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Microwave sintering and grain growth behavior of nano-grained $BaTiO_3$ materials

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Abstract

In this paper, we investigated the effect of microwave sintering parameters on the development of the microstructure of nano-grained $BaTiO_3$ materials co-doped with Y and Mg species. It is observed that the materials can not only be sintered densely at a lower temperature (1150 °C) and a shorter soaking time (20 min), but also the grain growth can be suppressed by 2.45 GHz microwave heating process. However, the grain growth exhibits a unique tendency in some processing conditions such as microwave sintering for longer intervals ($\geqq$60 min) or at higher temperatures (1200 °C). The grain growth behavior after densification was investigated in terms of the phenomenological kinetics, and the activation energy for grain growth using microwave sintering (59.4 kJ/mol) is considerably less than that of the conventionally sintered ones (96.0 kJ/mol), which indicates that microwave sintering process can accelerate the densification rate of the $BaTiO_3$ materials comparing with the conventional sintering process.

Keywords: A. Grain growth; A. Microwave processing; B. Microstructure-final; D. $BaTiO_3$ and titanates

1. Introduction

Barium titanate ($BaTiO_3$)-based ceramics have attracted much interest and have received a favorable review, both from fundamental and from applied aspects, such as multilayer ceramic capacitors (MLCCs) and positive temperature coefficient resistors (PTCRs) etc. [1]. Pure $BaTiO_3$ is a typical ferroelectric material with high dielectric constant ($k \sim 10000$). Its dielectric properties can be modified by adding either acceptor or donor dopants. For instance, $BaTiO_3$ can co-doped with abundant Y_2O_3 and MgO species to achieve high temperature stability of dielectric constant for X7R type MLCCs applications [2,3]. With the miniaturization of MLCCs, however, high dielectric constant material with fine grains is required for thinner dielectric layer to achieve large-capacitance MLCCs with small size, and that also to improve the DC degradation and voltage breakdown strength [4]. In view of this, a sintering process which can effectively densify the materials without inducing the growth of grains is thus demanded. Previously, many materials have been successfully sintered and fine grain size, uniform microstructure and significant energy savings were achieved by microwave sintering [3,5–7]. The advantages of microwave sintering were not only found to include higher energy efficiency, higher post sintering density and low sintering temperatures, but also reduced activation energy compared to conventional sintering [7]. At present, there are only few reports concerning the densification of $BaTiO_3$-based materials by using microwave sintering [3,8]. In this paper, therefore, microwave-sintering technique was adopted to densify the nano-grained $BaTiO_3$ materials co-doped with Y and Mg species. The effect of processing parameters on the densification behavior and the related microstructural characteristics of these $BaTiO_3$ materials were examined. The results were compared to that obtained by conventional sintering process.

2. Experimental procedures

Commercial $BaTiO_3$ (the particle size is of about 70 nm, TPL Inc, USA) were used as starting materials. Co-doped with

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3 mol% yttrium nitrate ($Y(NO_3)_3{\cdot}6H_2O$) and 2 mol% magnesium acetate ($Mg(CH_3COO)_2{\cdot}4H_2O$) by chemically precipitated coating method [9]. The co-precipitated powder was mixed with 3 mol% sintering aids ($(Ba_{0.6}Ca_{0.4})SiO_3$, which has stronger microwave absorbability and does not induce marked grain growth of the $BaTiO_3$ materials [10], by ball-milling for 24 h and dried. After being calcined at 950 °C for 2 h, the as-calcined mixtures were ball-milled again for 10 min by an attritor. The mixtures were pressed at about 50 MPa into pellets using a die with 10 mm diameter and then sintered at 950–1200 °C for 0.1–30 min in a CEM MAX-7000 microwave furnace (MS series), using 2.45 GHz microwaves generated from a commercial source. The temperature profile was measured using Pt–13%Rh thermocouples placed near the sample surface. The heating rate and the cooling rate were 30 °C/min. For comparison, samples were also prepared by a conventional sintering process (CS series), that is, sintering at 1100–1250 °C for 2 h in an electrical furnace. The heating rate and the cooling rate were 10 °C/min.

