Analysis of Early-Stage Sintering Mechanisms of Mechanically Activated BaTiO$_3$

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Abstract: Barium-titanate powder was mechanically activated in a planetary-ball mill for 60 and 120 minutes. Non-isothermal sintering of non-activated and activated powder samples was investigated using a dilatometer in the temperature interval from room to 1380°C with three different heating rates (10, 20 and 30°C/min). Early-stage sintering mechanisms for all three types of samples were analyzed, showing significant differences between the non-activated and mechanically activated samples.

Keywords: BaTiO$_3$, Mechanical activation, Sintering mechanism

Introduction

Materials based on barium-titanate have excellent dielectric and electromechanical properties and are thus often used in multilayer ceramic capacitors (MLLC), piezoelectric devices, electroluminescent panels, and polymer-matrix composites for integral passive devices. Other applications also include coatings for shielding and electro-static control [1]. In order to reduce particle size and modify physico-chemical properties mechanical activation of initial powders by high-energy ball milling is often used [2]. Soft agglomerates often form in mechanically activated powders as a result of increased surface energy of mechanically activated powders, while the particle morphology remains relatively irregular. The constant heating method has been often used to investigate sintering mechanisms of different materials, such as for example UO$_2$ [3], Ni-Zn ferrites [4], and CeO$_2$ [5]. In this paper we have investigated the influence of mechanical activation on non-isothermal sintering of BaTiO$_3$ by analyzing early stage (initial and intermediate stages) sintering mechanisms.

Based on the general equation for isothermal initial-stage sintering proposed by Woolfrey and Bannister [6],

$$\frac{d}{dt}\left(\frac{\Delta L}{L_0}\right) = A_0 \exp\left(-\frac{Q}{RT}\right)\left(\frac{\Delta L}{L_0}\right)^m$$

(1)

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where $\Delta L/L_0$ is relative shrinkage, $t$ is time $A_0$ is a constant depending only on the material parameters and sintering mechanisms and $m$ has different values depending on dominant mass transport mechanisms ($m=0$ for viscous flow, $m=1$ for volume diffusion, $m=2$ for grain boundary diffusion [7]). Young and Cutler [8] derived several equations for describing initial sintering by measuring powder compact shrinkage at constant heating rates, either using shrinkage or shrinkage-rate. The first using shrinkage is in the following form:

$$(\Delta L / L_0) / T = A_1 \exp \left[ -\frac{Q}{(m+1)RT} \right]$$

(2)

In logarithmic form:

$$\ln[(\Delta L / L_0) / T] = -\frac{Q}{(m+1)RT} + \ln A_1$$

(3)

The second one uses the shrinkage rate in the following form:

$$T^2 d(\Delta L / L_0) / dt = A_2 \frac{Q}{(m+1)RT} \frac{1}{L_0} \left( \frac{\Delta L}{L_0} \right)$$

(4)

where $A_1$ and $A_2$ are constants depending only on the material parameters and sintering mechanisms. Both shrinkage and shrinkage-rate equations are used for data analysis [6]. No assumptions are made regarding geometry or the sintering mechanism, except that one rate-controlling mechanism dominates.

The value of $m$ can be obtained using either isothermal or non-isothermal techniques [5]. Woolfrey and Bannister [6] obtained $m$ by performing experiments with different heating rates.

In the case when only one heating rate is used or shrinkage depends on the heating rate the Dorn method is used to determine the instantaneous effect of a small change in temperature on the shrinkage rate [6]. If $V_1$ is the shrinkage rate at temperature $T_1$ just before the temperature change and $V_2$ is the shrinkage rate at $T_2$ just after the change, then the apparent activation energy of the process responsible for sintering is given by [3,6]:

$$Q = \frac{RT_1 T_2}{T_2 - T_1} \ln \left( \frac{T_2 V_2}{T_1 V_1} \right)$$

(5)

This method does not need a theoretical model, as the use of different theoretical equations that depend on the densification state studied is not necessary [3].

