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Microwave Sintering of Base-Metal-Electroded $BaTiO_3$ Capacitor Materials Co-Doped with MgO/Y_2O_3 Additives

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Abstract. In this paper, we systematically investigated the effect of microwave sintering parameters on the characteristics of $BaTiO_3$ capacitor materials co-doped with Y_2O_3/MgO species. It is observed that the granular structure of the materials is relatively insensitive to the sintering temperature and soaking time such that the $BaTiO_3$ capacitor materials possessing X7R dielectric constant-temperature (K-T) characteristics can be obtained in a wide range of sintering conditions. TEM examinations reveal that the detailed microstructure of these materials is extremely complicated. The unique K-T properties of these materials are ascribed to the duplex structure of the samples, viz. fine grains of paraelectric phase and large grains of ferroelectric phase.

Keywords: microwave sintering, base-metal-electroded capacitor, X7R-type capacitor

1. Introduction

High performance and small sized multilayer ceramic capacitors (MLCC), which possess high reliability and compatible with surface mounting technology, have great potential for industrial applications [1]. Technology for MLCC mainly involves the co-firing of dielectrics and electrode materials (Ag/Pd alloy). However, utilization of large Pd content electrode materials increases the manufacturing cost tremendously. The development of inexpensive electrode materials such as base metals (Cu and Ni) is thus urgently needed for reducing the production cost for MLCC [2, 3]. The base-metal-electroded (BME) capacitors need to be fired under reducing atmosphere, since the Cu (or Ni) metal is subjective to oxidation during sintering in air. Many approaches have been reported being able to successfully maintain high insulation resistance of the $BaTiO_3$ materials, even when they were sintered in reducing atmosphere [3–10]. Moreover, the variation of capacitance with operation temperature is one of the major concerns in circuit application. In X7R type MLCC materials, the capacitance variation ($\Delta C/C_{25}$)-value must be within 15% from -55°C to 125°C temperature regime, where C_{25} is the capacitance at 25°C. The key factor resulting in low capacitance variation ($\Delta C/C_{25}$) of dielectric properties is presumed to be the presence of the core-shell microstructure [11–14], which can be achieved by critically controlling the doping species and concentration [15–17]. However, the microstructure and hence the related dielectric properties are extremely sensitive to the processing parameters, which are presumed due to growth of the grains during sintering, altering the core-shell microstructure for the materials. In view of this, a sintering process which can effectively densify the materials without inducing the growth of grains is thus demanded. Microwave sintering process can markedly reduce the temperature necessary for densification of the materials [18–20]. Grain growth phenomenon is thus pronouncedly suppressed such that high-density materials containing fine grain microstructure can be obtained, which is expected to improve the processing reliability.

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In this paper, microwave-sintering technique was adopted to densify the $BaTiO_3$ materials co-doped with Y_2O_3 and MgO species. The effect of processing parameters on the microstructure and hence dielectric properties of these $BaTiO_3$ materials were examined. The results were compared to that obtained by conventional sintering process.

2. Experimental

The commercial $BaTiO_3$, BTO, powders with Ba/Ti = 0.998 and particle size around 0.2 μm (BATIO-BT-02H, Batio Tech Co.) were mixed with the additives, which include 2.0 mol% Y_2O_3, 0.4 mol% MnO_2 and 1.5 mol% MgO as donor/acceptor dopants and 3 mol% $(Ba_{0.6}Ca_{0.4})SiO_3$, (BCSO), as sintering aids. The BCSO sintering aids were prepared by mixed-oxide method, in which the $BaCO_3$, $CaCO_3$ and SiO_2 of nominal composition were calcined at 1000°C for 2 h, followed by pulverization down to 0.3 μm size. The mixture was pressed into pellets about 10 mm in diameter and 1.2 mm in thickness and then microwave sintered in Al_2O_3-SiO_2 setter at 1100–1250°C for 0.1–20 min, using SiC rods as microwave absorption susceptors. The 2.4 GHz microwave generated by microwave generator, Gerling, GL 107, was injected into the sintering chamber through the WR284 waveguide. The sintering temperature of the samples was measured by using a thermocouple placed in touch with the pellets. To avoid the interference of microwave with the temperature measurement, the thermocouple was encapsulated in a stainless-steel sheath and was oriented in perpendicular to the electric field of the incident microwave. It should be noted that the microwave sintering was proceeded in air atmosphere for convenience. Such an approach does not loss generality, as only the densification/grain-growth behavior of the materials will be examined. Moreover, the composition of the samples have already been proved to be resistant to sintering under reducing atmosphere [17]. There is no doubt that the results observed in this study can also be applied when the sintering was proceeded in reducing atmosphere.

