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Mechanochemical synthesis of barium titanate

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Abstract

A powder mixture of BaO and TiO_2 was mechanochemically treated in a planetary ball mill in an air atmosphere for up to 4 h, using zirconium oxide vial and zirconium oxide balls as the milling medium. Mechanochemical reaction leads to the gradual formation of $BaTiO_3$ phase. Phase evolution during synthesis and changes in powder size and morphology were monitored by XRD, DSC, IR and TEM analysis and it was shown that the formation of $BaTiO_3$ phase was initiated after 60 min. Extended time of milling directed to formation of higher amount of $BaTiO_3$ perovskite phase. Barium titanate with good crystallinity was formed after 240 min sintering without pre-calcination step was performed at 1330 °C for 2 h within heating rate 10 °C/min.

Keyword: Barium titanate

1. Introduction

A characteristic feature of all solid-state reactions is that they involve the formation of product phase(s) at the interfaces of the reactants. Further, growth of the product phase involves diffusion of atoms of the reactant phases through the product phase, which constitutes a barrier layer preventing further reaction. The solid-state reactions initiated by intensive milling in high-energy ball mills could be good choice for the ceramic powder preparation. An important criterion for intensive milling is the formation of highly dispersed phased materials typical for metal powders or oxide based materials (*mechanical activation*) or the formation of new product because of a solid-state reaction (*mechanochemical synthesis*).[1,2] Intensive milling increases the area of contact between the reactant powder particles due to reduction in particle size and allows fresh surfaces to come into contact. This allows the reduction to proceed without the necessity for diffusion through the product layer. As a consequence, solid-state reactions that normally require high temperatures will occur at lower temperature during mechanochemical synthesis without any externally applied heat. In addition, the high defect densities induced by intensive milling in high-energy mills favor the diffusion process. Alternatively, the particle refinement and consequent reduction in diffusion distances (due to microstructural refinement) can at least reduce the reaction temperatures significantly, even if they do not occur at room temperature. Further, mechanical treatment of ceramic powders can reduce particle size and enable obtainment of nano-structured powders, which are of the main interest in current trend of miniaturization and integration of electronic components.[3,4]

It was shown that the mechanochemical treatment is convenient to synthesis polycrystalline piezo, pyro, and ferroelectric ceramics.[5–8] Named materials are extremely important for electronic purpose, because of their various properties applicable as capacitors, multilayer capacitors, piezo generators, piezo motors, piezo and electrostrictive actuators, relaxors, positive temperature coefficient of resistivity, gas and humidity sensors, non-volatile memories, buffer layers, etc. Many of named components and units obtained based on barium titanate—$BaTiO_3$ (BT).

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Progress in processing of materials fabricated on the basis of BT both at the powder synthesis stage and subsequent densification to solid component is caused by increasing demands on the quality of the electronic ceramics. Sintering process is generally improved by liquid phase sintering with titanium reach composition at the temperature above 1320 °C or by mechanical activation of initial powders $BaCO_3$ and TiO_2.[9–15]

It was noticeable that the processing during mechanical activation of BT lead to increase in specific surface area, as a consequence of destruction of agglomerates and the particles of the starting materials. XRD analysis of mechanically activated powders was shown the small amount of perovskite phase; however after calcination the perovskite cubic phase of $BaTiO_3$ increases with increase of activation time. Gomez et al.[12] analyzed the effect of long-term milling up to 78 h in an attritor on the structure and chemical behavior of the initial constituents $BaCO_3$ and TiO_2. It was shown that mechanical activation accelerated the formation rate of $BaTiO_3$. Otherwise, long term-milling provoked the formation of Ba_2TiO_4 besides BT phase. Welham obtained $BaTiO_3$ as a result of the milling of $BaO + TiO_2$ in a ball mill during 100 h, however high temperature treatments were needed to preserve the BaO in pure state, prior to the milling.[16] Abe and Suzuki using the milling in the planetary ball mill and starting from the mixture of $Ba(OH)_2 \cdot 8H_2O + TiO_2$ obtained a $BaTiO_3$ powder which had poor crystallinity, so an annealing treatment was necessary.[11] Milling of the mixture of powders of Ba + Ti constituents followed by an oxidation heat treatment in an atmosphere of pure oxygen gave also $BaTiO_3$ as product. Evidently, the formation of perovskite phase of BT occurs during thermal treatment slightly lower after mechanical activation of initial powders. On the other hand, the mechanical activation could be associated with the formation of transient phases formed during grinding.

