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Low sintering of X7R ceramics based on barium titanate with SiO_2–B_2O_3–Li_2O sintering additives in reducing atmosphere

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Abstract

Development of a low-temperature sintered dielectric material derived from barium titanate for X7R characterized dielectric ceramics application is discussed in this paper. By addition of SiO_2–B_2O_3–Li_2O sintering additives to commercial $BaTiO_3$ powder, more than 95% of the theoretical density was obtained at a sintering temperature of 950 °C in H_2/N_2 atmosphere. The influence of the composition and procedures on the microstructures, lattice parameters and properties of ceramics materials were systemically studied. After explaining the reason for lower isolated resistivity (IR) in the previous experiment, several methods are tried out to improve the IR properties, which have reached the application requirement level of 10^{12} Ω cm. These ceramics sintered between 900 °C and 950 °C in H_2/N_2 atmosphere are promising candidates for fabrication of Cu electrode MLCCs.

Keywords: A. Sol–gel processes; $BaTiO_3$; Low sintering; B_2O_3–Li_2O–SiO_2

1. Introduction

In recent decades, multilayer ceramic capacitors (MLCCs) have been used as surface mount devices (SMDs) in many commercial products, including TVs, cell phones, and personal computers [1]. The quantity of shipment of MLCCs has grown to over one trillion in 2009 and the demand will further increase in the future. Some noble metals, such as, Pt, Au, Pd, are traditional internal electrodes. Because of the increase of noble metal price, the electrode materials have become a big share of the cost. So base metal inner-electrode, for instance, copper, nickel, has become a significant developing trend of MLCCs. However, Ni and Cu electrodes are readily oxidized in the thermal treatment when the atmosphere is even slightly rich in oxygen, therefore it is necessary to use a reducing atmosphere while co-firing base metal with $BaTiO_3$ dielectrics.

Actually, the melting point of copper is just 1084 °C, thus the sintering temperature should be lower than 1000 °C. Besides, higher temperature will accelerate the diffusion between the ceramics and electrodes and reduce the coverage of the electrodes [2].

In order to decrease the sintering temperature, for one thing, it is effective to use small grain and homogenous barium titanate, whose grain size is about 110 nm in the research. For another, sintering aids should be added. Oxides glass formers with low melting phase, such as B_2O_3–ZnO [3], LiF [4] and Li–B glass could enhance the densification. The flux is usually melted and quenched to get the low melting-point glass, which is easier to form liquid phase during the sintering procedure. But the glass may remain on the grain boundary, which will also lead to the reduction of dielectric and electric properties. Therefore, in this paper, no glass B_2O_3–Li_2O–SiO_2 (BLS) flux was selected as the sintering aids.

2. Experimental

The high purity commercial hydrothermal $BaTiO_3$ powder (GuoTeng Co. Ltd., Shandong, China) was used as starting material, which was synthesized hydrothermally with particle size of 100 nm. The powder was calcined at 720 °C for 2 h, and the grain size grew up to approximately 120 nm. All the additives used here, such as Y_2O_3, MgO, MnO_2 and CaO,

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were of reagent grade purity. The flux agent B_2O_3–Li_2O–SiO_2 was obtained in two ways: the first one, mixing lithium carbonate, boric acid, and silicon dioxide together in certain proportion, produces BLS; the other one, sol–gel method [5], produces small size flux aids called BLS-SG. The calcined BT powder, the additives and 0.2–1.2 wt% BLS were mixed in a nylon jar by ball milling for 24 h. After drying, the powder was pressed into small disks (1 mm in thickness and 10 mm in diameter) under the pressure of 1 MPa. The disks were sintered at 950 °C for 3 h, 5 h and 8 h under pO_2 of 10^{-11} to 10^{-13} Pa, respectively, followed by a similar re-oxidation schedule at 900 °C for 2.5 h and 3.5 h in pO_2 1–50 Pa. Furthermore, the heating rate for each sintering process is 4 °C/min.

The phase structures and lattice parameters were identified by an X-ray diffractometer (D/max-rB, Rigaku, Japan) with Cu Kα radiation. The microstructure of the samples was characterized by SEM (Leo-1530, German) and TEM (JEOL200CX, Tokyo, Japan). 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 1Vrms (root mean square). Electric properties of ceramic discs were characterized by HP4140B (Hewlett-Packard Co., USA).

