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Densification and micro-structure evolution of $BaTiO_3/ZrO_2$ composites

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Abstract

The sintering of $ZrO_2/BaTiO_3$ composites was studied by stepwise, individual and non-isothermal dilatometry methods. The composites were prepared by slurry mixing followed by drying, sieving and powder compaction by uniaxial pressing. High density sintered compacts were obtained by a variable time stepwise densification method using a starting mixture with 10 mol% zirconia. Addition of ZrO_2 to $BaTiO_3$ reduced the temperature at which sintering began and a broad range of temperature of high sintering rate was observed for the composite with 10 mol% ZrO_2 in the initial mixture. The addition of ZrO_2 suppressed abnormal grain growth and allowed more than 97% dense ceramics to be produced by stepwise isothermal densification in short dwell time. Kinetic parameters of sintering (exponent n, specific rate constant K_t and apparent activation energy E) were evaluated from which it can be found that the mechanism of sintering is constant in the temperature range from 1260 to 1310 °C.

Keywords: Sintering; Thermal analysis; Kinetics; Composite materials

1. Introduction

The piezoelectric ceramic materials such as $BaTiO_3$, $(Ba,Sr)TiO_3$ and $Pb(Zr,Ti)O_3$ (PZT) have many technical applications as actuators and sensors [1–3].

It is desirable to bring down the sintering time and temperature for the production of these ceramics. Lower sintering temperatures and time reduces the energy consumption and the evaporation of components in the process. A lot of effort has been done during the last two decades to reduce the sintering temperature of these materials while retaining or improving thermal, mechanical and electrical properties [4–10]. Among the methods investigated, are sintering of ultra-fine powders and use of additives [11,12].

Dielectric properties and structure of $BaTiO_3$ ceramics have been shown to be significantly influenced by small addition of some additives [13]. Observations revealed enhanced microstructural uniformity and retarded grain growth with ZrO_2 addition, depending on sintering temperature. The composite has a flattened dielectric constant response with temperature and significantly lower dielectric loss.

Many physical and chemical changes occur during ceramic consolidation, ranging from macro-scale changes in the volume of the entire ceramic body to micro-scale changes in the size or shape of the individual grains that comprise the ceramic body.

It is therefore desirable to monitor the micro-structural evolution during the entire course of densification. The properties of the final ceramics strongly depend on a green body microstructure and on conditions under which the green body is sintered. Specially, the temperature program during sintering is one of the most important parameters.

For this reason, dilatometry experiments are well suitable method to study the densification kinetics during sintering [14–16].

Despite all studies conducted on titanates, the densification kinetics of $BaTiO_3/ZrO_2$ has not been thoroughly studied before.

2. Experimental

Barium titanate and ZrO_2 powders with a mean particle size of 1–2 μm were used as starting materials. Desired amounts of these powders were mixed in water by a mechanical stirrer. The slurries were then dried at 150 °C for 3 h. The powders were die pressed at a pressure of 5 MPa in a 1-cm diameter steel die. The

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green bodies were first heated at 300 °C for 30 min in air and then sintered in air at 1270–1310 °C using different temperature programs. The sintering kinetics was observed with the help of a dilatometer (Netzsch 402 PC) applying the methods of stepwise isothermal dilatometry (SID) and non-isothermal dilatometry (NID). In the SID method, the temperature of the cylindrical sample was increased up to a definite temperature at a constant rate of 5 K/min. Then the isothermal steps at different time duration were programmed. The heating rate between isothermal holdings was 5 K/min. In the NID method, the temperature was increased up to final temperature by constant rate of 5 K/min. In addition to this, samples were measured also at each isothermal holding using each time new sample. This procedure is known as individual isothermal dilatometry (IID).

The shrinkage rate reports densification in only one dimension, whereas the densification rate reports densification in three dimensions, therefore, in the present study, sintering kinetics was studied with the densification rate as a function of density. The micro-structure of the fractured surface of the sintered samples was observed by scanning electron microscopy (SEM) (Philips XL30).