In view of above, our paper reports on work carried out on fine $BaTiO_3$ powders synthesized via the mechanical activation of BaO_2 and TiO_2 directly during high-energy milling. The resulting $BaTiO_3$ powders have been evaluated for powder characteristic.

2. Experimental procedure

The barium titanate was prepared starting from barium oxide (BaO) and titanium oxide. TiO_2, in a rutile crystal form was commercially available (Fluka, 99.8% purity). BaO was obtained from $BaCO_3$ thermally treated at 1300 °C for 4 h to complete decomposition of carbonates to oxides controlling the carbonate presence. These oxide powders exhibited a particle size distribution in the range 2–4 μm for TiO_2 and 1–5 μm for BaO. To make a batch required for stoichiometric $BaTiO_3$ composition, corresponding amount of prepared BaO and TiO_2 were weighed and loaded into zirconium jars together with zirconium milling balls ~10 mm in diameter. Mechanical activation, i.e. mechanochemical synthesis was performed in air atmosphere in a planetary ball mill (Fritsch Pulverisette 5) that was operated at basic disc rotation speed 320 min^{-1} and rotation speed of discs with jars ~400 rpm for 30, 60, 120 and 240 min. The relation between powders and balls during milling was 1:20. Phase development in the mechanically activated powders was monitored using an X-ray difractometer (XRD, Model D500, Siemens) and using DSC (Model STA 409 Netzsch) and DTA-TG analysis (Model 414/2, TASC). Transmission electron microscopy (TEM, Model 213, Philips) and scanning electron microscopy (SEM, Model SM-300, Topcon) were used to study their particle size and powder morphology. Infrared spectroscopy (Model 400-IR/FT, IMPACT) was used to indicate the presence of carbonates in barium titanate powders.

3. Results and discussion

It is well known that multiple advantages of the solid-state method for preparing $BaTiO_3$ are that it is a single process and a low cost technique. Despite the advantages, there are some problems to be solved. The high calcination temperatures lead to coarsening of the $BaTiO_3$ particles that are unsuitable for manufacturing fine grained ceramics and that, even the nominal ratio Ba/Ti in starting materials is 1, intermediate phases or $BaCO_3$ can persist as an end-product preventing to complete reaction between the starting materials. Otherwise, it was established that the barium titanate ceramic materials and its solid solutions may be prepared directly during high-energy milling or at low calcination temperatures as the result of physical, chemical and physico-chemical changes due to influence of mechanical energy. It means that the formation of perovskite phase of BT occurs slightly easier after mechanical activation of initial powders. Also, lowering the calcination temperature could prevent anomalous grain growth.[9]

Practically all known papers are devoted to investigations of mechanical activation of $BaCO_3$ and TiO_2 and only few articles are addressed to mechanical synthesis of this material from oxides milling in nitrogen atmosphere. According to the same literature data when the mixed oxides of BaO and TiO_2 were mechanically activated in air, the formation of $BaCO_3$ was triggered and the formation of perovskite $BaTiO_3$ phase could not be realized.[16]

In spite of those observations, our intention was to prepare barium titanate by milling in air atmosphere starting from oxides. In order to obtain barium titanate by mechanical activation of BaO_2 and TiO_2 in air atmosphere, we used milling in a planetary ball mill during various time of mechanical activation. As one would expect, the formation of barium titanate was detected by XRD analysis. Fig. 1a–g shows the XRD patterns for initial powders BaO_2 (a) and TiO_2 in the rutile crystal form (b) and diffractograms for powders that have been mechanically activated for various time periods: 30, 60, 120 and 240 min ((c)–(f)). Certain amount of perovskite cubic $BaTiO_3$, indicated by the peaks at 2θ angles at 22.0°, 31.4°, 38.7°, 45.0°, 55.9° and 65.5° was observed together

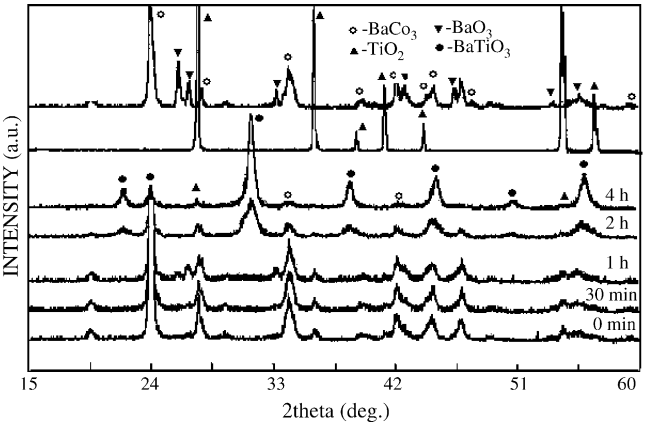

Fig. 1. X-ray diffraction patterns of initial powders: BaO_2, TiO_2 rutile, and mechanically activated powders at 0, 30, 60, 180 and 240 min.

