

B. WODECKA-DUŚ*, M. PLOŃSKA*, D. CZEKAJ*

SYNTHESIS, MICROSTRUCTURE AND THE CRYSTALLINE STRUCTURE OF THE BARIUM TITANATE CERAMICS DOPED WITH LANTHANUM

SYNTEZA, MIKROSTRUKTURA I STRUKTURA KRYSZALICZNA CERAMICZNEGO TYTANIANU BARU DOMIESZKOWANEGO LANTANEM

In the present study BaTiO_3 and $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ (0.1-0.4mol.% La) ceramic powders were synthesized by the conventional mixed oxide method (MOM). The characterization of the ceramic powders was carried out using a simultaneous thermal analysis (STA), with a combined DTA/TG/DTG system (Netzsch STA409). The results of thermal analysis allowed to determine the optimal temperature of synthesis. Microstructure was investigated by scanning electron microscopy (SEM), crystalline structure was studied by X-ray diffraction method (XRD). The EDS investigations showed that samples exhibited conservation of stoichiometry according to the chemical composition formula. The X-ray diffraction analysis confirmed formation of the desired crystalline structure both pure and La^{3+} -doped BaTiO_3 ceramics exhibiting a perovskite-type structure ABO_3 with tetragonal symmetry $P4$ mm.

Keywords: $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x/4}\text{O}_3$ ceramics, La^{3+} doping, microstructure, perovskites

W prezentowanej pracy przeprowadzono badania ceramiki BaTiO_3 i $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x/4}\text{O}_3$ (BLT) dla koncentracji x z przedziału $0,001 \leq x \leq 0,004$ (0,1-0,4mol.% La). Ceramikę BLT wytworzono z mieszaniny prostych tlenków La_2O_3 , TiO_2 i BaCO_3 (wszystkie o czystości 99,9+%, Aldrich Chemical Co.) Proszki ceramiczne otrzymano metodą konwencjonalną w stanie stałym (metodą MOM) i poddano badaniu mikrostruktury i struktury krystalicznej. Mieszaniny proszków poddano analizie termicznej. Wyniki analizy termicznej określiły optymalną temperaturę syntezy oraz procesy zachodzące podczas ogrzewania proszków. Następnie proszki formowano w dyski pod ciśnieniem 300MPa w matrycach ze stali nierdzewnej o średnicy 10 mm. Syntezę przeprowadzono w $T_S = 950^\circ\text{C}$ $t = 2$ godz. Ostatnim krokiem technologii było bezcisnieniowe spiekanie metodą swobodnego spiekania w $T = 1350^\circ\text{C}$ przez $t = 2$ godziny.

Morfologię otrzymanego materiału ceramicznego obserwowano metodą skaningowej mikroskopii elektronowej. Ceramikę BLT badano również pod względem składu chemicznego metodą EDS. Analizę strukturalną przeprowadzono metodą dyfrakcji rentgenowskiej. Badania mikrostruktury i struktury krystalicznej ceramiki przeprowadzono w temperaturze pokojowej. Badania EDS potwierdziły zachowanie stechiometrii otrzymanych próbek według wzoru chemicznego.

Rentgenowska analiza dyfrakcyjna potwierdziły wytworzenie pożądanej struktury krystalicznej zarówno czystej ceramiki BaTiO_3 jak i z domieszką La^{3+} . Otrzymana ceramika wykazuje strukturę typu perowskitu ABO_3 o symetrii tetragonalnej $P4$ mm. Stwierdzono, że wraz ze wzrostem stężenia La^{3+} w BaTiO_3 następuje zmniejszenie wielkości ziarn krystalicznych, zmniejszenie średniego wymiaru krystalitów, zmniejszenie objętości komórki elementarnej oraz wzrost obliczonej rentgenowskiej gęstości.

1. Introduction

Solid solutions of complex oxides crystallizing in the perovskite-type structure (ABO_3) represent an important class of materials. Electrical properties of these materials vary from those of insulators to superconductors as the function of their composition and structure. At room temperature, BaTiO_3 adopts a tetragonal perovskite type structure and is a ferroelectric with high permittivity. It transforms to the cubic, paraelectric state at the Curie temperature, T_C , of approximately to 130°C [1]. Undoped BaTiO_3 is electrically insulating, but oxygen deficiency can occur at high temperatures ($T > 350^\circ\text{C}$, in air) and/or in reducing atmospheres [2].

