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# Dielectric Properties of Barium-titanate Sintered from Tribophysically Activated Powders

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***Abstract***

*It has been well known that the tribophysical (mechanical) activation could be used as a method for modification of physicochemical properties of dispersed systems such as polycrystalline mixture of oxides. In this study, we consider the properties of $BaTiO_3$ obtained from tribophysically activated initial powders. The mixture of 50 mol% $BaCO_3$ and 50 mol% $TiO_2$ powders was tribophysically activated in high energy vibromill during 0, 3, 30, 90 and 180 min, calcinated at 800°C for 1 h and reaction sintered at 1100, 1200 and 1300°C for 2 h. The surface specific areas, densities (green and sintered), phase compositions and dielectric properties were evaluated. © 1999 Elsevier Science Limited. All rights reserved*

*Keywords*: calcination; sintering; X-ray methods; dielectric properties; $BaTiO_3$ and titanates.

## 1 Introduction

It is well known that tribophysics and tribochemistry (or mechanical and mechanochemistry) can deal with physical, chemical or physicochemical changes due to influence of mechanical energy.[1] The influence can be expressed as the increase of total free surface and internal energy of materials, changes in crystal lattice and in some cases as chemical changes.[2,3] However, the nature of this modification has not been explained in many cases. The main reason could be the nature of dispersed systems as a specific multiparameter object.

As the diffusion is the most prominent mechanism of mass transport during sintering, it can be expected that mechanical activation of starting powders has a profound influence on sintering processes. Corresponding to that, it can be also expected a reduction of sintering temperature and an increase of densities of sintered compacts previously tribophysically activated, in comparison with non-activated samples.

The influence of tribophysical activation has been perceived in various oxide systems[1,3] but most frequently from viewpoints of processing parameters and mechanisms of solid state reaction during thermal treatment. Taking into account the importance of barium-titanate with a sintered electronic material the present paper was concerned with the influence of tribophysical activation on structure and dielectric properties of $BaTiO_3$ ceramics.

## 2 Experimental

The mixture of 50 mol% $BaCO_3$ (Merck, p.a., 99%) and 50 mol% $TiO_2$ (Ventron, p.a., 99·8%) powders were homogenized and activated in high energy vibromill with rings (CUP Mill, MN 954/3 KHD Humboldt Wedag AG) during 0, 3, 30, 90 and 180 min. Determinations of surface specific areas were carried out using BET method with $N_2$ absorbate. After calcination at 800°C for 1 h, specimens were sintered at temperatures of 1100, 1200 and 1300°C for 2 h. Phase composition and crystallographic data of initial, activated, calcinated and sintered powders were determined by X-ray powder diffraction (XRPD) method using a Philips-1820 diffractometer. The dielectric constant and dielectric losses were determined as a function of temperature in the range from 20 to 140°C.

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## 3 Results and Discussion

Previous investigations of the tribophysical activation effects on sintering process have showed an intensification of the process with increase of amount of activation.[1] In fact, it was noticeable that the activation process leads to changes in specific areas, as a consequence of destruction of agglomerates and the particles minimization of the starting materials. The values of specific surface areas of 2·84, 2·93, 4·36, 4·53 and 3·87 $m^2g^{-1}$ were obtained for non-activated powder and powders activated for 3, 30, 90 and 180 min, respectively. According to this, the small decrease of specific surface area after activation at 180 min can be ascribed to repeated agglomeration.

To provide information about influence of activation on solid-state reaction and sintering process, XRPD analyses were performed, primarily in order to analyze changes of phase compositions. Qualitative analysis of initial non-activated powders, $BaCO_3$ and $TiO_2$, was indicated as witherite $BaCO_3$ modification and mixture of approximately 1·05:1 rutile to anatase $TiO_2$ modifications. The analysis of activated mixtures showed, that during milling in high energy vibro-mill *only tribophysical* activation occurred. Semiquantitative analysis of rutile to anatase ratio indicated significant increase from 1·05:1 at initial mixture to 1·30:1 at mixture activated for 180 min. XRPD analysis of calcinated specimens showed the presence of four different crystal phases: witherite, anatase, rutile and cubic barium-titanate phase (Fig. 1). The percentage of the cubic $BaTiO_3$ was changed as 11·05, 15·34, 20·83 and 25·27 wt% for 0, 30, 90 and 180 min of tribophysical activation, respectively and those were in agreement with recently published results.[5] This increase of cubic $BaTiO_3$ content has been attributed to the influence of tribophysical activation on acceleration of solid-state reaction. At the same time, the diffraction line broadening analysis of presented crystal phases, pointed out a significant increase of full width at the half maximum (FWHM) which is closely related to effects of tribophysical activation. On the other hand, the investigation of sintered specimens pointed out that solid-state reaction proceeded entirely to the end with formation of tetragonal $BaTiO_3$ modification, (Fig. 2).