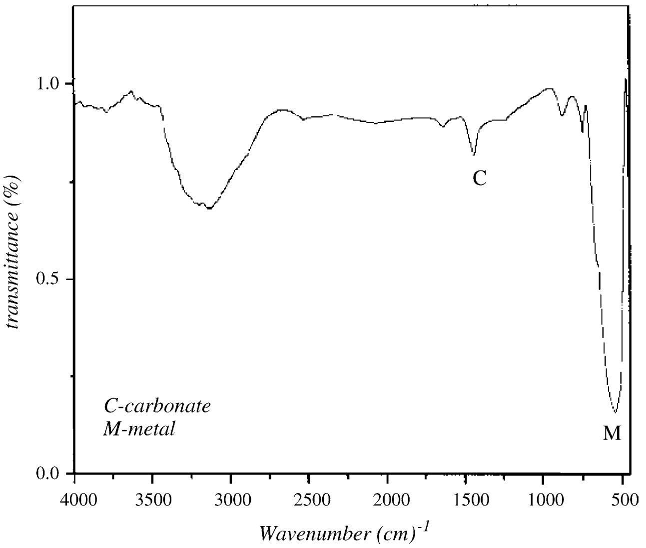

Fig. 2. IR measurement carried out on a 240 min mechanically activated barium titanate sample.

with the much-weakened and broadened peaks of TiO_2 and BaO. The presence of unreacted components is more evident when the powder mixture was subjected to mechanical activation for shorter time. Thus, the observation indicates that the formation of small amount of amorphous $BaTiO_3$ phase triggers after 60 min of mechanical activation. Therefore, besides rather amorphous phase of barium titanate, the peak broadening of initial oxides implies that shorter time of mechanical activation is not enough to obtain good crystallinity of pure $BaTiO_3$. A degree of amorphization decreased with extended time of mechanical activation and after 240 min only a minor amount of initial oxides is still observed. In this case, we can see the effectiveness of the milling process.

It is necessary to emphasize that it was observed the presence of visible amount of $BaCO_3$ triggered unless of two main reasons. First, initial barium oxide was not used as a fresh prepared constituent. Taking this in account, the probability of barium carbonate formation is rather high and the XRD analysis of initial barium oxide (Fig. 1a) confirmed this observation. Besides, during milling in air atmosphere, the formation of $BaCO_3$ could be effected. Meanwhile, during extended time of milling, besides possibility of phase transformation of γ-$BaCO_3$ in α-$BaCO_3$, the decomposition of carbonate to oxide is facilitated favoring after the mechanochemical reaction. By IR analysis was confirmed the presence of small amount of $BaCO_3$ even the powder was mechanochemically activated 240 min (Fig. 2).

Comparison DSC curves (Fig. 3) of 30 and 240 min mechanically activated mixtures helps to establish the influence of mechanical activation on solid-state reaction and phase formation of barium titanate. Obviously, the time of mechanical activation has strong influence on the process. The endothermic hump in the range 400–700 °C associated with the stronger endothermic thermal peak and recorded in the powder milled for shorter time coincides to allotropic transition of $BaCO_3$ and thermal decomposition of carbonates. Other event observed at ∼1000 °C could be pertaining to solid-state reaction between oxides and formation of barium titanate. Comparing with XRD results seems that barium titanate was formed only to a limited extend. The DSC curve for extended milling time within the same temperature range did not show any distinctive event. Otherwise, after 240 min of mechanical activation, the barium titanate phase as the major ones seems to have been only formed.

