



Effects of Kaolinite addition on the densification and dielectric properties of BaTiO₃ ceramics

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ABSTRACT

Commercial Kaolinite was employed as sintering aid to reduce the sintering temperature of BaTiO₃ ceramics. The effects of Kaolinite content and sintering temperature on the densification, microstructure and dielectric properties of BaTiO₃ ceramics have been investigated. The density characterization results show that the addition of Kaolinite significantly lowered the sintering temperature of BaTiO₃ ceramics to about 1200 °C. XRD results show BaTiO₃ ceramics with a low amount of Kaolinite exhibited perovskite structure, but 10.0 wt% Kaolinite additions resulted in the formation of a secondary phase, BaAl₂Si₂O₈. BaO–TiO₂–Al₂O₃–SiO₂ glass phase was formed and improved the average breakdown strength of ceramics, which was supported by SEM–EDX results. The Kaolinite content had shown a strong influence on the dielectric constant and the diffuse transition. BaTiO₃ ceramic with 4.0 wt% Kaolinite addition possessed well temperature stability of dielectric constant.

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1. Introduction

As one of the most important ferroelectric materials, BaTiO₃-based ceramics are widely used in electronic devices such as multilayer ceramic capacitors (MLCCs) [1–3] and positive temperature coefficient resistors (PTCRs) [4,5]. However, BaTiO₃ ceramics are usually sintered at temperatures above 1350 °C. Therefore, it is required to develop capacitor materials which can be fully densified at a low sintering temperature. Recently, numerous researches have been applied to the sintering of BaTiO₃-based ceramics for the purpose of lowering the sintering temperature and optimizing properties of the components and devices as well [6–13].

In general, the sintering temperature of BaTiO₃ ceramics can be lowered through methods as following. Firstly, chemical processing [6,7] such as sol–gel method can obtain a high degree of chemical uniformity, make the mixture of reactants at the molecular level, and can obtain grains from nanometer to micrometer-size, thereby reducing the sintering temperature. Secondly, the sintering temperature can be reduced by using small grain and homogenous BaTiO₃ [8,9], particularly for the superfine powder, since smaller particle has higher surface energy. Moreover, adding glass or oxides as sintering aids is considered to be an effective method. Several glass powders such as ZnO–B₂O₃–SiO₂ [6,10], BaO–B₂O₃–SiO₂ [11], and BaO–SiO₂ [12] compositions have been used to decrease the sintering temperature of BaTiO₃ ceramics. Oxides [13] such as

Bi₂O₃, B₂O₃, SiO₂, and Al₂O₃ have been added as the sintering aid, which can effectively lower the sintering temperature of BaTiO₃-based ceramics. However, the addition of sintering aids may not always result in the desired dielectric properties which include a high and almost temperature independent dielectric constant and a low dielectric loss. This is especially true if the dielectric constant is lowered by the presence of a continuous low ϵ grain boundary phase. Therefore, it is important to choose a suitable sintering aid composition which can reduce the sintering temperature and produce densification without deterioration of dielectric properties of material. Among varieties of additives, Kaolinite which possesses high content of Al₂O₃ and SiO₂ used as sintering aid was few reported.

In this paper, Kaolinite used as sintering aid was discussed, aiming at obtaining high density dielectrics by low temperature sintering in the presence of an optimal amount of liquid phase without any undesirable phase formation. The microstructures and dielectric properties of BaTiO₃ ceramics were also investigated.

