Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 8, Issue, 01, pp.25281-25284, January, 2016

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

CHARACTERIZATION OF ZIRCONIUM DOPING BARIUM TITANATE POWDERS BY RAMAN SPECTROSCOPY

[1,2*]Abdelhalim Elbasset, [1]Taj-dine Lamcharfi, [2]Farid Abdi, [1]Salaheddine Sayouri , [2]Lamiae Mrharrab and [3]Zouhairi Mohamed

[1]LSSC Department of Electrical Engineering, Faculty of Sciences and Techniques, University Sidi Mohmmed ben Abdelah, Fes, Morocco
[2]LPTA, Physics Department, Faculty of Science University Sidi Mohmmed ben Abdelah, Fes, Morocco
[3]Laboratory of Chemistry of Condensed Matter FST, B. P. 2202, Fes Morocco

ARTICLE INFO

Article History:
Received 24th October, 2015
Received in revised form
15th November, 2015
Accepted 09th December, 2015
Published online 31st January, 2016

Key words:
Raman Spectroscopy,
The adjustment,
Full width at half maximum (FWHM),
Frequency.

ABSTRACT

This product for bute to present zirconium effect on Raman modes and structure of Barium Titanate Powders. The adjustment of raman indque modes of $BaTiO_3$ Doping by 15% zirconium causes significant broadening of the modes E $(LO_4)/A_1(L0_3)$ and $E(TO_3+ LO_2)/B_1$ (50% higher) characteristic of quadratic phase $BaTiO_3$. The results obtained show that when zirconium rate increases, the lattice parameters increase along the axes (a) and (c) against the quadracité decrease and change of the lattice parameter following the axis (a) is more important than that the axis (c).

Copyright © 2016 Abdelhalim Elbasset et al. *This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.*

Citation: **Abdelhalim Elbasset, Taj-dine Lamcharfi, Farid Abdi, Salaheddine Sayouri , Lamiae Mrharrab and Zouhairi Mohamed, 2016.** "Characterization of zirconium doping barium titanate powders by raman spectroscopy", *International Journal of Current Research,* 8, (01), 25281-25284.

INTRODUCTION

Barium titanate (BT) is certainly the most studied ferroelectric material compounds. These dielectric properties found many technical applications in various fields of technology. Furthermore, $BaTiO_3$ is a chemically and mechanically very stable compound which has ferroelectric properties in a temperature range including room temperature (Megaw *et al*., 1947). It is relatively easy to develop and can be prepared as single crystals or ceramics. Because of its less complicated structure than that of many other ferroelectric materials; it also provides a better approach to the phenomena. These different characteristics have made him "the equivalent iron" of ferroelectric materials and so far the number of jobs that are done in the world on the influence of various parameters (especially doping) on physical properties chemical barium titanate is impressive. In particular, when replacing the B-site of the structure, it may in some cases lead to disordered dipolar compounds having advantageous physical properties with regard to the original multiple industrial applications. In effect the structural properties of BTZx depending on the Zr content was reported by several authors (Hennings *et al*., 1982, Kuang *et al*., 2009, Julphunthonga *et al*., 2013, Reddy *et al*., 2007). For example Hennings *et al* (Hennings *et al*., 1982) show that these crystallize in the ceramic tetragonal phase up to 25% zirconium and in the cubic phase in the range of x = 0.25 to 1 and Kuang *et al* (Kuang *et al*., 2009) That show the structure of the system is BZxT Undergoing a transformation from tetragonal (for BT) to orthorhombic (for $BZ_{0.12}T$) at room temperature, one hand Phongthorn l'autre *et al* (Julphunthonga *et al* ., 2013) aussi indicate indication, the crystal structure of rhombohedral to BZxT Was Transformed , tetragonal and cubic phase with respectivement Increasing zirconium happy. However, the effect of the rate of the dopant on the mid-height width and the position of the Raman modes BT was not reported. In this study, the structural properties and the evolution of the Raman modes of barium titanate according to zirconium ratio was taken.