It is well known that La, Ce, Nd, Gd etc. donor-doped BaTiO_3 ceramics exhibit a positive temperature coefficient of resistivity effect (PTCR) that manifests it self as a sudden increase in resistivity around the Curie temperature (T_C) [3]. PTCR ceramics are used in a wide variety of applications such as an overcurrent protection, self-regulating heaters and temperature sensors [4].

When pure, this material is highly resistive at room temperature ($\rho > 10^{10}\Omega\text{cm}$), but its electrical resistivity can be dramatically lowered by some dopants, like rare earth elements [5].

Much lower room-temperature bulk resistivities of the order of $\rho = 10^3 \div 10^5\Omega\text{cm}$ can be obtained for sintered BaTiO_3

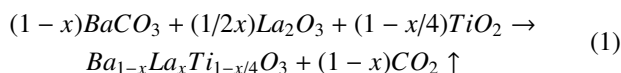
* UNIVERSITY OF SILESIA, DEPARTMENT OF MATERIALS SCIENCE, 2 SNIEZNA STR., 41-200 SOSNOWIEC, POLAND

ceramic with 0.1÷0.3 mol.% rare-earth dopants, such as La, Sm and Ce. This is attributed to the occupation of A sites by the La^{3+} (or other rare earth) ions in the perovskite lattice by replacing Ba^{2+} ions. Upon replacement of a Ba^{2+} ion by a La^{3+} ion, an extra positive charge results. Due to the requirement of electrical neutrality, a Ti^{4+} ion must trap an electron (e^{1-}) [6].

Goal of the present research was to fabricate undoped and La-doped BaTiO_3 ceramics, study the influence of La^{3+} doping ions on microstructure and crystalline structure.

2. Experimental

In the present study pure BaTiO_3 (BT) and lanthanum-doped $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x/4}\text{O}_3$ (BLT) compositions for x within the range $0.001 \leq x \leq 0.004$ (0.1-0.4mol.% La) were prepared by the conventional solid state, mixed-oxide method (MOM). Appropriate amounts of BaCO_3 , La_2O_3 and TiO_2 (all 99.9 + % purity, Aldrich Chemical Co.) were intimately mixed, with an agate mortar and pestle, until dry, to give the desired compositions. To reveal characteristic features of the synthesis of BT and BLT ceramics the stoichiometric mixture of powders corresponding to the chemical solid-phase reaction given below:



Pellets were prepared by pressing powders to 30 MPa in 10 mm diameter stainless-steel die. The synthesis was performed at $T_S = 950^\circ\text{C}$ for $t = 2\text{h}$. The final step was a pressureless sintering (free sintering method) at $T = 1350^\circ\text{C}$ for $t = 2\text{h}$. The technological process was described in details elsewhere [7]. The characterization of the ceramic powders was carried out using a simultaneous thermal analysis (STA), with a combined DTA/TG/DTG system (Netzsch STA409).

Microstructure was investigated by scanning electron microscopy (FESEM-HITACHI S-4700 and EDS-NORAN Vantage). The EDS investigations showed that samples exhibited conservation of stoichiometry according to the chemical composition formula. The crystal structure was studied by X-ray diffraction method at room temperature (diffractometer XRD, Philips PW 3710, $\text{CoK}_{\alpha 1}$ radiation, Θ - 2Θ method, data angle range $2\Theta = 10$ - 90° , scan step size $\Delta 2\Theta = 0.01$, scan step time $t = 8\text{s}$, $\lambda = 1.789007\text{\AA}$).

3. Results and discussion

To reveal characteristic features of synthesis of BT and BLT ceramics the stoichiometric of powders corresponding to the chemical solid-phase reaction (Eq. 1) was investigated by STA within the temperature range $T = 20$ - 1350°C . Fig. 1 shows the traces of DTA, TG and DTG recorded at heating rate $10\text{deg}/\text{min}$. As result of the thermogravimetric measurements the specific temperature ranges corresponding to different rates of the chemical reaction have been stated. The temperature of synthesis was chosen as $T_S = 950^\circ\text{C}$. Also the temperature at which the chemical reaction runs at maximal rate was determined $T > 1000^\circ\text{C}$ (i.e., minimum at DTG curve).

Thus on the base of results of the thermogravimetric measurements the temperature regimes for the technological process of BT ceramics fabrication have been determined.

All dried ceramics powders exhibited a total weight loss is around $\Delta m \approx 16\%$ for pure BaTiO_3 and doped BaTiO_3 . As result of the thermogravimetric measurements the specific temperature ranges corresponding to different rates of the chemical reaction have been stated.