2. Experimental

Commercial BaTiO₃ ($\geq 99.5\%$, Zhongxing Electronic Material Co. Ltd., Xiantao, China) and Suzhou Kaolinite ($\geq 98.0\%$, Impurity content: Fe₂O₃ $\leq 0.04\%$, TiO₂ $\leq 0.12\%$, Na₂O $\leq 0.22\%$, MgO $\leq 0.11\%$, CaO $\leq 0.10\%$, K₂O $\leq 0.17\%$, Kaolinclay Co. Ltd., Longyan, China) powders were used as the starting materials. The Kaolinite powder was added in BaTiO₃ powder in the ratio corresponding to the following chemical composition: (100– x) wt% BaTiO₃– x wt% Kaolinite, where $x=0$ –10.0. These powders were weighted according to the nominal compositions, and mixed in distilled water by ball milling for 4 h. The slurries were filtered and dried at 90 °C for 8 h. The powders were granulated in a 3.0 wt% PVA (polyvinyl alcohol solution) in a proportion of 90.0 wt% of powder and 10.0 wt% of PVA solution. Disks with 13.60 mm in diameter were prepared by unidirectional pressing (60 MPa). The disks were baked at 800 °C

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for 30 min for binder removal. The samples were sintered at a certain temperature ranging from 1100 to 1390 °C in air. The soaking time at the sintering temperature was 2 h, while a slow heating rate of 2–3 °C/min aimed to prevent deformation of the samples.

The crystal structure of the samples was identified using an X-ray diffractometer (XRD; Model D-MAX 2200pc, Rigaku Co., Tokyo, Japan), in conjunction with Cu K α radiation, operated at 50 kV, 100 mA, and a scanning rate of 3°/min within the range of 2 θ from 15° to 80°. Lattice parameter of samples was worked out using the Bragg law for the tetragonal system:

$$d = \left[\left(\frac{h^2}{a^2} \right) + \left(\frac{k^2}{a^2} \right) + \left(\frac{l^2}{c^2} \right) \right]^{-1/2} \quad (1)$$

Two strongest peaks in XRD patterns for each sample were chose to calculate a and c . For dielectric measurements, Ag electrodes were screen printed with Ag paste on both sides of the pellets and heat treated at 650 °C for 20 min. The DC breakdown measurement was performed using a withstanding voltage tester (Model ET2671B, Entai, Nanjing, PR China) at room temperature. All samples were immersed in silicone oil to prevent surface flashover. The frequency dependence of the dielectric properties were measured using a precision LCR Meter (Model E4980A, Agilent Tech., CA, U.S.) over a frequency range from 20 Hz to 2 MHz at room temperature, and the temperature dependence of dielectric properties were measured over a temperature range from –60 to 160 °C at 1 kHz. The microstructure of the sintered samples was studied on polished and then thermally etched surfaces using a scanning electron microscope (SEM; Model JSM-6390A, Tokyo, Japan) equipped with energy dispersive X-ray (EDX) spectrometer for element analysis.

3. Results and discussion

Bulk and relative density of BaTiO₃ ceramics with different Kaolinite additions as a function of sintering temperature were studied. The bulk density of ceramics sintered at different temperatures was measured by the Archimedes method. Nearly 94.5% of the theoretical density was obtained for pure BaTiO₃ when the sintering temperature reached to 1350 °C. For BaTiO₃ ceramics with Kaolinite addition, since Kaolinite reacted with part of BaTiO₃ during sintering (see XRD analysis), and the amount of generated phase increased with increasing Kaolinite content, it was difficult to accurately calculate the theoretical density of the sample. In order to approximately estimate the densification, assuming no interaction had taken place between Kaolinite and BaTiO₃, the theoretical density of samples can be calculated from [14]:

$$D = \frac{(W_1 + W_2)}{(W_1/D_1 + W_2/D_2)} \quad (2)$$

where W_1 and W_2 were the weight percentages of BaTiO₃ and Kaolinite in the mixture, respectively. D_1 and D_2 , representing the theoretical density of BaTiO₃ and Kaolinite, were 6.02 and 2.62 g/cm³, respectively.

