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Effect of silica sintering additive on the sintering behavior and dielectric properties of strontium barium niobate ceramics

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Abstract

$Sr_{0.5}Ba_{0.5}Nb_2O_6$ powders were prepared in the partial coprecipitation method. Using amorphous SiO_2 as the sintering additive, $Sr_{0.5}Ba_{0.5}Nb_2O_6$ ceramics were sintered at different temperatures and the effects of the additive on the sintering behaviors and dielectric properties were studied. The phase structure, microstructure and dielectric properties of the samples were investigated in X-ray diffraction (XRD), SEM and LCR analyzer respectively. The results indicated that the amorphous SiO_2 additive could accelerate the pore elimination, shorten the sintering time and enhance the density for $Sr_{0.5}Ba_{0.5}Nb_2O_6$ ceramics. The well development of microstructure promoted by the additives can result in the improvement of the dielectric constant and the weakening of the relax behavior. With the help of the additive of 1.5 wt.%, the relative density of the sample sintered at 1300 °C only for 2 h can reached 94.3% and the dielectric constant was up to 4322.

Keywords: Strontium barium niobate (SBN); Partial coprecipitation; Sintering additive; Sintering behavior; Dielectric property

1. Introduction

Strontium barium niobate ($Sr_{1-x}Ba_xNb_2O_6$, $0.25 \leq x \leq 0.75$, abbreviated as SBN) has the tetragonal tungsten bronze (TTB) structure. It has drawn much attention as a lead-free electroceramic, due to its excellent pyroelectric,[1,2] electro-optic[3,4] and photo-refractive properties.[5,6] However, the high-density SBN ceramics are difficult to obtain because of the abnormal grain growth.[7] Researches have been done to improve the density of SBN in many ways, such as dual-stage sintering,[8] hot pressing,[9] reaction singtering[10] and atmosphere sintering[11] etc. For instance, the relative density of SBN synthesized by partial coprecipitation method[12] could reach 92.25% by sintered at 1300 °C for more than 24 h. With high purity starting powders, SBN sample with a high relative density (~98.7%) could be obtained by reaction sintering in oxygen atmosphere.[11] Although the two ways mentioned above had effectively improved the density, they both increased the complexity of fabrication to some extent. The first one required twice long-time grinding and a long sintering time, while twice precursor calcinations and a controlled atmosphere were essential to the second.

In this paper, amorphous SiO_2 was introduced as the sintering additive to improve the density of SBN, and SBN precursor used in this process was synthesized by partial coprecipitation method. Our concern was the effect of sintering additive on the sintering behavior, microstructure and dielectric properties of SBN.

2. Experiment

The $Sr_{0.5}Ba_{0.5}Nb_2O_6$ powders were prepared in the partial coprecipitation method. $SrCl_2{\cdot}6H_2O$ (99.5%, Tianjin Dibo Chemicals, China), $BaCl_2{\cdot}2H_2O$ (99.5%, Shanghai Aibi Chemicals, China) and Nb_2O_5 (99.5% Shanghai Chemical Reagent, China) were used as starting materials. Nb_2O_5 was wet-ball-milled in agate jars for 4 h. 2% citric acid solution was added to decrease segregation. Aqueous solution of $(NH_4)_2CO_3$ was added dropwise in a light excess after the addition of aqueous solution of $SrCl_2$ and $BaCl_2$ with continuously mechanical stir. Then $NH_3{\cdot}H_2O$ was added to adjust pH to a value of 10. The precipitate was filtered, washed with water and alcohol subsequently after the overnight settlement, and was dried in air at 80 °C. The dried powders were calcined at 1150 and

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1200 °C respectively in air for 2 h. Then the powders calcined at 1150 °C were mixed with 0.5, 1.0 and 1.5 wt.% amorphous SiO_2 respectively (abbreviated as SBN0.5, SBN1.0 and SBN1.5 respectively). After that, the mixed powders were uniaxially pressed in a die of 12 mm diameter at a pressure of 200 MPa. The green compacts were sintered in air at 1250, 1280, 1300 and 1320 °C for 2 h respectively and the heating rate was maintained at 2.5 °C/min.

