

Microwave and Conventional Sintering and Grain Growth Behavior of Nano- Nb Doped BaTiO₃ Prepared from Microwave Hydrothermal Powders

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Microwave-assisted hydrothermal synthesis of nano- Nb doped BaTiO₃ was performed at 150°C for 2 hours, using C₁₆H₃₆O₄Ti, Ba(OH)₂·8H₂O, NbCl₅ and NaOH as starting chemicals. The resulting powder deposited on to Al₂O₃ substrates with print screen method and were sintered by Microwave Sintering (MS) of 2.45 GHz at 950°C for 20 min and Conventional Sintering (CS) at 950°C for 90 min in the air atmosphere. It is observed that the grain growth can be suppressed by 2.45 GHz microwave heating process. The grains size distribution of sample sintered for 20 min with microwave heating process was rather uniform with lower grain size and higher surface area. Microstructure, surface morphology and grain size of the thick films were studied by Field-Emission Scanning Electron Microscopy (FE-SEM), Atomic Force Microscopy (AFM) and the surface area analysis with the Brunauer – Emmett – Teller (BET) method and the Barrett – Joyner – Halenda (BJH) method used for the pore size distribution.

Keywords: *nanomaterials, thick film, structure characterization, perovskites.*

УДК 539.51

INTRODUCTION

Barium titanate is one of the most important ferroelectric materials used in electronics ceramic industry [1–3]. Numerous studies on developing synthesis methods for purer and finer BaTiO₃ powders have been reported in literature. It is necessary to site here a few sources, at least]. The hydrothermal method, a genuine low-temperature process, have enjoyed success in preparation of high-purity homogeneous and ultrafine powder of BaTiO₃ under environmentally friendly conditions. Compared to the traditional solid-state reaction and other wet-chemical routes (including sol–gel processing, oxalate route, and homogeneous precipitation), the hydrothermal method is low-cost and convenient to prepare BaTiO₃ nanoparticles without a following high temperature calcination process [4–9]. The microwave-assisted hydrothermal process is often found to be rapid and has the potential to enhance the crystallization kinetics of hydrothermal process. The term microwave-hydrothermal process was coined by Komarneni and colleagues in 1992 [10], and this process has been used for the rapid synthesis of numerous ceramic oxides, hydroxylated phases, porous materials, and metal powders.

On the other hand, Microwave Sintering (MS) is a self-heating process which is accomplished by absorbing the electromagnetic energy by a dielectric material. A higher heating speed and efficiency can be obtained with a low thermal stress gradient by the microwave volumetric heating. At room temperature, most of the ceramics have low dielectric loss

factor so that it is impossible to raise the temperature. The conventional sintering (CS) is time- and energy consuming; as a result, some researchers have shown a possibility of using microwave energy for rapid sintering [11]. In the MS, the material itself generates heat and this volumetric heating mechanism makes the sintering process rapid and selective [12, 13]. Microwave heating offers greater flexibility than conventional heating in the thermal treatment of materials. Depositing energy in the centre of the material enables rapid heating with the generation of uniform temperature profiles, offering fine grained/uniform microstructures, faster production rates, and high controllability. The present study focuses on the use of the microwave-assisted technology as compared with the CS process of print-screened niobium-doped BaTiO₃ thick films. Microstructure, surface morphology, and grain size of thick films were studied by the Field-Emission Scanning Electron Microscopy (FE-SEM), Atomic Force Microscopy (AFM) and the surface area analysis with the Brunauer – Emmett – Teller (BET) method and the Barrett – Joyner – Halenda (BJH) method used for the pore size distribution.

