UDK 662.785: 553.689: 549.6

Low Temperature Sintering of Mechanically Activated $BaCO_3$-TiO_2

V. P. Pavlović[1], B. D. Stojanović[2], V. B. Pavlović[3*], Lj. Živković[4], M. M. Ristić[5]

[1] Faculty of Mechanical Engineering, University of Belgrade, Belgrade, Yugoslavia
[2] Center for Multidisciplinary Studies, University of Belgrade, Belgrade, Yugoslavia
[3] Faculty of Agriculture, University of Belgrade, Belgrade, Yugoslavia
[4] Faculty of Electronic Engineering, University of Nis, Nis, Yugoslavia
[5] Serbian Academy of Sciences and Arts, Belgrade, Yugoslavia

(*Dedicated to Professor Dr. Drago Kolar in memory of a great scientist and a great man*)

Abstract: *In this article low temperature sintering of mechanically activated $BaCO_3$-TiO_2 system was studied. A stoichiometric mixture of $BaCO_3$ and TiO_2 powders was mechanically activated in a high-energy vibromill for 0, 30, 90 and 180 min, calcined at 800°C for 1 h and reaction sintered at 1100°C and 1200°C for 2 h (heating rate of 10°C/min). Phase compositions and crystallographic data of initial, activated, calcinated and sintered specimens were obtained by the XRPD method. It was noticed that mechanical activation enhanced and lowered the temperature of the formation of tetragonal $BaTiO_3$. Scanning electron microscopy was used to study and characterize microstructures of the samples.*

Keywords: *Sintering; Mechanical activation; $BaCO_3$-TiO_2; $BaTiO_3$; Microstructure.*

Резюме: *В данной работе исследовано низкотемпературное спекание механически активированной системы $BaCO_3$-TiO_2. Смесь порошков $BaCO_3$ и TiO_2 в стехиометрическом соотношении механически активирована в высокоэнергетической вибрационной мельнице в течение 0, 30, 90, 180 мин. Кальцинирование проведено при 800°C в течение 1 часа и реакционное спекание при 1100 и 1200°C в течение 2 часов (скорость нагрева 10°C/мин.). Фазовый состав и кристаллические данные исходных и активированных смесей, а также кальцинированных спеченных образцов полученых рентгеновским методом. При помощи сканирующей электронной микроскопии исследована микроструктура образцов. Установлено, что механическая активация ускоряет процесс спекания и понижает температуру образобания тетрагонального титаната бария.*

Ключевые слова: *Спекание; механическая активация; $BaCO_3$-TiO_2; $BaTiO_3$; микроструктура.*

* Corresponding author (vlaver@beotel.yu).

Садржај: *У овоме раду је проучавано нискотемпературно синтеровање механички активираног система $BaCO_3$-TiO_2. Прах $BaCO_3$ и TiO_2 у стехиометријском односу је механички активиран у високоенергетском вибрационом млину током 0, 30, 90 и 180 min, калцинисан на 800°C током једног часа и реакционо синтерован на 1100 и 1200°C током два часа (брзина загревања је износила 10°C/min). Фазни састав и кристалографски подаци почетних и активираних смеса, као и калцинисаних и синтерованих узорака добијени су рендгенском методом. Сканирајућом електронском микроскопијом проучена је микроструктура узорака. Утврђено је да механичка активација убрзава процес синтеровања, уз снижавање температуре формирања тетрагоналног баријум-титаната.*

Кључне речи: *Синтеровање; механичка активација; $BaCO_3$-TiO_2; $BaTiO_3$; микроструктура.*

Introduction

Ceramic materials with a perovskite or perovskite related structure such as undoped and doped barium titanate have found wide application as capacitor dielectrics, resistors, self regulated heaters, thermal sensors etc. Their applicability mostly stems from their ferroelectric nature below the Curie temperature; $BaTiO_3$ based materials exhibit a spontaneous polarization which is reorientable with an applied electric field, giving rise to hysteresis behaviour and a high dielectric constant. Since ferroelectric properties are highly dependent upon grain size, domain structure and composition, controlled processing conditions of these materials, both at the powder synthesis stage and subsequent densification to a solid component, must be achieved. The sintering process of materials fabricated on a barium titanate basis can be improved by liquid phase sintering at temperatures below 1320°C [1-2], or by mechanical activation of initial powders $BaCO_3$ and TiO_2 [3-4].

