Study on the effect of Bi dopant on the structural and optical properties of BaTiO$_3$ nanoceramics synthesized via sol-gel method

M Tihtih$^1$, J F M Ibrahim$^1$, E Kurovics$^1$, M Abdelfattah$^1$

$^1$Institute of Ceramics and Polymer Engineering, University of Miskolc, Miskolc, Hungary
$^2$IGREX Engineering Service Ltd, Igrici, Hungary

E-mail: medtihtih@gmail.com, fememese@uni-miskolc.hu, jamalfadoul@gmail.com

Abstract. In this study the preparation of pure and Bismuth (Bi) doped barium titanate (BaTiO$_3$) nanoceramics by sol-gel process is reported. The structural and optical properties of the samples were investigated using X-ray diffraction (XRD) and UV-visible spectroscopy. XRD results show that the samples are crystallized in the pure perovskite structure when calcined at relatively low temperature ($800 \, ^\circ\mathrm{C}$) for 3 h, without the presence of secondary phases. Both Bi doping (1%, 2%) decrease the lattice parameters, tetragonality and the crystallite size. The decrease of their sizes can be explained by the replacement of large ionic radii of Ba$^{2+}$ (1.35 Å) ion by smaller ionic radii Bi$^{3+}$ (1.03 Å) ion. A close investigation of the results shows that BT is a tetragonal-phase ferroelectric. The band gap of the Bi-doped BaTiO$_3$ nanopowders is lower compared to that of pure BaTiO$_3$, as determined from the analysis of UV absorbance spectra.

1. Introduction

Lately, the research development in the area of technical ceramics has drawn great interest [1-27]. Perovskite type structured ceramic materials with high dielectric constant and electrical conductivities are considered as a promising material for applications in tunable devices such as ferroelectric phase shifters and electrochemical devices [28-29].

Barium titanate (BaTiO$_3$) is the most commonly utilized ferroelectric material and even after seventy-five years after its disclosure, it remained as the most essential multilayer dielectric ceramic material. Also, it is one of the most extensively studied lead-free ferroelectric materials due to its broad range of device applications for instance, capacitors, transducers, positive temperature coefficient (PTC) thermistors, ferroelectric non-volatile memories FRAM’s, detection of gaseous pollutants like CO and many more [30, 31]. Two major approaches are generally considered for the manufacturing of BaTiO$_3$ ceramics, traditional and advanced processing. Barium titanate is normally prepared by solid-state reaction method carried out at relatively high temperatures which yield a particles with different grain size distribution, some degree of porosity and multiple phases that occur due to impurity and inhomogeneity associated with the powder processing stage. The basic wet chemical techniques including hydrothermal, precipitation method, microemulsion approach and sol-gel process have been developed to provide several advantages [32]. Specially, the low-temperature sol-gel method gives an interesting capability for the preparation of high
purity, ultrafine and monodispersed powders through which electronic components with tailored and expected behaviours can be synthesised [33]. Moreover, the doping of barium titanate nanoceramics by introducing small amounts of trivalent ions (such as Bi$^{3+}$, La$^{3+}$, Y$^{3+}$, etc.) in the Ba-site is an interesting topic in the last few years because it has pronounced effect on structural, optical and electrical properties of BaTiO$_3$ owing to their good behaviour. Bismuth is also used as a donor dopant based on BaTiO$_3$ as elements to obtain semiconductor grains, Bi$^{3+}$ replaces barium ions in the lattice and Bi$^{5+}$ titanium ions [34]. To date, several works on the synthesis and characterization of Bi-doped BaTiO$_3$ nanoceramics have been reported. Sareecha et al [35] have investigated the effect of Bismuth doping influence on structural and electrical properties of Barium titanate nanopowders. Mahapatra et al [36] have reported the effect of Bi on the structural, optical and dielectric properties of BaTiO$_3$ prepared via microwave sintering properties in order to develop new MLCCs. Sreenu et al [37] have carried out the synthesis via sol-gel method and characterization of undoped and Bi-doped BaTiO$_3$ in the Ti-site. In this work synthesis of Bismuth doped barium titanate nanoceramics through the sol-gel method is reported. The samples were thoroughly characterized by X-ray Diffraction (XRD) and UV-visible spectroscopy, in order to study the crystal size, lattice parameter, lattice strain, and band gap energy. The aim of this study is to investigate the effect of Bi dopant on the structural and optical properties of BaTiO$_3$.