EXPERIMENTAL

The Microwave Hydrothermal (MH) reactions were performed using a laboratory-made microwave-heating-autoclave system with a polytetrafluoroethylene (PTFE) inner vessel, that operates at a 2.45 GHz frequency. The system can operate at 0–100% of full power, at 900W, with controlled

temperature up to the maximum of 220°C and an auxiliary cooling/heating device that is fitted to the system, which enables it to operate at a fixed temperature for a long time, while maintaining the input power of the microwave radiation during the reaction. Reagents $C_{16}H_{36}O_4Ti$, $Ba(OH)_2 \cdot 8H_2O$, $NbCl_5$ and $NaOH$ were used as raw materials. The molar ratio of Ti/Nb was kept at 0.97/0.03. The starting materials of $Ba(OH)_2 \cdot 8H_2O$, $NbCl_5$, and $C_{16}H_{36}O_4Ti$ were mixed in distilled water, containing 1M $NaOH$ at 70°C to control the pH under stirring until it turned into a homogeneous solution. The solution was transferred into a sealed PTFE autoclave followed by distilled water until the total volume reached 100 ml, that is, 80% of the capacity of the autoclave. The system was heat treated at 150°C for 2 hours. The resulting powders were centrifuged and washed with distilled water and finally oven dried at 85°C for 24 h. The obtained powders were characterized by the X-ray powder diffraction (XRD) with $Cu-K\alpha$ radiation in the 2θ range from 20° to 70° and the microstructural characterization was performed by the FE-SEM.

The powders were then used to make the respectively slurries for processing thick films. The screen-printable pastes were prepared by mixing the organic vehicles with the Nb doped Barium Titanate powder, in the ratio of 30:70. The organic vehicles were prepared by mixing the polyvinyl alcohol (PVA-19wt%), poly acrylic acid (PAA-6wt%) and Bi_2O_3 (5% wt.) powder. The PVA was used as an organic binder for getting correct viscosity of the paste for screen printing, the PAA was used as dispersant, and a small percentage of Bi_2O_3 powder (a bonding agent) was added to the mixture in order to improve the adhesion of the film to the Al_2O_3 substrate. To form homogeneous paste, the mixture was stirred using magnetic stirrer at the speed of 130 rpm and 40°C for 15 minutes. The printed films were dried at 100°C for 15 min and the organics were decomposed at 300–400°C in a conventional heating furnace before the films were processed in a microwave applicator too [14–17]. Thick films were sintered by a microwave of 2.45 GHz at 950°C for 20 and by a conventional furnace at the same temperature for 90 minutes in the air atmosphere. Microstructure, surface morphology and grain size of thick films were studied by the FE-SEM, AFM and the surface area analysis with the BET-method and the Barrett – Joyner – Halenda (BJH) method used for the pore size distribution.

RESULTS AND DISCUSSION

Figure 1a shows the X-ray powder diffraction patterns for the microwave-hydrothermal niobium-doped barium titanate (Nb doped $BaTiO_3$) powders prepared at 150°C for 2 h (The XRD result com-

pared with the known standard JCPDS 01-075-2116). The nanoparticles were pure perovskite $Nb-BaTiO_3$, minus the intermediate carbonate phase that usually was observed in the 2θ equals to 24° or 42° in the solid state method [18]. The diffraction patterns were around 45° of 2θ , where there was a characteristic splitting of the (200) reflection for the tetragonal form but not a symmetric peak for the cubic form, and no characteristic separation of the peak at 2θ equal to 45°, which corresponds to the tetragonal structure, was found. An eventual tetragonal peak splitting of the reflections cannot be resolved due to overlapping of the (0 0 2) and (2 0 0) planes. However, XRD peaks of nanoparticles are wider than the larger one, thus the cubic structure cannot be totally excluded and often makes this splitting difficult to determine [19]. The FE-SEM of the prepared $BaTi_{1-x}Nb_xO_3$ compound (where $x = 0.03$) is shown in Fig. 1b. In the MH process, the microwave radiation can couple with and be absorbed by the dielectric material, thus the smaller $BaTiO_3$ will dissolve more quickly. According to the dissolution/recrystallization mechanism, this will lead to the larger particles growing faster, too [20, 21]. Substitution of Nb^{5+} with a longer ionic radius for Ti^{4+} increases the crystallite size. The decreased crystal size in the MH method might be due to the increased nucleation rate and the high energy, which both activate chemical reactions at low temperatures.