Fig. 1 shows relative density of BaTiO₃ ceramics with different Kaolinite additions as a function of sintering temperature. The relative density of ceramics gradually increased and then decreased with increasing sintering temperature, namely, it had a maximum value. The sintering temperature corresponding to the maximum value was defined as the suitable sintering temperature (SST) [11]. The lower density shown by all samples sintered below the SST might be due to the fact that the liquid phase was too viscous to penetrate the voids between BaTiO₃ particles [15]. While the lower density above the SST can be attributed to the oversintering phenomenon. The ceramics when $x = 2.0, 4.0, 6.0, 8.0,$ and 10.0 , obtained its SST at 1260, 1240, 1230, 1220, and 1210 °C with estimated relative densities of 94.9, 95.1, 95.7, 95.6, and 95.3%, respectively. It was because more liquid phase was formed with increasing Kaolinite content, thus, solid particles were fully wetted by liquid phase, which resulted in the densification and decreasing of sintering temperature. As for the decrease in relative density when $x = 10.0$, it was presumably due to the crystallization of liquid phase according to the XRD results which led to less liquid phase presenting in sample and resulted in decrease of densification. It can be concluded that Kaolinite enhanced the densification of BaTiO₃ ceramics at lower

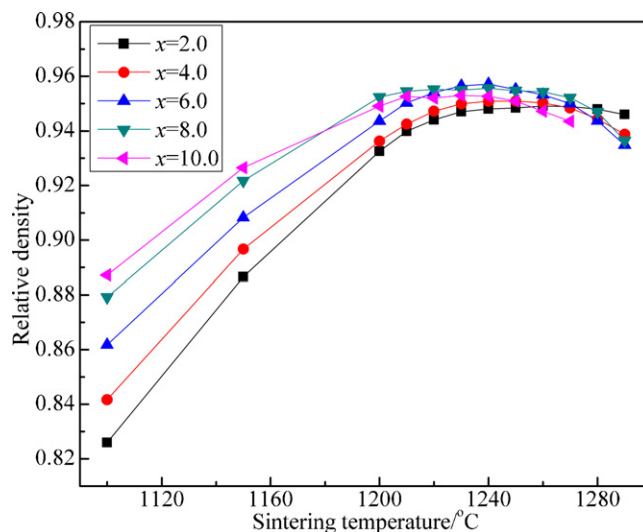


Fig. 1. Relative density of BaTiO₃ ceramics with different Kaolinite additions as a function of sintering temperature.

Table 1

Lattice parameters for BaTiO₃ ceramics with different Kaolinite additions.

	$x = 0$	$x = 2.0$	$x = 4.0$	$x = 6.0$	$x = 8.0$	$x = 10.0$
a (Å)	3.9999	3.9999	3.9999	3.9999	3.9998	3.9998
c (Å)	4.0179	4.0179	4.0179	4.0179	4.0181	4.0180

sintering temperatures in the presence of liquid phase. In the rest of this paper, all the samples were prepared at their SSTs.

Fig. 2 shows the XRD patterns for BaTiO₃ ceramics with different Kaolinite additions. The crystalline phase of pure BaTiO₃ at room temperature was tetragonal. With the addition of Kaolinite ($x = 2.0$ – 8.0), no new crystalline phase was observed in the XRD results. It can be attributed to that additives are incorporated into the perovskite or as a residual glassy phase located at triple points during sintering in the presence of liquid phase. However, the lattice parameters of the perovskite phase were hardly changed, which had been calculated and were listed in Table 1. It was suggested that the constituents of Kaolinite did not work as dopants incorporating into the perovskite lattice but reacted with part of