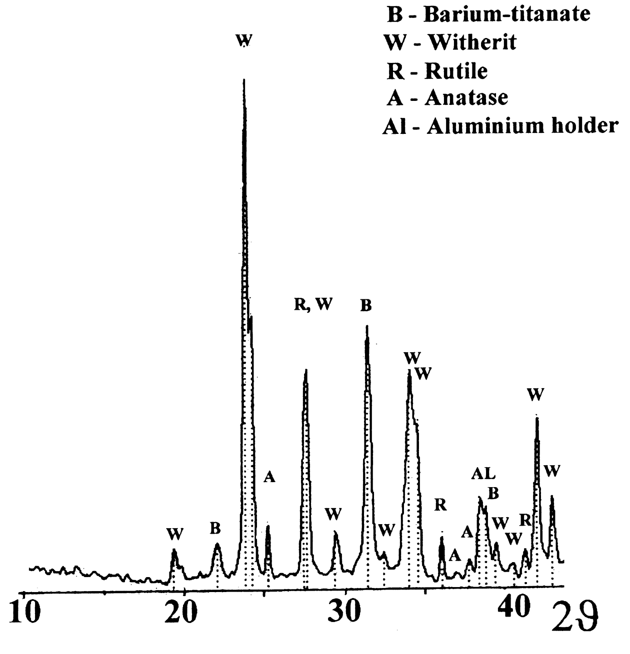

**Fig. 1.** X-ray pattern of specimen calcinated at 800°C, from mixture activated for 180 min.

It can be observed that the values of the dielectric constant $\varepsilon_r(t)$ and the dielectric loss tangent $tg\sigma(T)$, made on specimens sintered at 1100, 1200 and 1300°C, (Fig. 3), pointed out tribophysical activation effects. The values of $\varepsilon_r(T)$ and $tg\sigma(T)$ at $T < T_c$ varied from $\varepsilon_r = 227$, $tg\sigma = 0{\cdot}15$ (for non-activated specimens, sintered at 1100°C) to $\varepsilon_r = 480$, $tg\sigma = 0{\cdot}033$ (for the 180 min activated specimens, sintered at 1300°C) (Table 1). The small values of $\varepsilon_r$ were obtained owing to the low densification. Relatively low densities are probably the consequence of the relative high heating rate (30°C $min^{-1}$) and short sintering time. For example, for the above presented specimens the green densities were in the range 2·1–2·7 g $cm^{-3}$. The values of sintered densities were from 3·15 to 4·15 g $cm^{-3}$ independent of sintering temperature and time of activation. The maximum of the curve $\varepsilon_r = f(T)$, that corresponded to the transition from the ferroelectric to the paraelectric states, were closely linked to the time of tribophysical activation. It can be observed that the Curie temperatures ($T_c$) were displaced towards lower temperatures, as the time of tribophysical activation increased (from 127°C at non-activated specimen to 112°C for 180 min activation). One could notice that such behavior has been primarily caused by effects of tribophysical activation, generating strains within $BaTiO_3$ particles and thereby affecting the lower temperature of tetragonal to cubic phase transition.

## 4 Conclusion

The dielectric properties of $BaTiO_3$ ceramics obtained from tribophysically activated initial powders have been studied. The temperature dependence of the dielectric constant ($\varepsilon_r$) and dielectric loss factor ($tg\sigma$) on the time of tribophysical activation has been established in the temperature range 20–140°C. It was noticed that tribophysical activation has a prominent influence

