

The structure and dielectric properties of low temperature sintering barium titanate based X7R ceramics

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Abstract In this paper we try to do systematic investigation on the structure and dielectric properties of low temperature sintered barium titanate based X7R ceramics, which are doped with rare earth oxide, Nb_2O_5 , Co_3O_4 using $\text{ZnO-B}_2\text{O}_3$ as the sintering aids. The dielectric ceramic powder can be sintered at the temperature below 950°C to satisfy X7R requirement and also with good permittivity and low dielectric loss. The research strongly suggest that this doped BaTiO_3 based ceramic, which can be sintered at a rather low temperature, may be used in the production of MLCC with low content of Pd in the Ag–Pd electrode, and for sure, the production cost would be greatly reduced.

Keywords X7R · Barium titanate · Low temperature sintering · Dielectric property

1 Introduction

With the rapid development of the 3C (Computer, Communication, Consumer Electronics) industry, the techniques of the multilayer ceramic capacitor (MLCC), of which the X7R MLCC is the major product, have been greatly pushed forward. The X7R performance requirement of the Electronic Industries Association (EIA) means that a stable temperature coefficient of capacitance (TCC) which should be within $\pm 15\%$ between -55 and 125°C .

Usually the barium titanate based ceramics are sintered at a temperature above $1,300^\circ\text{C}$, while the alternate layers

of ceramics and the internal electrodes are cofired at this temperature. Some noble metals, i.e., Pt, Au, Pd, are chosen as the internal electrode. However, the high cost of them imposes a major constraint to the commercial production of MLCC.

There are two ways to reduce the cost of the internal electrode [1]. One is to use base metals as the electrode, such as Ni, Cu. However, in this way the ceramics must be sintered in a reducing atmosphere. Apparently, it will raise the production cost. The alternative one is to reduce the amount of Pd content in the alloy of Ag–Pd. This reduction of Pd content is directly related to the reduction of the sintering temperature of the barium titanate based ceramics. If the sintering temperature can be reduced to 950°C , an alloy of Pd 10%–Ag 90% could serve the purpose as well, and thus considerable cost saving can be achieved.

In order to decrease the sintering temperature, addition of the sintering aids could be an efficient way [1]. Because most of them are non-ferroelectric materials, their doping may “dilute” the ferroelectric properties of the barium titanate: depress the permittivity of the material and raise the dielectric loss. Accordingly, it is pivotal to choose sintering aids. In this paper, $\text{ZnO-B}_2\text{O}_3$ solution is chosen as the sintering aids. The sintering temperature is successfully decreased, while the “core-shell” structure, which promises the X7R performance of the material, is not ruined. We investigate the structure and dielectric properties of this low-temperature sintered ceramics and make a comparison with the undoped sample.