The powders morphology was studied by the scanning electron microscopic (SEM) techniques (JEOL Company, Japan; JSM-6390LV). The densities of the samples were measured by the Archimedes method. The phase composition was analyzed by XRD (Model D/max-rB, Japan) using Cu Kα ($\lambda = 1.54056$ Å). The scan rate of 2θ was kept at 5°/min. The samples were well polished and sputtered gold electrodes for dielectric properties measurements and SEM investigation. The dielectric constants were measured by LCR meter (TH2819-GDS-100) from −20 to 150 °C in different frequencies.

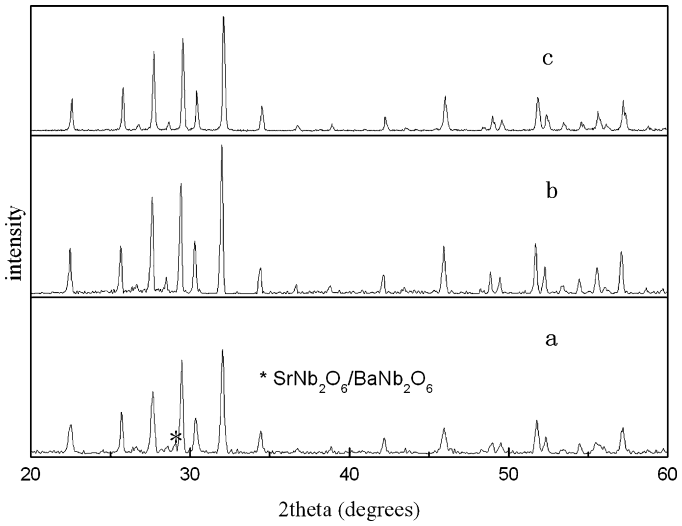

Fig. 1. X-ray diffraction patterns of (a) powder calcined at 1150 °C and (b) powder calcined at 1200 °C and (c) ceramic sintered at 1250 °C from powder (a).

3. Results and discussion

3.1. Characterization of powder

The X-ray diffraction patterns of powders are shown in Fig. 1. As shown in Fig. 1, the crystal phases of SBN have been completely formed at 1150 °C (see Fig. 1(a)), though there are few interim phases ($SrNb_2O_6$ or $BaNb_2O_6$), which disappear when the calcining temperature increases to 1200 °C (Fig. 1(b)). The intensities of diffractive peaks at 1200 °C are obviously stronger than those at 1150 °C. It is due to the increase of the crystallization level of the tungsten bronze phase at higher calcining temperatures. Compared to the powders calcined at 1200 °C, the powders calcined at 1150 °C have a larger surface energy and are more easily sintered at the same sintering conditions. Thus they are selected as the starting powders. Fig. 1(c) shows that their interim phases have disappeared after the sample was sintered at 1250 °C for 2 h.

Fig. 2(a) and (b) shows the SEM images of the synthesized precursor powder before and after calcination at 1150 °C respectively. A larger Nb_2O_5 particle (∼5 μm) is selected to observe the morphology of the precipitates on the particle surface before calcination. As shown in Fig. 2(a), some fine precipitates of $BaCO_3$ and $SrCO_3$ were evenly attached on the surface of Nb_2O_5, which is consequently favorable for the solid phase reaction in the heat treatment process.

As shown in Fig. 2(b), the particle sizes range about from 0.5 to 1.5 μm after calcination. The mean diameter of the powders is obviously smaller than the sizes of those before calcination. This result illustrates that the particle sizes can be reduced dramatically after calcination because of the solid reaction between the precipitates and Nb_2O_5 particles.

3.2. Densification behavior

Fig. 3 shows the sintering densification behavior of SBN with different sintering additive amounts at various sintering temperatures. The figure indicates that the densities of the samples have close relation with the sintering temperature and the additive amount.