Corresponding author: Abdelhalim Elbasset,
LSSC Department of Electrical Engineering, Faculty of Sciences and

Experimental procedure

The samples BTZx were prepared using barium acetate ($Ba(CH_3CO_2)_2$; $3H_2O$), zirconium acetate (Zr(CH3CO2)4; xH_2O), and and titanium alcoxide. The modification was based on the substitution of Z^{4+} in sublattice B (Ti^{4+}). The process of the preparation of BTZx is detailed in another works (Elbasset *et al*., 2015). Phase identification of the samples was performed using X-ray diffraction (Cu K ray, λ = 1.5418 Å) and Raman spectrum.

RESULTS AND DISCUSSION

The Figure.1 shows the XRD spectra of the powders BTZx (x = 0, 0.025, 0.05, 0.075, 0.01, 0.125 and 0.15), calcined at 900°C for 4 hours. It shows the crystallization all of the powders in the perovskite phase with the presence of secondary microphase. Increasing the doping level causes the displacement of the peak position (220) towards lower angles (Figure 1.b), due to the fact that the ionic radii of Zr^{4+} (0.72 Å) is higher than Ti^{4+} (0.605 Å), therefore, the substitution of Ti^{4+} by Zr^{4+} increase the ceramic lattice parameter. To highlight the influence of zirconium on the structural state of $BaTiO_3$, we calculated lattice parameters a and c of BTZx, by the use of CMPR program. The evolution of the parameters a and c as well as the c/a ratio (quadracité) and their difference for tenure Zr studied, is shown in tableau.1 and shown in Figure 2. The results show that when the zirconium rate increases, the lattice parameters increase along the axes (a) and (c) against the quadracité decrease. For x <5% there is a slight variation depending on the parameter but from 7.5% there is a change in linearity (Fig .2). It is also noted that the change of the lattice parameter following the axis (a) is greater than that of the axis (c) (Fig .3). In fact the rate of change of these parameters respectively (a and c) between x = 0 and x = 15% of zirconium, calculated by equation (1) is 3.86 10^{-1} 8.41 10^{-3}.

Rate of change = ($\Delta g/g$) *100=(g_2-g_1/ g_2) *100 (1)

or

g_1: The lattice parameter value for x = 0
g_2: The lattice parameter value for x = 0

As regards the evolution of the lattice parameter (a) of the BTZx powder with x up to 15%, the same trend was observed by Jong-Yoon Ha *et al* (Ha *et al*., 2007) in the case of $(BA_{0.6}Sr_{0.4})$ $(Ti_{1-x}Zr_x)$ O_3 $(0.05 \leq x \leq 0.3)$. On the other hand it is observed that the higher the zirconium rate increases over the tetragonality of phase decreases and is accompanied by the approximation of the lattice parameters a and c, and especially from 7.5%. This Will Lead to Reduced internal stress due to the formation of 90 deg ferroelectric domains. Calculating the volume from the cell parameters (Table 1), shows an increase of cell volume with the increase in the zirconium fraction (from 64.719 to 65,227$Å^3$). Referring to the Vegard's law (Fournet, G., 1953) which states that in solid substitution solutions, the network parameter varies with the atomic composition, it suggests that the formed main phase would probably be a solid solution in which zirconium atoms occupy certain positions in the titanium crystal lattice of $BaTiO_3$. This increase in volume is due to the size effect of the substituent atom. Indeed the ionic radius of zirconium (0.74Å) being greater than that of titanium (0.61 Å). This results in a slight distortion of the mesh. This type of variation is typical to that observed by some authors in $CaTi_{1-2x}Fe_xNb_xO_3$ compounds (Koopmans *et al*., 1983). The Raman spectrum in dependence of the composition of solid-solution $BaTi_{1-x}Zr_xO_3$, is shown in Fig .3 for a wide range of frequency 100-1000 cm^{-1} and carried out at room temperature. On the Raman spectrum of pure barium titanate, we observe