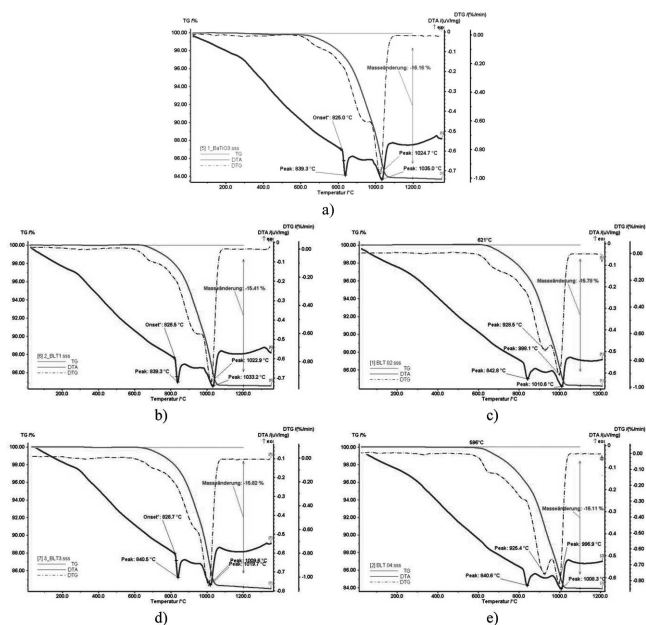
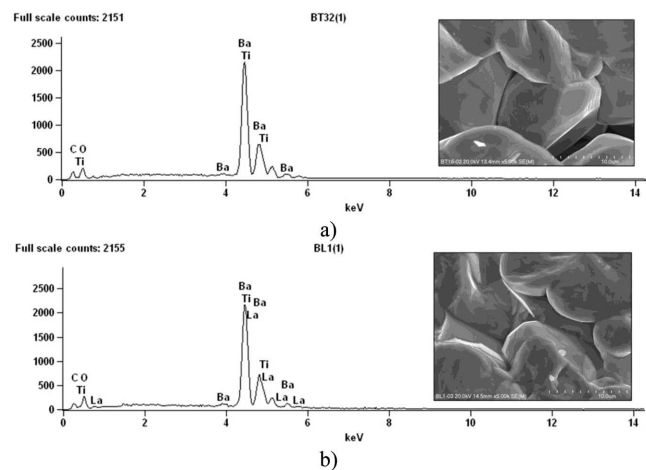


Fig. 1. Thermal analysis data of pure BaTiO_3 (a), BaTiO_3 +0.1 mol.% La (b), BaTiO_3 +0.2 mol.% La (c), BaTiO_3 +0.3 mol.% La (d) and BaTiO_3 +0.4 mol.% La (e)

EDS spectrum and SEM photographs of the microstructure fracture for pure BaTiO_3 and doped BaTiO_3 ceramic samples are given in Fig. 2. The insets in Fig. 2 show photographs of the microstructure of ceramics.

One can see that fabricated ceramic materials exhibit well-shaped grains that decrease with an increase in La-content. Theoretical content of elements (calculation for simple oxides) for BT and BLT ceramics were calculated. The small deviations from the theoretical composition of BT and BLT have occurred but they do not exceed a value of $\pm 5\%$ what is consistent with the resolution of the utilized method of investigation.