3. Results and discussion

In order to investigate the effect of ZrO_2 on the shrinkage of $BaTiO_3$, several composites with different mole ratios of $ZrO_2/BaTiO_3$ were prepared. The samples were pressed at 5 MPa, dried at 300 °C for 30 min, and then heated in an electrical kiln to 1270–1330 °C with 20 min holding time at each final temperature. Fig. 1 shows the dependence of the volume shrinkage of the samples on the mole fraction of zirconia. As it can be seen, the volume shrinkage of the composite sample with 10 mol% of ZrO_2 is greater than that of monolithic $BaTiO_3$ and also other composite samples. Then the subsequent experiments were conducted on this composite. Fig. 2 illustrates the longitudinal, radial and volume shrinkages of a $ZrO_2/BaTiO_3$ cylindrically shaped composite sample with 10 mol% of zirconia (10 mm diameter and 10 mm length) *versus* temperature. The shrinkage was anisotropic and the radial shrinkage varied proportional to the longitudinal shrinkage when the temperature of sintering increased. The volume shrinkage or densification rate was a favorable parameter for studying the kinetics of sintering.

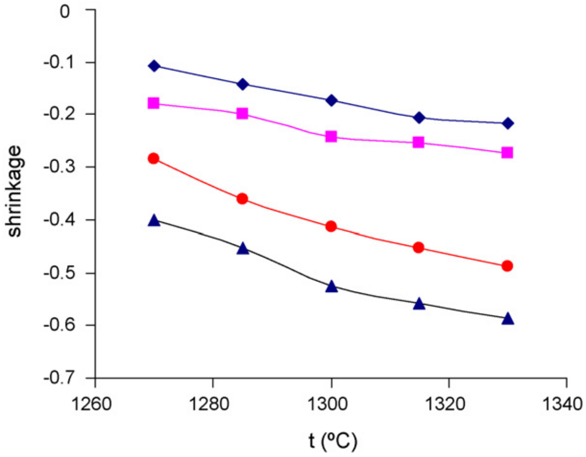

Fig. 2. Dependencies of shrinkage of a $ZrO_2/BaTiO_3$ composite with 10 mol% ZrO_2 on the temperature of sintering: (♦) longitudinal, (■) radial, (▲) volume, and (●) volume shrinkage of monolithic $BaTiO_3$ (dwell time 20 min).

Fig. 3 shows the typical dependence of the longitudinal shrinkage *versus* temperature and time in a non-isothermal dilatometric analysis (NID). The temperature profile is shown on the secondary axis for an easier analysis of the shrinkage data. The curves numbered 1–4 were obtained by NID with the final temperature of sintering 1270, 1280, 1290, and 1300 °C, respectively. It is clear that by increasing the final temperature of sintering the longitudinal shrinkage of the sample increases, however, the rate of linear shrinkage remains without change. A change of the sintering rate was observable in the temperature range of 1150–1250 °C. However, for a more suitable description of the micro-structure evolution in this temperature range, the plot of densification rate was prepared as a function of the relative density. The variation of the densification rate ($d\rho/\rho_f dT$) *versus* the relative density calculated by Eq. (1) is shown in Fig. 4. The study of these diagrams (Figs. 3 and 4), reveals that the samples are stable when the temperature increases up to 1010 °C. Then the rate of sintering increases and around 1150 °C (which corresponds to the relative density of 71%) experiences its first peak. As the temperature ramping continues, a second sharp increase in the shrinkage rate appears around 1250 °C corresponding to a relative density of 83%. Previous dilatometry of monolithic barium titanate had also indicated sintering rate peaks at 1170 and 1300 °C [17]. The first peak is related to grain boundary solid-state diffusion, while the higher temperature peak is considered to be due to liquid phase sintering [17]. Addition of ZrO_2 reduces the temperature at which sintering

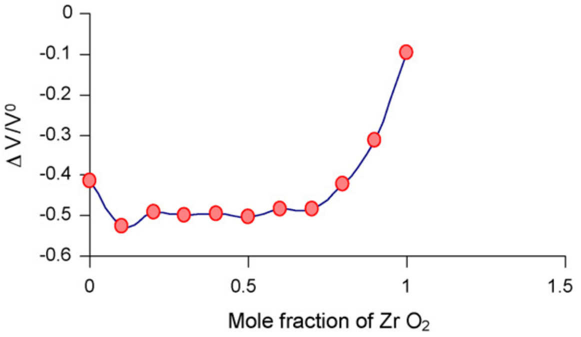

Fig. 1. Plot of volume shrinkage *vs.* mole fraction of ZrO_2 in the composite samples sintered at 1300 °C for 30 min.

