$$
$$= SrCO_3 \downarrow + 2NH_4NO_3 + H_2O \qquad (1)$$
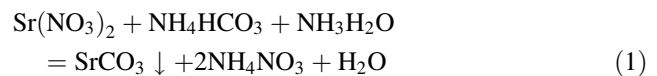
The precipitation reaction was instantaneous. Finally, the obtained precipitates were thoroughly washed with distilled water and ethanol and air-dried at room temperature led to the coated BTSO ($BaCO_3$, TiO_2 and $SrCO_3$) powders. The coated BTSO powders were calcined at 950–1,050 °C for 2 h to obtain the BST powders, which will be hereinafter referred to as the HP powders. The calcined powders were then pressed into the form of discs (diameter = 13 mm, thickness = 2 mm) using polyvinyl alcohol (5 wt.% with respect to the weight of the powders) as the binder and sintered at 1,280–1,330 °C for 2 h in air. This will be hereinafter referred to as the HPC ceramics.
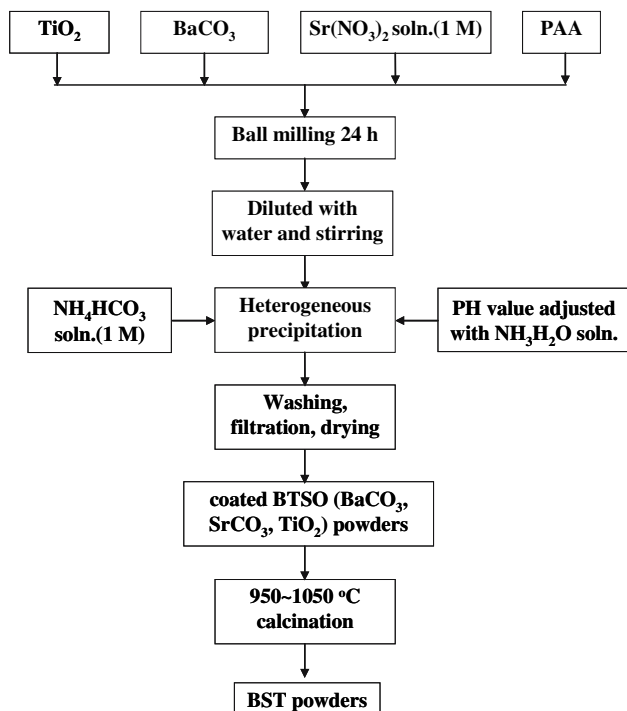
For comparison, conventional solid-state reaction process was also used to prepare the $Ba_{0.70}Sr_{0.30}TiO_3$ ceramics [14]. Single phase BST powders which will be hereinafter referred to the CS powders could be obtained at a calcination temperature of 1,150 °C. The sintering conditions were determined at 1,280–1,360 °C for 2 h. The ceramics obtained will be hereinafter referred to as the CSC ceramics. All of the raw materials used in this process were the same grade as that used in the heterogeneous precipitation method.

The microstructure of the coated BTSO powders was investigated by transmission electron microscopy (TEM) with energy dispersive spectroscope (EDS; Model JEM-2100F, JEOL, Tokyo, Japan). X-ray diffraction (XRD) with CuK_α radiation (Model Rax-10, Rigaku, Tokyo, Japan) was carried out to examine the phase of the BST powders. The densities of the sintered samples were measured according to the Archimedes principle. Scanning electron microscopy (Model JSM-6700F, JEOL, Tokyo, Japan) was used to observe the microstructures of the thermally etched samples. Average grain sizes were estimated by assessing the size of all grains in several micrographs. Dielectric properties were measured by an impedance analyzer (HP4284A) at 0.1, 1, 10, and 100 kHz using Ag as the electrode on both faces of the samples.