As shown in Fig. 3, the density of pure SBN maintains a low level below 1300 °C, although it increases rapidly when the

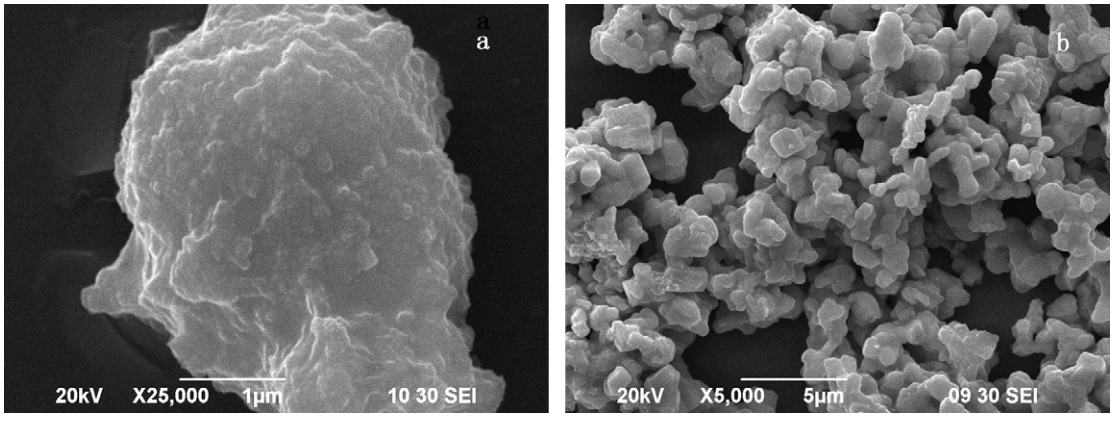

Fig. 2. The SEM images of the synthesized precursor powder (a) before and (b) after calcination at 1150 °C.

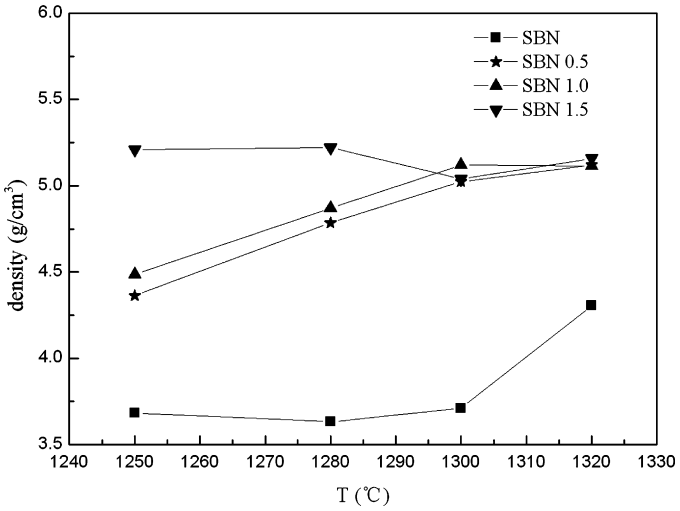

Fig. 3. The densities of SBN added with different sintering additive amounts at different temperatures.

sintering temperature is close to 1320 °C and is still much less than that of the samples with sintering additives. The density of pure SBN sintered at 1320 °C for 2 h only reaches to 4.3 g/cm^3 (∼79.43% Dth). When the amorphous SiO_2 was introduced as the sintering additive, the things were changed.

The densities of SBN0.5 and SBN1.0 increase rapidly until the sintering temperature reaches to 1300 °C, but there is only a slight increase in density when the temperature rises from 1300 to 1320 °C. The densities of SBN0.5 sintered at 1320 °C, SBN1.0 sintered at 1300 °C and SBN1.5 sintered at 1280 °C all for 2 h, can reach to 94.5, 94.4 and 96.3% respectively. The result is similar with that of P.K. Patro et al.,[12] in which the density of the sample sintered at 1300 °C for 24 h stands at 92.3%. Such long sintering time not only incurs higher preparation cost but also brings to abnormal grain growth easily. This has supported the view that the sintering additive can remarkably shorten the sintering time and enhance the density. In the sintering process, the amorphous SiO_2 can generate a uniform liquid phase by its own or with other impurities on the grain boundary. The uniform liquid phase can accelerate the mass transfer process and restrain the abnormal grain growth resulting from localized liquid phase produced.[8,13]

Fig. 3 also shows that the additive amount has significant effect on the densities of SBN. When the sintering temperature is below 1300 °C, the densities of SBN increase dramatically with the increase of the additive amounts. However, the effect is not obvious when the sintering temperature rise to 1300 °C and above. It is also worth noticing that the sintering temperature is not a key factor in densification when the additive amount is up to 1.5 wt.%. It means that 1.5 wt.% SiO_2 is sufficient for the SBN densification and the sintering range of the ceramics could be broadened obviously.

