Spark plasma sintering of fine-crystalline $BaTiO_3$ synthesized in sub- and supercritical water

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Barium titanate is a prominent ferroelectric which has wide industrial applications as a material for base-metal-electrode capacitors, piezoelectric actuators, thermistors and electro-optic devices [1,2]. The progress in this field requires submicron-grained ceramics produced from fine-crystalline $BaTiO_3$ powders. A perfect powder for microelectronics production should perform high purity, homogeneous composition, uniformity of particles and weak agglomeration of crystals [3]. Recently, a novel method of synthesis based on the use of sub- and supercritical water was successfully used for nanocrystalline $BaTiO_3$ preparation [4-6].

The current study is to perform the connection between the conditions of synthesis in water medium and the capability of $BaTiO_3$ powders to be used as raw material for high-density dielectric ceramics. The proposed method of synthesis operates with barium and titanium oxides as reagents and subcritical vapor or supercritical water as a reaction medium. It was reported [6,7] that during the synthesis in these conditions water molecules provided hydration and hydroxylation of the starting metal oxides accompanied by breaking of metal – oxygen bonds and formation of metal – hydroxyl bonds. These processes led to a dramatic increase of solid-state mobility and facilitated solid-state diffusion of barium ions into TiO_2 structure followed by the formation of $BaTiO_3$ structure. This reaction between BaO and TiO_2 had a similar mechanism in sub- and supercritical water. Nevertheless, H_2O molecules in supercritical region possessed more degrees of freedom than in subcritical state and their reactivity towards oxides was higher. Due to this the reaction in supercritical water yeilded nearly full conversion while in subcritical medium it reached only about 80%. Besides, the contents of volatile admixtures in the product obtained in supercritical water was nearly four times lower (0.241 mass.%) than in case of synthesis in subcritical vapor (0.884 mass.%).

Table 1. Conditions of $BaTiO_3$ powder synthesis in sub- and supercritical water

Reagents	T (°C)	P (MPa)	t (h)	Sample
BaO, TiO_2	230	2.94	20	LC
	400	26.00	20	HC

The synthesis of $BaTiO_3$ was carried out in sub- and supercritical water at 230°C, 2,94 MPa and 400°C, 26,00 MPa, respectively, with the use of BaO and TiO_2 equimolar mixture as starting reagents (Table 1). The detailed procedure to obtain $BaTiO_3$ was described elsewhere [6]. The powder synthesized in subcritical conditions consisted of $BaTiO_3$ with traces of starting TiO_2. The product of synthesis in supercritical medium was single-phase $BaTiO_3$ within the limits of XRD sensitivity. From TEM study, $BaTiO_3$ crystals in the sample LC were distributed around 101 nm, the sample HC consisted of nanosized crystals of about 80 nm with a minor fraction of submicron crystals up to 370 nm in size. Spark plasma sintering (SPS) technique was chosen as a method of ceramics manufacturing as it provides effective sintering due to simultaneous application of heating and pressuring. Based on the data on powders shrinkage rate [5,6], the following conditions of SPS were applied for the powders LC and HC: 1170°C, 50 MPa. The dwell time varied from 1 to 10 min.

The values of the density of the ceramics manufactured from the powders LC and HC related to the theoretical value of 6.02 g cm^{-3} were shown in Fig. 1. The highest relative density reached in the LC series was 97.4% and lowered with the dwell time. In another series produced from the powder HC the density was not almost affected by the dwell time and reached 98.3-99.9%. The results obtained for the both series were superior to the densification during pressureless sintering. The density of 86% was reported for the powder synthesized in subcritical water vapor (LC type) [8] and 89% for the powder produced in supercritical water (HC type) [9].

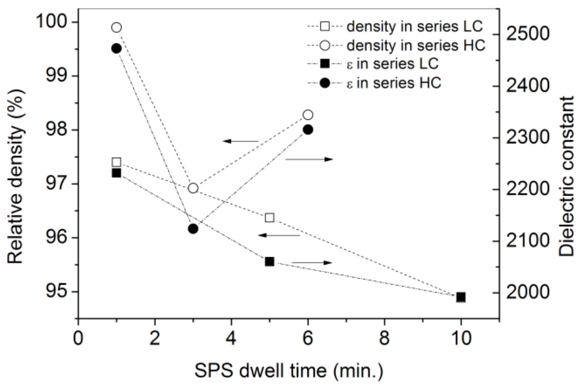

Figure 1. Relative density and dielectric constant at 1 MHz of the $BaTiO_3$ ceramics produced by SPS technique

Fig. 2 showed the microstructure of the ceramics produced from powders LC and HC with different SPS duration. Formation of a structure with hardly visualized grain boundaries and round-shaped pores was observed after 1 min. of sintering of LC powder. The observed type of microstructure pointed to the liquid-phase mechanism of sintering due to the presence of TiO_2 in the LC powder. Prolongation of sintering up to 10 min. led to a significant increase in porosity and appearance of lamellar abnormal grains. The mean size of normal grains was 331±55 nm. The abnormal grain growth was caused by phase inhomogeneity in the powder LC and was accompanied by undesired dedensification of ceramics [10,11]. Dense ceramics with homogeneous microstructure was sintered from the HC powder. The ceramics of HC series performed negligible grain growth. Mean size of grains was 142±31 nm and 147±31 nm after 1 min. and 6 min. of sintering, respectively.

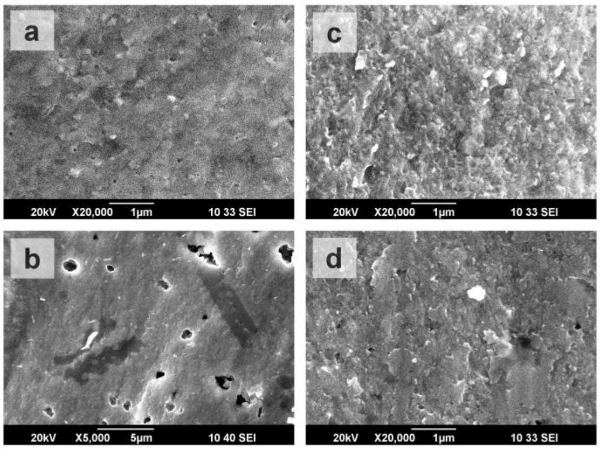

Figure 2. Fracture surfaces of $BaTiO_3$ ceramics sintered by SPS at 1170°C, 50 MPa from powders LC (a – 1 min. dwell; b – 10 min. dwell) and HC (c – 1 min. dwell; d – 6 min. dwell)

The dielectric constant calculated from capacitance measurements by a contact method correlated well with the density of ceramics (Fig. 1). The highest value of ε = 2473 was reached for the sample of 99.9% density manufactured from HC powder. This value corresponded to the data reported on dense $BaTiO_3$ ceramics considering the grain-size effect [12].

$BaTiO_3$ powder synthesized in supercritical water showed excellent properties as a raw material for high-density, homogeneous, and fine-grained dielectric ceramics. Increased values of pressure and density along with high molecular mobility of supercritical water in respect of subcritical vapor provided formation of well-crystallized single-phase $BaTiO_3$ fine powder. This work supplemented the results reported previously on supercritical water as a proper medium for high-quality oxide preparation [13]. Also, in current study the SPS technique allowed manufacturing of highly dense materials in contrast to a conventional sintering technology.

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