The microstructures of the samples, which were polished and then chemically etched, were examined using scanning electron microscopy (SEM, Joel TSM-840 A). The Cu-paste was screen printed onto the sintered samples, followed by firing at 900°C for 10 min in 30 ppm Po_2 to serve as electrodes. The dielectric

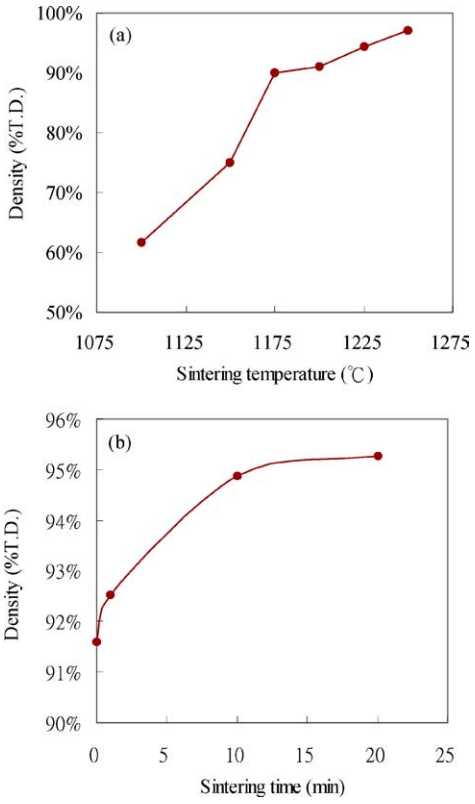

Fig. 1. Effect of (a) sintering temperature and (b) soaking time on the densification behavior of $BaTiO_3$ materials, which were co-doped with 2.0 mol% Y_2O_3 and 1.5 mol% MgO and 0.4 mol% MnO_2.

properties of the capacitor materials were measured from −55 to 150°C using HP 4278 capacitance meter. The capacitance of the samples was measured at 1 MHz only, as it is the frequency conventionally used in the industry for evaluating the dielectric properties of the materials. The detailed microstructure was examined using transmission electron microscopy (TEM, Joel 2000 FX II).

3. Results and Discussion

Microwave sintering process can densify the BTO materials very efficiently. Figure 1(a) shows that the density of the samples already reach 90%T.D. (theoretical density) by microwave sintering the materials at 1175°C for 10 min. The density of the samples increases gradually with the sintering temperature, reaching 97%T.D., for 1250°C sintered ones. SEM micrograph shown Fig. 2(a) indicates that, typically, the microwave-sintered materials contain very fine grains

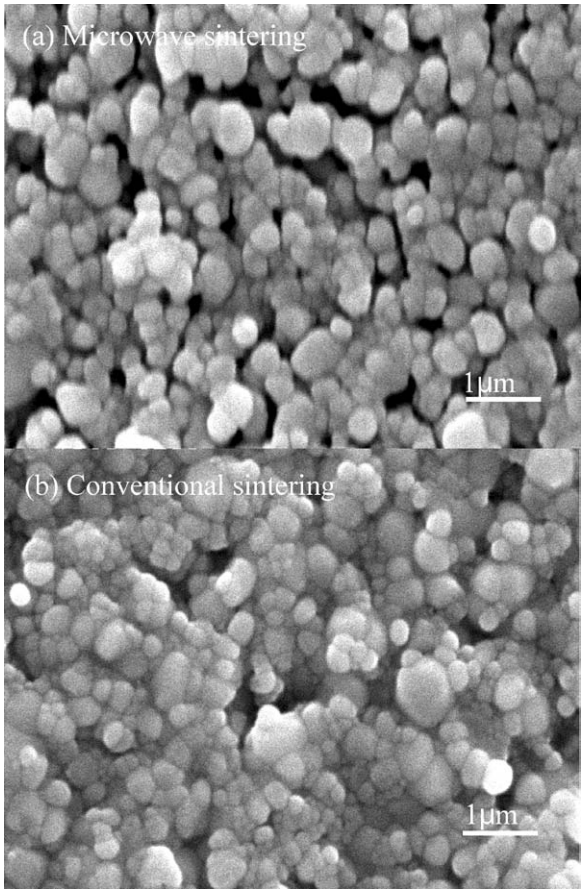

Fig. 2. SEM microstructure of $BaTiO_3$ materials, which were co-doped with 2.0 mol% Y_2O_3 and 1.5 mol% MgO and 0.4 mol% MnO_2 and were densified by either (a) microwave sintering process at 1225°C for 10 min or (b) conventional sintering process at 1250°C for 180 min.