**Experimental**

A commercial BaTiO$_3$ powder (Merck 99.8% purity Ba/Ti ratio of 1:1, mean grain size ~ 1 $\mu$m) was used as the starting material. The powder was mechanically activated in a planetary-ball mill in a continuous regime for 60 and 120 minutes. After mechanical activation samples of the powders obtained and the non-activated powder were pressed into pellets 6 mm in diameter with an average thickness of 4 mm. Non-isothermal sintering of these samples was carried out in a dilatometer (Bahr Geratebau GmbH) at three heating rates (10, 20 and 30°C/min) up to 1380°C.

**Results and discussion**

Fig. 1 shows plots calculated using eq. 4 for the non-activated (fig. 1a) and samples activated for 60 (fig. 1b) and 120 minutes (fig. 1c). According to Woolfrey and Bannister [6] the slope of this plot is correct irrespective of the sintering mechanism.
Differences between the plots calculated for the non-activated and activated samples can be noted. The linear curve parts represent stages in which one sintering mechanism was dominant, while non-linear parts represent transition regions between two mechanisms. According to Young and Cutler [8] a change in the slope could be caused by a particle size distribution, a change in mass transport mechanism or by a change in relation between sintering mechanisms (which is dominant).

For the non-activated powder shrinkage started at the temperature of 1070°C and there is one linear stage between 2 and 8% in the temperature range of 1150-1210°C. It is followed by a transition region between 1210-1240°C, while the final stage was for shrinkage between 13 and 20%. They were the same irrespective of the heating rate. Both activated powders showed similar behaviour. Shrinkage started at lower temperatures than was the case for the non-activated powder. The early sintering stage until achieving a maximal shrinkage rate is characterized by several segments, while the slope of the final stage of sintering is much steeper for both activated powders compared to the non-activated one.

For the powder activated 60 min three linear curve parts were noted with transition regions in between compared to one for the non-activated powder until the maximum shrinkage rate was achieved. The values of shrinkage and temperature of these stages are given in tab. I. One can note that these three stages occurred at similar temperatures for all three sintering rates though the shrinkage values were different and depended on the heating rate.

Similar behaviour was noted for the powder activated 120 min (three linear stages) and the values obtained are given in tab. I. Compared to the powder activated for 60 minutes the first linear stage started at lower temperatures for the powder activated 120 minutes, while the other two linear stages were at slightly higher temperatures.
Tab. I Shrinkage (denoted as $s$ in %) and temperature of three sintering stages of BaTiO$_3$ powder activated for 60 and 120 minutes where one sintering mechanism is dominant

<table>
<thead>
<tr>
<th>Powder activated 60 minutes</th>
<th>stage</th>
<th>heating rate $10 , ^{\circ} \text{C/min}$</th>
<th>heating rate $20 , ^{\circ} \text{C/min}$</th>
<th>heating rate $30 , ^{\circ} \text{C/min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$s_1$</td>
<td>$s_2$</td>
<td>$T_1$</td>
</tr>
<tr>
<td>I</td>
<td>2.73</td>
<td>3.83</td>
<td>945</td>
<td>1027</td>
</tr>
<tr>
<td>II</td>
<td>4.25</td>
<td>5.21</td>
<td>1050</td>
<td>1084</td>
</tr>
<tr>
<td>III</td>
<td>11.4</td>
<td>14.4</td>
<td>1179</td>
<td>1209</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Powder activated 120 minutes</th>
<th>stage</th>
<th>heating rate $10 , ^{\circ} \text{C/min}$</th>
<th>heating rate $20 , ^{\circ} \text{C/min}$</th>
<th>heating rate $30 , ^{\circ} \text{C/min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$s_1$</td>
<td>$s_2$</td>
<td>$T_1$</td>
</tr>
<tr>
<td>I</td>
<td>2.05</td>
<td>4.76</td>
<td>854</td>
<td>1046</td>
</tr>
<tr>
<td>II</td>
<td>6.81</td>
<td>7.63</td>
<td>1113</td>
<td>1133</td>
</tr>
<tr>
<td>III</td>
<td>15.89</td>
<td>17.23</td>
<td>1231</td>
<td>1240</td>
</tr>
</tbody>
</table>