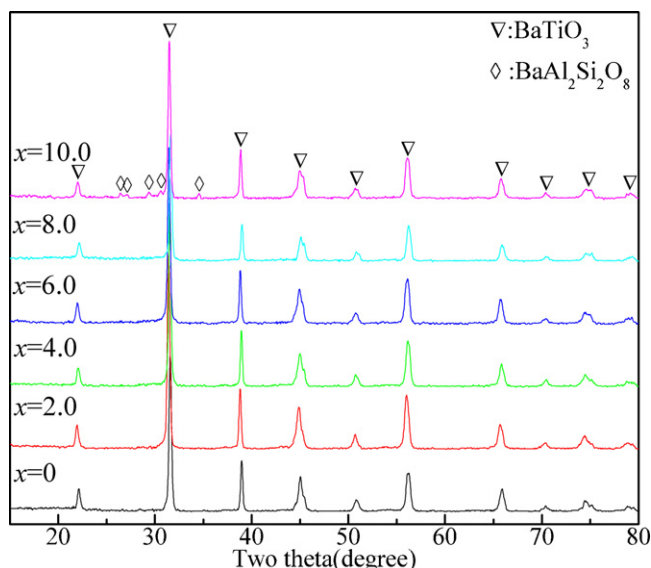


Fig. 2. XRD patterns for BaTiO₃ ceramics with different Kaolinite additions.