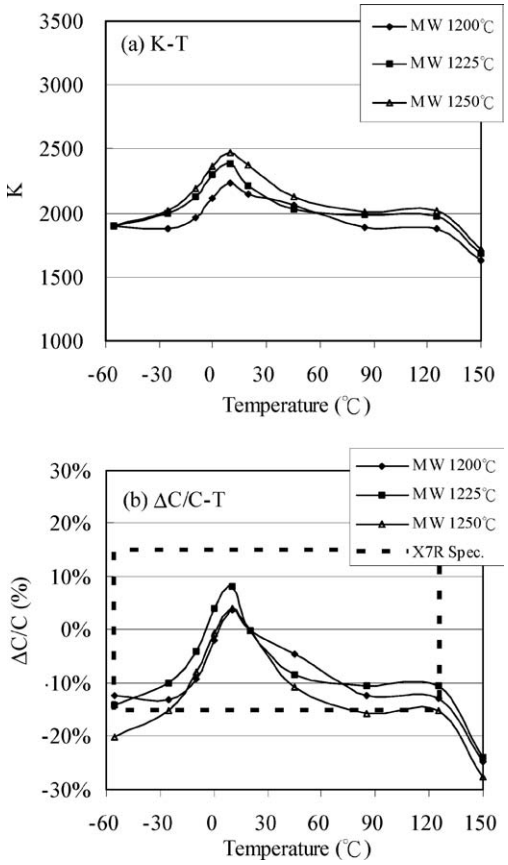

Fig. 3. (a) Dielectric constant-temperature, K-T, and (b) capacitance variation-temperature, ΔC/C-T, properties of the $BaTiO_3$ materials densified by microwave sintering process at 1200–1250°C for 10 min.

(0.2 μm) and the grain size distribution is very uniform. The microstructure of the samples microwave-sintered at other temperature (1100–1250°C) is not markedly different from that shown in Fig. 2(a). Moreover, granular microstructure of these samples is essentially the same as that of the materials prepared by conventional sintering process, which is illustrated in Fig. 2(b).

The dielectric constant-temperature (K-T) characteristics of these BTO materials shown in Fig. 3(a), indicate that the materials possess high room temperature dielectric constant ($K = 2000$) with very flat K-T properties, as long as the samples possess high enough density. High dielectric constant peak, which usually occurred at Curie temperature of BTO materials, is completely suppressed. Only a small hump is observed at around 10°C, which is typical characteristics of a heavily doped materials. This figure shows that increasing the sintering temperature from 1200° to 1250°C does not induce any pronounced change on the K-T characteristics of the samples. All the three samples possess small capacitance variation (ΔC/C), which meets X7R specification (Fig. 3(b)). Contrarily, for the conventional BTO materials process, the K-T curve was modified markedly and the ΔC/C-T characteristics shift off the X7R specification when the sintering temperature was increased, say from 1250°C (180 min) to 1300°C (180 min) [17].

On the other hand, Fig. 1(b) indicates that, when sintered at 1225°C, the density is higher than 94.5%T.D., which is sufficient for insuring high insulating resistance for these materials. In contrast, it needs at least 1250°C (180 min) to sinter the BTO materials to the same high density by conventional sintering process

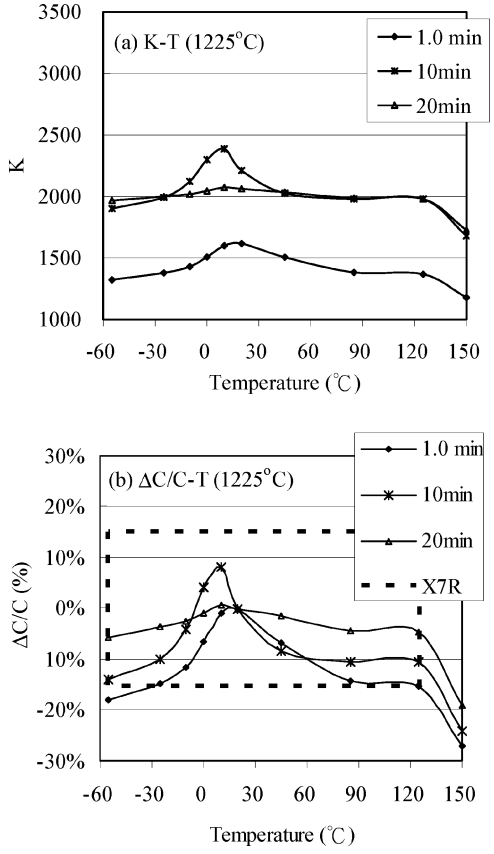

Fig. 4. (a) Dielectric constant-temperature, K-T, and (b) capacitance variation-temperature, ΔC/C-T, properties of the $BaTiO_3$ materials densified by microwave sintering process at 1225°C for 1.0, 10 or 20 min.