The sintered density was measured using Archimedes' method. The average grain size, G, as described by Mendelson [11], is obtained as $G = 1.56L$, where L is the average grain-boundary intercept length of a series of random lines on the micrographs. In microstructural analysis, a scanning electron microscopy (SEM, Jeol 6500F) was employed to examine microstructural characteristics.

3. Results and discussion

Microwave sintering process can densify the nano-grained $BaTiO_3$ materials very efficiently. Fig. 1(a) shows that the relative density of the samples already reach 90%T.D. (theoretical density) by microwave sintering the materials at 1100 °C for 20 min. The density of the samples increases gradually with the sintering temperature, reaching 96%T.D., for 1200 °C sintered ones. Furthermore, Fig. 1(b) shows that the density of the 1150 °C-sintered samples for various soaking time. The density of the samples rises gradually with the soaking time and reaches a maximum value, 95.5%T.D., at soaking time in the 20–30 min.

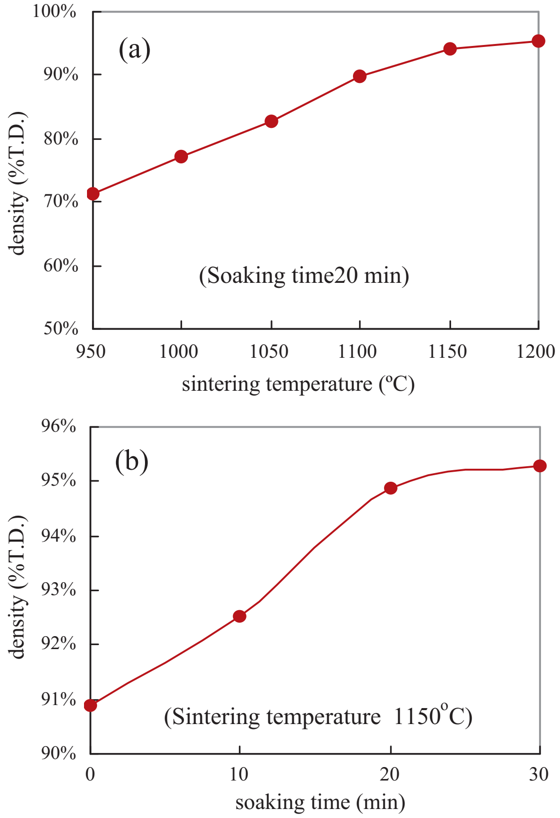

Fig. 1. Effect of (a) sintering temperature and (b) soaking time on the densification behavior of microwave-sintered $BaTiO_3$ materials which were co-doped with 3 mol% Y and 2 mol% Mg species.

To further understand how the different sintering processes influence the densification behavior of the $BaTiO_3$ materials, the samples are sintered using an electrical furnace. Fig. 2 shows a comparison of relationships between the relative density and the sintering temperature of $BaTiO_3$ materials using microwave (MS) and conventional sintering (CS) process. It reveals that, at the same sintering temperature, the density of the MS samples is much higher than that of the CS samples. Furthermore, it is evident that it needed only 1100 °C to densify the $BaTiO_3$ materials to a density of 92.5%T.D., whereas it required at least 1200 °C to reach the same density for $BaTiO_3$ materials using conventional sintering. This indicates that the microwave sintering process is more easy to achieve higher densification at lower temperature. Besides, it is noticed that the density of the samples microwave sintered for only 20 min (refer MS-20 curve) is superior to that of the samples conventionally sintered for 2 h when the sintering temperature is the same. For example, at 1200 °C, the density of the $BaTiO_3$ materials for microwave and conventional sintering processes are found to be 96%T.D. and 92%T.D., respectively. The result implies that the microwave sintering process substantially enhances the densification rate of $BaTiO_3$ materials such that the sintering time needed is markedly shortened.