2. Experimental details

Different processing steps were followed for the synthesis of Bi-doped BaTiO$_3$ nanoceramics as shown in Figure 1.

![Figure 1. Flowchart for the preparation process of Bi-doped BaTiO$_3$ nanoceramics](image)

The pure and Bi-doped BaTiO$_3$ nanopowders were prepared by the sol-gel method using barium acetate trihydrate (Ba(CH$_3$CO$_2$)$_2$.3H$_2$O), bismuth acetate Bi(CH$_3$CO$_2$)$_2$ and titanium alkoxide Ti[OCH(CH$_3$)$_2$]$_4$ as precursors, lactic acid (CH$_3$CH(OH)CO$_2$H) as peptizing agent, acetic acid to dissolve, bismuth acetate and...
distilled water as solvent. The first step is to prepare a colloidal solution of TiO₂; the preparation of 250 ml of titanium sol requires 150 ml of distilled water, 11.92 ml of lactic acid and 94.95 ml of titanium alkoxide. The aqueous lactic acid solution is stirred at 80 °C for a few minutes. Then, the titanium alkoxide is added carefully and quickly to the mixture to avoid as much as possible hydrolysis of the alkoxide. The obtained mixture was stirred continuously at 70 °C for 24 hours. A transparent floor with adequate proportions has been obtained. Then 12.5g of barium and bismuth acetates were dissolved in distilled water separately, with a few drops of acetic acid. These solutions are mixed in stoichiometric proportions, according to the chemical formulation Ba₁₋ₓBixTiO₃ (x = 0, 0.01, 0.02) with continuous stirring for 30 min. Finally, the produced nanopowders, after grinding, were calcined in the air in a programmable oven at 800 °C for 3 h.

3. Results and discussion

3.1 Structural studies

The structure and crystallinity of the prepared samples were analyzed using X-ray diffraction [XPERT-PRO diffractometer with Cu-Kα radiation (λ = 1.540598 Å)]. Figure 2 illustrate the room temperature X-ray diffraction patterns of the as-prepared Ba₁₋ₓBixTiO₃ powders (x = 0, 1 and 2%) calcined at 800 °C for 3h. A.K. Nath et al [38] obtained BBixT samples, prepared by the conventional solid-state reaction, after calcination at 1050 °C for 4 h, but with the presence of the secondary phase Bi₂Ti₂O₇. As observed from Figure 2, it is clear that all BBixT powders crystallize in the perovskite phase without presence of secondary phases; this indicates that formation of pure perovskite ceramic powders is achieved. The X-ray analysis shows the presence of peaks of the planes (200) and (002) around 2θ = 45°, which are characteristic of the single tetragonal phase. In addition, the position of (101) peak in the Bi-doped BaTiO₃ nanoceramics slightly shifts to larger angle compared to the peak position in the pure BaTiO₃, which is indicative of incorporation and effect of Bi-doping on BT structure. Lattice parameters and unit cell volume are given in Table 1. The reduction of volume of the unit cell is due to the difference between ionic radii of Ba²⁺ (1.35Å) and Bi³⁺ (1.03 Å) [36] the occupation of Ba-sites by Bi³⁺ ions (Bi³⁺ is then surrounded by 12 oxygen atoms) gives rise to strains and consequently to a compression of the unit cell which manifests itself by a shift of X-ray diffraction peaks to higher angles, as observed on Figure 2 for BBixT samples.

