SYNTHESIS OF BARIUM TITANATE NANOPowDERS BY MECHANO CHEMICAL ACTIVATION TECHNIQUE

1. INTRODUCTION

Since its discovery at the middle of the last century, barium titanate, as well as barium titanate based ceramics become the most studied ceramics both for their exceptional dielectric and ferroelectric 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, electrotactical 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 superparaelectric 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 commination of the raw materials and initiates 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 these investigations were:
• To synthesize 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 nanoparticles with high reactivity
• To prepare ceramic bodies from this nanopowder with different grain sizes by sintering at different temperatures.

4. RESULTS

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 BaTiO3, 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 PM400 planetary ball mill. The mill operated at a rotation speed 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.

3. EXPERIMENTAL

The densification process is illustrated in figure 4 where one can see that between 1350°C 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 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 BaTiO3 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 2 μm 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 grains samples. Figure 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 Tc 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.

5. SUMMARY

Single phase BaTiO3 was synthesised by mechanochemical process from BaO and TiO2, after 50 h of milling in a high energy ball mill. The resulting perovskite phase of BaTiO3 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.