Results and discussion

Coated structure characterization

Figure 2 shows the coated structure of the BTSO powders prepared by the heterogeneous precipitation method. There is a uniform coating layer on the surface of the BTO powders. Figure 3 shows the EDS spectra of two kinds of coated structures which take $BaCO_3$ (Fig. 3a, c) and TiO_2 (Fig. 3b, d) serving as the cores, respectively. It can be

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┌──────┐ ┌───────┐ ┌──────────────────┐ ┌─────┐
│ TiO₂ │ │ BaCO₃ │ │Sr(NO₃)₂ soln.(1 M)│ │ PAA │
└──┬───┘ └───┬───┘ └────────┬─────────┘ └──┬──┘
   │         │              │               │
   └─────────┴──────┬───────┴───────────────┘
                    ▼
          ┌───────────────────┐
          │  Ball milling 24 h│
          └─────────┬─────────┘
                    ▼
          ┌───────────────────┐
          │   Diluted with    │
          │ water and stirring│
          └─────────┬─────────┘
                    ▼
┌──────────────┐ ┌───────────────┐ ┌───────────────────┐
│  NH₄HCO₃     │ │ Heterogeneous │ │ PH value adjusted │
│ soln.(1 M)   │→│ precipitation │←│with NH₃H₂O soln.  │
└──────────────┘ └───────┬───────┘ └───────────────────┘
                    ▼
          ┌───────────────────┐
          │     Washing,      │
          │ filtration, drying│
          └─────────┬─────────┘
                    ▼
          ┌────────────────────┐
          │coated BTSO (BaCO₃, │
          │SrCO₃, TiO₂) powders│
          └─────────┬──────────┘
                    ▼
          ┌───────────────────┐
          │   950~1050 ºC     │
          │    calcination    │
          └─────────┬─────────┘
                    ▼
          ┌───────────────────┐
          │   BST powders     │
          └───────────────────┘
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Fig. 1 Synthesis flowchart for the preparation of the $Ba_{0.70}Sr_{0.30}TiO_3$ powders by the heterogeneous precipitation method

seen that the peak intensity ratios of Sr/Ba and Sr/Ti at the edge field (Fig. 3a, b) are much higher than that in the center field (Fig. 3c, d). It is clear that this is a typical coated structure. The core is the $BaCO_3$ or TiO_2 particles with the coating layer of $SrCO_3$ nanoparticles. These observations show that the nuclei from the precipitation of the $SrCO_3$ in the slurry grow on the surface of the BTO particles instead of forming discrete precipitates. The surface of the BTO particles serves as the heterogeneous nucleation site.

Figure 4a shows the molecular formula of PAA. Figure 4b shows the forming process of the coated structure of BTSO powders. In order to prepare the coated BTSO

powders, the initial stable BTO slurry is important. PAA is an effective dispersant which has been widely used as a superabsorbent polymer, a scale inhibitor [15]. It can cover at the surface of BTO powders and prevent the sedimentations of the $BaCO_3$ and TiO_2 particles. As mixed and milled for 24 h, the stable BTO slurry could be easily obtained. Furthermore, PAA is a typical anion surface active agent with lots of carboxyls in the branched chain as the hydrophilic group. The Sr^{2+} ions were adsorbed on the surface of the BTO particles by this effective anion surfactant. When the precipitators were added into the slurry, the heterogeneous precipitation on the surface of BTO powders occurred. As a result, the coated structure formed.

It seems that most $SrCO_3$ particles grow on the surface of BTO powders in some certain orientations. This offers some information to the orientated growth of nanoparticles. But it is not the interest of this paper.