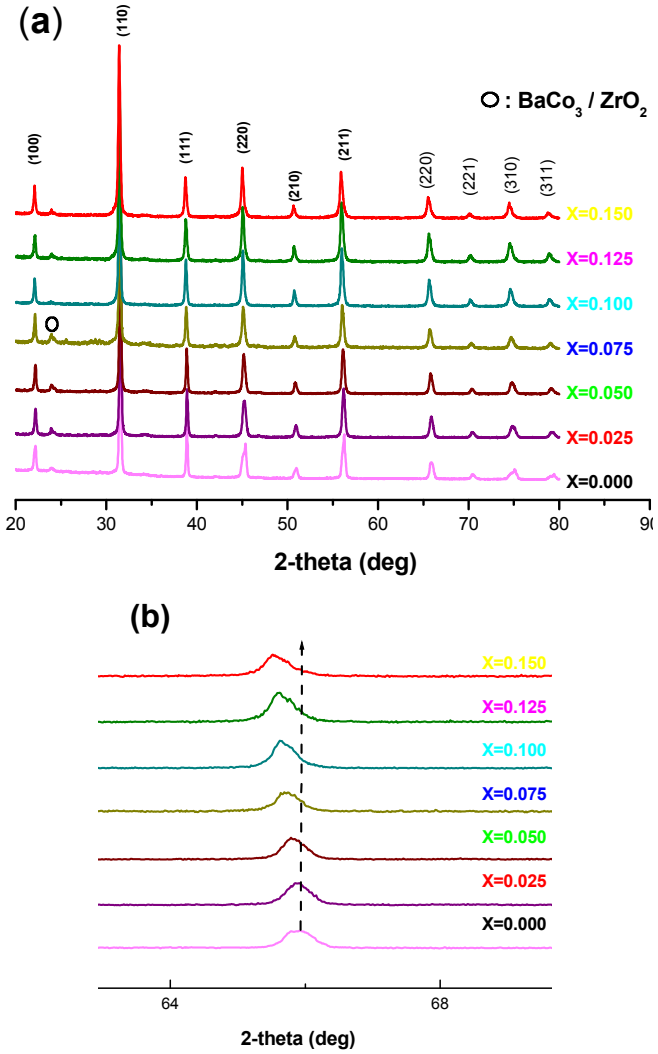

Fig. 1. (a) X-ray diffraction patterns of samples calcined at 900°C, (b) 110 the insets show the reflection 2θ between 64 and 68°.

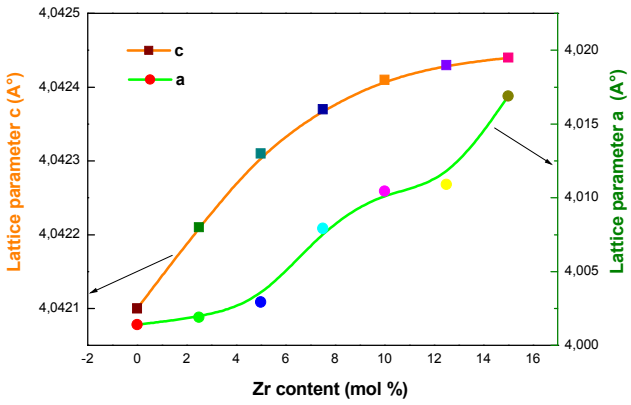

Fig. 2. Variation of the lattice parameters of BTZx.

certain active modes of phonons. Indeed, there is the existence of a narrow band 305cm^{-1} associated with modes B_1 and E(TO_3+LO_2) which are attributed to the tetragonal phase and a broad and asymmetric band at 520 cm^{-1} associated with modes $A_1(TO_3)$ and E(TO_4). Finally, it is another broad band (low intensity) to 720 cm^{-1} associated with A_1 modes (LO_3) and E(LO_4) characteristic of the presence of quadratic $BaTiO_3$ phase, which is in agreement with the results of X-ray. On the other hand we note the presence of three small peaks located respectively at 200cm^{-1}, 230cm^{-1} and 285cm^{-1} associated with modes A (TO_1), A (LO_1) and A (TO_2), which are part of Raman spectrum pure BT. For the doped barium titanate to 2.5% zirconium (Fig .3), it is noted that the two peaks at 230 and 285cm^{-1} in the barium titanate ($BaTiO_3$), are transformed into a single broad band between 210 and 290 cm^{-1} and $BTZ_{2.5}$ mode A_1(TO) moves to lower frequencies. However, the increase rate of the zirconium causes the total distribution of these three modes in one broader fashion and significant decrease in the intensity of the latter. This is a clear indication that the addition of zirconium causes the disorder in the $BaTiO_3$ structure. On the other hand there is much the decrease in intensity of E manual (TO_3 + LO_2) / B_1 and the widening of the band E (LO_4)/A_1 (LO_3).