The morphology of the barium titanate powder after mechanical activation is presented in Fig. 4. It is possible to identify the rather strong agglomeration of powders after milling time of 240 min. $BaTiO_3$ powder consists of agglomerates of varying size and morphology. A detailed study at high magnifications showed that agglomerate consists from approximately 100 grains with grains mostly rounded shaped in the range 20–50 nm. Nanoparticles are observed clearly, although they have aggregated together to form irregularly shaped agglomerates. The needle like

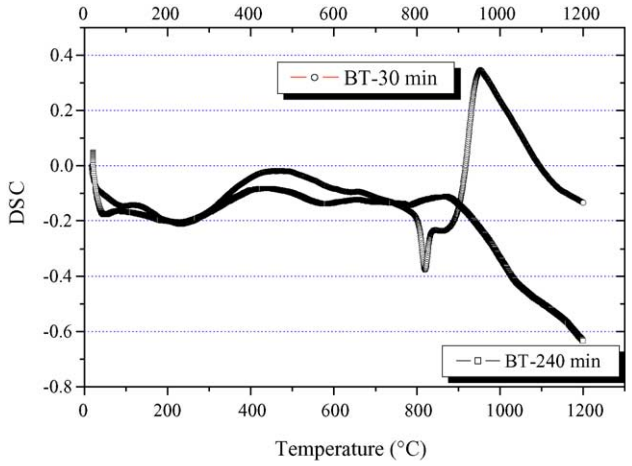

Fig. 3. DSC curves of samples prepared from powders mechanically activated at 30 and 240 min.

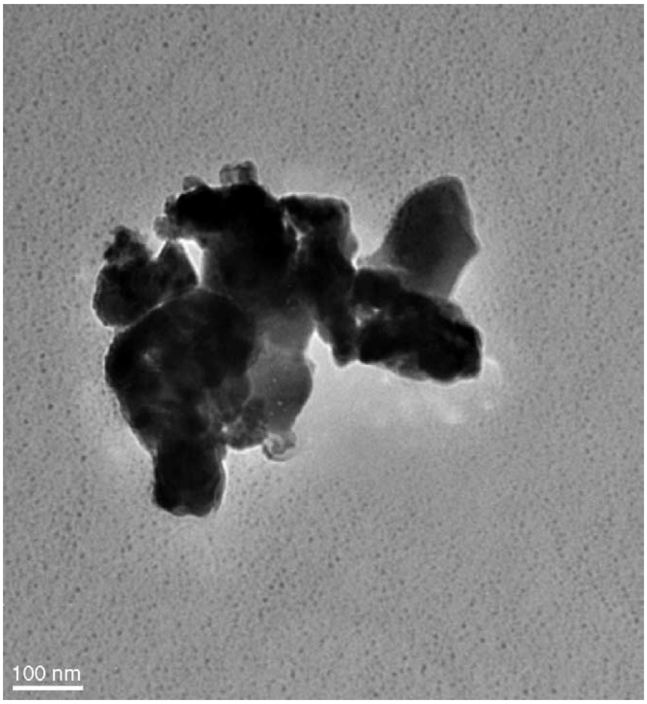

Fig. 4. TEM of barium titanate powders mechanically activated 240 min.

grains were not observed in mechanically activated powders indicating that Ba_2TiO_4 phase was not formed and what was in agreement with XRD results.

The effect of mechanochemical activation can be detected after carrying out thermal treatments on the samples. For example, samples prepared from 240 min of mechanical activation and sintered at 1330 °C for 2 h, without pre-calcination step, possess clear tetragonal crystal structure of barium titanate (Fig. 5).

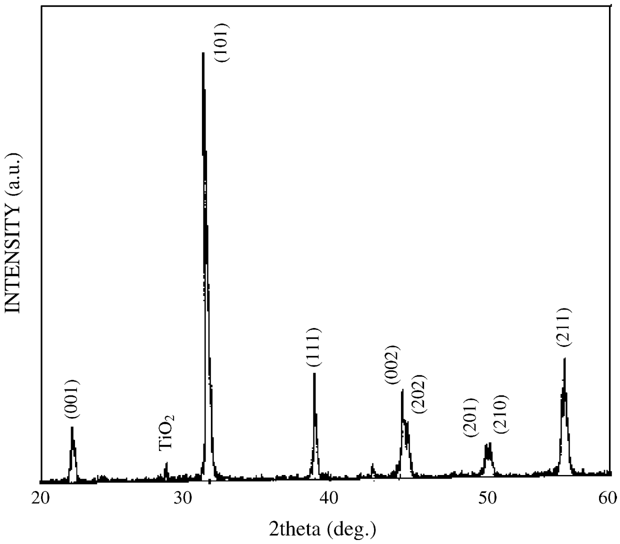

Fig. 5. XRD powder patterns obtained on sample sintered at 1330 °C for 2 h and prepared from mechanically activated powders for 240 min.