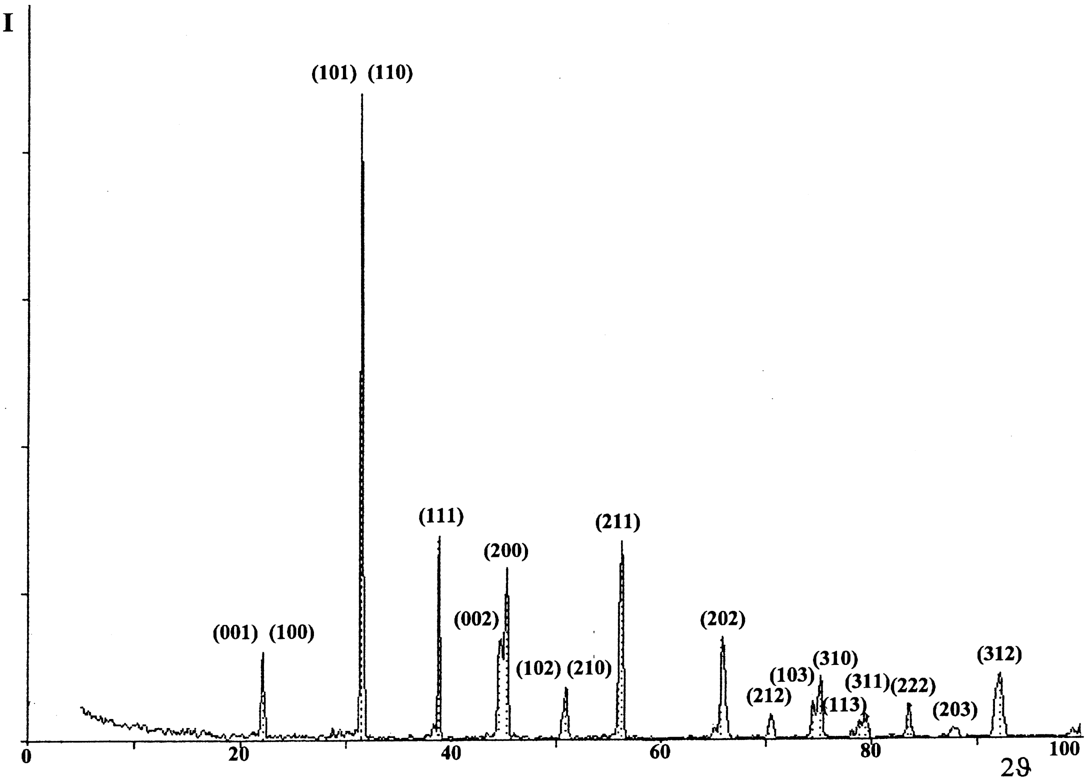

**Fig. 2.** X-ray pattern of specimen sintered at 1200°C, from mixture activated for 180 min.

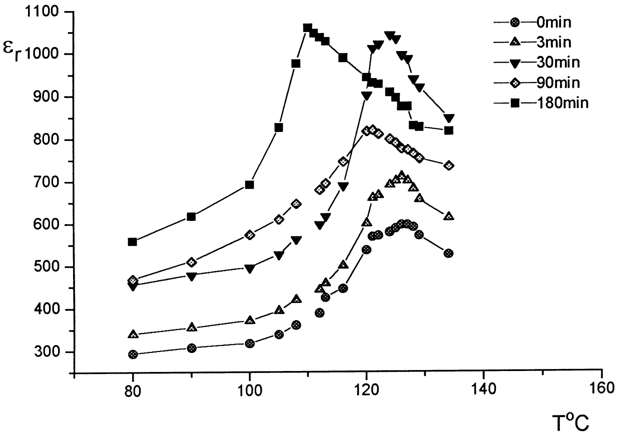

**Fig. 3.** The influence of tribophysical activation time on dielectric constant for $BaTiO_3$ ceramics sintered at 1300°C.

**Table 1.** The influence of tribophysical activation on dielectric properties of $BaTiO_3$

| *Sintering temperature (°C)* | *Time of Activation (min)* | *Dielectric constant* ($\varepsilon_r$) | *Dielectric loss factor* (tgσ) | Curie point (*°C*) |
|---|---|---|---|---|
| 1100 | 0 | 230 | 0·18 | 124 |
| | 30 | 330 | 0·12 | 126 |
| | 90 | 450 | 0·06 | 118 |
| | 180 | 350 | / | < 100 |
| 1200 | 0 | 250 | 0·13 | 127 |
| | 30 | 350 | 0·09 | 126 |
| | 90 | 350 | 0·17 | 126 |
| | 180 | 500 | 0·11 | 115 |
| 1300 | 0 | 300 | 0·04 | 127 |
| | 30 | 450 | 0·025 | 127 |
| | 90 | 450 | 0·11 | 121 |
| | 180 | 550 | 0·03 | 112 |

on structure and properties of $BaTiO_3$ ceramics. The dielectric constant and dielectric losses factor are functions, not only of the sintering regime, but also the time of tribophysical activation. The Curie temperature goes to lower values with increasing of tribophysical activation time ($T_c = 112$–115°C for 180 min of activation, in comparison with $T_c = 124$–127°C for non-activated specimens).

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