![Figure 2. X-ray diffraction patterns of BBixT samples](image-url)
3.2 Crystallite size and strain

Variation of the crystallite size (D) was estimated according to the Debye Scherrer formula [39]:

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

(1)

Where \( \lambda \) denotes the X-ray wavelength, \( \theta \) is the Bragg diffraction angle, and \( \beta \) is the full width at half maximum (FWHM) of the XRD peak; \( k \) is a dimensionless shape factor, with a typical value of 0.9, D is the crystallite size.

The lattice strain (\( \varepsilon \)) of the BBixT samples was estimated using the following tangent formula [40]:

\[ \varepsilon = \frac{\beta}{4 \tan \theta} \]  

(2)

The information on structural properties of samples including, lattice parameters, volume of the unit cell, tetragonality c/a, crystallite size and lattice strain of the all samples obtained according to the XRD spectra of the preferential crystallographic (101) peak orientation are listed in Table 1. The calculated average crystallite size (D), lattice parameters, and the lattice strain were found to be decreased with increasing Bi contents. This can be explained by the fact that Bi has an ionic radius smaller than that of barium.

Table 1. Physical parameters of BBixT samples

| Sample   | a (Å)   | c (Å)   | c/a   | V (Å³)  | 2θ  (degree) | Crystallite size (nm) | Lattice strain | Band gap (eV) |
|----------|---------|---------|-------|---------|--------------|----------------------|---------------|--------------|
| BT       | 3.9917  | 4.0261  | 1.00861 | 64.15054| 31.4668      | 33.16                | 0.003968      | 3.219        |
| BBi1T    | 3.9915  | 4.0206  | 1.00729 | 64.05648| 31.50058     | 31.84                | 0.004063      | 2.984        |
| BBi2T    | 3.9916  | 4.0191  | 1.00688 | 64.03580| 31.54598     | 29.15                | 0.004144      | 2.7973       |

3.3 Optical analysis

Figure 3 depicts the UV absorbance spectrum of Bi-doped BT nanoceramics recorded at room temperature. The optical band gap energy (Eg) can be estimated by drawing the optical absorption (\( \alpha h\nu \)) versus incident photon energy (\( h\nu \)) (as shown in Figure 3), based on the following Tauc equation [41]:

\[ \alpha h\nu = A(h\nu - E_g)^n \]  

(3)

Where \( \alpha \) is the absorption coefficient of the material, \( A \) is an energy-independent constant, \( h\nu \) is photon energy; \( E_g \) is band gap energy; and \( n \) is a constant which determines the type of optical transition (\( n = 1/2 \), for direct allowed transition and \( n = 2 \), for indirect allowed transition). The optical band gap energy decrease with increasing Bi contents. This may be attributed to the change of the lattice constants due to creation of A-site vacancies and distortions in the \([\text{TiO}_6]\) clusters [36], these distortions in the \([\text{TiO}_6]\) increase with increasing the doping elements which create localized electronic levels in the band gap of the samples, hence influencing on the values of the band gap, as seen in Table 1. Based on the comparison of the growth of the crystallite size and the \( E_g \) of the prepared samples as demonstrated in figure 4, the characteristics of these two parameters have shown large similarity which reveals that the defects stimulated by Bi can highly influence all the physical behaviours of nanoceramics.
Figure 3. Plots of \((ahv)^2\) versus \(h\nu\) spectra of Ba\(_{1-x}\)Bi\(_x\)TiO\(_3\) (\(x = 0, 0.01\) and 0.02) nanocermics

Figure 4. Comparison of the energy band gap and crystallite size behaviours of BBi\(_x\)T (\(x = 0, 1,\) and 2\%) samples