SEM micrograph shown Fig. 3(a) indicates that, typically, the MS samples contain very fine grains and the grain size

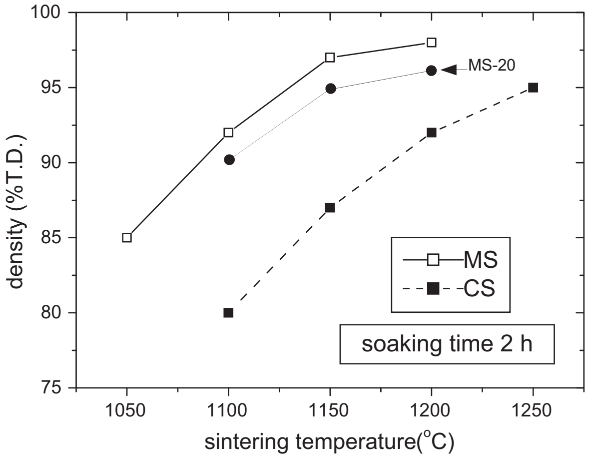

Fig. 2. Relative density as a function of sintering temperature of microwave-sintered (MS) and conventionally sintered (CS) $BaTiO_3$ materials which were co-doped with 3 mol% Y and 2 mol% Mg species materials (MS & CS: soaking time of sintering is 2 h; MS-20: soaking time of sintering is 20 min).