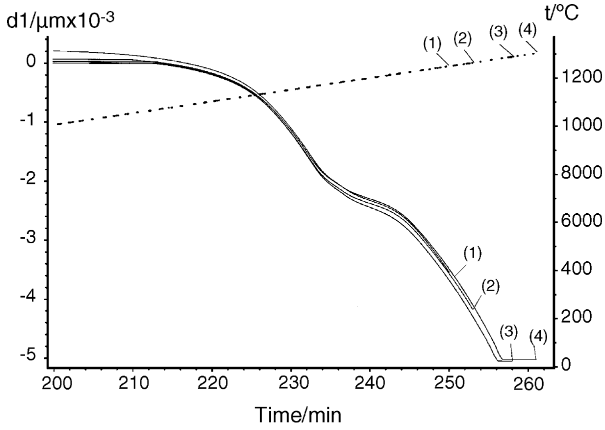

Fig. 3. Longitudinal shrinkage of a composite sample of $ZrO_2/BaTiO_3$ with 10 mol% ZrO_2 *vs.* temperature (dotted lines) and sintering time obtained by NID. Heating rate was 5 K/min. The final temperature of sintering was (1) 1270 °C, (2) 1280 °C, (3) 1290 °C and (4) 1300 °C.

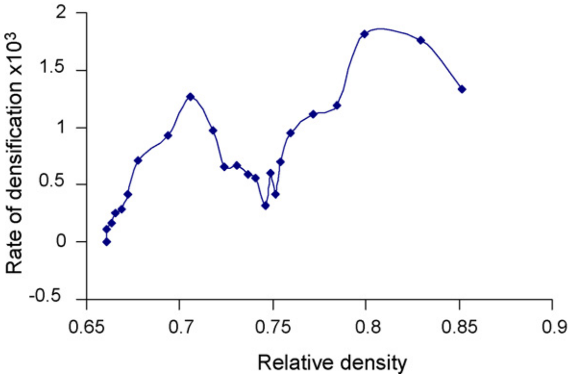

Fig. 4. Variation of densification rate *vs.* relative density calculated by Eq. (1).

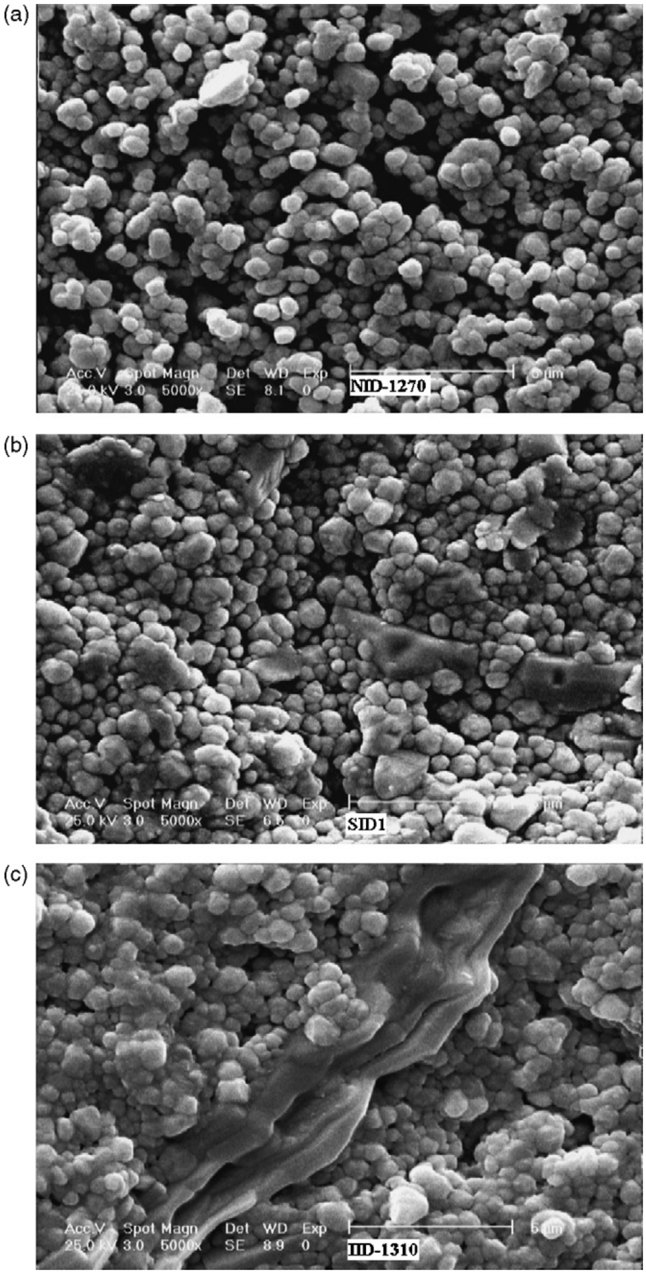

Fig. 5. SEM images of a $ZrO_2/BaTiO_3$ composite sample with 10 mol% ZrO_2 sintered by (a) NID method at 1270 °C, (b) SID method at a maximal temperature of 1310 °C after a dwell time of 10 min, (c) IID method at 1310 °C after a dwell time of 60 min.