4. Conclusion
In conclusion, this work presents the elaboration and characterization of pure and Bi-doped BaTiO\(_3\) nanocermics. Samples were synthesized using sol-gel method in quite low temperature. Structural and optical properties have been investigated, the average crystallite size was calculated using the Debye Scherer formula. The XRD patterns of Bi-doped BaTiO\(_3\) show that the samples were crystallized into tetragonal phase with a perovskite structure at \(x = 0.01, 0.02\) %. The modification in the structural properties after doping indicates that Bi has successfully doped into BaTiO\(_3\) lattice. The optical band gap was estimated using the UV-Vis spectroscopy technique. The results obtained show decreasing in the band gap
after the doping with Bi (from 3.219 to 2.7973 eV), Bi (1 and 2%)-doped BaTiO$_3$ samples can be used in many optoelectronic applications shown better properties.

Acknowledgement
Thanks to the University of Miskolc (Hungary), University Sidi Mohamed Ben Abdellah USMBA (Morocco) to support this work.

References
[1] S Kulkov 2013 IOP Conf. Ser.: Mater. Sci. Eng. 47 012042 https://doi.org/10.1088/1757-899X/47/1/012042
[2] M Tihtih et al 2019 Épitoanyag-Journal of Silicate Based & Composite Materials, 71(6) 190-193 https://doi.org/10.14382/epitoanyag-jsbcm.2019.33
[3] A Buyakov et al 2018 Épitoanyag – Journal of Silicate Based and Composite Materials, 70 (1) 27–31. https://doi.org/10.14382/epitoanyag-jsbcm.2018.6
[4] M Abdelfattah et al 2019 MultiScience - XXXIII. microCAD International Multidisciplinary Scientific Conference, University of Miskolc ISBN 978-963-358-177-3 https://doi.org/10.26649/musci.2019.080
[5] M Abdelfattah et al 2019 XIIIth International Conference, Jahodná, 141-146 ISBN: 978-80-553-3314-4.
[6] J. F. M Ibrahim et al 2017. Advanced Ceramics Progress, 3 (4) 1-5.
[7] J.F.M. Ibrahim 2015. Enhancement of structural and magnetic properties of eu and fe doped gdmon3 and cr doped homno3 multiferroic ceramics.
[8] S Baba et al 2018 Épitoanyag- JSBCM 70 (6). https://doi.org/10.14382/epitoanyag-jsbcm.2018.34
[9] J. F. M Ibrahim et al 2019 MultiScience - XXXIII. microCAD International Multidisciplinary Scientific Conference, University of Miskolc, 23-24 May, ISBN 978-963-358-177-3. https://doi.org/10.26649/musci.2019.076
[10] T Kimura et al 2013 IOP Conf. Ser.: Mater. Sci. Eng. 47 012018 https://doi.org/10.1088/1757-899X/47/1/012018
[11] E Kurovics et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 175 012013 https://doi.org/10.1088/1757-899X/175/1/012013
[12] L A Gömze et al 2013 IOP Conf. Ser.: Mater. Sci. Eng.47 012023 https://doi.org/10.1088/1757-899X/47/1/012023
[13] S Kulkov et al 2015 J. Phys.: Conf. Ser. 602 012019. https://doi.org/10.1088/1742-6596/602/1/012019
[14] L A Gömze et al 2013 IOP Conf. Ser.: Mater. Sci. Eng. 47 012030 https://doi.org/10.1088/1757-899X/47/1/012030
[15] J F M Ibrahim et al 2019 Épitoanyag–JSBCM 71 (4) 120 https://doi.org/10.14382/epitoanyag-jsbcm.2019.21
[16] O B Kotova et al 2019 Épitoanyag–JSBCM 71 (4) 125 https://doi.org/10.14382/epitoanyag-jsbcm.2019.22
[17] E Kurovics et al 2019 Épitoanyag–JSBCM 71 (4) 114 https://doi.org/10.14382/epitoanyag-jsbcm.2019.20
[18] T Shchemelinina et al 2019 Épitoanyag–JSBCM 71 (4) 131 https://doi.org/10.14382/epitoanyag-jsbcm.2019.23
[19] J. F. M. Ibrahim et al 2019 Preparation of Ceramic Materials Proceedings of the XIIIth International Conference, Jahodná, 25th – 27th June, ISBN: 978-80-553-3314-4
[20] L A Gömze and L N Gömze 2013 IOP Conf. Ser.: Mater. Sci. Eng. 47 012033 https://doi.org/10.1088/1757-899X/47/1/012033
[21] László A. Gömze et al 2019 IOP Conf. Ser.: Mater. Sci. Eng. 613 012005
https://doi.org/10.1088/1757-899X/613/1/012005