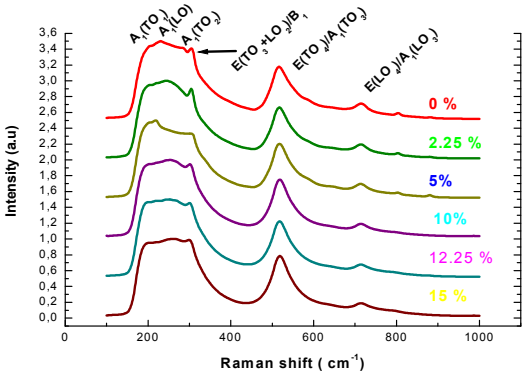

Fig. 3. Raman spectra for BTZx powders for different Zr concentration calcined at 900 °C for 4h

These are the consequence of the presence of different types of cations and anions, namely Ba^{2+}, Zr^{4+}, Ti^{4+}, O^{2-}, and confirmed well the disordered nature of the phase, indicating that the phase is pseudo-cubic . These results are consistent with those found on the barium titanate doped lanthanum (Liu, Y., 2009). It is possible that, in the case of pure $BaTiO_3$, BaO and TiO bonds characteristic of the tetragonal structure oscillate with different frequencies and, therefore, they display two different absorption bands A_1(TO), A_1(LO). The addition of the dopant appears to couple these two links, this resulting in the appearance of a single wide band which, in our case, is between 190 and 290 cm^{-1}.

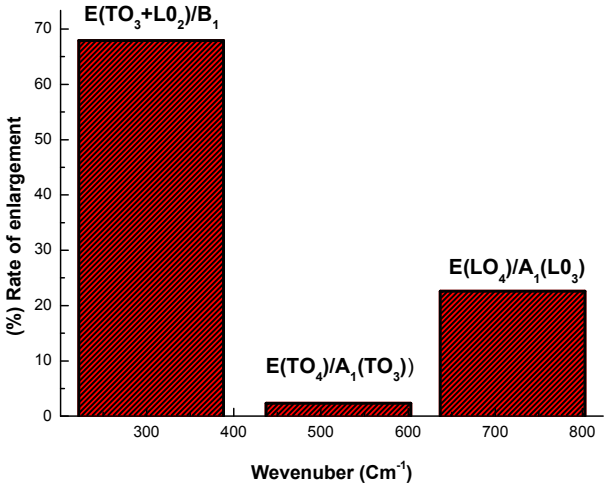

Fig. 4. The enlargement rate of the modes E(LO_4) / A_1 ($L0_3$), E (TO_3 + LO_2) / B_1 and E (TO_4) / A_1 (TO_3) of BTZx

To better exploit the Raman spectra of BTZx, we have adjusted to determine the settings for each mode are: mid-height width FWHM (full width at half maximum) and the center (frequency). On the results after the adjustment by cushioning response of an oscillator function that satisfies the Boltzmann statistics (~ 1-exp(-x)/KT), the results obtained (tableau. II) shows the positions of E modes (TO_3+LO_2)/B_1 and

Table 1. Result of lattice parameter, c/a ratio, volume as a function of Zr concentration for BTZx powders

Content of Zr (x%)	Lattice parametres		c/a ratio	Volume(Å^3)
	c (Å)	a (Å)		
0	4,04210	4,0014	1,0102	64,7189
2.5	4,04221	4,0019	1,0101	64,7371
5	4,04231	4,0029	1,0098	64,7718
7.5	4,04237	4,0079	1,0086	64,9343
10	4,04241	4,0105	1,0080	65,0170
12.5	4,04243	4,0109	1,0079	65,0322
15	4,04244	4,0169	1,0064	65,2267

Table 2. The Raman shift and half-value width of the modes as a function of Zr concentration change for BTZx powders.

