SYNTHESIS OF FINE-CRYSTALLINE TETRAGONAL BARIUM TITANATE IN LOW-DENSITY WATER FLUID

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ABSTRACT

Barium titanate was synthesized in mild conditions of low-density water fluid media (230°C, 2,94 MPa, 20 h.). The product consisted of uniform crystals with average size 165-170 nm. Post-synthetic treatment of $BaTiO_3$ samples included washing in acid and water and heating in air at 500°C for 1 h. It was found that the sequence of the treatment has an influence on phase content of crystalline $BaTiO_3$. This effect is useful in producing of highly tetragonal $BaTiO_3$ powder. Ceramics sintered from the synthesized powder possess high dielectric permittivity of 2320.

INTRODUCTION

Below the Curie temperature 120°C barium titanate ceramics perform high ferroelectric characteristics. Dielectric permittivity of $BaTiO_3$ discs was reported to reach 5000 at ambient temperature and 10000 at 120°C [1]. This property makes $BaTiO_3$ an important material for multilayer ceramic capacitors, piezoelectric transducers, positive temperature coefficient transducers and electro-optic devices [2-4]. It's known that physical properties of ceramics strongly depend not only on sintering process, but also on starting powder characteristics [5]. General requirements for $BaTiO_3$ powder in this connection are dispersivity, uniformity, crystallinity, low water and hydroxyl groups content and submicron size [6]. A large number of methods such as sol-gel, solvothermal, Pechini, oxalate, catecholate, aerosol pyrolisis, molten salt and their modifications allow producing fine $BaTiO_3$ powders meeting these requirements [2, 7-12]. An important place belongs to processes in aqueous media - hydrothermal method and synthesis in supercritical water fluid. These conditions are favorable to obtain $BaTiO_3$ particles as small as 4-110 nm and 9-100 nm, respectively [13, 14].

In addition to requirements mentioned above $BaTiO_3$ powder is desired to be tetragonal at room temperature. Though tetragonal modification is thermodinamically stable at these conditions, wet-chemically synthesized $BaTiO_3$ crystals often retain high-temperature cubic or pseudocubic state below 120°C. Lattice defects and also high surface tension in case of nano-sized particles obstruct spontaneous polarization [15]. Conversion from cubic to tetragonal phase requires heating of $BaTiO_3$ crystals at temperature higher than 1000°C and lead to particle aggregation. Hence, it is of interest to produce directly tetragonal $BaTiO_3$ crystals [16].

Low-density water fluid has been successfully used as reaction media for synthesis of crystalline $LaAlO_3$, $Y_3Al_5O_{12}$ and other complex oxides [17]. $BaTiO_3$ nanocrystals (50-80 nm) were obtained in this medium at 200-280°C and equilibrium pressure and showed cubic or pseudocubic structure at room temperature [18, 19].

Current work is directed to developing of synthesis in low-density water fluid so as to produce $BaTiO_3$ crystals in ferroelectric tetragonal modification.

MATERIALS AND METHODS

Synthesis in low-density water fluid was carried out in laboratory stainless steel autoclaves with PTFE inner containers. $Ba(OH)_2 \cdot 8H_2O$ and TiO_2 (71% rutile and 29% anatase) were thoroughly mixed in wooden mortar with pestle and put into PTFE container. Calculated amount of distilled water was added into the autoclave outside the container. Hermetically closed autoclave was heated up to 230°C and hold at this temperature for 20 h. After that the bottom of the autoclave was dramatically cooled so as vapor inside it rapidly condensed and the reaction stopped. This way was used for synthesis of two couples of samples: A-1 and A-2, B-1 and B-2 (**Table 1**).