The influence of mechanical activation of $BaTiO_3$ is closely related with different structural changes such as phase transitions, generations of dislocations and crystal lattice microstrains etc. [5]. The driving force of all these processes is excess enthalpy, obtained by activation in high-energy mills [6]. As a result, mechanical activation could lower the sintering temperature of an activated material [7].

Experimental procedure

A mixture of 50 mol% $BaCO_3$ (Merck p.a. 99 %) and 50 mol% TiO_2 (Ventron p.a. 99.8 %) powders was homogenized in a planetary ball mill for 120 min. The homogenized powders were activated in a high-energy vibromill with rings (Tm MN 954/3) in air, for 0, 30, 90 and 180 min. After addition of an organic binder (aqueous solution of 2 % polyvinyl alcohol) the powders were dried and pressed at 400 MPa. After calcination at 800°C for 1 h, pellets were crashed, sieved and after addition of the organic binder, dried up to 300°C and pressed into pellets. All samples were reaction sintered in air at 1100°C and 1200°C for 2 h (heating rate of 10°C/min). Specific surface area determinations of initial and activated powders were carried out using the BET method with N_2 absorbate. XRPD analysis of initial powders, non activated and activated mixtures, as well as calcined and sintered specimens were performed using a Philips 1820 with a graphite monochromator and CuKα radiation.

Scanning electron microscopy was used to study and characterize microstructures of the samples.

Results and discussion

In order to obtain barium titanate of acceptable purity, numerous factors such as quality of raw materials, granulometry, mixture homogeneity and nature of the reaction atmosphere must be controlled. Mechanical activation, as the process which affects some of the mentioned factors, can improve reactivity of the initial mixture, which leads to the lowering of temperature of barium titanate formation. It was noticed that specific surface area of $BaCO_3$-TiO_2 mixtures increased with the increase of activation time, as a consequence of destruction of agglomerates and particle minimization of starting materials. The values of specific surface areas of 2.84, 4.36, 4.53 and 3.87 m^2/g were obtained for non-activated powder and powders activated for 30, 90 and 180 min, respectively. According to SEM investigations, the small decrease of specific surface area after activation for 180 min can be ascribed as repeated agglomeration. As a result of mechanical activation, zones of remaining strain are formed in some particles and formation of new surface was accompanied by the concentration of energy on the surface layer of particles [8]. XRPD analysis of activated mixtures that we have performed pointed out to an important increase of diffraction line broadening, as a consequence of milling in high energy vibromill, related to the increase of the concentration of structural defects (primarily to the dislocation densities) with the activation time. Since the formation of new surfaces and the increase of the concentration of structural defects is accompanied by the increase of free energy, reactivity of starting mixture increased and lowering of the temperature of reaction sintering occurred, as well as the increase of the solid state reaction rate.

The influence of activation on the initial temperature of solid state reaction was confirmed by the phase analysis of diffraction patterns of calcined specimens. The presence of four different crystal phases (witherit, anatase, rutile and cubic barium titanate phase) was noticed after calcination (Fig. 1a), while the percentage of BaTiO3 phase changed as 11.05, 15.34, 20.83 and 25.7 wt.% for 0, 30, 90 and 180 min of mechanical activation, respectively.