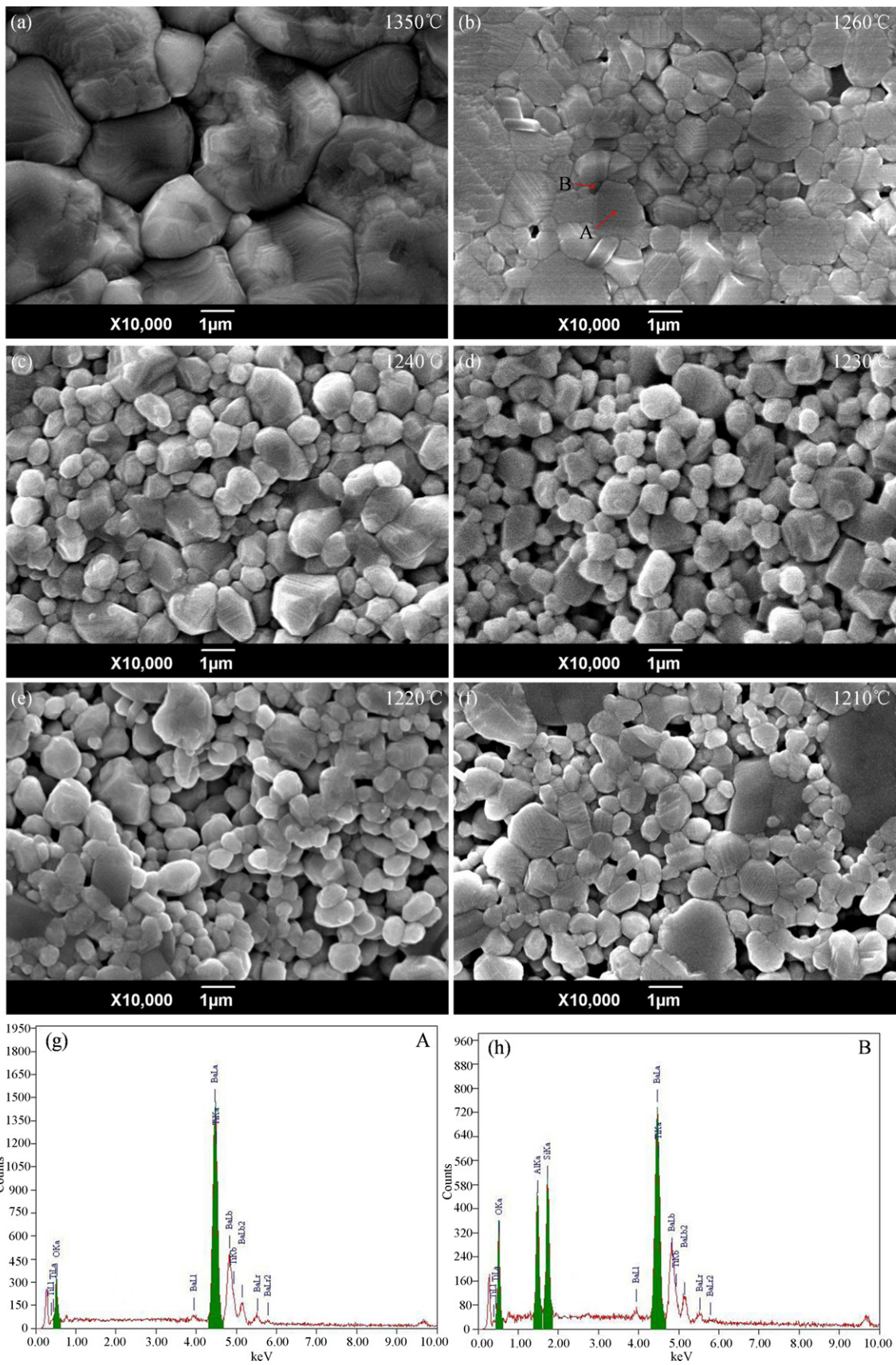


Fig. 3. SEM micrographs of the polished surface of BaTiO₃ ceramics with different Kaolinite additions sintered at different temperatures, $x=0$ (a), 2.0 (b), 4.0 (c), 6.0 (d), 8.0 (e), 10.0 (f), and the EDX spectra for grain (g) and grain boundary (h), respectively.

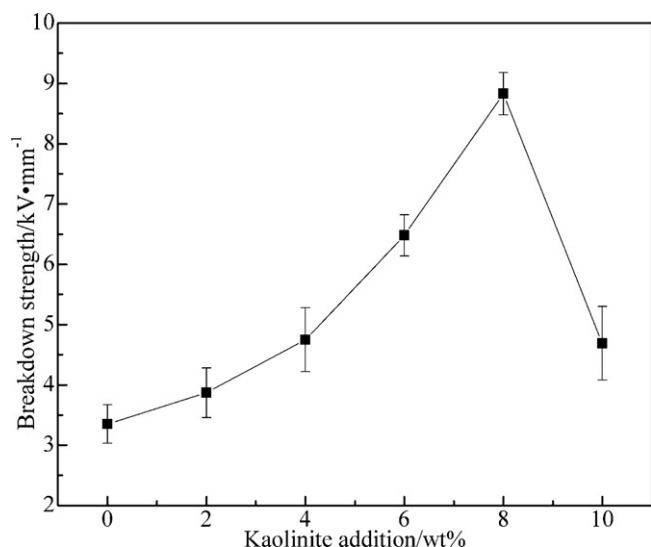


Fig. 4. Average breakdown strength of BaTiO₃ ceramics with different Kaolinite additions.

BaTiO₃ and resulted in the formation of BaO–TiO₂–Al₂O₃–SiO₂ glass [16–18] locating at triple points, which was supported by the SEM-EDX evidences (see Fig. 3). However, when $x=10.0$, tiny barium feldspar (BaAl₂Si₂O₈) phase, which was reported by Herczog [18] in the BaO–TiO₂–Al₂O₃–SiO₂ system, was formed according to the XRD analysis. It can be attributed to the crystallization of present glass which resulted from inhomogeneous distribution of Ba²⁺ in glass phase during sintering. In fact, it was well known that the thermodynamic stability of a glass depended on the connectivity of the glass structure, while BaO acted as a typical glassy network modifier in the present glass, excess modifier cations would break the network linkage and make the glass easy to crystallize.