3.3. Microstructure

The SEM images of the samples of pure SBN, SBN0.5, SBN1.0 and SBN1.5 sintered at 1300 °C for 2 h are shown in

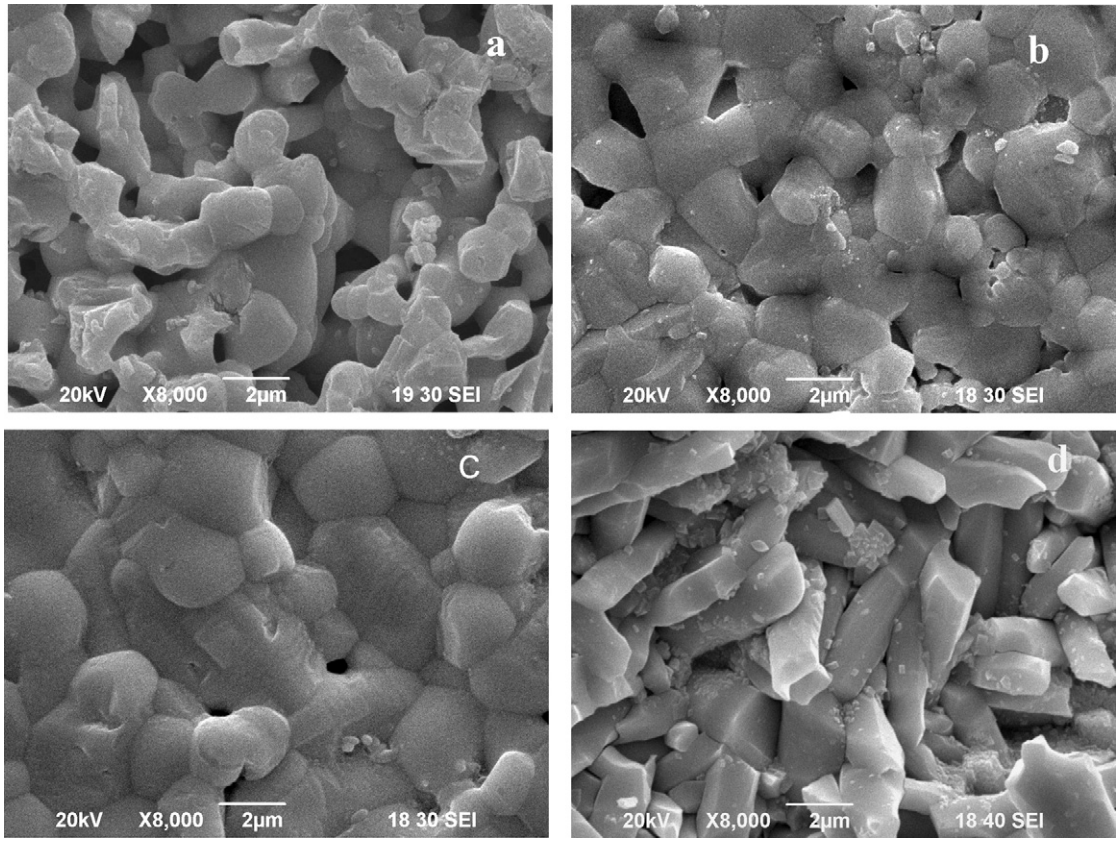

Fig. 4. The SEM images of the samples of pure SBN (a), SBN0.5 (b), SBN1.0 (c) and SBN1.5 (d) sintered at 1300 °C for 2 h.