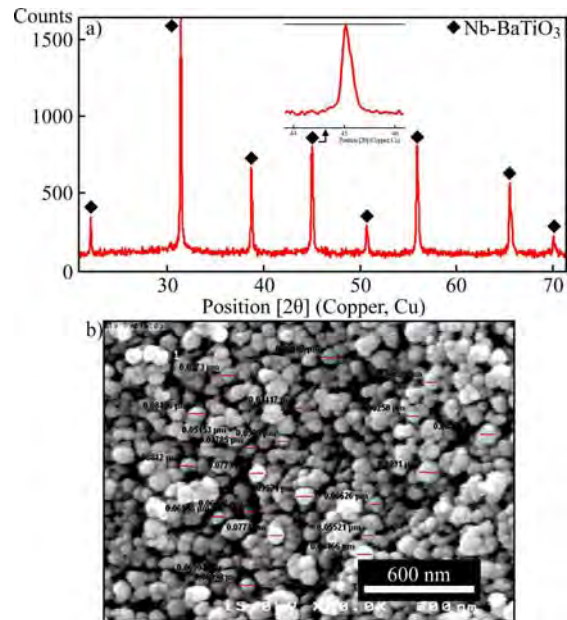
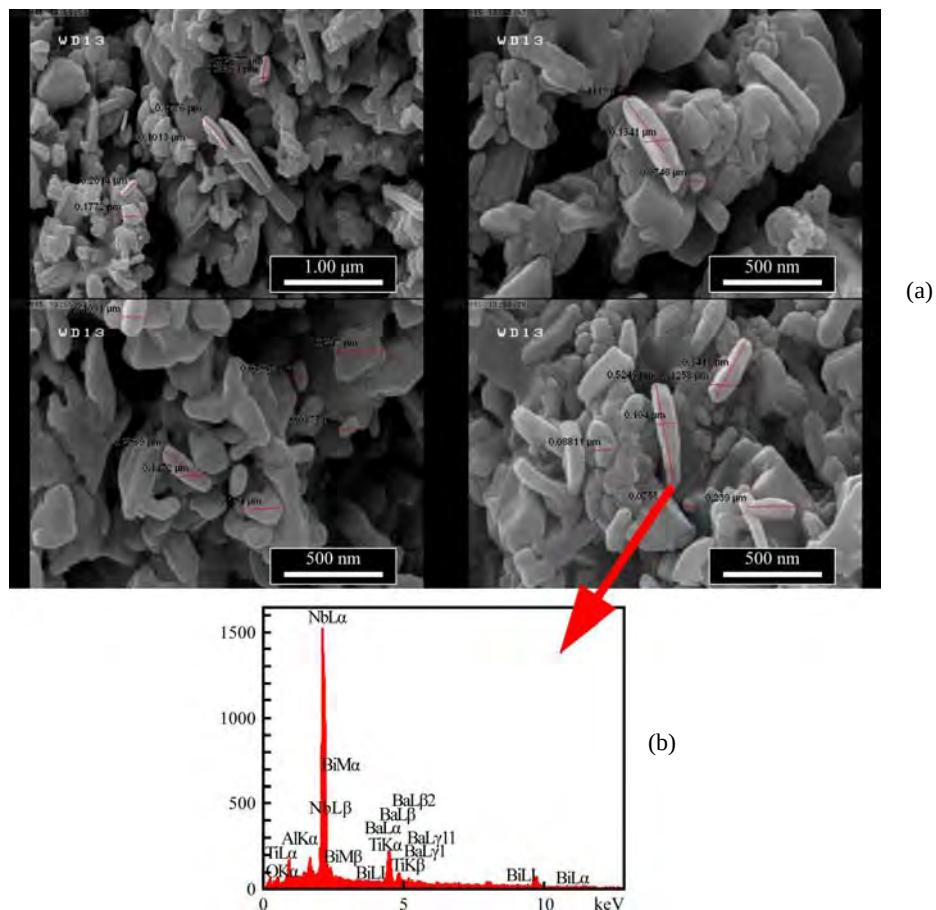


Fig. 1. (a) X-ray diffraction pattern; (b) SEM of $Nb-BaTiO_3$ nanoparticles.