[22] E Kurovics et al 2019 IOP Conf. Ser.: Mater. Sci. Eng. 613 012025
https://doi.org/10.1088/1757-899X/613/1/012025

[23] L A Gömze and L N Gömze 2008 Építőanyag–JSBCM 60 (4) 102
http://dx.doi.org/10.14382/epitoanyag-jsbcm.2008.16

[24] A Hamza et al 2019 IOP Conf. Ser.: Mater. Sci. Eng. 613 012051
https://doi.org/10.1088/1757-899X/613/1/012051

[25] L A Gömze and L N Gömze 2010 Építőanyag–JSBCM 62 (4) 98
http://dx.doi.org/10.14382/epitoanyag-jsbcm.2010.18

[26] L A Gömze and L N Gömze 2011 IOP Conf. Ser.: Mater. Sci. Eng. 18 082001
http://dx.doi.org/10.1088/1757-899X/18/8/082001

[27] L A Gömze and L N Gömze 2017 IOP Conf. Ser.: Mater. Sci. Eng. 175 012001
http://dx.doi.org/10.1088/1757-899X/175/1/012001

[28] S. Sheng and C.K. Ong 2010 Microelectronic Engineering 87 (10) 1932.
https://doi.org/10.1016/j.mee.2009.11.126

[29] A. Ecija et al 2013 Solid State Ionics 235 14. https://doi.org/10.1016/j.ssi.2013.01.010

[30] D. Sette at al 2015. Thin Solid Films 589 111. https://doi.org/10.1016/j.tsf.2015.04.087

[31] G. Catalan and J.F Scott 2009 Advanced materials 21 (24) 2463
https://doi.org/10.1002/adma.200802849

[32] M.R Mohammadi and DJ Fray 2011 Particuology 9 (3) 235
https://doi.org/10.1016/j.partic.2010.08.012

[33] V. Vinohini at al 2006 Ceramics international 32 (2) 99
https://doi.org/10.1016/j.ceramint.2004.12.012

[34] O. Steigelmann and P. Goertz 2004 Key Engineering Materials 264 1161
https://doi.org/10.4028/www.scientific.net/KEM.264-268.1161

[35] N. Sareecha at al 2018 Physica B: Condensed Matter 530 283
https://doi.org/10.1016/j.physb.2017.11.069

[36] A. Mahapatra et al 2015 JOM 67 (8) 1896. https://doi.org/10.1007/s11837-014-1266-7

[37] K. Sreenu et al 2014 Science, Technology and Arts Research Journal 3 (1) 39
http://dx.doi.org/10.4314/star.v3i1.7

[38] A.K. Nath and N. Medhi 2012 Materials Letters 73 75 https://doi.org/10.1016/j.matlet.2011.12.113

[39] U. Holzwarth and N. Gibson 2011 Nature nanotechnology 6 (9) 534
https://doi.org/10.1038/nnano.2011.145

[40] G.K. Williamson and W.H. Hall 1953 Acta metallurgica 1 (1) 22
https://doi.org/10.1016/0001-6160(53)90006-6

[41] D.L. Wood and J.S. Tauc 1972 Physical Review B 5 (8) 3144 https://doi.org/10.1103/PhysRevB.5.3144