The microstructure of BaTiO₃ ceramics with different Kaolinite additions was observed by SEM. Two effects of Kaolinite addition on the microstructure could be observed. On the one hand, the grain size reduced obviously. As shown in Fig. 3, pure BaTiO₃ had large grains with an average size of over 4.0 μm, while the average grain size was reduced to about 1.5, 1.0, and 0.5 μm, respectively ($x=2.0$ –6.0). No continued reduction in the grain size was observed with further addition of Kaolinite ($x=8.0$ –10.0). On the other hand, a uniform distribution of grain sizes was observed. It can be interpreted that the liquid phase presented at the grain boundaries hindered the ion diffusion and inhibited the grain growth. According to the EDX spectra for grain (Fig. 3(g)) and grain boundary (Fig. 3(h)) of ceramic ($x=2.0$), it was proved that a strong interaction between BaTiO₃ particles and Kaolinite occurred and resulted in the formation of BaO–TiO₂–Al₂O₃–SiO₂ glass. But, unfortunately, abnormal growth of grains and decrease in densification of sample were observed in Fig. 3(f), it was because barium feldspar crystallized from glass phase in accordance with the XRD results. It indicated that the sintering property of BaTiO₃ ceramics can be greatly improved when $x=4.0$ –6.0.

Fig. 4 shows the average breakdown strength of BaTiO₃ ceramics with different Kaolinite additions. Ten samples for each composition were measured to obtain average breakdown strength. The pure BaTiO₃ had an average breakdown strength of 3.35 kV/mm, and the breakdown strength of BaTiO₃ ceramics was remarkably improved with increasing addition of Kaolinite but a notable decrease when $x=10.0$. Generally, two factors contributed to the breakdown strength of ceramics. One was the densification of sample, and the other was the distribution of grain sizes [19]. With increase in Kaolinite content, grain sizes of ceramics decreased gradually and densification of ceramics was enhanced in the

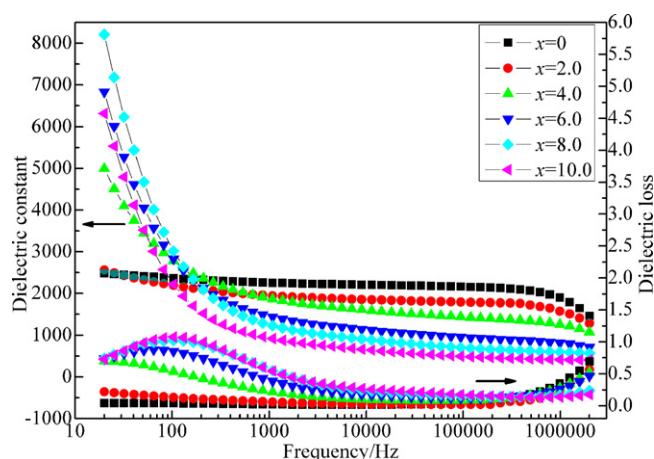


Fig. 5. Frequency dependence of dielectric constant and dielectric loss for BaTiO₃ ceramics with different Kaolinite additions.

presence of glass phase in accordance with Fig. 3. However, densification of ceramics when $x=10.0$ decreased resulting from crystallization of glass phase according to density analysis. Among all the measured samples, ceramics when $x=8.0$ shown the highest average breakdown strength of 8.83 kV/mm, which was 2.64 times higher than that of pure BaTiO₃.

The frequency dependence of dielectric properties for BaTiO₃ ceramics with different Kaolinite additions was presented in Fig. 5. The dielectric constant of samples gradually decreased with increase in frequency, which was particularly true for Kaolinite containing ceramics. The Kaolinite containing ceramics had higher dielectric constant than pure BaTiO₃ over the frequency range of 20–100 Hz. It resulted from the space charge polarization. The glass phase, locating at the grain boundary or surrounding the grains, impeded the transfer of free charge, and then, resulted in accumulation of charges or ions in intergranular areas and, therefore, formation of macro-dipoles dispersion. In addition, the dielectric constant increased with increase in Kaolinite content ($x=2.0$ –8.0). It was because more glass phase was formed, and which enhanced the space charge polarization effect. Meanwhile, the dielectric loss increased with increase in Kaolinite content. As for the decrease in dielectric constant when $x=10.0$, it was presumably due to the crystallization of glass in accordance with the XRD results, for the barium feldspar possessed a low dielectric constant [20,21]. Conversely, the Kaolinite containing ceramics had lower dielectric constant than pure BaTiO₃ ceramic over the frequency range of 100 Hz–2 MHz. It was because the space charge polarization was unable to keep pace with the variation of electric field over this frequency range, and it was the orientation polarization that played a major role in polarization of ceramics. Researches [12,22] have shown that two factors contribute to the dielectric constant, one is the densification and grain size distribution of ceramic, the other is the additive amount and property of glass. In this paper, samples were prepared with well densification and suitable grain sizes. The decrease in dielectric constant with increase in Kaolinite content can be attributed to that low ϵ glass phase dilutes the high ϵ BaTiO₃ phase. As for the higher dielectric loss for Kaolinite containing ceramics over this frequency range, it was because of the higher dielectric loss of glass phase.