The FE-SEM of the thick films were sintered by a microwave of 2.45 GHz at 950°C for 20 minutes and by the conventional heating for 90 minutes in the air atmosphere, which is shown in Fig. 2 and Fig. 3, respectively. The SEM morphology observation indicates that in sintering with the microwave



heating, the grain growth is, in fact, insignificant and no sintering occurs. In this case a rapid densification takes place with a relatively slow grain growth. When sintering with a conventional furnace is done for 90 minutes at the same temperature of 950°C, the grain growth is considerably faster. The SEM morphology result for the conventional method represents the normal densification process of ceramic, indicating that there is no densification without grain

growth. It seems that driving forces for densification and the grain growth are comparable in magnitude, both being proportional to the reciprocal grain size in this final-stage sintering.

With the Microwave Sintering (MS) method, very fine grains are formed and the grain size distribution (about 100 nm) is very uniform. But samples sintered by a conventional method exhibit markedly larger grain size distribution (300–800 nm) and an

abnormal grain growth, in contrast to that of microwave-sintered. According to the above experimental results, the MS process is observed to effectively densify the BaTiO₃ materials without elevating the growth of grains at a very rapid rate. The MS is a self-heating process which is accomplished by absorbing electromagnetic energy by a dielectric material. A higher heating speed and efficiency can be obtained with a low thermal stress gradient by microwave volumetric heating [22, 13].

It can be seen that the grain size, estimated by the intercept line method, is about 200 nm, but there are many “beams” in sintered samples. The dimensions of the “beams” are about 100–150 nm in length and 300–700 nm in diameter, which are far larger than those of the grains. The “beams” in nanocrystalline hydrothermal microwave Nb-doped BaTiO₃ are caused by the nanopowder agglomerates during sintering. It is well known that nanopowders have extremely large specific area and strongly tend to be agglomerated. The bonding between the particles of these agglomerates is expected to be much stronger than the bonding between particles that are only attracted by the van-der-Waals interaction. In order to investigate the structure and chemical composition of the “beams”, the EDX of them is also shown in Fig. 3b. The result indicates that the “beam” is composed of Ba, Ti, Nb and O. So the nanoparticles were pure perovskite Nb-doped BaTiO₃, without some intermediate phase that usually is observed in the sintered body.

The BET analysis based on N₂ adsorption has been used to determine the surface area and the pore size distribution using the BJH method. The quantity of the adsorbed gas on the solid surface is measured at discrete pressure (P) steps over the relative equilibrium pressure (P/P_0) range of 0.003 to 0.300 at constant temperature (Analysis Bath Temp.: 75.921 K). During the experiment, the pressure systematically increases up to the condensation pressure (adsorption branch) followed by the reduction of pressure from P_0 (desorption branch) and the data are reported as the adsorption isotherm. So, Fig. 4 depicts the BET surface area plot of the samples sintered with microwave and conventional methods for 20 and 90 minutes, and the quantity of gas adsorbed per mass expressed as moles or volume in cm³/g (S.T.P.) as a function of the relative equilibrium pressure (P/P_0). The results show that the single point surface area of the samples sintered for (a) microwave sintering for 20 min and for (b) CS for 90 min at $P/P_0 = 0.300$ shrunk from 123.52 m²/g to 73.29 m²/g, respectively.

The isotherm linear plots of the samples sintered via the microwave and conventional methods for 20 and 90 minutes are given in Fig. 5a and b, respectively. In literature, pore-sized nomenclature is

varied and a wide variety of terminology is used for pores with different sizes (e.g. nanopore, mesopore, micropores) [23]. The International Union of Pure and Applied Chemistry [IUPAC] recommends the following classification of pores according to their size:

1. Micropores: pores with pore-size below 2 nm.
2. Mesopores: Pores with pore-size between 2 nm to 50 nm.
3. Macropores: Pores with pore-size greater than 50 nm [24].

