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Effect of Mg on the Dielectric Properties of BaTiO3 Ceramic Materials Produced by Sol-Gel Process: (Ba1-xMgxTiO3)

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Effect of Mg on the dielectric properties of $BaTiO_3$ ceramic materials produced by sol-gel process: ($Ba_{1-x}Mg_xTiO_3$)

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Abstract

In this work the effect of doping with magnesium on the structural and physical properties of $BaTiO_3$ were studied. The ceramic materials of composition $Ba_{1-x}Mg_xTiO_3$ were prepared by the sol-gel process at low sintering temperature (700°C). In our preparation, $Ba_{1-x}Mg_xTiO_3$ were synthesized using magnesium acetate $Mg(CH_3COO)_2,3H_2O$, titanium alkoxide $Ti[OCH(CH_3)_2]_4$ and Barium acetate ($Ba(CH_3COO)_2$. Analysis of the various RX spectra obtained shows the appearance of three distinct domains. The first domain ranges from x=0 to 0.15, the second domain ranges from x=0.2 to 0.8 and the last domain for $x \geq 0.9$. The analysis of the Raman spectra of $BaMg_xTiO_3$ compounds shows the presence of three domains confirming the results obtained by XRD. The difference of the rays and the atomic numbers between Ba and Mg, causes the progressive distortion of the quadratic mesh to the pseudo cubic phase. Dielectric measurements (ε_r) were performed using an impedance analyzer HP 4284A in the frequency range from 1kHz to 1.8MHz depending on the temperature, ranging from ambient up to 200 °C, with a heating rate of 5°C / min. When the level of the magnesium inserted increases, the peaks of the transition from the ferroelectric phase to the para-electric phase become more and more spread out. It is also observed that the value of Tm remains independent of the frequency.

Keywords: Ceramic, sol-gel, Dielectric properties, Doping, BMxT.

1. Introduction

Perovskite-type ferroelectric materials are characterized by a very high dependence of some of their properties both with the electric field, the mechanical and thermal stresses applied and also with the procedure for their production. $BaTiO_3$ has been extensively used in the electronics industry due to its high dielectric constant and low loss characteristics [1–5].

Barium titanate has been emerged as a new material, which typically undergo a marked relaxation in dielectrics properties and induced to a decrease in relative permittivity by frequency, with a resonance peak in the dielectric loss at a narrow frequency band. $BaTiO_3$ has been attracting attention due to its particular multilayer capacitors, optical devices, thermistors and electromechanical properties [6].

$BaTiO_3$ can also exist in the orthorhombic phase at a temperature of 0°C, in the rhombohedral phase below -90°C, $BaTiO_3$ exists in the hexagonal phase above 1460°C. Although the primitive cube is the idealized structure, the differences in radius between cations A and B can modify the structure at several different so-called distortions, whose inclination is most

frequent. With the inclination of perovskite, the octahedron BO6 twists. Along one or more axes to accommodate the difference. The ferroelectric properties of ABO_3 type ceramic perovskite (here barium titanate) can be effectively controlled by doping using different doping elements [7-9].

Several synthesis methods have been used to prepare BT powders including nonconventional ones such as, oxalate, hydrothermal synthesis, citrates and polymeric precursors method, mainly based on the Pechini-type process and the sol-gel method [10-11].

The sol-gel method offers numerous advantages such as an excellent control of the stoichiometry, a good homogeneity of the powders and low processing temperature [12].

2. Experimental Procedure

The synthesis of various compounds of Barium titanate, doped with magnesium $Ba_{1-x}Mg_xTiO_3$ (BMxT) corresponding to substitutions the Mg^{2+} by Ba^{2+} was performed by sol-gel method. The $Ba_{1-x}Mg_xTiO_3$ materials are prepared from solutions of magnesium acetate, barium acetate and titanium sol, mixed in stoichiometric proportions. The BMxT solutions obtained are dried in an oven at 80 °C for 72 hours leading to the formation of a gel. The latter is dried, crushed and then calcined at 1000 °C for 4 hours. Phase identification of the samples was performed using X-ray diffraction (Cu K ray, λ = 1.5418 Å), scanning electron microscopy and Dielectric spectrum.

3. Materials characterization and analyses

3.1. X-ray diffraction (XRD) analysis

The XRD analysis (Fig. 1) revealed that BMxT ceramic samples for $0 \leq x \leq 1$ sintered at 1000° C for 4 hours, shows the appearance of three distinct domains. The first domain ranges from x=0 to 0.15, the second domain ranges from x=0.2 to 0.8 and the last domain for $x \geq 0.9$ [13]