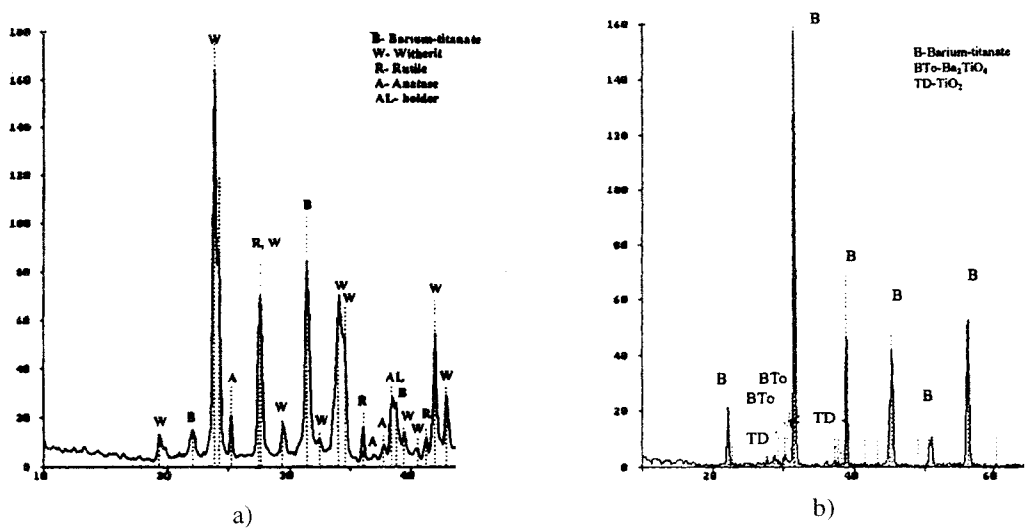
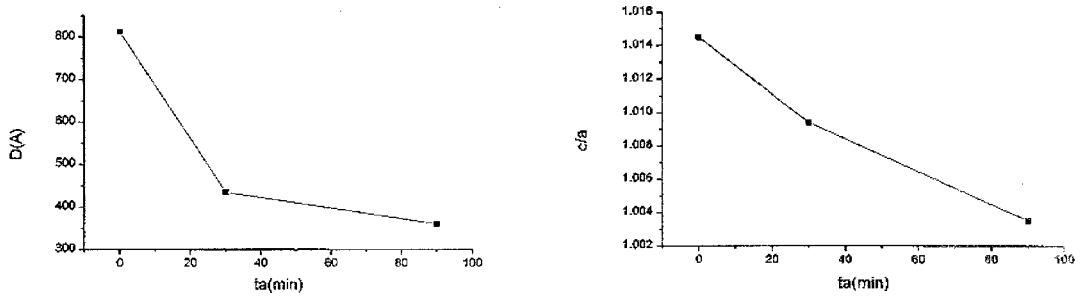


Fig. 1 Diffraction patterns: a) calcined sample (mechanically activated for 180 min); b) sample sintered at 1100°C (mechanically activated for 180 min).

After sintering it was noticed that for the samples sintered at 1100°C a solid state reaction proceeded almost to the end, with the formation of a tetragonal barium titanate with small amounts of Ba_2TiO_4 (Fig. 1b). For the samples sintered at 1200°C the solid state reaction proceeded entirely to the end, with formation of tetragonal barium titanate modification. Diffraction line broadening analysis showed that the mean crystallite size and tetragonal ratio c/a of barium titanate decreased with the increase of activation time, thus influencing an abrupt change of crystal lattices of the samples (Fig. 2a,b). According to this, after a certain time of mechanical activation the tetragonal crystal lattice of $BaTiO_3$ should approach the cubic lattice, causing a prominent change in dielectric properties of the material [8-9].



a) b)

Fig. 2 a) The dependence of mean crystallite size D on the activation time t_a; b) The dependence of tetragonal ratio c/a on the activation time t_a.

Microstructural analysis of sintered specimens showed that activation of the initial $BaCO_3$-TiO_2 mixture decreased the average grain size and porosity, which led to the formation of a more homogeneous microstructure. Microstructure of the samples contained two distinct areas: dense and locally porous one. Structures of the dense areas were rather uniform, although loosely packed and agglomerated (Fig. 3). A more detailed study of the microstructure showed that the agglomerate size decreased with the increase of the activation time, while their morphology stayed more-or-less square (Fig. 4).

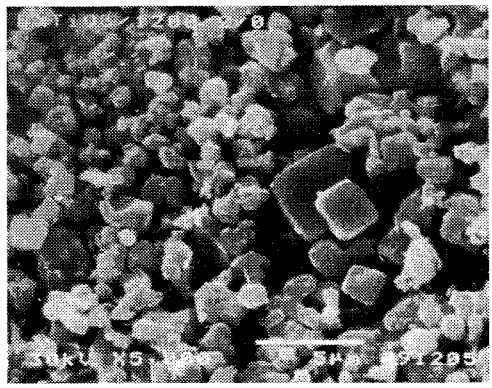


Fig. 3 Microstructure of the sample sintered at 1200°C.