3. Results and discussion

3.1. The dielectric properties and lattice parameters

A series of ceramics with 0.2–1.2 wt%BLS flux content were sintered at 950 °C for 5 h. The ceramics whose flux content is smaller than 0.5 wt% exhibit lower than 90% density. Fig. 1 only shows the dielectric properties of ceramics with 0.5–1.2 wt% BLS flux content. Dielectric constant was reduced by increasing the content of BLS flux broadly. "Core–Shell" structure is a typical structure in temperature stable barium titanate ceramics [6,7], which was observed by Hennings and Rosenstein [8] first in 1984. The core is nearly pure BT and retains a ferroelectric phase, while the shell is paraelectric due to the additive elements partially dissolved in the BT lattice, which reduces the Curie temperature [8,9]. Although more flux was beneficial for ceramics densification and mass transfer, more paraelectric phase in the shell of the grain would dilute the ferroelectric properties and depress the permittivity. All TCC curves meet the X7R specification (within ±15% of its 25 °C permittivity value over −55 °C to +150 °C). And the dielectric loss of all the samples is under 2%.

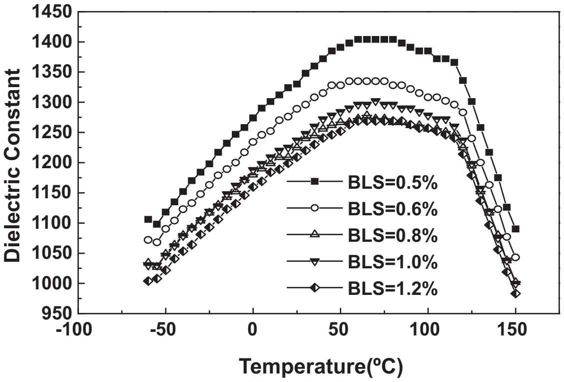

Fig. 1. Dielectric constant-temperature curves of the barium titanate (BT)-based ceramics with 0.5–1.2 wt%BLS content sintered at 950 °C for 5 h.

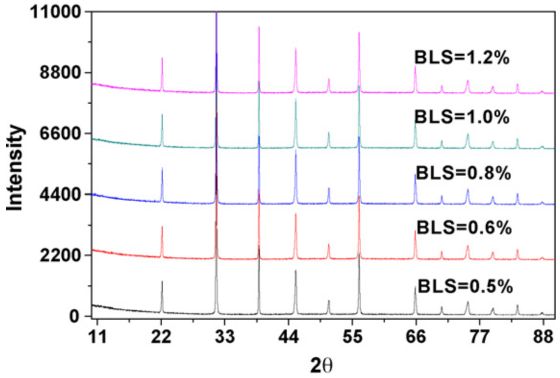

Fig. 2. XRD patterns of the barium titanate (BT)-based ceramics with 0.5–1.2 wt% BLS content sintered at 950 °C for 5 h.

BLS flux aid has a low melt point [10], and will form liquid phase during the sintering process. Fig. 2 shows the XRD patterns, which analyze the phase of different samples. It can be seen that only barium titanate phase occurred in the patterns while no other phases were found. That's because the flux content is so little that its liquid phase will easily be consumed in 900 °C. Consequently, there is no liquid phase remaining on the boundary after sintering. And the element totally diffused into the grains.

Table 1 shows the lattice parameters. It can be found that c/a increases with the BLS content, while parameter a decreases and parameter c almost keeps the same. The reason is concerned with the diffusion of Lithium. Randall et al. [9] had discussed the effect of Lithium ion in $BaTiO_3$–LiF system, and show the defect chemistry equation:

$$2[\mathrm{V}_{\mathrm{Ba}''}] + 4[\mathrm{V}_{\mathrm{Ti}''''}] + n + 3[\mathrm{Li}_{\mathrm{Ti}'''}] = p + 2[\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}] \tag{1}$$

The radius of lithium ion is smaller than that of Ti^{4+}, but bigger than that of interstitials in BT. Hence, if Li^+ get into the interstitials, lattice would stretch a bit, and lattice parameters would be enhanced. However, parameter a decreased when BLS content was increased, due to Li^+ occupied Ti^{4+} site.

Table 1
Lattice parameters of ceramics with 0.5–1.2 wt% BLS flux aids.