began and a broad range of high sintering rate from ∼1150 to 1250 °C is observed for the composite samples with 10 mol% zirconia. The micro-structure of the specimen sintered in a NID experiment (final temperature of sintering 1270 °C) is shown in the SEM photograph (Fig. 5a), where the onset of abnormal grain growth (AGG) is not observed. Xue and Brook studied the increase of the sintering rate of monolithic $BaTiO_3$ at 1300 °C and they observed that the increase in densification rate is correlated with the onset of AGG [16]. This suggests that the presence of ZrO_2 at the grain boundaries can suppress the AGG of $BaTiO_3$ and that the onset of the abnormal grain growth occurs at higher temperature or after a long time of sintering. Conversely, in the SEM photographs of the samples sintered by IID or SID the existing of AGG is clearly observable (Fig. 5b and c). Therefore, it can be concluded that the AGG occurs in the final stage of the sintering.

As cited before, measurement of final longitudinal and radial shrinkage of the samples indicated that the shrinkage was anisotropic. The time-dependent relative density was calculated from the following expression:

$$\rho(t) = \left\{ \frac{[1+(L_\mathrm{f}-L_0)/L_0][1+(\varphi_\mathrm{f}-\varphi_0)/\varphi_0]^2}{[1+\Delta L(t)/L_0][1+\alpha\Delta L(t)/L_0]^2} \right\} \rho_\mathrm{f} \qquad (1)$$

L_f and L_0 are the final and the initial length of the specimen. φ_f and φ_0 are the final and the initial mean diameter of the specimen and $\Delta L(t)$ is the change in the length of the specimen. ρ_f is the final relative density, and α is the anisotropic shrinkage factor given as

$$\alpha = \frac{(\varphi_\mathrm{f}-\varphi_0)L_0}{(L_\mathrm{f}-L_0)\varphi_0} \qquad (2)$$

Fig. 6 compares the SID and IID curves of the sintering of $ZrO_2/BaTiO_3$ which are the base for the kinetic analysis of the processes. Curve 1 shows the linear shrinkage as a function of temperature which was increased stepwise from 1260 °C (20 min), 1270 °C (20 min), 1280 °C (20 min), 1290 °C (15 min), 1300 °C (10 min) and 1310 °C (10 min). The overall step time in the SID experiment (95 min) was the same as in the IID method. The curve nos. 2–5 were obtained by IID method with the temperature steps of 1260 °C (95 min), 1270 °C (95 min), 1280 °C (95 min), 1290 °C (95 min) and 1310 °C (60 min), respectively. It can be seen from Fig. 6 that in both cases the sintering is identical up to 1290 °C and the main difference between these methods appears at 1300 °C where sintering slows in IID. This behavior is due to onset of AGG in the final stage of sintering.

In the SID method, reducing the duration time of the isothermal heating steps at 1300 °C and above can cause the sintering process to proceed due to a more extensive normal grain growth (NGG) resulting in higher densification. In the IID method the high initial sintering rate accelerates the grain growth which traps the pores that cannot be easily removed during further sintering. In the IID method grain growth also occurs abnormally fast (Fig. 5c) and reduces the temperature range of high sintering rate.

Table 1
Kinetic parameters of sintering of a $ZrO_2/BaTiO_3$ sample with 10 mol% ZrO_2 for two different methods

IID method			SID method				
t (°C)	1310	1290	1270	1310	1300	1290	1280	1270
K_t ($\times 10^4\ s^{-1}$)	20.8 (5.2)	5.9	2.11	15.31	10.2	4.01	1.67	1.10
n	1.01 (1.06)	1.05	1.03	1.08	1.13	1.15	1.00	1.16
E (kJ/mol)	1161					1437		

K_t, n and E are the rate constant, reaction order and activation energy of sintering process, respectively. The numbers in parentheses are data related to the monolithic $BaTiO_3$.