Since the gas is below its critical point, capillary condensation becomes important in these experiments which give us the information of pore-sizes. At 77 K, N₂ is the most commonly used gas for the surface area and mesopore characterization. So, subcritical N₂ gas adsorption at liquid nitrogen (LN₂) temperature and subatmospheric pressure is used to characterize the surface area and pore-structure. The shape of the isotherm and its hysteresis pattern provide useful information about the physisorption mechanism, the solid and gas interactions, and can be used to qualitatively predict the types of pores present in the adsorbent.

IUPAC (International Union of Pure and Applied Chemistry) classified the adsorption isotherms into six types [23, 25, 26]. The isotherm linear plots of both samples sintered with microwave and conventional methods are very close to Type IV. So, the samples are nearly predominantly mesoporous material and will have a characteristic hysteresis loop, which is associated with capillary condensation and evaporation taking place in mesopores. At a lower relative pressure ($P/P_0 < 0.4$), the isotherm profiles are similar to Type II isotherms, indicating a monolayer to multilayer adsorption mechanism on the walls of meso- and macropores. At higher relative pressures, the gas condenses in the mesopores to bulk liquid at pressures below the saturation vapor pressure with the formation of a gas–liquid meniscus (capillary condensation). The isotherm profiles exhibit a plateau with reduced adsorption at a high P/P_0 . The limiting adsorption plateau at a high P/P_0 indicates complete filling of mesopores and subsequent adsorption on the external surfaces.

The hysteresis loop in Type IV isotherms is characteristic of mesopores. Non-connecting cylindrical mesopores can show hysteresis due to differences in the meniscus shapes during the capillary condensation (adsorption) and evaporation (desorption) process. Capillary condensation is preceded by a metastable fluid state with a cylindrical meniscus while capillary evaporation occurs with a hemispherical meniscus resulting into lower equilibrium pressures P of the phase transition for the same pore size. Other mechanisms that contribute to hysteresis include pore network and pore connectivi-

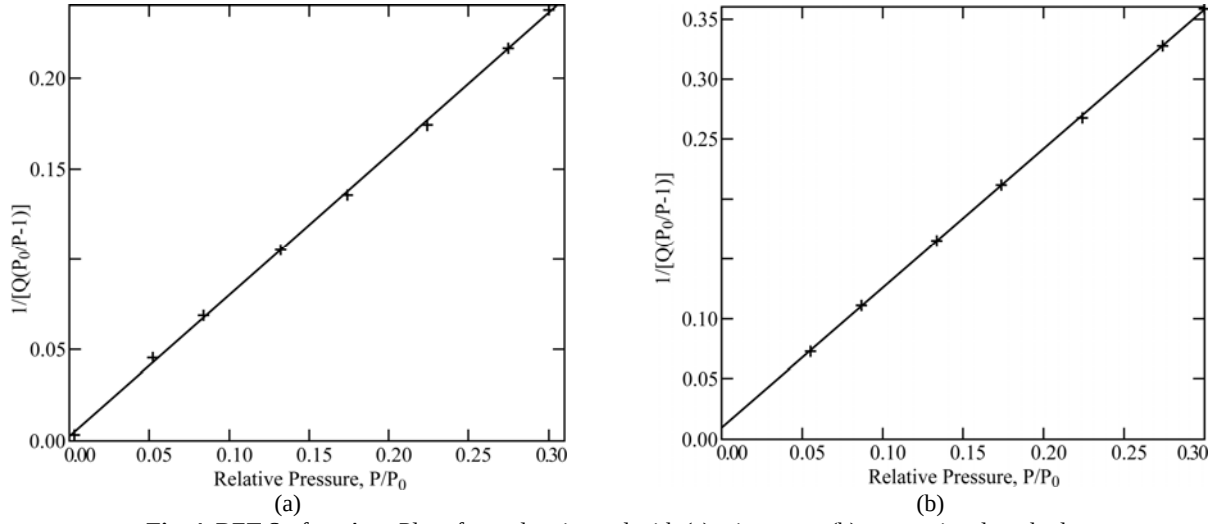


Fig. 4. BET Surface Area Plot of samples sintered with (a) microwave (b) conventional method.