BLS (wt%)	a	c	c/a
0.5	3.997451	4.011788	1.003587
0.6	3.9964	4.01199	1.003901
0.8	3.996234	4.01253	1.004078
1.0	3.994558	4.011801	1.004317
1.2	3.994381	4.013095	1.004685

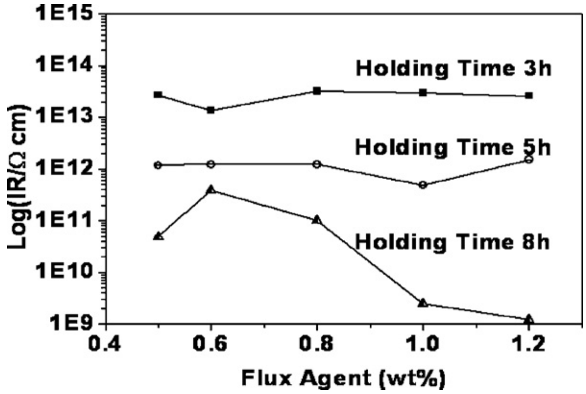

Fig. 3. The logarithm values of insulated resistance of ceramics with different flux content and various holding time.

Table 2
Dielectric and electric properties of ceramics with different BLS flux aids.

BLS	D (cm)	e_{25}	Tand$_{25}$	R (10^{12} Ω cm)
BLS	8.06	1141	0.007	0.1224
BLS-SG	8.06	1200	0.009	2.2962

Table 3
Resistivity of ceramics with different re-oxiding time.

BLS (wt%)	R (10^{12} Ω cm) when $T_{RO} = 2.5$ h	R (10^{12} Ω cm) when $T_{RO} = 3.5$ h
0.5	0.68553	1.18694
0.6	0.64796	1.1436
0.8	0.52326	1.00827
1.0	0.22964	0.28677
1.2	0.1156	0.16115

3.2. Changing sintering process and type of BLS flux aid

But these ceramics did not exhibit eligible electric properties. The isolated resistivity was only at $10^{11}\,\Omega$ cm level, and was smaller by one order of magnitude than standard. Then, the ceramics were sintered with 3–5 h holding time and 2.5–3.5 h re-oxiding time (call T_{RO} for short), and the result is shown in Fig. 3 and Table 2. Resistivity was sub-standard when holding time was longer than 5 h, and it reduced greatly when the samples contained more flux. There was the dilemma of holding time: better dielectric constant needed longer holding time while better IR needed shorter holding time. And increasing the re-oxiding time could make up for the problem caused by extending the holding time.

We compared the effect of BLS with BLS-SG. The BLS-SG was prepared by the following processes: H_3BO_3 (99%, Beijing Finechemical Co. Ltd.) and Li_2CO_3 (99%, Beijing Finechemical Co. Ltd.) were dissolved and mixed in deionized water with polyethylene glycol as a dispersant to achieve a homogeneous inorganic solution. Secondly, tetraethylorthosilicate ($SiO_2 \geq 28.0\%$, Beijing Finechemical Co. Ltd.) was dissolved in ethanol by adjusting the pH value to 2 with acetic acid solution to obtain a transparent organic solution. Finally, the inorganic and organic solutions were mixed with stirring to transform into a stable sol. After drying, the sol turned into a gel. BLS-SG was obtained by calcining the gel at 500–800 °C for 3 h. Adding the same content BLS and BLS-SG to the ceramics powder, and the measurement result is shown in Table 3. And the microstructure is shown in Fig. 4. As can be seen, Ceramics with BLS-SG exhibited qualified resistivity, larger