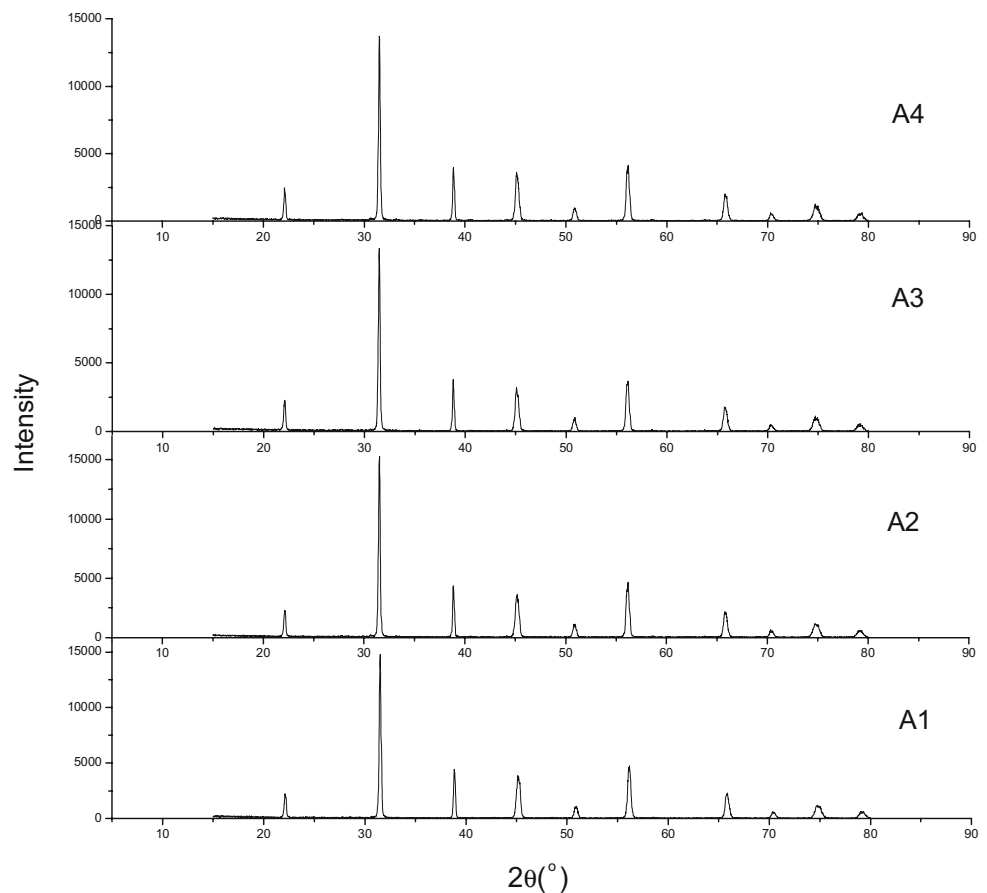
2 Experiments

High purity commercial BaTiO_3 with the average grain size of 100 nm (Guoteng Co., Ltd., Shandong, China) was

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Fig. 1 X-ray diffraction patterns of the samples A1–A4 sintered at 950 °C

* Damping Factor



adopted as starting material. The barium titanate powder was pre-calcined at 1,050 °C in the air, and then doped with Nb_2O_5 , Co_3O_4 , rare earth oxide and $\text{ZnO-B}_2\text{O}_3$ solution. Marked as A1–A4, the amount of the sintering aids content in the four samples increased gradually. Another sample, as B1, was prepared, which contains the same amount of oxide as A1 but without sintering aids. The mixture powders were milled, dried for hours, after then pressed into small disks (1 mm in thickness and 10 mm in diameter). The pellets were sintered at 950 °C in the air, and then cooled to room temperature.

The microstructures of the samples were observed by scanning electron microscopy (SEM JEOL JSM-6301F). The phase structures were identified by a X-ray diffractometer (D/max-rB, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation. Silver paste electrodes were fired on both surfaces of the samples. The permittivity and dielectric loss of the samples were measured using an impedance analyzer (Model HP 4192A LF Hewlett-Packard Co., USA) from –60 °C to +150 °C at 1 kHz and 1 Vrms (root mean square). The densities of the samples were measured by the Archimedes' method.

3 Results and discussion

Figure 1 shows the X-ray diffraction (XRD) profiles of the samples, A1–A4 respectively. All the samples were found

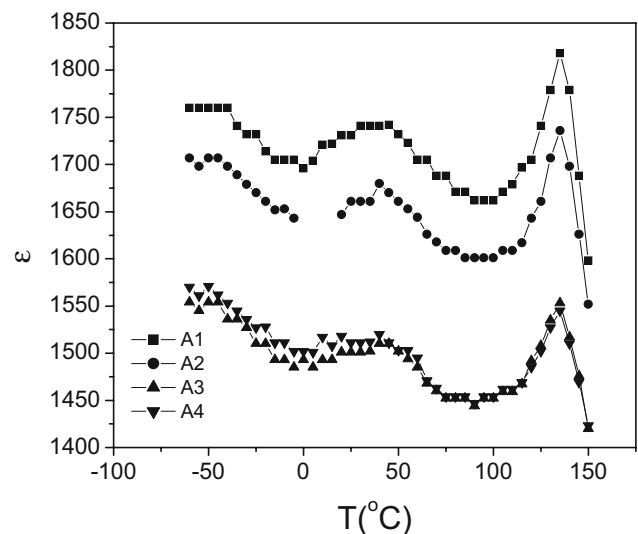


Fig. 2 The permittivity-temperature behaviors of the samples A1–A4 sintered at 950 °C

Table 1 Sintering character and dielectric properties of the samples A1–A4 and B1.

