Effect of High Energy Milling on the Preparation and Properties of Barium Titanate


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ABSTRACT

A high energy ball milling technique was used to prepare BaTiO$\textsubscript{3}$ powder from equal molar mixture of BaCO$\textsubscript{3}$ and TiO$\textsubscript{2}$ powder. The effect of the milling time, calcination time, and calcination temperature on the BaTiO$\textsubscript{3}$ formation and its sintering behavior were investigated. It was found that, a milling time of 7.5 hours was quite sufficient to form single phase BaTiO$\textsubscript{3}$ at 750°C/10hrs. Irrespective of the milling time, the rate of formation of BaTiO$\textsubscript{3}$ phase increases with the increase in calcination time and calcination temperature. In addition, the TMA results showed that the shrinkage of BaTiO$\textsubscript{3}$ compact proceeds at lower temperature upon increasing the milling time.

Key Words: Ferroelectric Materials / Barium Titanate (BTO) / preparation& Properties.

INTRODUCTION

Several ceramic materials with ferroelectric properties have been developed and utilized for a variety of applications. The perovskite family having a structure of the type ABO$\textsubscript{3}$ such as; barium titanate (BaTiO$\textsubscript{3}$), lead titanate (PbTiO$\textsubscript{3}$), lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT), and lead magnesium niobate (PMN, relaxor ferroelectrics) is the most popular type. Among these, barium titanate is the most widely used material due to its high dielectric constant and low dielectric loss. BaTiO$\textsubscript{3}$ is a good candidate for a variety of applications, such as multilayer ceramic capacitors (MLCCs), electro-optic devices, piezoelectric actuators, and positive temperature coefficient resistors (PTCR) due to its excellent dielectric, ferroelectric and piezoelectric properties.$^{(1)}$

The recent development of thinner multilayer ceramic capacitors (MLCCs) has increased the demand for high purity fine barium titanate powders with uniform particle size distribution. During the last decade a wide number of synthetic methods have been developed for the preparation of barium titanate powders, but large scale production is frequently based on solid-state reactions of mixed oxides. In this process, barium titanate powders were conventionally synthesized by solid-state reaction between BaCO$\textsubscript{3}$ and TiO$\textsubscript{2}$ at high temperatures, 1100-1200,$^{(2,3,4)}$.

The high calcination temperature required by the solid-state reaction process leads to many disadvantages in the BaTiO$\textsubscript{3}$ produced such as; large particle size, broad size distribution and high degree of particle agglomeration, which generally limits the ability to fabricate reliable electronic components.$^{(5)}$ So it is desirable to lower preparation temperature in order to obtain fine and homogenous BaTiO$\textsubscript{3}$ powder, which might enable the use of base metal electrodes such as Ni electrode in the capacitors, and consequently reduce its the cost.$^{(5)}$. Some authors reported that, the formation temperature of BaTiO$\textsubscript{3}$ could be reduced by mechanical activation of raw materials during
powder processing, using high energy milling (6-9). The aim of this work is to study the effect of the high-energy ball milling on the formation of barium titanate powder by solid state reaction.

EXPERIMENTAL PROCEDURE

An equimolar mixture of commercial BaCO₃ (99% purity, Aldrich Chemical Company, USA) powder together with a very fine titanium dioxide (TiO₂) were used as the starting materials. The TiO₂ was accidentally obtained upon inconvenient storage conditions of TiCl₄ (Aldrich Chemical Co. Ltd., Gillingham-Dorset-England) by oxidation and hydrolysis. The obtained TiO₂ had a surface area of 86 m²/g. A slurry of BaCO₃-TiO₂ powder mixture in alcohol was milled in the planetary mill (Retsch PM400-Fritsch, Germany) for different milling times: 2.5, 5, 7.5, 10, and 12.5 hours. Two 250 ml plastic polyamide bowls and 32 agate balls (for each bowl) having a diameter of 15mm and 5.6 gm weight were used as a milling medium. The milling speed was set at 200rpm. The milling was stopped for 5 min every 30 min of milling to cool down the system. The slurry was dried at 90°C in the drying Furnace (NEY Furnace, M-525) and then crushed in Agate Mortar (Fritsch, Germany) to break the agglomerates. The powder was sieved by passing through 112 µm sieve. The sieved powder was calcined (Carbolite Furnace, GPC 1300, UK) at different temperatures (600-900°C) and different calcinations times, with a heating rate of 10°C/min, then furnace cooled. The thermal analysis was studied using differential thermal analyzer (DTA-50, Shimadzu-Japan), the thermo-gravimetric analyzer (TGA-50, Shimadzu-Japan), and the thermo-mechanical analyzer (TMA-50, Shimadzu-Japan). X-ray diffractometer (XRD-3A, Shimadzu-Japan, CuKα-Ni filter) was used for phase analysis.