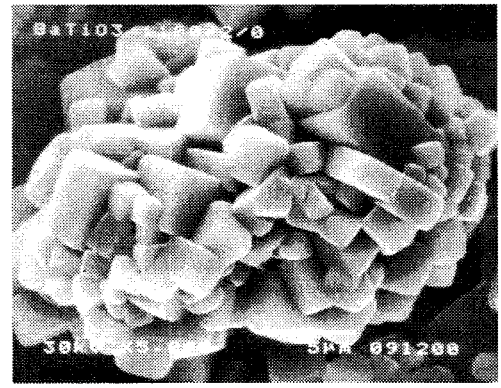


Fig. 4 Microstructure of an agglomerate.

According to our investigations, formation of agglomerates is influenced by the existence of remnant agglomeration of the $BaCO_3$-TiO_2 mixture, especially for 180 min of activation. Fig. 5 illustrates the interconnection of regions that make up the agglomerate and their rearrangement. These regions range from a few grains strung together as a chain to large

groups that formed irregular mass up to 5 μm in size. It should be noticed that agglomeration can influence the development of microstress, microstructural deffects and exaggerated grains, thus affecting the microstructural development of a sintered material. However, the effect of agglomeration depends on the size distribution, degree of agglomeration and relative density.

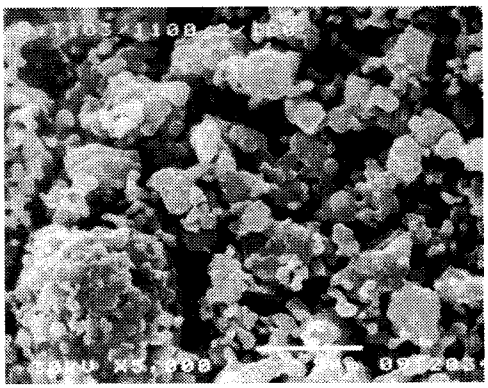


Fig. 5 Microstructure of the sample sintered at 1100°C and activated for 180 min.

Conclusion

Low temperature sintering of mechanically activated stoichiometric mixture of $BaCO_3$ and TiO_2 was studied. It was found that mechanical activation can improve reactivity of the initial mixture, lowering the temperature on which formation of barium titanate occurs and, at the same time, influencing the mean crystallite sizes and tetragonal ratio c/a of the specimens. It was shown that due to agglomeration, mechanical activation had a prominent influence on microstructural development of activated samples.

References

1. T. R. Armstrong, J. Amer. Ceram. Soc., **73** (1990) 700.
2. V. Pavlovic, B. Stojanovic, Lj. Zivkovic, G. Brankovic, M. M. Ristic, Ferroelectrics, **186** (1996) 165.
3. J. Xue, J. Wang, D. Wan, J. Am. Ceram. Soc., **83** (2000) 1.
4. P. G. McCormic, F. Froes, JOM, **11** (1998) 61.
5. B. D. Stojanovic, V. B. Pavlovic, V. P. Pavlovic, S. Djuric, B. A. Marinkovic, M. M. Ristic, J. Europ. Ceram. Soc., **19** (1999) 1081.
6. K. Tkacova, Mechanical Activation of Minerals, Elsevier, Amsterdam, 1998.
7. V. P. Pavlovic, V. B. Pavlovic, B. D. Stojanovic, T. Sreckovic, B. Marinkovic, M. M. Ristic, in "Advanced Science and Technology of Sintering", Eds. B.D. Stojanovic et al., Kluwer Academic/Plenum Publishers, New York, 1999, p. 403.
8. B. A. Marinkovic, B. D. Stojanovic, V. B. Pavlovic, V. P. Pavlovic, M. M. Ristic, Mat. Structures, **62** (1999) 1.
9. W. Y. Shih, W. H. Shih, I. A. Aksay, Phys. Rev. B, **21** (1994) 50.