SYNTHESIS OF BARIUM TITANATE NANOPOWDERS BY MECHANOCHEMICAL ACTIVATION TECHNIQUE

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1. INTRODUCTION

Since its discovery at the midle of the last century, barium titanate, as well as barium titanate based ceramics become the most studied ceramics both for their exceptional dielectric and feroelectric properties. It is enough to mention only some of the main fields of application such as multilayer ceramic capacitors, high dielectric constant materials for microwave resonators, positive temperature coefficient thermistors, piezoelectric transducers, electrooptical devices and so forth. The characteristics of such electroceramics are markedly influenced by their morphostructure. Consequently, efforts are made to get more information and experimental data regarding the effect of crystallite size on the properties of dense bulk ceramics of barium titanate. In many phenomena there is a so called superparaferoic behavior for very fine crystals whose origin is not yet fully understood. Therefore efforts are made to prepare materials with grain sizes within a very large range using new advanced methods. One such method is the mechanochemical activation process for powder synthesis, in which the high mechanical energy produces a fine cominution of the raw materials and initiate the chemical reaction between the raw oxides to form the new compound. The experimental results obtained in preparing fine powder of barium titanate by mechanochemical synthesis together with some of the main properties of ceramics made from such powder are presented here.

2. OBJECTIVES

The main objectives of this investigations were:

- To synthetize a nanometric barium titanate powder by mechanochemical activation process from raw oxides of barium and titanium
- To find out the practical preparation conditions able to produce barium titanate nanopowders with high reactivity
- To prepare ceramic bodies from this nanopowder with different grain sizes by sintering at different temperatures.
- To investigate the main properties of these ceramics and to evidence the influence of the morphostructure on the dielectric and piezoelectric properties.

3. EXPERIMENTAL

The starting raw materials used for the preparation of barium titanate were barium oxide and titanium dioxide of p.a. purity. The oxides, with a particle size distribution in the 1-5 μm range were weighted to make batches of 30 g of stoichiometric $BaTiO_3$ and they were loaded into agate jars, of 500 ml together with 100 agate balls of 10 mm diameter corresponding to a ball/oxide powder ratio of 5/1. In order to prevent the ground material from sticking to the jars and balls we added 5 ml of methanol to allow a better dispersion and to reduce the agglomeration of smaller particles. The jars usually called “the planets” were mounted in their corresponding places on the sun wheel of a Retsch PM 400 planetary ball mill. The mill operated at a rotation speed of the sun wheel of 350 min^{-1} and a speed ratio of 1:-2, which means that the grinding jar rotates twice for each sun wheel rotation thus providing a high fineness of the powder in a relatively short time. Centrifugal forces carry the balls in the direction in which the jar is rotating and the differences between the speeds of the grinding jar and the balls results in strong frictional forces.

4. RESULTS

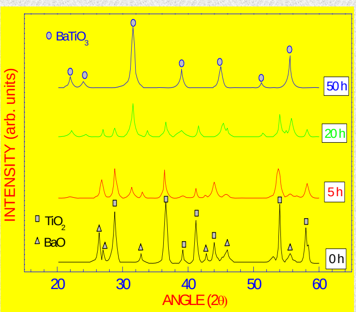

Fig. 1. XRD pattern of mechanically activated oxide powder for different milling times

POWDER The conventional way to synthesize barium titanate by the solid state reaction is a simple and low cost process, but it has the disadvantage to require high temperatures for calcinations and to produce coarse grained powder. The mechanochemical synthesis produces directly fine grained powder without being necessary the calcinations step. Figure 1 shows the XRD patterns of mixed powders mechanically activated for different times. One can see that the XRD for initial mixture of oxides show only the peaks for BaO and TiO_2. After 5 hours of milling the well-known perovskite structure begin to appear being slightly visible at 2θ=31.4°, 38.7° and possible at 45°. After 20 hours the barium titanate seems to be formed in a much higher amount and eventually after 50 hours the synthesis of $BaTiO_3$ is completed. The morphology of the powder milled for 50 hours is illustrated in figure 2. The majority of grains show spherical shapes but some others show faces at different angles. This is probably due to the fact that the grains synthesized in the beginning were much more errodated by milling while the other formed afterwards, were not enough errodated.

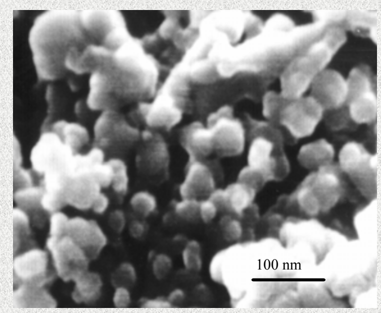

Fig. 2. Morphology of barium titanate powder after 50 hours of milling

SINTERED CERAMICS The synthesized powders were uniaxially pressed as discs with 10 mm diameter and about 1 mm thick and were sinterized on platinum boats in air at temperatures between 1200° and 1450 °C for 4h. Figure 3 shows images of as fired surfaces of samples sintered at different temperatures.