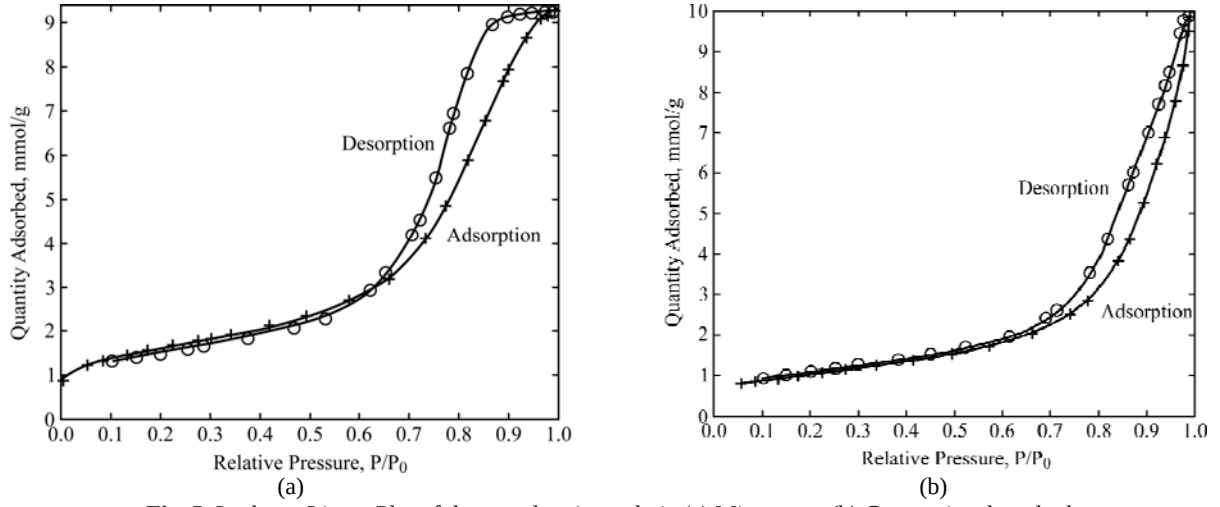


Fig. 5. Isotherm Linear Plot of the samples sintered via (a) Microwave (b) Conventional method.

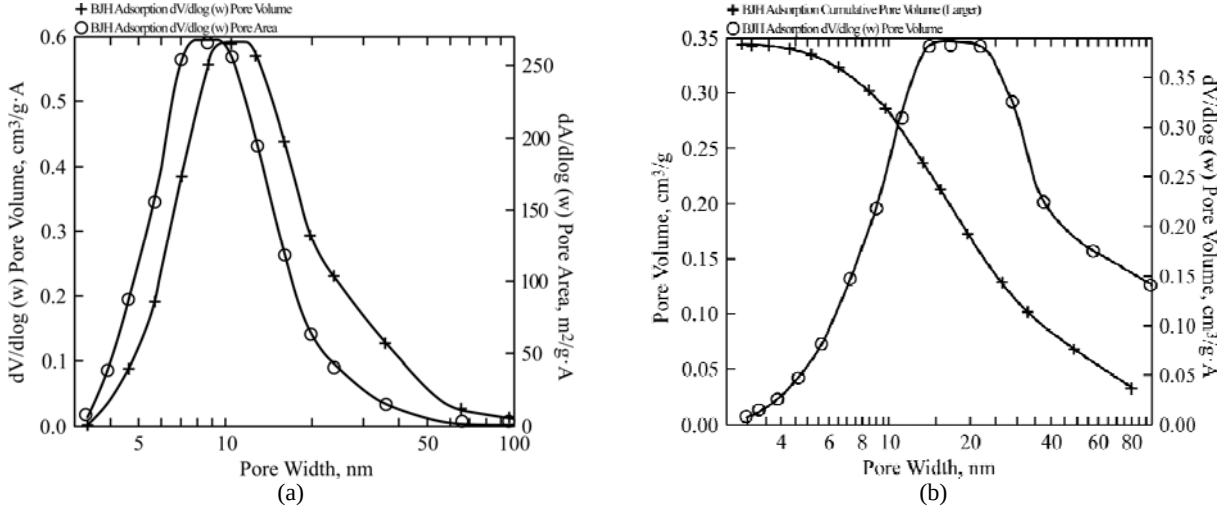


Fig. 6. BJH adsorption $dV/d\log(w)$ pore volume and pore area ($dA/d\log(w)$) for the samples sintered via (a) microwave and (b) conventional methods.