Powders characterization

Figure 5 shows the X-ray diffractions of the BST powder synthesized at different temperature. It can be seen in Fig. 5a that the characteristic reflections corresponding to perovskite phase appear after the powders were calcined at 950 °C. There were two weak lines appearing at $2\theta = 28.8°$ and 29.3° which may be attributed to some intermediate phase formed during the calcination of the powders in Fig. 5b. At high temperature these peaks disappeared and a pure phase was obtained at 1,050 °C (Fig. 5c) which is much lower than that of the conventional solid-state reaction. Compared to the mixture obtained by the direct ball milling of the $BaCO_3$, $SrCO_3$ and TiO_2 powders during the conventional solid-state process, this coated structure of BTSO powders is effective for the low temperature synthesis of BST powders as this structure can make the reactants contact more closely and increase the reaction activity because the $SrCO_3$ particles serving as the coating layer are nanoscaled.
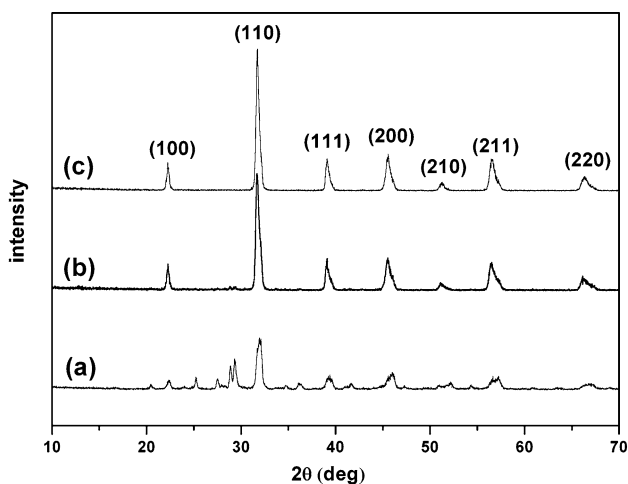
Fig. 2 TEM images of the powders with $SrCO_3$ nanoparticles coated on the surface of the BTO particles
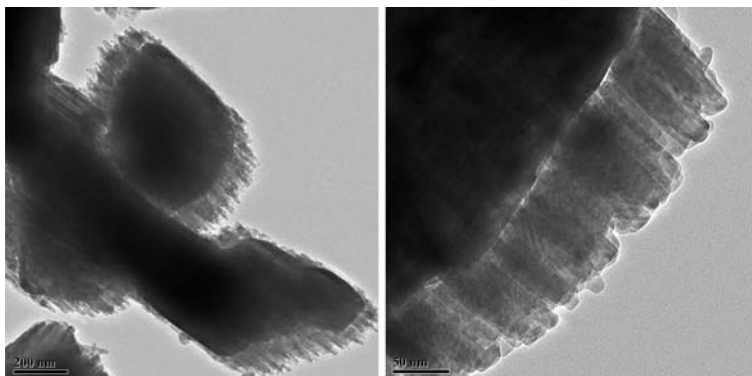
Fig. 3 EDS spectra of two kinds of coated structures: BaCO$_3$ as the core, (**a**) at the edge field, (**c**) at the center field; TiO$_2$ as the core, (**b**) at the edge field, (**d**) at the center field
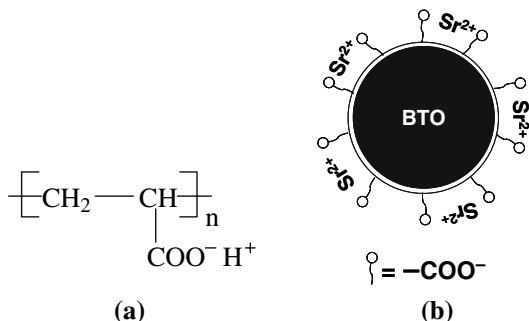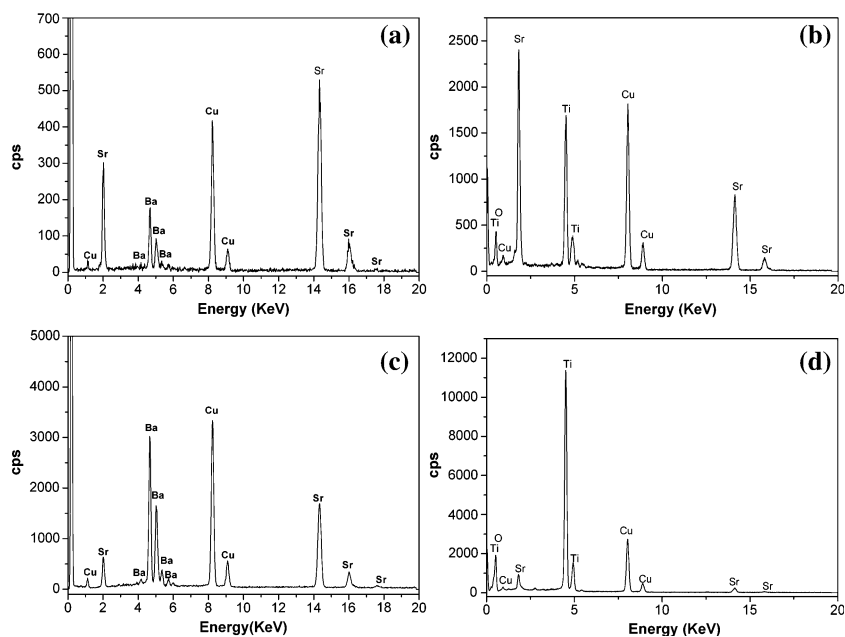
**Fig. 4** The molecular formula of PAA (**a**). The forming process of the coated structure (**b**)