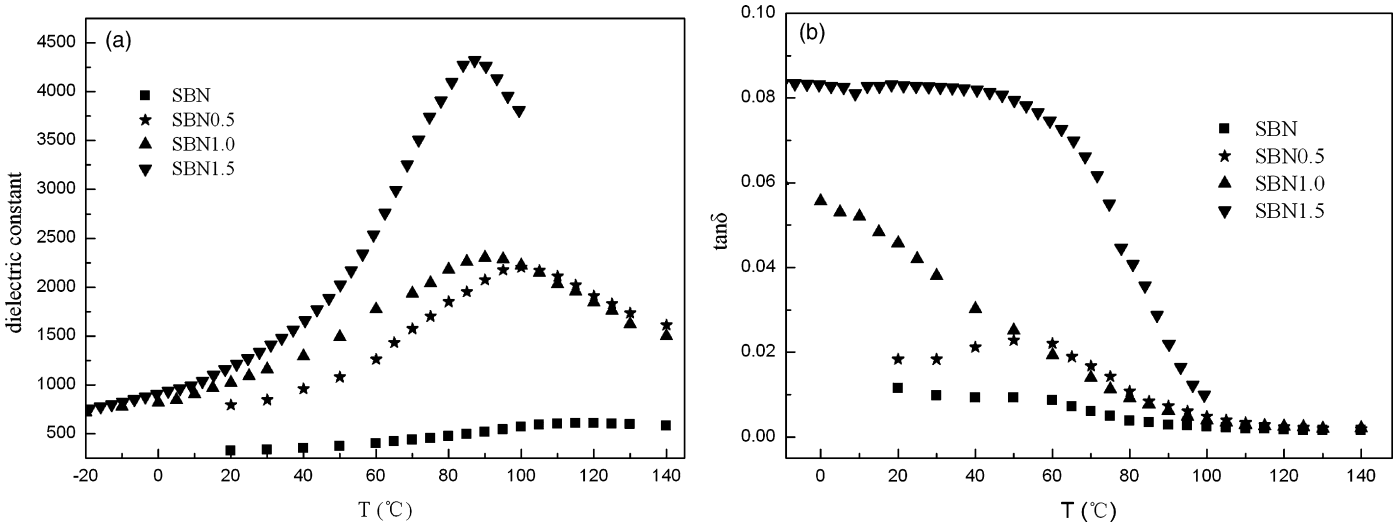

Fig. 5. The effect of the sintering additive on the dielectric constant (a) and loss (b) of the samples sintered at 1300 °C in 10 kHz.

Fig. 4(a)–(d) respectively. Fig. 4(a) shows a high porosity in pure SBN sample whose grain sizes range from 1.5 to 2.0 μm. Most of grains appear irregularly spherical. It illustrates that the pore elimination is just in initial stage of sintering. As shown in Fig. 4(b), the porosity decreases dramatically and the grain shapes tend to be regular. It indicates the pores have been mostly eliminated and the grains begin to grow, whose sizes range from 1.5 to 2.5 μm. Compared with Fig. 4(b), the grain sizes in Fig. 4(c) become larger and the grain shape becomes more regular. The pore elimination draws to a close.

As shown in Fig. 4(d), the unidirectionality in grain growth is observed and the grains appear elongated with the average size of 3.5 μm, which causes loose packing of the grains and a light decrease of the density of SBN1.5 sample sintered at 1300 °C (see Fig. 3). The results indicate that the amorphous SiO_2 could effectively speed up pore elimination, improve the grain growth and shorten the sintering time. The abnormal grain growth can be restrained to some extents.