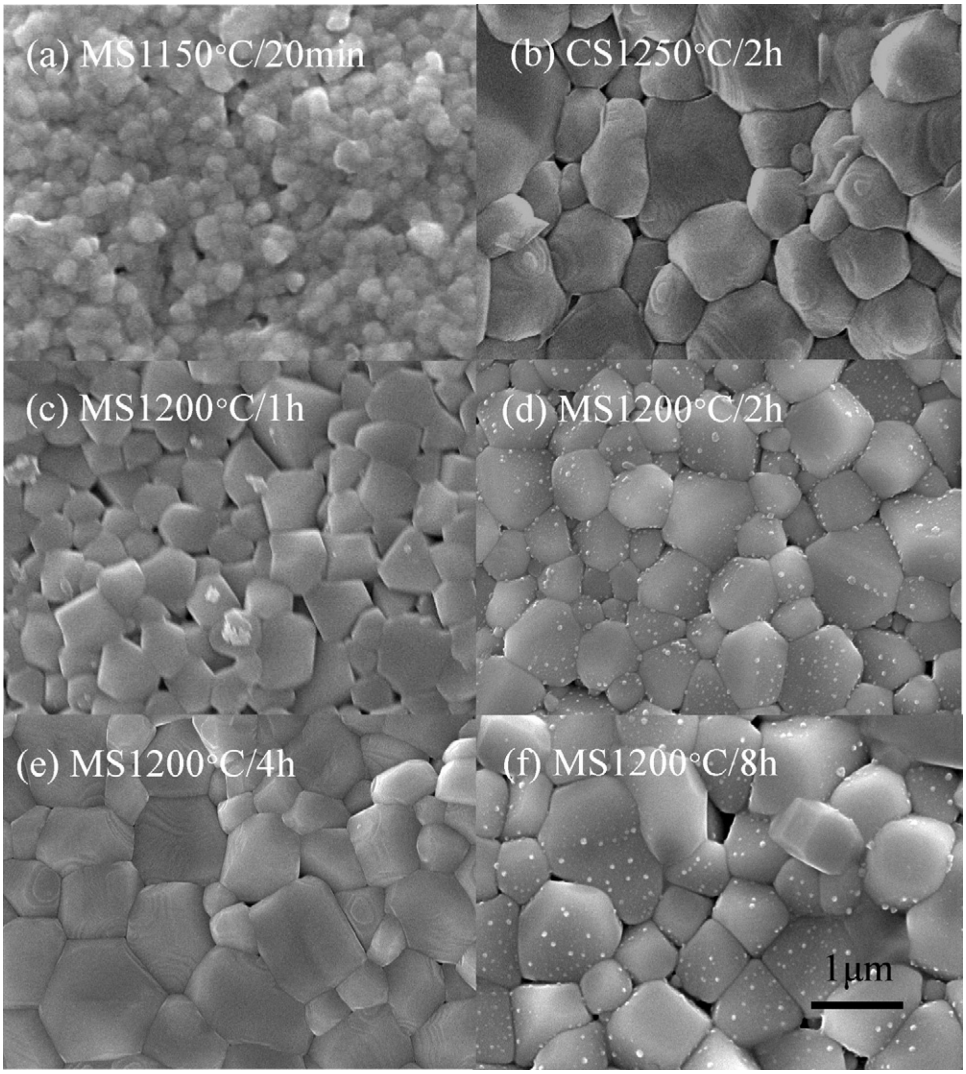

Fig. 3. SEM micrographs of (a): microwave-sintered (MS) $BaTiO_3$ materials densified at 1150 °C for 20 min; (b): conventionally sintered (CS) $BaTiO_3$ materials densified at 1250 °C for 2 h; (c)–(f): microwave-sintered (MS) $BaTiO_3$ materials densified at 1200 °C for 1, 2, 4 and 8 h, respectively.

distribution is very uniform. On the other hand, Fig. 2 indicates that, when sintered at 1150 °C for 20 min, the density already reach 95%T.D., which is sufficient for insuring high insulating resistance for these materials. In contrast, it needs at least 1250 °C (120 min) to sinter the $BaTiO_3$ materials to the same high density by a conventional sintering process. However, granular microstructure of the conventionally sintered samples, which is illustrated in Fig. 3(b), is markedly different from that of the materials prepared by microwave sintering process. These conventionally sintered samples exhibit markedly larger grain size than that of microwave-sintered ones. According to the above experimental results, the microwave sintering process is observed to densify effectively the $BaTiO_3$ materials without inducing the growth of grains at a very rapid rate and at a substantially lower temperature.

The grain growth, however, is also observed with the increase of sintering temperature and it already started at 1200 °C. The evolution of microstructure with sintering interval is shown in Fig. 3(c)–(f) for the 1200 °C-sintered MS samples which soaked for 1, 2, 4 and 8 h, respectively. The grain size of these fully densified MS samples is increased gradually with the soaking period. Most of the grains of MS samples are of faceted geometry and their size is still smaller than that of CS samples (Fig. 3(b)). The average grain size versus soaking period for $BaTiO_3$ materials sintered at various temperatures by microwave and conventional process is plotted in Fig. 4. The grain size is found to increase with soaking time and this trend is more significant at higher sintering temperatures. In another word, grain growth takes place by diffusion when the temperature is high enough and time of heat treatment is long enough.

Generally, grain growth occurs in polycrystalline materials to decrease the free energy of the system by decreasing the total grain boundary energy. The grain growth behavior of polycrystalline materials was reported to obey the equation: $G_n - G_0^n = kt$, where G_0 is the initial grain size, G is the grain size at time t, n is a grain growth exponent, k is the growth rate constant [12]. If G_0^n is negligible compared with G^n, then the above equation becomes $\log(G) = (1/n)\log(k) + (1/n)\log(t)$. Moreover, the k is a temperature dependent parameter, given as $k = k_0 \exp(-Q/RT)$ where k_0 is a constant, Q is the activation

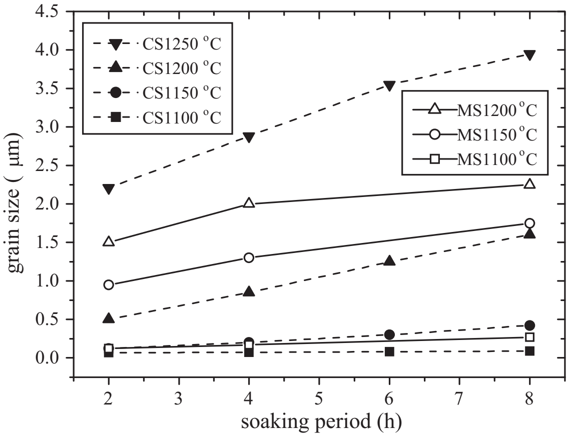

Fig. 4. Average grain size versus soaking period for $BaTiO_3$ materials sintered at various temperatures using a microwave (MS) and a conventional (CS) sintering process.