Fig. 5 X-ray diffractions of the BST powder synthesized at different temperatures (**a**) 950 °C, (**b**) 1,000 °C, (**c**) 1,050 °C

## Sintering behavior and microstructure

Figure 6a, b show the densities of the HPC and CSC ceramics. The densities of the BST ceramics sintered from the HP powders increase from 92.35% at 1,280 °C to a maximum of 95.33% at 1,320 °C. However, in order to achieve densification, the sintering temperature should be increased to 1,350 °C by using the CS powders. The sintering behavior of the BST powders reveals that the powders obtained by the heterogeneous precipitation method could be sintered to a high density at a relatively lower temperature than that of the conventional solid-state reaction, which implies the better sintering behavior of the HP powders. These density values assume a theoretical density of 5.763 g cm^{-3}, as calculated from refined unit cell parameters.

The SEM images of the polished and thermally etched surfaces of BST ceramics are shown in Fig. 7. Figure 7b shows that the grains sintered from the CS powders are very coarse and unhomogenized. The grain size is in the range of 3–7 μm with an average grain size of 4.07 μm. Meanwhile, the grains of the ceramics (Fig. 7a) sintered from the HP powders are fine and uniform. Most of them are pentagonal and hexagonal. The grains is in the size range of 0.8–2.5 μm with an average grain size of 1.34 μm. This can be attributed to the better sintering behavior of the HP powders than that of the CS powders. From Figs. 6, 7, we can conclude that the heterogeneous precipitation method is an effective process for the synthesis of the dense and fine-grained BST ceramics.

Fig. 6 The densities as a function of temperature sintered from (**a**) HP powders, and (**b**) CS powders
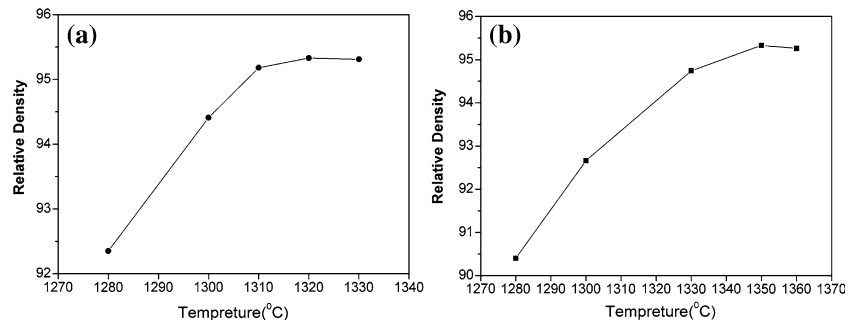
Fig. 7 SEM images of the polished and thermally etched surfaces of BST ceramics sintered from (**a**) HP powders at 1,320 °C, and (**b**) CS powders at 1,350 °C
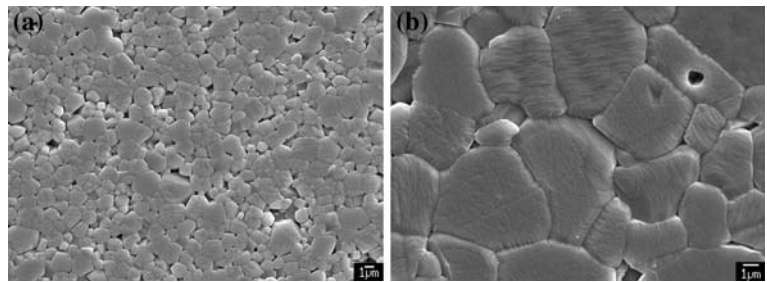