Table 1: Conditions of $BaTiO_3$ synthesis and treatment

Sample	Synthesis	Post-synthetic treatment	
		I	II
A-1	230°C, 2,94 MPa, 20 h.	Washing with acid, filtration, drying	Heating in air at 500°C for 1 h.
B-1			
A-2		Heating in air at 500°C for 1 h.	Washing with acid, filtration, drying
B-2			

The synthesis of samples A-1 and B-1 was followed by washing in acetic acid solution from residual $Ba(OH)_2$ and $BaCO_3$, filtration, washing with distilled water and drying in air at 70°C. Then A-1 and B-1 were heated in air at 500°C for 1 h. The samples A-2 and B-2 were firstly heated and then washed and dried in the same way (**Table 1**). Samples from series B were used for verification of results obtained for series A. The sample A-1 was sintered into ceramic disc by SPS method (Labox-625) at 1220°C, 60 MPa for 2 min. Permittivity of ceramics was detected at LCR meter E7-12 at 1 MHz. XRD patterns of the samples were scanned at Rigaku D/Max-2500 diffractometer with CuKα radiation in range $10° \leq 2\theta \leq 70°$ with step 0,02° 2θ. SEM study was performed at JSM-6390 LA.

RESULTS

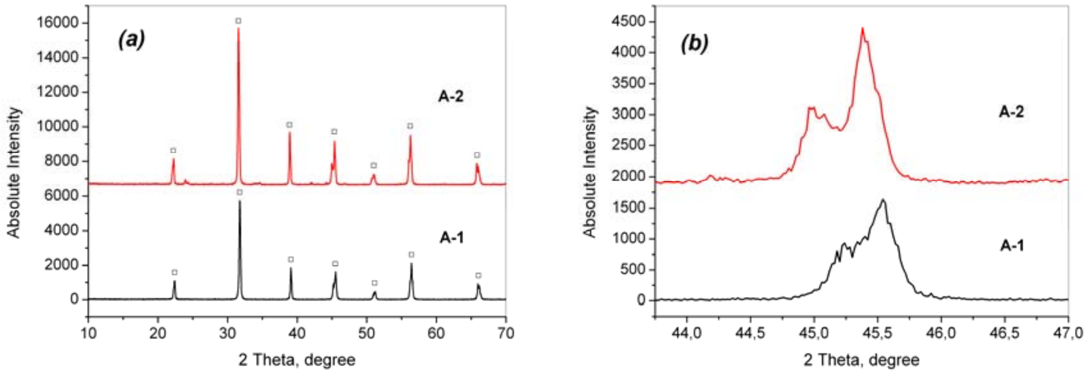

Figure 1: XRD patterns of A-1 and A-2 samples in ranges a) $10° \leq 2\theta \leq 70°$, b) $43{,}75° \leq 2\theta \leq 47°$.

Figure 1 shows XRD patterns of samples A-1 and A-2, which were synthesized in the same conditions and differ in order of treatment after that (**Table 1**). Marked peaks in the patterns at **Fig. 1a** are consistent with tetragonal $BaTiO_3$ phase (00-073-1282 in PDF-2). Sample A-2 also contains traces of $BaCO_3$. Evidently, the patterns of A-1 and A-2 samples are not identical. Asymmetry and splitting of reflections in 2θ range 44°-46° at **Fig. 1b**, indicating the presence of tetragonal phase of $BaTiO_3$, could be interpreted in two ways. Some authors [20, 21] consider the sample as single tetragonal phase of $BaTiO_3$ and characterize it by the degree of tetragonality *c/a*. Another way is to suppose the powder consisted of mixed cubic and tetragonal $BaTiO_3$ phases and estimate percentage of each phase [22, 23]. Anyway, asymmetry and splitting could be used for visual estimation of tetragonality.

The tetragonality of A-2 with distinctly splitted peak at 44°-46° 2θ is apparently higher than tetragonality of A-2, which has asymmetrical, but not splitted peak in the same 2θ range. Comparison of XRD patterns of samples B-1 and B-2 gave similar results. Samples heated directly after the synthesis are characterized by higher tetragonality, than samples heated after washing.