ty effects. In such interconnected pore-networks systems, the path dependence is due to varying sequence in which the probe molecule encounters the pores during the adsorption and desorption process, resulting in hysteresis [25–26].

The microwave sintered samples hysteresis loop types are mostly seen in materials with a narrow distribution of cylindrical or tubular pores. The conven-

tional sintered samples hysteresis loop types also result from slit-shaped pores, but are associated with micropores in general.

The BJH adsorption $dV/d\log(w)$ pore volume and pore area ($dA/d\log(w)$) for the samples sintered via microwave and conventional methods for 20 and 90 minutes, respectively, are given in Fig. 6.

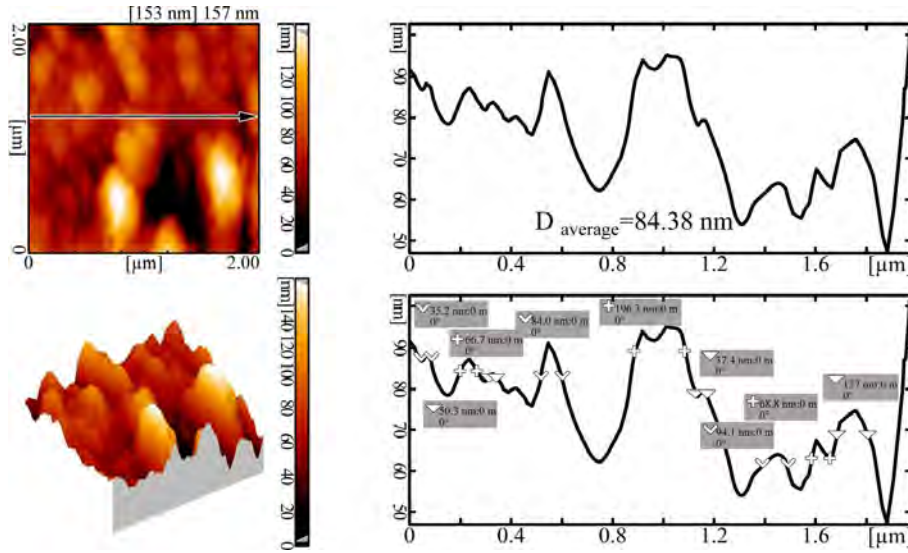


Fig. 7. AFM image of the surface of samples sintered via microwave method for 20 min.