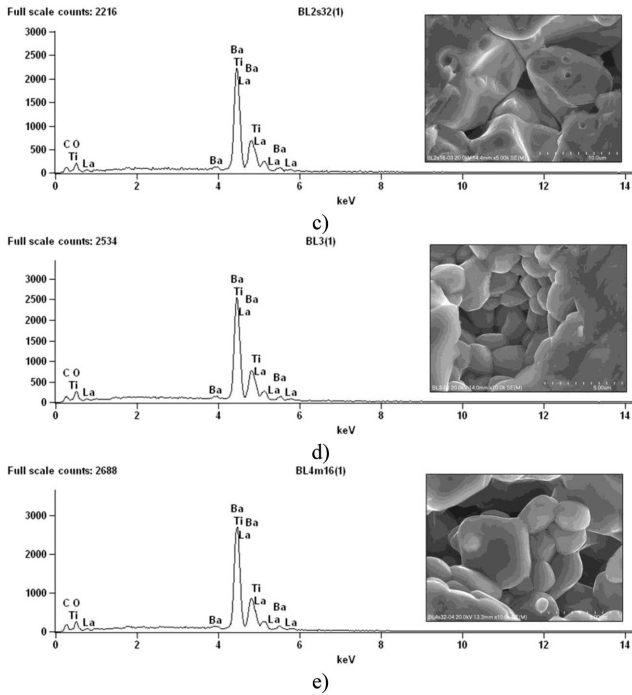


Fig. 2. EDS spectrum and SEM photographs of the microstructure fracture for pure BaTiO₃ (a), BaTiO₃+0.1 mol.% La (b), BaTiO₃+0.2 mol.% La (c), BaTiO₃+0.3 mol.% La (d) and BaTiO₃+0.4 mol.% La (e)

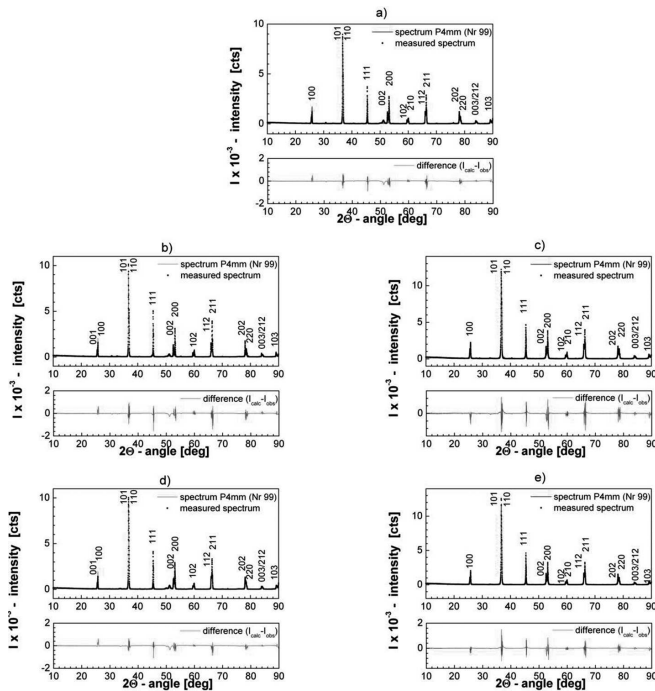


Fig. 3. X-ray diffraction patterns for pure BaTiO₃ (a), BaTiO₃+0.1 mol.% La (b), BaTiO₃+0.2 mol.% La (c), BaTiO₃+0.3 mol.% La (d) and BaTiO₃+0.4 mol.% La (e)

The X-ray diffraction analysis confirmed formation of the desired crystalline structure. A careful examination of the XRD reflection intensities further indicates that no preferred orientation could be found for any sample. The lattice parameters for BaTiO₃ and Ba_{1-x}La_xTi_{1-x/4}O₃ were calculated for tetragonal phase using the Rietveld refinement [8], embedded into the computer programme PowderCell 2.4. For fitting the diffraction profile the pseudoVoigt2 function was used and

the following *uvw* parameters. Although numerical criteria of goodness of fit (i.e. *R*-values) are very important, it is necessary to point out that they do not fully reflect the quality of fitting. Graphical criteria such as plots of the calculated and observed intensities as well as a plot of the difference between the calculated and observed intensities are also necessary. From the trace on the bottom of Fig. 3 one can see that there are no gross errors of fitting coming from bad scaling parameters, or incorrect crystalline structure used for simulation, or incorrect unit cell parameters.

The calculated unit cell parameter and X-ray diffraction the volume of the elementary cell for supposed tetragonal symmetry space group P4 mm are given in Table 1. The X-ray diffraction the volume of the elementary cell increased from $V = 64.36 \times 10^{-30} \text{ m}^3$ (pure BaTiO₃) to $V = 64.20 \times 10^{-30} \text{ m}^3$ (doped BaTiO₃+ 0.1, 0.2, 0.3 and 0.4 mol.% La).