RESULTS AND DISCUSSION

1. Thermal analysis:

Figure (1) shows the DTA and the TG results obtained for the barium carbonate starting powder (BaCO₃). The DTA shows three endothermic peaks at 838.3°C, 991, 1260°C. The first endothermic peak at 838.3°C corresponds to polymorphic transformation of BaCO₃ from the witherite orthorhombic (?) to rhombohedral (β) structure. The second, a relatively small endothermic peak, at 991°C corresponds to the rhombohedral/ cubic (α) phase transformation. The thermogravi-metric analysis (TG), showed no weight change during these phase transformations. The third endothermic peak at 1260°C is accompanied with a weight loss of 22.39% in the TG curve, corresponding to the decomposition of BaCO₃ to BaO. The temperature, 838.3°C, at which the first endothermic peak occurs, is in agreement with the results of Seveyrat et al. (3) who detected the endothermic peak at 830°C when using heating rate 10°C/min, while it is relatively higher than that obtained by Basahel and Diefallah, (2) and Pavlovnic et al. (7). This discrepancy might be a result of using different heating rates and room temperatures.

Figure (2) shows the DTA-TG curves for the BaCO₃-TiO₂ milled powder mixtures (12.5hrs). It can be seen from the figure that, the DTA curve does not show any endothermic or exothermic peaks during heating up till a temperature of 1000°C. While the thermo-gravimetric (TG) results show a weight loss of 18.5% upon heating to the same temperature. This might be due to the reaction taking place gradually not at a specified temperature or time. This depends upon the population of the dissimilar BaCO₃-TiO₂ contacts relative to that of similar contacts (TiO₂-TiO₂, BaCO₃-BaCO₃) and may as well reflect an amorphous nature of milled powder mixture due to prolonged milling. This is in good agreement with Brzozowski et al. (9), who found that the activation caused by milling led to fast decomposition of BaCO₃ that could mask the ? to β transition. Similar results were obtained by Berbeni et al. (10).
In order to obtain detail results from the TG curve shown in Figure (2), a differential curve (DTG) was reproduced and shown in Figure (3) together with the TG curve. The figure shows a weight loss of 2.46% starting from the room temperature and ending at 220°C, this is represented by DTG peak at 40°C, which corresponds to the elimination of the remainder of the ethanol used in the wet milling. Another 2% weight loss occurred in the temperature range 220-430°C, represented by DTG peak at 293°C corresponds to the release of absorbed water from the TiO$_2$ powder. Then in the temperature range from 430 to 1000°C, TG curve shows 15.8% weight loss and the DTG shows three peaks at 612, 729, and 915°C. The first peak at 612°C can be attributed to the formation of BaTiO$_3$ perovskite phase via the reaction between BaCO$_3$ and TiO$_2$ and release of CO$_2$ (according to the reaction: BaCO$_3$+TiO$_2$ ? BaTiO$_3$+CO$_2$). The second peak at 729°C might stand for the Ba$_2$TiO$_4$ intermediate phase formation (according to the reaction: BaTiO$_3$+BaCO$_3$ ? Ba$_2$TiO$_4$+CO$_2$). The last peak at 915°C is due to the reaction between the Ba$_2$TiO$_4$ intermediate phase and TiO$_2$ (according to the reaction: Ba$_2$TiO$_4$+TiO$_2$ ? 2BaTiO$_3$), besides the reaction between the residual BaCO$_3$ and TiO$_2$ powders. Based on these results, the BaTiO$_3$ formation reaction starts at 600°C, which is well below the temperature required to start the decomposition of pure BaCO$_3$ as shown in Figure (1).
2. Phase analysis:

The XRD patterns of powder mixtures milled for 7.5, 10, and 12.5hrs and calcined at different temperatures from 600 to 900°C for one hour are shown in Figures (4), (5), and (6), respectively. Figures (4) and (5) show that for powder mixtures milled for 7.5 and 10hrs, the formation of BaTiO$_3$ started at 600°C (BaTiO$_3$ phase appears at $2\theta$ = 31.5°). On the other hand, the XRD patterns for the powder mixture milled for 12.5hrs (Figure 6) shows that the formation of BaTiO$_3$ started at 700°C, which is 100°C higher than that for powders milled for 7.5 and 10hrs. XRD patterns for the powders calcined at 800°C, irrespective of the milling time, showed small amounts of an intermediate phase with a composition Ba$_2$TiO$_4$ (orthotitanate phase at $2\theta$ = 28.6°) in addition to BaTiO$_3$, TiO$_2$ and BaCO$_3$ phases. From Figures 4-6, it can be seen that the amount of BaTiO$_3$ formed after calcination increases with the increase in calcination temperature at constant time. At 900°C, the reaction between BaCO$_3$ and TiO$_2$ reaches an end by 100% formation of perovskite single phase BaTiO$_3$. The temperature at which the formation of BaTiO$_3$ is complete depends on the calcination time as well as the activation of the powder mixture related to the milling time.
Fig. (4): XRD patterns of powder mixture milled for 7.5 hrs and calcined at different temperatures.

Fig. (5): XRD patterns of powder mixtures milled for 10 hrs and calcined at different temperatures.
In order to have a better understanding of the effect of milling time on the BaTiO$_3$ formation, the fractions reacted were calculated from the integrated peak area of line (011) for BaTiO$_3$, (111) for BaCO$_3$, and (200) for TiO$_2$. The results of these calculations are given in Table (1). It can be seen that the fraction reacted increases with the milling time up to 10 hours. It can be seen that, a milling time greater than 10hrs does not show increase in the fraction reacted, contrarily a decrease was observed. This might be attributed to the formation of agglomerates that decreased the amount of the dissimilar BaCO$_3$-TiO$_2$ contacts.

Figure (7) shows the effect of the calcination time on the amount of BaTiO$_3$ phase formed after calcination at 750°C of the powder mixtures, milled for 7.5hrs. It can be seen from the figure that, the formation of BaTiO$_3$ phase increases with the increase in the calcination time and single phase BaTiO$_3$ was formed after calcination of the powder mixture for 10 hrs. The figure shows that, a trace of an intermediate phase (Ba$_2$TiO$_4$) could be observed in the XRD patterns of the powders calcined for 2 and 5hrs. Upon increasing of the calcination time to 7 hrs this intermediate phase disappeared. Formation of BaTiO$_3$ from the solid-state reaction between BaCO$_3$ and TiO$_2$ at such low temperature is comparable with the published data for BaTiO$_3$ formation through wet-chemical methods (11-13). This result agrees also with Kong et al. (6) who found that the BaTiO$_3$ phase was formed at a calcination temperature of 800°C/2hrs (the milling time was 10hrs). On the other hand, it disagrees with the result published by Seveyrat et al. (3), who stated that a temperature of 1100°C is required for the formation of BaTiO$_3$. These discrepancies might be a result of differences in the starting powders and the parameters of the mechanical activation (7,14). The mechanical activation may lead to the formation of a new surface with similar or dissimilar contacts and/or to the formation of agglomerates.
Table (1): The fraction reacted of BaCO$_3$-TiO$_2$ powder mixture milled for different times and calcined at different temperatures and times.