These differences between shrinkage behaviour for the non-activated and activated powders are in accordance with our previous analysis where we established a correlation between shrinkage and densification rates and microstructure evolution [9]. Then, we divided the increasing part of the densification rate curve for mechanically activated samples into three processes. The first process was attributed to intra-agglomerate particle sintering; the second one to the sintering of grains between the aggregates and the third process was attributed to aggregate sintering. Microstructure analysis also showed differences in the structure of the non-activated powder and the activated ones.

As shrinkage of the activated powders depended on the heating rate Dorn’s method (eq. 5) was used to determine apparent activation energy values for both activated powders and the non-activated powder. The values obtained for the non-activated powder and powder activated 60 and 120 minutes are given in tab. II. The apparent activation energy value obtained for the non-activated powder is in accordance with the values determined by Genuist and Haussonne [10]. For the activated powders apparent activation energy values are lower than for the non-activated powder and are similar for both activation times. Mechanical activation led to intensification of transport processes and thus increased sinterability.

**Tab. II** Values of apparent activation energy and $m$ for non-activated BaTiO$_3$ powder (a) and BaTiO$_3$ powder activated for 60 (b) and 120 (c) minutes, respectively

<table>
<thead>
<tr>
<th>Powder</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q$ [kJ/mol]</td>
<td>$m$</td>
<td>$Q$ [kJ/mol]</td>
</tr>
<tr>
<td>a</td>
<td>523</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>114</td>
<td>2.26</td>
<td>409</td>
</tr>
<tr>
<td>c</td>
<td>110</td>
<td>1.64</td>
<td>380</td>
</tr>
</tbody>
</table>

Plots of $\ln[\Delta L/L_0]$ versus $1/T$ using eq. 3 in the relative shrinkage range of 2-8% are given in fig. 2. The three curves corresponding to the three different heating rates exhibit almost the same slope. The average of all three slopes is used to calculate the value of the exponent $m$ reflecting the dominant sintering mechanism that is also given in tab. II.
6.75 6.80 6.85 6.90 6.95 7.00 7.05
-11.5
-11.0
-10.5
-10.0

heating rate [K/min]

10 20 30

\ln(\Delta L/L_0/T) 10^{-4}/T [K^{-1}]

Fig. 2 ln(\Delta L/L_0/T) versus 1/T for non-activated BaTiO_3

The plots of ln[\Delta L/L_0] versus 1/T using eq. 3 in the three analyzed shrinkage ranges for BaTiO_3 powder activated 60 and 120 minutes also exhibited almost the same slope for all three heating rates and the average values of m are also given in tab. II. An example is given in fig. 3.

An analysis of the values obtained for m show that different sintering mechanisms are dominant in the early sintering stage for the case of non-activated and activated powders. According to the definition of m by Woolfrey and Bannister [6] in the case of the non-activated powder it is volume (bulk or lattice) diffusion (m=1), while grain-boundary diffusion is dominant in the case of the activated powders (m≥2).

Conclusion

In this paper early stage (initial and intermediate stages) sintering mechanisms of mechanically activated BaTiO_3 powder were analyzed and compared with non-activated
BaTiO$_3$ powder. It was found that the shrinkage rate depended on the heating rate and that the early sintering stage of mechanically activated BaTiO$_3$ consisted of three stages where one sintering mechanism is dominant (grain boundary diffusion) interconnected with transition stages compared to non-activated BaTiO$_3$ where there was only one stage. Apparent activation energies were calculated using Dorn’s method and they were lower for the activated powder compared to the non-activated one.

Acknowledgements

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References