Table 2 performs the crystalline domains mean size calculated by Sherrer equation. The calculations were carried out using broadening value of (111) plane reflection, so long as this peak is single in both cubic and tetragonal $BaTiO_3$. The results present the mean size about 40 nm and show no significant difference in crystalline size between samples with different tetragonality.

Table 2: Crystalline mean size of $BaTiO_3$

Sample	A-1	A-2	B-1	B-2
Crystalline mean size, nm	37,6	42,2	40,9	39,9

SEM study (**Figure 2**) revealed well-dispersive slightly faceted crystals in each of investigated samples. Crystal mean sizes of samples A-1 and A-2 are 165 and 168 nm, respectively. There is no noticeable aggregation of particles after heating at 500°C for 1 h. The morphology of $BaTiO_3$ is not sensitive to the order of post-synthetic treatment.

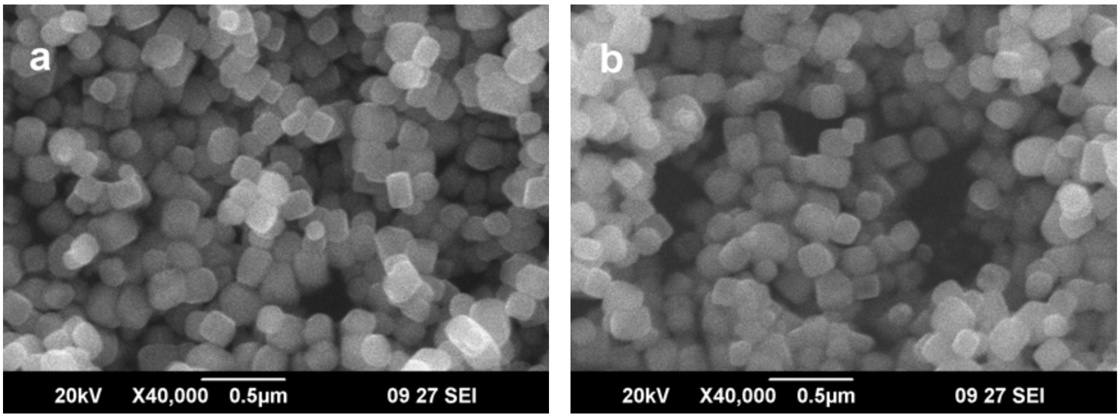

Figure 2: SEM images of samples a) A-1, b) A-2.

$BaTiO_3$ samples synthesized in low-density water fluid at 230°C show phase and morphological characteristics allowing the use of these powders as material for ceramics processing. Detected differences in degree of $BaTiO_3$ tetragonality could be connected with leaching behaviour of Ba^{2+} ions in water solutions [24, 25]. Deficiency of Ba^{2+} at the surface of particles causes difficulties for spontaneous polarisation and lead to pseudocubic phase formation. It's very likely that leaching of Ba^{2+} is more intensive in "fresh" $BaTiO_3$, washed right after the synthesis (samples A-1 and B-1), than in powder heated at 500°C (samples A-2 and B-2). Thus the tetragonality of samples, which were heated before washing, is higher, that this value of $BaTiO_3$ washed just after the synthesis.

Ceramic disc processed from the powder A-1 by SPS method performed dielectric permittivity of 2320 at 1 MHz. This result proves high sinterability of $BaTiO_3$ obtained in low-density water fluid.

CONCLUSION

Tetragonal $BaTiO_3$ was synthesized in low-density water fluid at 230°C and 2,94 MPa for 20 h. The powder consists of uniform, weakly aggregated, slightly faceted crystals with average size 165-170 nm and crystalline domain size of about 40 nm. Heating at 500°C for 1 h. following the synthesis before washing in acid allows obtaining crystals with higher tetragonality than this value for crystals washed right after the synthesis. Ceramics obtained from highly tetragonal powder shows the value of permittivity as high as 2320 at 1 MHz. Process in low-density water fluid performs satisfactory results in producing of crystalline $BaTiO_3$ for ceramic materials.