For BaTiO₃ occupied most of the volume in BaTiO₃ ceramics with different Kaolinite additions, it can be considered as a two-phase system which is composed of a ferroelectric continuous phase (BaTiO₃) and a non-ferroelectric spherical phase (Kaolinite). For spherical dispersions, the effective dielectric constant of

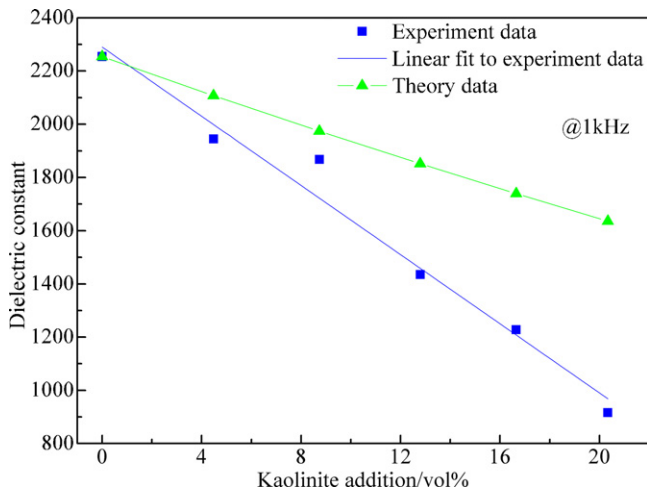


Fig. 6. Dielectric constant of BaTiO₃ ceramics with different Kaolinite additions.

ceramics can be described using the Maxwell-Garnett (MG) effective medium theory [23,24]:

$$\varepsilon_{eff} = \frac{\varepsilon_1[\varepsilon_2 + 2\varepsilon_1 + 2\nu_f(\varepsilon_2 - \varepsilon_1)]}{[\varepsilon_2 + 2\varepsilon_1 - \nu_f(\varepsilon_2 - \varepsilon_1)]} \quad (3)$$

where ε_1 is the dielectric constant of the continuous phase, ε_2 is the dielectric constant of the spherical phase, and ν_f is the volume fraction of the spherical phase. At room temperature, BaTiO₃ possesses high dielectric constant of about 2200 at 1 kHz, while Kaolinite only has 15. As shown in Fig. 6, ν_f of Kaolinite was calculated from its weight ratio. According to MG theory, effective dielectric constant of BaTiO₃ ceramics with different Kaolinite additions were calculated and illustrated. Experiment data of dielectric constant for ceramics were also presented in Fig. 6. The significant difference between theory and experiment data of dielectric constant can be attributed to the reaction between BaTiO₃ particles and Kaolinite. With increase in Kaolinite content, more BaTiO₃ particles reacted with Kaolinite, and bigger difference between theory and experiment data of dielectric constant was observed.