Sample	Basic composition	Doping style of ZnO–B ₂ O ₃	Sintering shrinkage of diameter/%	Relative density/%	Sintered level	K	D.F. */%	$\rho/\Omega^*\text{cm}$	T _c /°C
A1	BaTiO ₃	Solution method	15.8	94	Good	1,731	0.7	2.02E+12	135
A2			14.8	95	Good	1,661	0.7	2.91E+12	135
A3			15.7	94	Good	1,501	1.7	3.95E+10	135
A4			15.7	94	Good	1,511	3	4.69E+9	135
B1	BaTiO ₃	None	1.6	64	Unsintered	–	–	–	–

* Damping factor.

to exhibit a single tetragonal phase at room temperature. Apparently, addition of the sintering aids did not lead to the formation of any secondary phase.

The sintering character of samples with different amounts of ZnO–B₂O₃ was shown in Table 1. As can be seen, the sample B1, which contained no sintering aids, appeared a very small shrinkage in the diameter. The relative density of B1 was only 64%, indicating that the sample was still loose after sintering at 950 °C. On the other hand, the samples A1–A4, containing different amounts of sintering aids, showed about 15% shrinkage in the diameter, and their relative densities reached 94%, much higher than that of the sample B1. The sintering densification was greatly promoted with the sintering aids. This demonstrated that it was effective to decrease the sintering temperature of the barium titanate by the doping of ZnO–B₂O₃ solution.

The permittivity-temperature dependence behaviors of the samples A1–A4 were exhibited in Fig. 2. As shown, the permittivity at room temperature ($\epsilon_{25^\circ\text{C}}$) of the sample A1 was the highest, reaching 1731. As the amount of ZnO–B₂O₃ increasing, $\epsilon_{25^\circ\text{C}}$ decreased gradually. That is because with the increasing of the additives, the non-ferroelectric content “diluted” the ferroelectric properties of the barium

titanate, depressed the permittivity and raised the dielectric loss.

As temperature decreases, barium titanate undergoes three successive phase transition. That is from paraelectric cubic phase to ferroelectric tetragonal phase and then to ferroelectric orthorhombic phase and finally to low-temperature rhombohedral phase. Among them, the transition from cubic to tetragonal is significant for it is a transition from paraelectric to ferroelectric, which appears spontaneous polarization. For pure barium titanate, the transition temperature is 125 °C, called Curie point (T_c). The Curie point can be shifted by the doping of different additives. It is found that the structure of the tetragonal lattice of the BaTiO₃ based materials at room temperature is related to their Curie point: the change of the structure can lead to the shift of the Curie point. It can be seen in Fig. 2 that T_c of the samples A1–A4 was 135 °C. That is because *c/a* of the tetragonal lattice changed with the addition of the ZnO–B₂O₃ sintering aids, and the Curie point shifted from 125 to 135 °C. It is coherent with what previous papers reported [2].

Generally speaking, ZnO–B₂O₃ serves as a flux material, which provides active liquid to promote sintering. However, according to ZnO–B₂O₃ phase diagram, there is no liquid