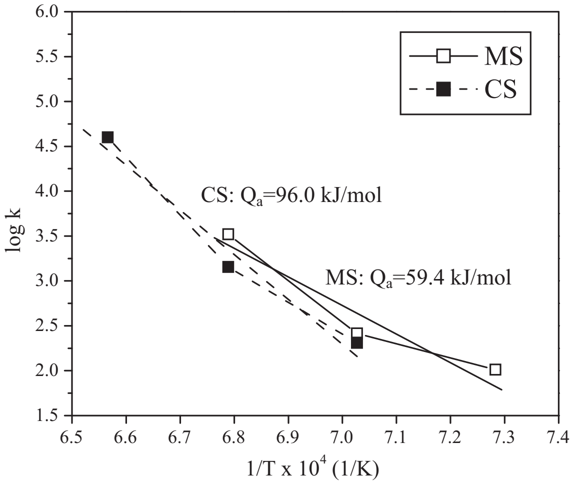

Fig. 5. The plots of log(k) versus 1/T for the calculation of activation energy (Q) for microwave-sintered (MS) and conventionally sintered (CS) $BaTiO_3$ materials which were co-doped with 3 mol% Y and 2 mol% Mg species.

energy for the grain growth, T is the sintering temperature (K) and R is the universal gas constant. The value of grain growth exponent n can be obtained from the straight line plots of logarithm of grain size (G) versus soaking time (t). The activation energy (Q) for grain growth can be deduced from the slope of the fitted straight line by plotting the graph between log(k) and 1/T based on the sintering temperatures (as shown in Fig. 5). The calculated activation energy for grain growth is 59.4 kJ/mol for the microwave-sintered specimen, which is much lower than activation energy calculated by conventional sintering (96.0 kJ/mol). The result indicates again that microwave energy consumed to sinter the $BaTiO_3$ materials is more efficient than that of conventional process. Besides, the decrease in activation energy might be attributed to microwave energy can interacts effectively with the sintering aids $(Ba_{0.6}Ca_{0.4})SiO_3$, which leads to rise fast the local temperature of a silicate-based liquid phase around the nano-sized $BaTiO_3$ grains and enhances consequently the rate of mass transport during the sintering period, i.e. the $(Ba_{0.6}Ca_{0.4})SiO_3$ addition is expected to be melted rapidly by absorbing incident microwave radiation and to form subsequently a silicate-based liquid phase at grain boundaries at the initial stage of microwave sintering period. The liquid phase is believed to offer a rapid path for matter transfer along the grain boundary. The above-mentioned results and discussion infer that the grain boundary diffusion should be a main diffusion mechanism for the nano-sized $BaTiO_3$ materials densified by microwave sintering, which would make the possibility for better densification.

4. Conclusions

The microwave sintering and grain growth behavior of nano-grained $BaTiO_3$ co-doped with Y and Mg species were investigated. It was found that the activation energies required for grain growth through two different sintering processes are 59.4 kJ/mol and 96.0 kJ/mol for microwave-sintered (MS) and conventionally sintered (CS) specimens, respectively, which indicates that microwave sintering process can enhance effectively the densification behavior at a lower temperature (1150 °C) and a shorter soaking time (20 min). The decrease in activation energy for the MS specimens might be attributed to microwave energy interacting effectively with the sintering aids $(Ba_{0.6}Ca_{0.4})SiO_3$, which leads to a fast rise of the local temperature of a silicate-based liquid phase around the nano-sized $BaTiO_3$ grains and enhances consequently the rate of mass transport during the sintering period.

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