[17]. Soaking interval in microwave sintering process imposes slightly larger influence on the K-T behavior of the $BaTiO_3$ samples. Figure 4(a) shows that the dielectric constant (K) of the materials increased with samples' density and already reached $K = 2000$ for the samples soaked for 10 min (1225°C). Figure 4(b) indicates that the 10 min-soaked samples already possessed flat ΔC/C-T characteristics, satisfying the X7R specification. Longer soaking time (20 min) leads to even more flat ΔC/C-T characteristics, without changing the dielectric constant value. That the 1 min-soaked sample possesses slightly inferior dielectric properties is ascribed to the insufficient sintered density for the materials. These results demonstrate clearly that X7R-type characteristics for $BaTiO_3$ materials can be achieved for wide range of sintering temperature and soaking time in microwave sintering process. In contrast, for

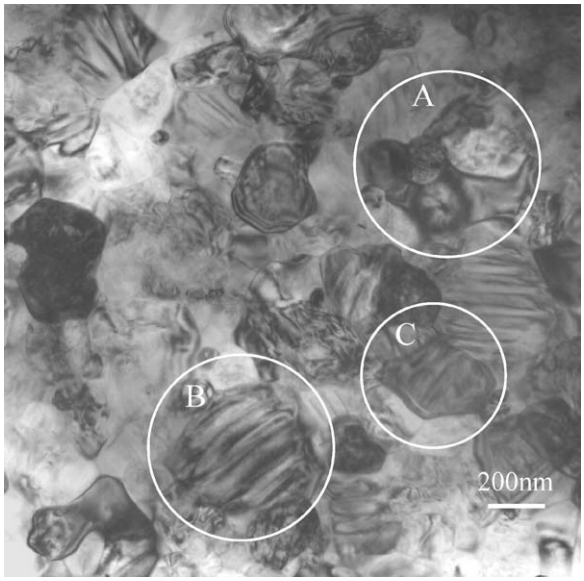

Fig. 5. TEM microstructure for $BaTiO_3$ materials, which were densified by microwave sintering technique at 1225°C for 10 min.

the $BaTiO_3$ materials prepared by conventional sintering process, the sintering parameters need to be critically controlled in order to maintain ΔC/C at small value.

Figure 5 reveals that the detailed microstructure of the microwave-sintered materials is surprisingly complicated. Most of the grains are very small (80–120 nm) and are highly strained (labeled as A). These fine grains contain no ferroelectric domains and are presumed to be paraelectric. Large grains (300–400 nm), which are frequently observed, contain clear domain structure and are ferroelectric (labeled as B). Core-shell structured grains (labeled as C) are seldom observed. The fine grains are probably resulted from the pronounced inward diffusion of dopants, Y_2O_3 and MgO, into the $BaTiO_3$ grains, which suppressed the grain growth mobility and induced large proportion of strains. The large grains contain smaller proportion of dopants and can grow to a larger size, preserving ferroelectric characteristics. The implication of the microstructure observed in Fig. 5 is that flat K-T behavior (small capacitance variation, ΔC/C) for $BaTiO_3$ materials can also be achieved by randomly mixing the paraelectric grains with the ferroelectric ones. Core-shell microstructure is not really necessary.

The significant feature of such a unique microstructure is that the kinetics of interdiffusion between

dopants (Y_2O_3/MgO) and $BaTiO_3$ grains are markedly enhanced in microwave sintering process. Most of the dopants can be incorporated into the grains in a very short period, resulting in highly strained paraelectric $BaTiO_3$ grains. There exist very few non-equilibrium grains, i.e., core-shell structured ones. Increasing the sintering temperature or extending the soaking times only increases the sintered density of the samples, without further modifying the microstructure. The desired flat K-T dielectric properties for the materials can be obtained for wide range of sintering temperature and soaking time. Restated, the control on the sintering parameters is markedly relaxed in microwave sintering process. In contrast, for the conventionally sintered $BaTiO_3$ materials, core-shell structured grains with large shell-to-core thickness ratio are needed to result in flat dielectric constant-temperature (K-T) properties for these materials. The core-shell structure is a non-equilibrium microstructure, which changes with sintering conditions profoundly. Therefore, the processing parameters need to be stringently controlled in order to maintain the desired microstructure and the flat K-T behavior for the $BaTiO_3$.

4. Conclusion

$BaTiO_3$ materials simultaneously co-doped with Y_2O_3/MgO species were sintered by microwave sintering process. The samples can be densified efficiently such that the density for the materials achieves 94.5%T.D. when sintered at 1225°C for only 10 min. The samples possessing high enough density exhibit small capacitance variance ($\Delta C/C$). The materials meet X7R specification for wide range of of sintering temperature and soaking time. TEM examinations reveal that the detailed microstructure is extremely complicated, although the grains are uniformly small for all samples. The unique dielectric constant-temperature (K-T) characteristics of the samples are ascribed to the duplex structure of the samples, which contain fine grains of paraelectric phase and large grains of ferroelectric phase.

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