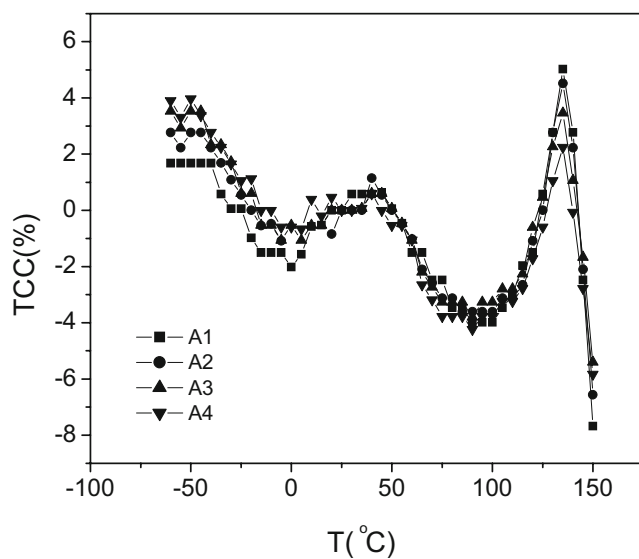


Fig. 3 TCC of the samples A1–A4 sintered at 950 °C

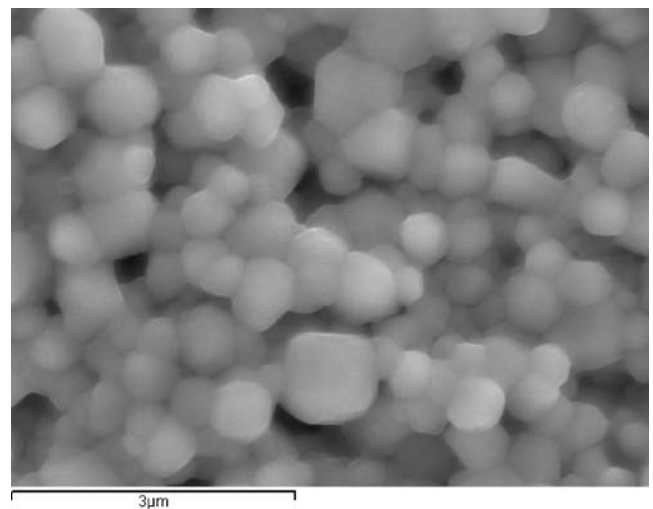
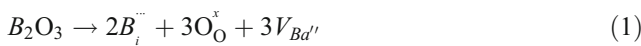
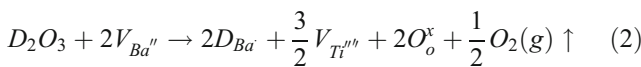


Fig. 4 The SEM micrograph of the sample A1 sintered at 950 °C, 18,000X

phase forming at 950 °C due to our proportion of B₂O₃. Therefore, we believe that in low temperature sintering, defects are the main reason that helps to decrease the sintering temperature. During barium titanate sintering, bulk diffusion through grain boundary is one of the most important matter transfer models. Some defects and distortions of lattice can decrease the activation energy of bulk diffusion, promote the matter transfer and thus enhance the sintering ability of samples. The radius of B³⁺ is 0.2 Å, while the radius of cations in BaTiO₃: Ba²⁺ 1.34 Å, Ti⁴⁺ 0.68 Å. B³⁺ is too small to occupy the sites of Ba²⁺ and Ti⁴⁺, so that B³⁺ ions form boron interstitials when they are incorporated in the lattice of BaTiO₃. Therefore, *c/a* of the tetragonal lattice and T_c were changed. The defect chemistry equation is written as:



where B_{*i*}^{··} stands for an interstitial boron with three positive charges, O_{*o*}^x for an neutral oxygen atom on an oxygen site, and V_{*Ba*}^{''} for a barium vacancy with two negative charges. The appearance of barium vacancy can promote the bulk diffusion of the rare earth oxide.



Because the diffusion of Nb⁵⁺ in barium titanate lattice is through titanium vacancy, the appearance of V_{*Ti*}^{''''} can boost the bulk diffusion of Nb₂O₅ [3].

With the interstitial ion and vacancy, the activation energy of bulk diffusion was decreased, so that the sintering temperature of BaTiO₃ based materials was decreased successfully. In this way, the relative densities of samples doped with sintering aids reached 94% or above, while in contrast the undoped one could hardly be sintered to dense body. This demonstrates that ZnO–B₂O₃ sintering aids can decrease the sintering temperature of BaTiO₃ based ceramic and promote its sintering densification effectively.

The temperature coefficient of capacitance (TCC) reveals the relationship between permittivity and temperature, calculated from Eq. 3 and shown in Fig. 3.

$$TCC = \frac{(\varepsilon(T^\circ C) - \varepsilon(25^\circ C))}{\varepsilon(25^\circ C)} * 100 \quad (3)$$

Here, ε(*T*°C) is the permittivity at each temperature and ε(25°C) the permittivity at 25°C. From–55°C to 125°C, TCC of the samples A1–A4 was within ±15%, which satisfied the X7R requirements of EIA. Apparently, the “core-shell” structure, which promised the X7R performance, was not ruined by the doping of ZnO–B₂O₃.

Figure 4 shows the microstructure of the sample A1. The grain was integrated and grew well. The average grain size was 400 nm.

4 Conclusions

Adding ZnO–B₂O₃ as the sintering aids to BaTiO₃ based X7R type ceramics, B³⁺ can be incorporated in the lattice of BaTiO₃ and forms defects. This will enhance the ion diffusion during sintering, and thus the sintering temperature can be decreased effectively, without ruin of the “core-shell” structure. Sintered at 950 °C, all the samples with sintering aids satisfied the X7R requirements. The maximal permittivity at room temperature was above 1,700, and the dielectric loss was less than 1%. Using this BaTiO₃ based ceramics to produce X7R type MLCC, people could lower the Pd content to 10% in the Ag–Pd electrode, and for sure, the production cost would be greatly reduced.

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