TABLE 1
Parameters of X-ray analysis of pure BaTiO₃ and doped BaTiO₃

Ceramics	a_0 [nm]	c_0 [nm]	$V \cdot 10^{30}$ [m ³]	Density [kg/m ³]	Rietveld <i>R</i> -factors		
					R_p	R_{wp}	R_{exp}
Pure BaTiO ₃	0.3994	0.4030	64.36	6023	23.65	37.58	13.88
BaTiO ₃ with 0.1 mol.% La	0.3993	0.4034	64.31	6020	26.61	38.88	11.22
BaTiO ₃ with 0.2 mol.% La	0.3993	0.4031	64.23	6028	25.53	31.98	11.76
BaTiO ₃ with 0.3 mol.% La	0.3994	0.4027	64.23	6028	23.92	40.33	11.72
BaTiO ₃ with 0.4 mol.% La	0.3992	0.4020	64.20	6029	25.88	33.03	11.20

To calculate the mean crystallite size the approximation method was used, utilizing the full width at half maximum of the six diffraction lines fitted with Gaussian function and based on the Scherrer's equation:

$$D = K\lambda/(\beta \cos\Theta). \quad (2)$$

were: *D* – mean crystallite size; *K* – Scherrer's constant; λ – X-diffraction wavelength; β – FWHM.

The dependence of β^2 on $\sin^2\Theta$ given in Fig. 4 helps to determine contribution of the mean crystallite size in to FWHM.

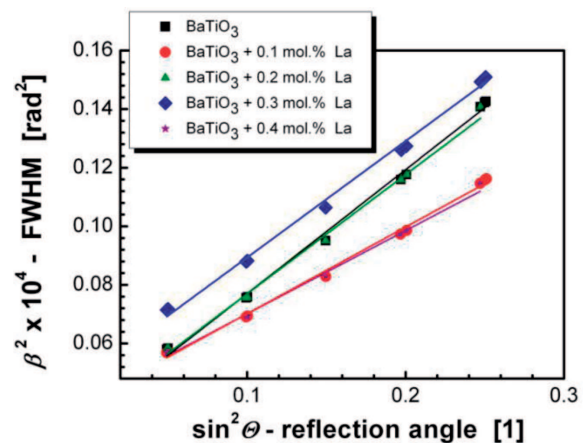


Fig. 4. FWHM vs. $\sin^2\theta$ for pure BaTiO₃, and doped BaTiO₃+ 0.1, 0.2, 0.3 and 0.4 mol.% La

Results of the calculations have shown that the mean crystallite size for pure BaTiO₃ ceramics is $D_1 = 40$ nm, whereas to 0.1 mol.% doped $D_2 = 36$ nm, for 0.2 mol.% doped $D_3 = 34$ nm, for 0.3 mol.% doped $D_4 = 33$ nm and for 0.4 mol.% doped $D_5 = 31$ nm.

4. Conclusion

In the present research both pure and La³⁺ – doped BaTiO₃ ceramics exhibiting a perovskite-type structure ABO₃ with tetragonal symmetry P4 mm (No. 99) were fabricated by MOM followed by 3-step sintering process. On the base of the thermogravimetric measurements the temperature regimes for the technological process of BT and BLT ceramics fabrication have been determined.

It was found that an increase in La³⁺ concentration causes: a reduction of crystalline grain size, a decrease in mean dimension of crystallites (D) and a decrease in volume of the elementary cell (V) and an increase in calculated (X -ray) density of BaTiO₃ ceramics.

Acknowledgements

The present research has been supported by Polish Ministry of Education and Science from the funds for science in 2010-2013 as a research project N N507 494338.

REFERENCES

- [1] K. Ćwikiel, E. Nogas-Ćwikiel, Dielectric and pyroelectric properties of the Ba_{0.3}Na_{0.7}Ti_{0.3}Nb_{0.7}O₃ ceramics obtained by sol-gel method, *Phase Transitions* **80**, 141-146 (2007).
- [2] Y. Xu, *Ferroelectric materials and their applications*, North Holland, New York, 1991.
- [3] B. Wodecka-Duś, D. Czekaj, Właściwości elektryczne modyfikowanej elektroceramiki na bazie tytanianu baru, *Ceramika/Ceramics*, **103**, 1, 241-246 (2008).
- [4] B.A. Boukamp, *Solid State Ionics* **169**, 65 (2004).
- [5] M.E.V. Costa, P.Q. Mantas, *J. Euro. Ceram. Soc.* **19**, 1077-1080 (1999).
- [6] H. Beltran, E. Cordoncillo, P. Escribano, D.C. Sinclair, A.R. West, *J. Am. Ceram. Soc.* **87**, 2132-2134 (2004).
- [7] B. Wodecka-Duś, D. Czekaj, Fabrication and dielectric properties of donor doped BaTiO₃ ceramics, *Archives of Metallurgy and Materials* **54**, 923-933 (2009).
- [8] R.A. Young, (Ed)., *The Rietveld Method*, Oxford University Press, 1995.