The kinetics of isothermal sintering can be expressed in terms of the volume shrinkage which according to Ali et al. [18] is given as

$$\frac{V_0 - V_t}{V_0 - V_f} = \frac{[K_t(t - t_{0,T})]^n}{1 + [K_t(t - t_{0,T})]^n} \tag{3}$$

where V_0 is the initial volume of the green body, V_t the volume at time t, and V_f is the volume of a fully densed sample; t is the sintering time, $t_{0,T}$ the formal beginning of isothermal sintering, K_t the specific rate constant, and n is the parameter related to the sintering mechanism. Eqs. (1) and (3), can be combined into the relation:

$$\frac{\rho_f(\rho_t - \rho_0)}{\rho_t(\rho_f - \rho_0)} = \frac{[K_t(t - t_{0,T})]^n}{1 + [K_t(t - t_{0,T})]^n} \tag{4}$$

which can be used to monitor the rate of isothermal densification by measuring volume shrinkage of specimens. Fig. 7 shows good agreement of the calculated values with the experimental data. Fitting Eq. (4) to the experimental curve for each isothermal stage yielded the values of the parameters K_t and n (Table 1). Since n is independent of temperature, the mechanism of sintering is indicated to be constant. The lower value of the activation energy obtained during IID as compared to the SID experiments may be related to the higher heating rate. It has been recognized that the shrinkage rate increases almost linearly with the heating rate and then activation energy decreases [19]. In the present investigation during the isothermal steps of the SID method the temperature is constant and the shrinkage slowing down so that the activation energy increases compared with the IID method.

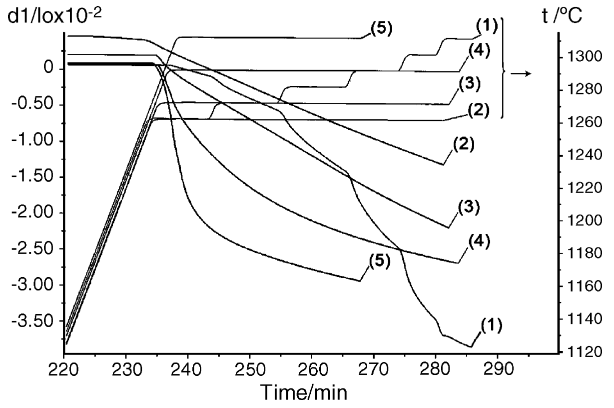

Fig. 6. Dependence of the longitudinal shrinkage on temperature and sintering time in the $ZrO_2/BaTiO_3$ composite sample with 10 mol% ZrO_2. (1) IID with the isothermal step at 1260 °C (holding time of 95 min), (2) IID with the isothermal step at 1270 °C (holding time of 95 min), (3) IID with the isothermal step at 1310 °C (holding time of 60 min) and (4) SID with the isothermal steps at 1260 and 1270 °C (holding time of 20 min), 1280 and 1290 °C (holding time of 15 min), 1300 and 1310 °C (holding time of 10 min).

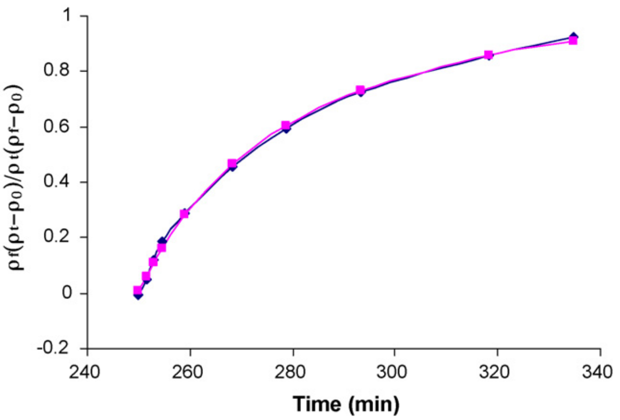

Fig. 7. Isothermal densification of a composite sample of $ZrO_2/BaTiO_3$ with 10 mol% ZrO_2. Comparison of experimental results obtained after IID (at 1190 °C, waiting time of 95 min) and values fitted with the help of Eq. (4).

4. Conclusion

The addition of 10 mol% of ZrO_2 to $BaTiO_3$ improves the shrinkage rate of the sintered samples. A stepwise isothermal densification with reduced heating times at temperatures higher than 1300 °C turned out to be a more suitable method than non-isothermal and individual isothermal sintering. Thereby more densified composites (97.2% theoretical density) can be obtained. At these conditions the sintering process proceeds more intensively by normal grain growth and in the final stage the onset of abnormal grain growth reduces the rate of sintering. The sintering mechanism occurs at a constant rate without phase transformation when the temperature is varied from 1260 to 1310 °C. Obviously, using finer powder, preparing green bodies with higher initial density, or sintering by hot isostatic presses higher densities near the theoretical one can be obtained.

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