Content of Zr (x%)	Raman shift			Half-value width (FWH)		
	E(TO+LO)/B_1	A_1(TO)/E(TO)	A_1(LO)/E(LO)	E(TO+LO)/B_1	A_1(TO)/E(TO)	A_1(LO)/E(LO
0	306,9886	513,8524	715,7409	9,6268	41,2150	41,8680
2.5	306,6989	514,1866	715,9784	10,7161	41,6420	43,9948
5	306,6358	514,349	716,2296	14,0337	41,9376	45,9999
7.5	303,5504	514,6675	716,8976	14,1084	42,0078	48,4335
10	302,2415	514,9975	716,9976	22,1084	42,1268	50,8335
15	301,7946	515,332	715,7409	29,9951	42,1922	54,0753

$E(LO_4)/A_1(L0_3)$ move toward the high frequencies with increasing zirconium rates against the E mode $(TO_3 + LO_2)/B_1$ moves toward the low frequencies that which is in agreement with the effect of strontium on the $BaTiO_3$ vibration modes (Kuo *et al*., 2001, Zhang *et al*., 2009 and Xia *et al*., 2012). However the change of peak positions (tableau.II) is accompanied by an increase in the FWHM for all studied modes (tableau.II) which confirms the incorporation and zirconium effect on the barium titanate structure . However it is of interest to note that the rate of enlargement mode E (LO_4) / A_1 (LO_3) and E $(TO_3+LO_2)/B_1$ is very important 22.07% and 67.91%, respectively (Fig. 4) which shows the gradual distortion of quadratic mesh and its evolution to the pseudo-cubic phase. This is in good agreement with several studies (Frey *et al*., 1996; Suzuki *et al*., 2006 and Cho *et al*., 1998). This work shows that these two bands are specific modes to the tetragonal phase of $BaTiO_3$ as they disappear above the Curie temperature (Tc) when the structure is cubic. In addition the small of enlargement (2.32%) mode $E(TO_4)/A_1(TO_3)$ (Fig. 4) may be connected to the relative increase in lattice parameter c.

Conclusion

The structural analysis results found by XRD and Raman spectroscopy showed that the effect of doping with zirconium, is to change the structure of the tetragonal phase to the pseudo cubic phase by the large increase in lattice parameter a. Therefore, increasing Zr promotes the increase of the symmetry. The adjustment of Raman spectra, helps provide additional information about the center and mid-height width FWHM of each peak. The doping of $BaTiO_3$ by 15% zirconium causes significant broadening of the modes E (LO_4) / A1 $(L0_3)$ (above 25%) and E $(TO_3 + LO_2)$ / B1 (above 50%) characteristic of the tetragonal phase $BaTiO_3$.

REFERENCES

Cho, W.S. and Hamada, E. 1998. *J. Alloys Compd*., 266:118

Elbasset, A., Abdi, F., Lamcharfi, T., Sayouri, S., Abarkan, M., Echatoui N. S. and Aillerie, M. 2015. *Indian Journal of Science and Technology*. 8(13), 56574

Fournet, G. 1953. le journal de physique et le radium. 14:374

Frey, M.H. and Payne, D.A. 1996. Phys. Rev. B. 54:3158

Ha, J.Y., Choi, J.W., Kang, C.Y., Kim, J.S., Yoon, S.J., Choi, D.J. Kim, H. J. 2007. *Journal of the European Ceramic Society*. 27:2747

Hennings, D., Schnell, A. and Simon, G. 1982. *J. Am. Ceram. Soc*., 65, No.11:539

Julphunthonga P., Chootina, S., Bongkarn, T. 2013. *Ceramics International*. 39. S415

Koopmans, H.J.A., Van G.M.H. de Velde, P. 1983. *J. Acta Crystallographica*. C 39, 1325

Kuang, S.J., Tang, X.G., Li, L.Y., Jiang Y.P. and Liu, Q.X. 2009. *Scripta Materialia*. 61:68

Kuo, S.Y., Liao, W.Y. and Hsieh, W.F. 2001. Physical Review B 64. 224103

Liu, Y., Feng, Y., Wu, X. and Han, X. 2009. *Journal of Alloys and Compounds*. 472:441

Megaw, H. D. 1947. Proc. Roy. Soc., 189: 261

Reddy, S. B., Raob, K. P. and Ramachandra Raoa, M.S. 2007. Scripta Materialia. 57:591

Suzuki, K. Kijima, K. 2006. *J. Alloys Compd*., 419, 234

Xia , W., Xu, Z., Wen , F. and Zhang, Z. 2012. *Ceramics International*, 38:1071

Zhang, J., Zhai, J., Chou, X., Shao, J., Lu, X. and Yao, X. 2009. Acta Materialia. 57:4491

****