REFERENCES

[1] DURAN, P., GUTIERREZ, D., TARTAJ, J., MOURE, C., Ceram. Int., Vol. 28, **2002**, p. 283.
[2] MAISON, W., KLEEBERG, R., HEIMANN, R.B., PHANICHPHANT, S., J. Eur. Ceram. Soc., Vol. 23, **2003**, p. 127.
[3] YOON, D.-H., LEE, B.I., J. Eur. Ceram. Soc., Vol. 24, **2004**, p. 739.
[4] JOSHI, U.A., YOON, S., BAIK, S., LEE, J.S., J. Phys. Chem. B, Vol. 110, **2006**, p. 12249.
[5] HSIEH, H.L., FANG, T.T., Ceram. Int., Vol. 16, **1990**, p. 39.
[6] PARISH, M., BOWEN, H.K., Ceram. Int., Vol. 10, **1984**, p. 75.
[7] MOHAMMADI, M.R., FRAY, D.J., Particuology, Vol. 9, **2011**, p. 235.
[8] KWON., S.-G., CHOI, K., KIM, B.-I., Mater. Lett., Vol. 60, **2006**, p. 979.
[9] VINITINI, V., SINGH, P., BALASUBRAMANIAN, M., Ceram. Int., Vol. 32, **2006**, p. 99.
[10] KHOLLAM, Y.B., DESHPANDE, A.S., POTDAR, H.S., DESHPANDE, S.B., DATE, S.K., PATIL, A.J., Mater. Lett., Vol. 55, **2002**, p. 175.
[11] PURWANTO, A., WANG, W.-N., LENGGORO, I.W., OKUYAMA, K., J. Eur. Ceram. Soc., Vol. 27, **2007**, p. 4489.
[12] ZHANG, Y., WANG, L., XUE, D., Powder Technology, Vol. 217, **2012**, p. 629.
[13] KUMAZAWA, H., KAGIMOTO, T., KAWABATA, A., J. Mater. Sci., Vol. 31, **1996**, p. 2599.
[14] HAYASHI, H., HAKUTA, Y., Materials, Vol. 3, **2010**, p. 3794.
[15] BEGG, B.D., VANCE, E.R., NOWOTNY, J., J. Am. Ceram. Soc., Vol. 77, **1994**, p. 3186.
[16] SUN, W., LI, CH., LI, J., LIU, W., Mater. Chem. and Phys., Vol. 97, **2006**, p. 481.
[17] DANCHEVSKAYA, M.N., IVAKIN, YU.D., TORBIN, S.N., MURAVIEVA, G.P., OVCHINNIKOVA, O.G., J. Mater. Sci., Vol. 41, **2006**, p. 1385.
[18] KHOLODKOVA, A., DANCHEVSKAYA, M., FIONOV, A., 4th International Conference NANOCON 2012, Brno, Czech Republic.
[19] KHOLODKOVA, A.A., DANCHEVSKAYA, M.N., FIONOV, A.S., XIV International Scientific Conference « High-Tech in Chemical Engineering-2012 », Tula, Russia.
[20] SREEKANTAN, S., NOOR, A.F.M., AHMAD, Z.A., OTHMAN, R., WEST, A. J. Mater. Proc. Res., Vol. 195, **2008**, p. 171.
[21] SUN, W., LI, J., Mater. Lett., Vol. 60, **2006**, p. 1599.
[22] KWON, S.-G., CHOI, K., KIM, B.-I., Mater. Lett., Vol. 60, **2006**, p. 979.
[23] BACHA, E., DENIARD, PH., RICHARD-PLOUET, M., BROHAN, L., GRUNDEL, H.W., Thin Solid Films, Vol. 519, **2011**, p. 5816.
[24] PINCELOUP, P., COURTOIS, CH., LERICHE, A., THIERRY, B., J. Am. Ceram. Soc, Vol. 82, **1999**, p. 3049.
[25] CHEN, CH., WEI, Y., JIAO, X., CHEN, D., Mater. Chem. and Phys., Vol. 110, **2008**, p.186.