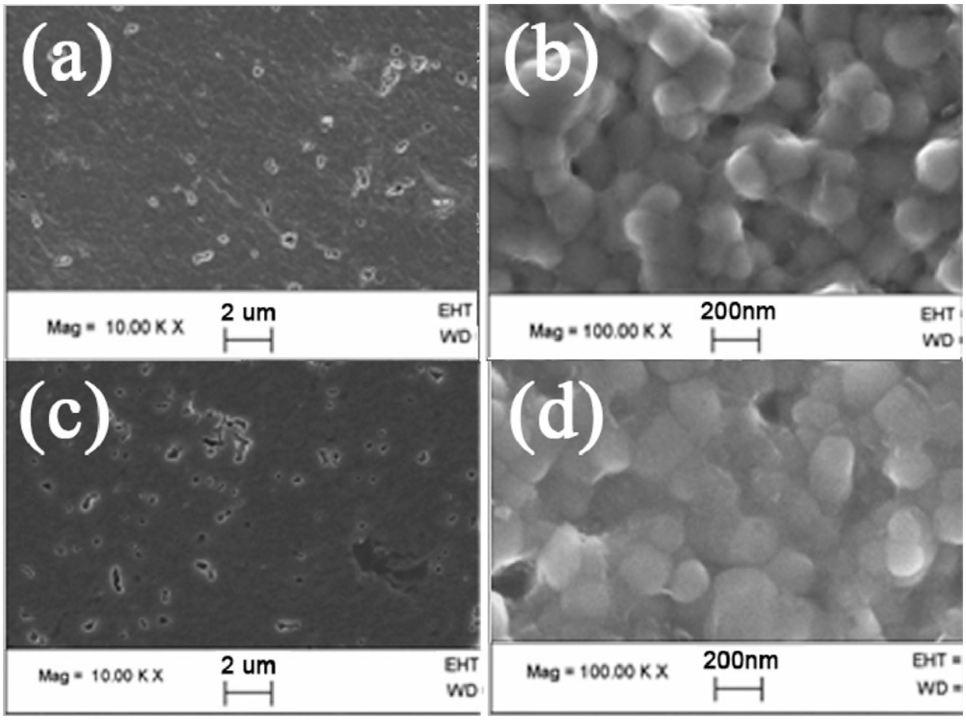

Fig. 4. The microstructure of (a) section and (b) surface of the ceramics with BLS-SG aids, and microstructure of (c)section and (d) surface of the ceramics with BLS.

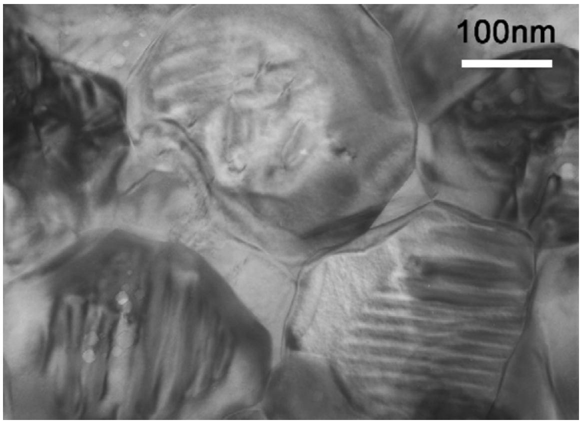

Fig. 5. The TEM microstructure of barium titanate ceramics with BLS flux.

dielectric constant and less pores. So sol–gel flux aid is an effective way to realize low temperature sintering.

3.3. Explanation of low resistivity

Generally, high isolated resistivity is required by lots of applications, and it is one of the most significant parameters of ferrite ceramics. Fig. 5 shows that the grain microstructure of the ceramics with BLS flux aids is "core–shell" structure, which consists of ferroelectric barium titanate core region and paraelectric doping grain boundary. Actually, the pure barium titanate sintered in reducing atmosphere has lower resistivity, whereas barium titanate doped has higher one. In this case, the resistivity of ceramics is determined mainly by the resistivity of grain boundaries. Isolated resistivity would be affected by many factors, for instance, density, grain size, composition stoichiometry, crystal structure perfection, impurity, macrostructure homogeneity, and so on [11]. Among these, two reasons are the most important: effect of porosity and oxygen vacancy [12]. Compared to BLS-SG flux, heterogeneous BLS may cause bigger pores. And they would provide possible conduction path of electricity due to impurities entrapped inside. Hence ceramics with BLS have substandard resistivity. Besides, with the same BLS flux, longer holding time and less re-oxiding time may facilitate more oxygen vacancies, which are harmful for resistivity.

4. Conclusions

Ceramics based on barium titanate with BLS flux agent have been successfully achieved through low-temperature sintering. Holding time and re-oxiding time were changed in the experiment. Proper holding time and re-oxiding time were beneficial to get samples with high dielectric and electric properties. That is because lithium will occupy the titanium site in $BaTiO_3$ crystal lattice, and produce oxygen vacancy to lower IR property. Using sol–gel method to prepare aids, ceramics with excellent properties were obtained. IR was at 10^{12} Ω cm order magnitude, and homogeneous microstructure. The low-temperature sintered $BaTiO_3$-based ceramics enables the usage of Cu and Ni as the internal electrode, thus greatly reducing the cost in MLCC production.

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