Fig. 7 illustrates the temperature dependence of dielectric properties for BaTiO₃ ceramics with different Kaolinite additions. All samples exhibited the Curie temperature (T_c) at about 120 °C, and the dielectric constant exhibited a broadened and diffuse ferroelectric–paraelectric phase transition for Kaolinite containing samples. The diffuse phase transition was related strongly to

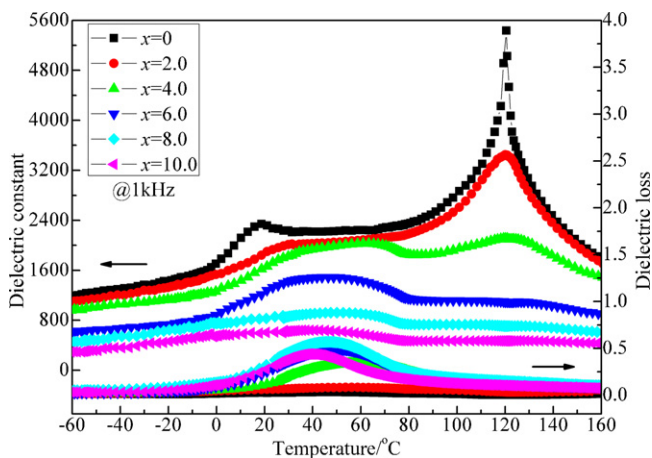


Fig. 7. Temperature dependence of dielectric constant and dielectric loss for BaTiO₃ ceramics with different Kaolinite additions.

the addition of Kaolinite. The glass phase resulting from the reaction between BaTiO₃ and Kaolinite led to the change of dielectric properties and the observation of relaxor behavior and diffuse transitions. Since the grain size decreased with addition of glass phase, more grain boundary emerged, while the phase locating at the grain boundary was mainly non-ferroelectric material. With increase addition of non-ferroelectric material, the content of ferroelectric material in ceramic decreased. According to Smolenski's composition fluctuation theory [25], assuming the sample was divided into many micro-areas, the phase transition temperatures in each micro-area had shown a certain distribution, and the T_c was the statistic of all the micro-phase transition temperatures. Since the increase in non-ferroelectric phase would make the micro-inhomogeneity of components increases, leading to the phase transition temperature varied in different micro-areas, thus causing phase transition in a wide temperature range. It also can be considered [26] the grain boundary caused a large stress against grains, and resulting in a change of the domain structure. So, the stress from the grain boundary was considered to depress the dielectric abnormality at the Curie temperature. As for the temperature dependence of dielectric loss, a dielectric loss peak was observed at about 40 °C, and this peak increased with increase in Kaolinite content ($x=2.0$ – 8.0). This is presumably due to the relaxation polarization of ceramics. The decrease of dielectric loss peak for ceramic when $x=10.0$ can be attributed to the formation of barium feldspar and less glass phase remained in sample. It was proved that BaTiO₃ ceramics with 4.0 wt% Kaolinite addition possessed well temperature stability of dielectric constant.

4. Conclusions

BaTiO₃ ceramics with different Kaolinite additions were prepared through conventional solid-state method. Kaolinite had a strong influence on the densification, microstructure and dielectric properties of BaTiO₃ ceramics. The density characterization results show that the addition of Kaolinite significantly lowered the sintering temperature of BaTiO₃ ceramics to about 1200 °C. BaO–TiO₂–Al₂O₃–SiO₂ glass phase was formed in accordance with the SEM-EDX analysis, leading to the reduction in the grain size and improvement of average breakdown strength of ceramics. A perovskite structure was revealed for all samples but the formation of a secondary phase, BaAl₂Si₂O₈ was crystallized from glass phase when the Kaolinite content reaches to 10.0 wt%. The reaction between BaTiO₃ and Kaolinite caused an uneven distribution of BaTiO₃ composition, giving rise to the strong broadening effects of the phase transition. BaTiO₃ ceramic with 4.0 wt% Kaolinite addition possessed well temperature stability of dielectric constant. These results provided useful information for the application of Kaolinite in electronic ceramics.

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