4. Conclusion

Using mixed oxides BaO and TiO_2 as the staring materials, the formation of singe phase $BaTiO_3$ compound could be obtained during mechanical activation. The formation of $BaTiO_3$ in air besides small amount of $BaCO_3$ was possible to trigger pointing to solid-state reaction occurrence during intensive milling. The nucleation of nanocristallites and subsequent growth of a highly activated oxide matrix forming a substantial amount of $BaTiO_3$ phase increased with an increasing degree of mechanochemical synthesis. The amount of carbonates was minimized during extended milling time. The resulting perovskite $BaTiO_3$ powder exhibited a particle size in the range of 20–50 nm. Mechanochemically synthesized $BaTiO_3$ powder was rather agglomerated after 240 min of milling in planetary ball-mill. After sintering, tetragonal structure of barium titanate was obtained.

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References

1. Wang, J., Wan, D. W., Xue, J. M. and Ng, W. B., *Novel Mechanochemical Fabrication of Electroceramics*. Singapore Patent 9801566-2, 1998.
2. Xue, J., Wan, D., Lee, S. E. and Wang, J., Mechanochemical synthesis of nanosized lead titanate powders from mixed oxides. *J. Am. Ceram. Soc.*, 1999, **82**(7), 1687–1692.
3. Ding, J., Ssuzuki, T. and Mc Cormic, P. G., Ultrafine particles prepared by mechanical/thermal processing. *J. Am. Ceram. Soc.*, 1996, **79**, 2956–2958.
4. Giri, A. K., Nanocrystalline materials prepared through crystallization due to instability in amorphous materials after grinding. *Adv. Mater.*, 1997, **9**, 163–166.
5. Boldyrev, V. V., Mechanochemistry and mechanical activation. *Mater. Sci. Forum*, 1996, **227**, 511–520.
6. Gaffet, E., Michael, D., Mazerolles, L. and Berthet, P., Effect of high-energy ball-milling on ceramic oxides. *Mater. Sci. Forum*, 1997, **235–238**(1), 103–108.
7. Francoise, D. M., Gaffet, E. and Mazerolles, L., Stabilized zircons prepared by mechanical activation. *J. Am. Ceram. Soc.*, 1993, **76**, 2884–2888.
8. Komattsubara, S., Isobe, T. and Senna, M., Effect of preliminary mechanical treatment on the microhomogenization during heating of hydrous gels as precursors for lead titanate. *J. Am. Ceram. Soc.*, 1994, **772**, 278–282.
9. Kostic, E. M., Kiss, S. J., Boskovic, S. B. and Zec, S. P., Mechanical activation of titanium oxide. *Am. Ceram. Soc. Bull.*, 1997, **76**, 60–64.
10. Stojanovic, B. D., Pavlovic V. B., Marinkovic, B. and Ristic, M. M., Influence of tribophysical activation on structure and properties of $BaTiO_3$ ceramics. In *Book of abstracts CIMTEC'98*, ed. P. Vincenzini and G. Galeati. Florence, 1998, pp. 40–41.

11. Abe, O. and Suzuki, Y., Mechanochemically assisted preparation of $BaTiO_3$ powders. *Mater. Sci. Forum*, 1996, **225**, 563–568.
12. Gomez-Yanez, C., Benitez, C. and Ramirez, H. B., Mechanical activation of the synthesis reaction of $BaTiO_3$ from a mixture of $BaCO_3$ and TiO_2 powders. *Ceram. Int.*, 2000, **26**, 271–277.
13. Randall, C. A., Kim, N. J., Kucera, P., Cao, W. W. and Shrout, T. R., Intrinsic and extrinsic size effects in fine-grained lead-zirconate titanate ceramics. *J. Am. Ceram. Soc.*, 1992, **71**, 978–985.
14. Berbenni, V., Marini, A. and Bruni, G., Effect of mechanical milling on solid state formation of $BaTiO_3$ from $BaCO_3$–TiO_2 rutile. *Thermochim. Acta*, 2001, **374**, 151–158.
15. Brzozovski, E. and Castro, M. A., Lowering the synthesis temperature of high-purity $BaTiO_3$ powders by modifications in the processing conditions. *Thermochim. Acta*, 2003, **398**, 123–129.
16. Xue, J., Wang, J. and Wan, D., Nanosized barium titanate powder by mechanical activation. *J. Am. Ceram. Soc.*, 2002, **83**(19), 232–234.