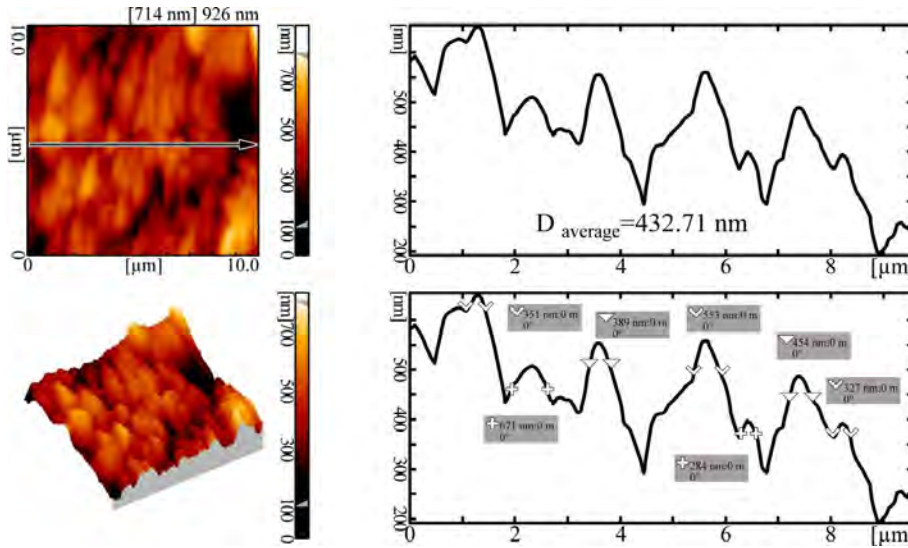


Fig. 8. AFM image of the surface of samples sintered via conventional method for 90 min.

The BJH distribution curve obtained for the samples sintered with microwave and conventional method for 20 and 90 minutes led to a cumulative surface area of pores between 1.7000 nm and 300.0000 nm width are 135.75 m²/g and 89.36 m²/g, and cumulative volume of pores between 1.7000 nm and 300.0000 nm width are 0.3409 cm³/g and 0.3439 cm³/g and average pore diameter are 10.039 and 15.39 nm, respectively. It must be also remarked that the BJH desorption distribution leads to an underestimated average pore diameter. This may be due to the fact that the thermodynamic gas-solid equilibrium is less stable at desorption when such non-cylindrical pores are involved. So it can be considered that microwave heating offers an ultra-fast method for ceramic with an ultra-large heating rate. The grain size is smaller than for other methods, while the grain size uniformity increases because of a few orders higher densification rate in a short sintering time.

The AFM surface images of the samples sintered with microwave and conventional methods for 20

and 90 minutes are presented in Fig. 7 and 8, respectively.

It is obvious from the AFM images of the samples that the surfaces of the print screened films are rough, and the average grain sizes of the samples sintered with microwave for 20 minutes and conventional method for 90 minutes are 84.38 nm and 432.71 nm, respectively. The results are in good agreement with BET and BJH results too.

CONCLUSIONS

In general, it is known to be difficult to prepare dense Nb-doped BaTiO₃ ceramics with fine grains via a sintering process. Nano-sized particles, due to the tendency to form agglomerates, can lead to microstructures with defects that cannot be eliminated during sintering. It is reported in the present paper that the driving forces for densification and the grain growth are comparable in magnitude; both being proportional to the reciprocal grain size in this final-stage sintering. But according to the above

experimental results, a few minutes of the microwave sintering method could effectively control the grain growth of first Nb-doped BaTiO₃ nanoparticles, realizing the uniform sintering of a thick film, to gain the stable microstructure. It seems that the sintering at inter-particle boundary is enhanced by the microwave driven high-frequency ion vibration, while a short time of the sintering process has no significant effect on the grain growth.

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Реферат

Гидротермальный синтез нано- Nb порошков легированных BaTiO₃ при микроволновом воздействии проводили при 150°C в течение 2 часов, используя C₁₆H₃₆O₄Ti, Ba(OH)₂·8H₂O, NbCl₅ и NaOH в качестве исходных химических веществ. Полученный порошок осаждали на подложках Al₂O₃ с помощью метода трафаретной печати и спекали с помощью микроволнового спекания (МС) при 2,45 ГГц и 950°C в течение 20 мин и методом обычного спекания (ОС) при 950°C

в течение 90 мин в атмосфере воздуха. Следует отметить, что рост зерен может быть подавлен при микроволновом нагреве с частотой 2,45 ГГц. Распределение размера зерен образца спеченного в течение 20 мин при микроволновом нагреве было достаточно однородным и с меньшим размером зерна и большей площадью поверхности. Микроструктура, морфология поверхности и размер зерна толстых пленок изучались методом автоэмиссионной сканирующей электронной микроскопии (FE-SEM), атомно-силовой микроскопии (АСМ) и анализа площади поверхности методом Брунауэра – Эмметта – Теллера (БЭТ) и методом Барретта – Джойнера – Халенды (БДХ) для исследования распределения пор по размерам.

Ключевые слова: наноматериалы, толстая пленка, характеристика структуры, перовскиты.