3.4. Dielectric properties

Fig. 5(a) shows the effect of the sintering additive on the dielectric constants of the samples sintered at 1300 °C in 10 kHz. As shown in Fig. 5(a), the dielectric constants of pure SBN sample appear very low due to inadequate sintering and high porosity (see Fig. 4(a)). Although the densities of the samples with different additive amounts sintered at 1300 °C are similar (see Fig. 3), the dielectric constants increase prominently with the increase of the additives own to the deferent microstructure. The maximum dielectric constant can reach a high value (∼4322) for SBN1.5, which is much higher than the results of previous researches[9,12,14,15] but is lower than that of the sample prepared by textured grain growth techniques.[16] We also can conclude from Fig. 4(a) that the Curie temperatures (T_c) shift to lower temperature and the relax behavior become weaker with the increase of additive. The results mentioned above indicate that microstructure, especially the grain size, has a significant

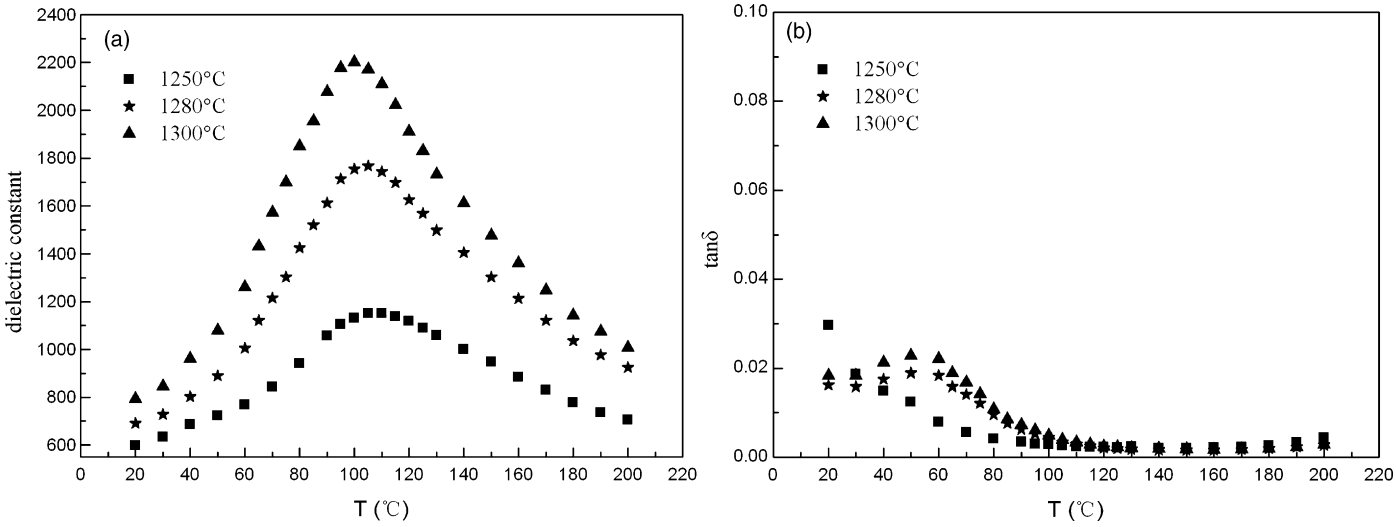

Fig. 6. The effects of the sintering temperature on the dielectric constant (a) and on the dielectric loss (b) for SBN0.5 in 10 kHz.