<table>
<thead>
<tr>
<th>Calcination temperature</th>
<th>Milling time 2.5hr</th>
<th>Milling time 5hr</th>
<th>Milling time 7.5hr</th>
<th>Milling time 10hr</th>
<th>Milling time 12.5hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>700/hr</td>
<td>16.5</td>
<td>28.2</td>
<td>48.72</td>
<td>50.5</td>
<td>50.11</td>
</tr>
<tr>
<td>750/5hrs</td>
<td>33.2</td>
<td>54.73</td>
<td>77.3</td>
<td>82.1</td>
<td>80.94</td>
</tr>
<tr>
<td>800/1hrs</td>
<td>-</td>
<td>43.3</td>
<td>68.9</td>
<td>70</td>
<td>69.8</td>
</tr>
</tbody>
</table>

Fig. (7): Effect of Calcination time on the formation of BaTiO$_3$, from BaCO$_3$-TiO$_2$ powder mixtures milled for 7.5hrs and calcined at 750°C.

3. Dilatometric analysis:

Thermo-Mechanical Analyzer (TMA) was used to study the shrinkage behaviors of the compacts made from the as milled BaCO$_3$-TiO$_2$ powder mixtures, milled for 7.5, 10, and 12.5hrs. The dilatometric curves were obtained using constant heating rate technique (CRH) at 5°C/min. Figure (8) shows the relative linear shrinkage of the different compacts. From the figure it can be seen that, irrespective of the milling time, the shrinkage took place in two stages: the first one started at ~654°C and ended at 895°C, which corresponds to the shrinkage that occurs due to the formation of BaTiO$_3$ from the reaction of BaCO$_3$ and TiO$_2$. In the second stage, significant shrinkage took place starting at ~1135°C and proceeding upon heating to the soaking temperature ~1320°C. This is due to the sintering of the powder compact. In this stage, the total shrinkage of the powder compact increases with the increase in the milling time. The shrinkage was: 16, 21.4, 23.4% for 7.5, 10, 12.5hrs milling time, respectively. This indicates that the sinterability increases with increasing milling time in agreement with pavlovic et al. (7) and Nicolic et al. (8) who reported that, mechanical activation led to intensification of transport processes, resulting in a less porous microstructure and a higher sinterability.
Fig. (8): The linear shrinkage of the different compacts made from BaCO$_3$-TiO$_2$ powder mixtures milled for 7.5, 10, and 12.5hrs.

Figure (9) shows the linear shrinkage rate versus temperature and time. From the figure it can be seen that the maximum shrinkage rate in the sintering stage (second stage) increases with increase of the milling time, which indicates that the milling process increases the powder activity. At the first stage (BaTiO$_3$ formation stage) the maximum shrinkage rate decreased with increase of milling time. This might be due to the formation of agglomerates, which decreases the amount of dissimilar contacts and thus slowing down the reaction. The maximums of the shrinkage rate occurred nearly at the same temperature, ~714°C for the first shrinkage stage and at ~1292°C for the second shrinkage stage, indicating that the milling time did not affect the temperature at which the maxima of the shrinkage rates occurred. In addition, in the first stage of shrinkage the figure shows that, after the 12.5hrs milling time there were two clearly observed maxima; the first one at 714°C and the second at 836°C. These might correspond to the formation of BaTiO$_3$ and Ba$_2$TiO$_4$ phases. For the 7.5 and 10 hrs milling times, only the maximum occurring at 714°C was observed, while the second one corresponding to the formation of the Ba$_2$TiO$_4$ intermediate phase was less significant (it broadened from ~775°C to ~895°C). This might be related to the agglomeration caused by the prolonged milling, which leads to the decrease in the rate of conversion of Ba$_2$TiO$_4$ phase.

Fig. (9): The linear shrinkage rate versus temperature and time.
CONCLUSION

The BaTiO$_3$ ferroelectric material was synthesized from 1:1 molar ratio BaCO$_3$-TiO$_2$ powder mixture. The starting powder mixture was mechanically activated using a high energy ball mill for different milling times. The effects of different parameters such as: the milling time, calcination time, and calcination temperature on the phase formation and the shrinkage behavior were studied. It was found that, 7.5hrs milling time is enough to yield 100% BaTiO$_3$ after calcination at 750°C for 10hr. The shrinkage of BaCO$_3$-TiO$_2$ compacts, proceeds in two stages: the stage of reaction and the stage of sintering. The shrinkage rate increases with milling time.

REFERENCES

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