Dielectric properties

Figure 8a, b show the variations of the dielectric constant with temperature under several frequencies for the HPC and CSC samples having different grain sizes of 1.34 and 4.07 μm, respectively. It can be seen that at the ferroelectric state, both of the dielectric constants of the two samples decreased when the frequency increased. But the decrease of the dielectric constant of the fine-grained sample was more than that of the coarse-grained one. This implies the better stability of dielectric constant vs. frequency of coarse-grained sample, which can be attributed to the different hopping height of the off-center Ti^{4+} ions in the samples of different grain sizes. Zhang [16] has shown that as the grain size decreased, the unit-cell volume and height of the potential barrier decreased. The decrease of the height will facilitate the hopping of Ti^{4+} ion among the potential wells, which lead to the better sensitivity of dielectric constant vs. frequency of fine-grained samples. At paraelectric state, this effect disappeared, thus the

dielectric constant almost did not vary as the frequency changed. In Fig. 8, it should be noted that in the fine-grained HPC ceramics, there was an evident diffuse phase transition and the T_c, tetragonal (ferroelectric) to cubic (paraelectric) transition temperature, decreased about 0.6 °C compared to that of the coarse-grained CSC samples. This could be attributed to the increased internal stress which helped the fine-grained material overcome the energy barrier of the transition [17]. As the grain size decreased, the internal stress increased [18]. Samara [19] has shown the transition temperature decreasing with hydrostatic compression in ceramic $BaTiO_3$, and has interpreted this as a stabilization of the cubic phase, with decreased volume under hydrostatic pressure, because the tetragonal to cubic transition accompanies a small decrease in unit-cell volume and the pressure favors the smaller volume. Furthermore, whatever phase the BST ceramics was, the dielectric constant increased when the size of the grain decreased from 4.07 to 1.34 μm. At ferroelectric state, this grain size effect could be attributed to the total effects of

Fig. 8 Dielectric constant as a function of temperature at various frequencies for BST ceramics: (**a**) HPC samples; (**b**) CSC samples
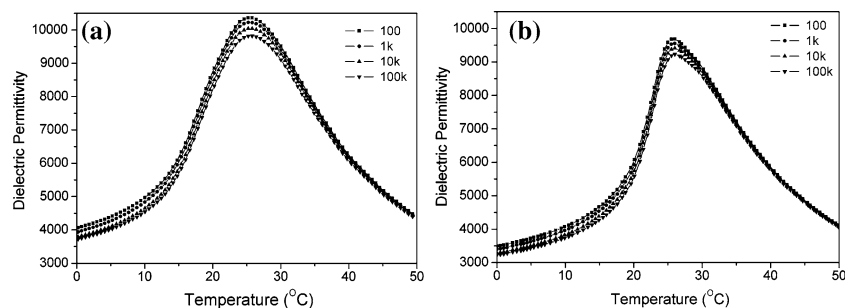
the internal stress, grain boundary and domain wall contributions to the dielectric constant, which was similar to the result of $BaTiO_3$ that has been discussed by Shaikh [18] in more detail. At paraelectric state, the behavior of the dielectric properties can be depicted by the Curie–Weiss law [20], describing the temperature decay of permittivity in the paraelectric state:

$$\varepsilon_r = C/(T - T_0).$$

Fit of experimental data to this equation shows that C (Curie constant) is considerably decreased from 1.614×10^5 to 1.458×10^5 in coarse-grained samples. Meanwhile, the T_0 (Curie–Weiss temperature) was almost equal to each other. In this case, the decreased dielectric constant at paraelectric state with increasing grain size could be easily understood from the Curie–Weiss law because the value of C decreased with increasing grain size.

Conclusions

Coated BTSO powders were successfully fabricated by the heterogeneous precipitation method, which was very effective for the low temperature synthesis of BST powders. The pure-perovskite BST powders could be obtained at 1,050 °C. The fine-grained BST ceramics with an average grain size of 1.4 μm were obtained by sintering these powders at 1,320 °C. Compared to the relatively coarse-grained material, the fine-grained sample exhibits the better sensitivity of dielectric constant vs. frequency. Dielectric data shows a broad phase transition and increased value of ε due to the fine grains. This novel method, requiring simple raw materials and processes, will offer an available and practical scheme for the preparation of fine-grained BST and other electron ceramics.

References

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