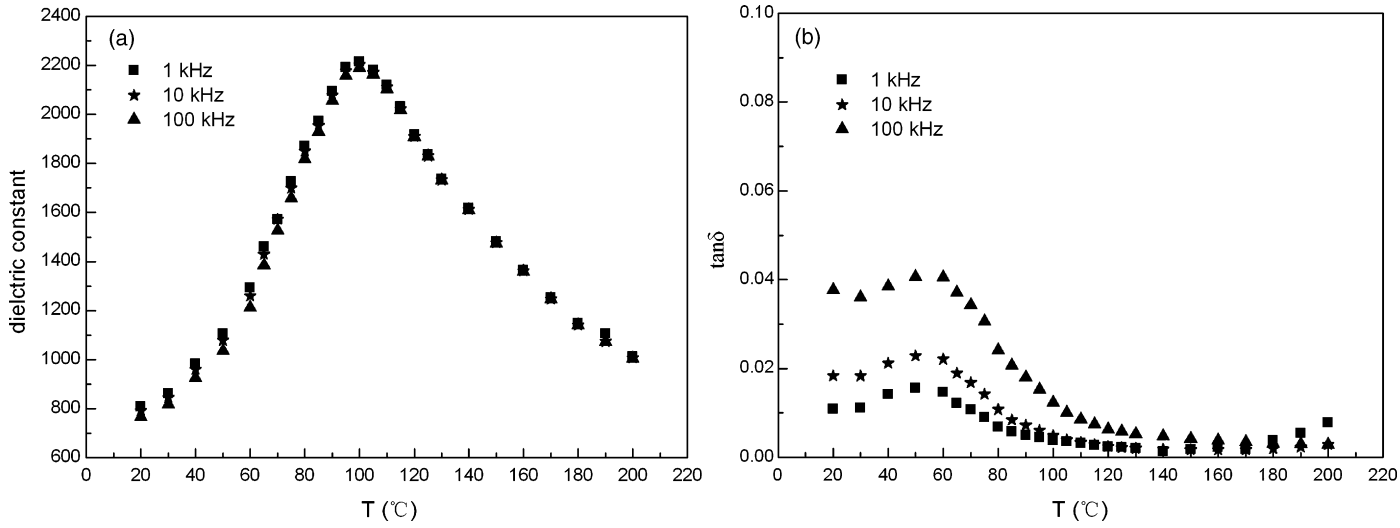

Fig. 7. The effects of the applied frequency on the dielectric constant (a) and loss (b) of SBN 0.5 ceramics sintered at 1300 °C for 2 h.

effect on the dielectric property and the larger grain size as well as the smaller pores can improve the dielectric constant (see Fig. 4(c) and (d)). The sintering additive can enhances the diffusion coefficient on the grain boundary, speeds up the grain boundary movement and enlarges the grain sizes. In return, the larger grains improve the dielectric constants, weaken the degrees of diffuse phase transition (DPT) and decrease the Curie temperatures (T_c).

Fig. 5(b) shows the effect of the sintering additive on the dielectric loss of the samples sintered at 1300 °C in 10 kHz. The dielectric losses increase significantly with the increase of the additive, which may be concerned with the increasing glass phase in the grain boundary and grain unidirectional growth (see Fig. 4(d)). But the values of the dielectric loss are always below 0.1. In addition, the dielectric loss sharply declines when the testing temperature enters the Curie zone.[13] The reason may be that the ionic displacement polarization plays a more important role rather than the dipole polarization after phase transition and that the glass phases in the grain boundary have less effect on the displacement polarization. It can be also found that the peak values of dielectric constants and losses are not at the same temperature points, which is one of typical features of the diffuse phase transition.

Fig. 6(a) and (b) shows the effects of the sintering temperature on the dielectric constant and loss of SBN0.5 in 10 kHz. As shown in Fig. 6, the dielectric constants rise sharply and the T_c declines slightly with the increase of sintering temperature, which is also due to the increase of the densities and grain sizes. The loss does not vary so much as that shown in Fig. 5(b) with the various sintering temperatures and stay at a very low level (less than 0.04). The losses at the room temperature remain at about 0.01 (Fig. 6(b)). These results show the amount of SiO_2 is one of main factors that affect the dielectric loss.

Fig. 7(a) and (b) shows the effects of the applied frequency on the dielectric constant and loss of SBN0.5 ceramics sintered at 1300 °C for 2 h. The peak values of dielectric constant decrease slightly (Fig. 7(a)) and the tan δ values enhance consequently Fig. 7(b)) as the frequency increases. The maximum losses are 0.015, 0.02 and 0.04, at 1, 10 and 100 kHz respectively, which are much lower than that of other researchers.[9] It shows that the appropriate amount of sintering additive does not affect the dielectric loss dramatically.

4. Conclusions

Introducing amorphous SiO_2 as sintering additive is an effective way to improve the sintering behavior and dielectric constant of SBN ceramics. The sintering additive can remarkably accelerates the pore elimination, improve the grain growth and advance the dielectric properties of the SBN ceramics. For SBN1.5 ceramics sintered at 1300 °C only for 2 h, the density can reach ~5.11 g/cm^3 (~94.3% Dth) and the dielectric constant is up to 4322, while the dielectric loss remains below 0.1. The Curie temperatures shift to lower temperature and the relax behavior weakens with the increase of SiO_2 additive.

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