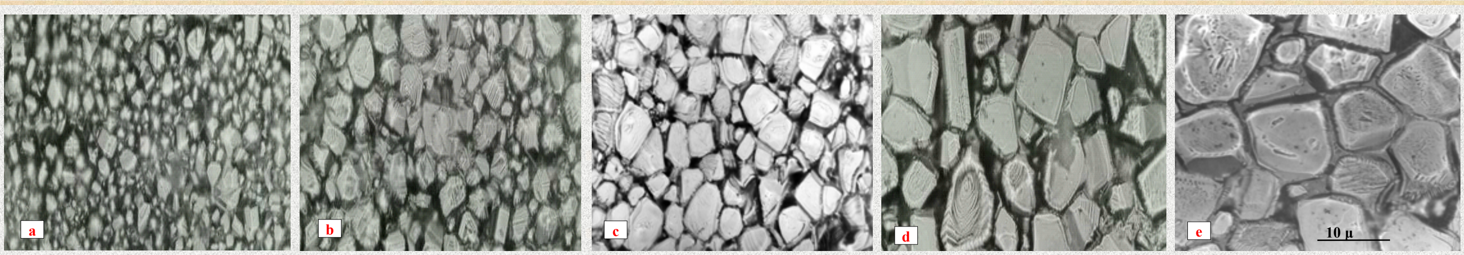

Fig. 3. Images of as fired sample surfaces for BT sintered at: a) 1200 °C; b) 1250 °C; c) 1300 °C d) 1400 °C and e) 1450 °C)

PROPERTIES The densification process is illustrated in figure 4 where one can see that between 1350° and 1400 °C the samples are fully densified and the density reaches maximum values of about 98% of theoretical density. Above 1400 °C the density decreased, probable due to the fact that crystallites increase were rapidly and a greater number of pores are formed. The average grain size vs sintering temperature is shown in figure 5. The grain size increases rather steadily with increasing sintering temperature. The dielectric properties of the fine and coarse grains samples of $BaTiO_3$ are shown in figures 6 and 7. Figure 6 shows the behavior of the relative dielectric constant as a function of the grain size. One can see that there is an optimum grain size of 2μm for which the dielectric constant shows a maximum value of 5800. For samples with smaller or greater grain size the dielectric constant decreases, this process being more pronounced for coarse grained samples. Fig. 7 illustrates the behavior of the dielectric constant with temperature. The first observation to be made is that the dielectric constant in the ferroelectric state strongly depends on grain size and very slightly on temperature, being rather constant up to 100 °C. In the paraelectric state, above the Curie point, it is almost independent on grain size but strongly on temperature. The peak around T_C is sharp for both samples but the maximum value for fine grained sample (nearly 16000) is higher than that for coarse grained samples (12500). The electromechanical planar coupling factor for fine and coarse grained specimens were different along the whole temperature interval from room temperature up to the Curie point.

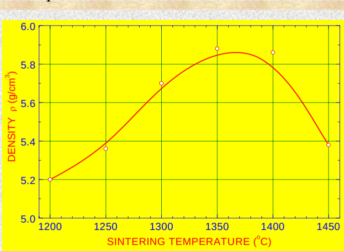

Fig. 4. Density vs. sintering temperature for BT

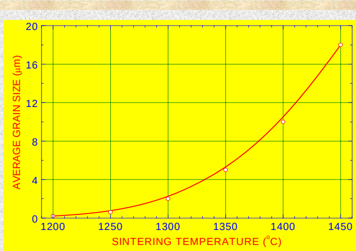

Fig. 5. Grain size behavior of BT powders as a function of sintering temperature.

Fig. 6. Dielectric constant for BT sintered samples with different grain size.

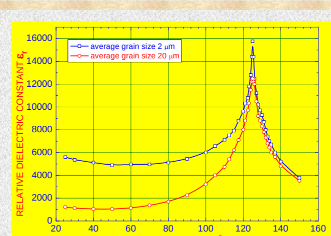

Fig. 7. Dielectric constant as a function of temperature for BT sintered samples with average grain sizes of 2μm and 20 μm respectively.

5. SUMMARY

Single phase BaTiO3 was synthesised by mechanochemical process from BaO and TiO_2, after 50 h of milling in a high energy ball mill. The resulting perovskite phase of $BaTiO_3$ powder exhibited particle size of about 50 nm. The best dielectric properties were obtained in fine grained ceramics with average grain size of 2 μm where the dielectric constant at room temperature was 5800 compared with only 1000 for coarse grained ceramics.