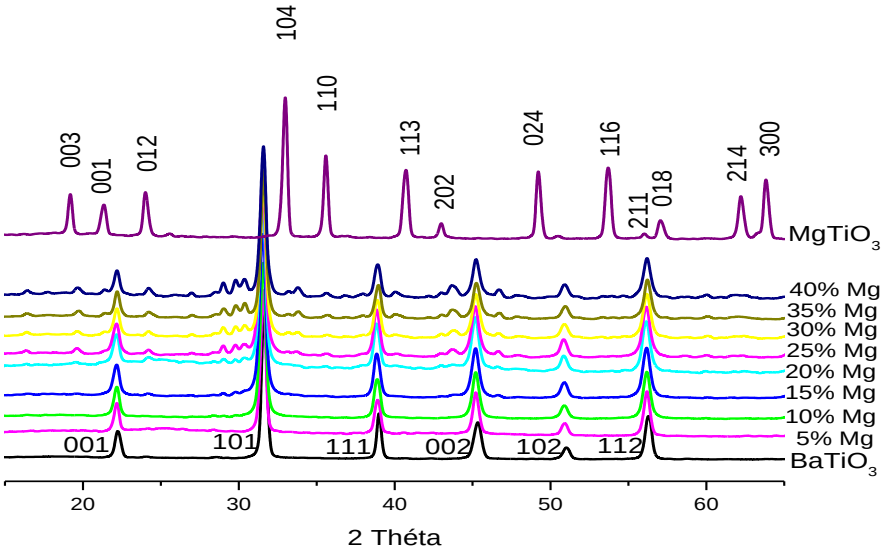

Figure 1: XRD spectra of the $Ba_{1-x}Mg_xTiO_3$ phases heat treated at 1000°C for 4h

3.2. Microstructure analysis

The SEM micrographs of ceramic samples (BMxT) sintered at 1100°C for 8h are shown in Fig.2. Show the morphology and appearance of grains of BMxT ceramic (x = 0, 0.1, 0.2, 0.3 and 0.4), they show an almost homogeneous structure with grains of different sizes and low porosity.

It is observed that the size of the grains progressively increases with the concentration of Mg. Indeed, the latter diffuses from the interfaces between the grains in the joints, thus favoring the enlargement of the grains with the increase magnesium rate in materials of composition $Ba_{1-x}Mg_xTiO_3$

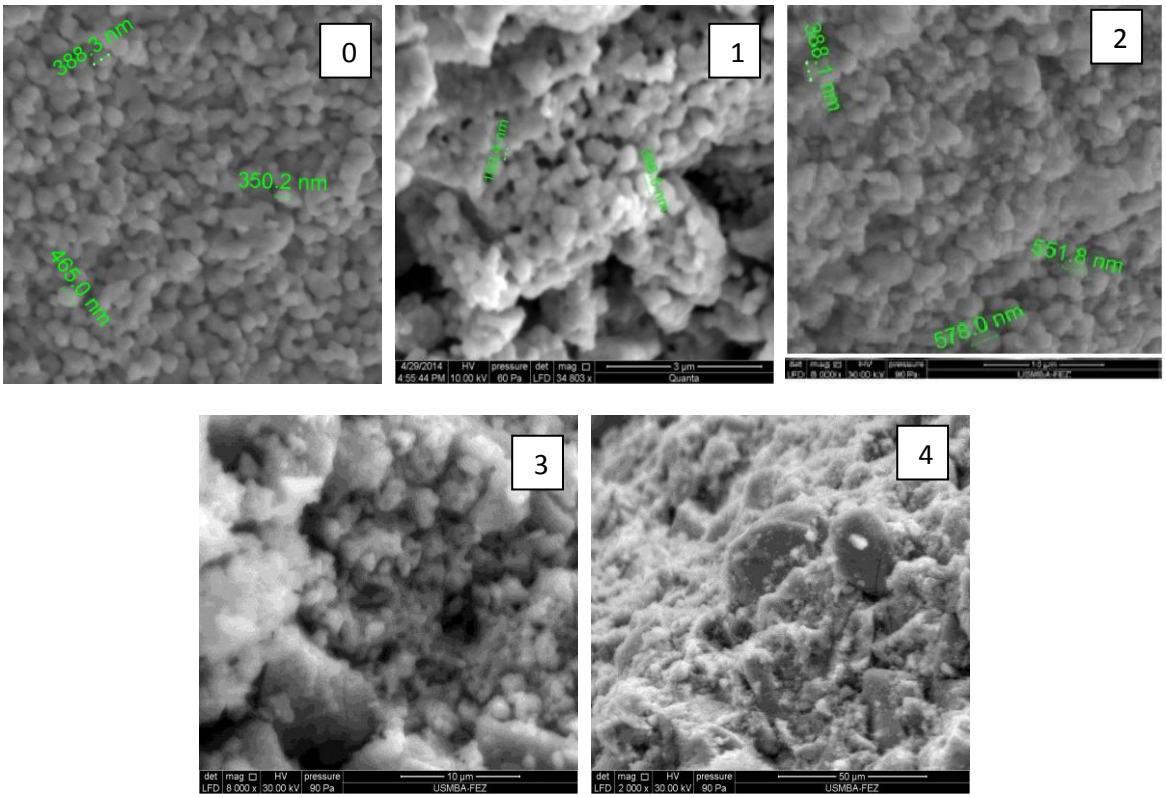

Figure 2. SEM micrographs of the $Ba_{1-x}Mg_xTiO_3$ (x=0, 1, 2, 3 and 4) ceramic sintered at 1100°C for 8h

The average grain size for the sample BMT(0) (Fig. 2) varies from approximately 350.2 nm to 465 nm and from approximately 388.1 and 578 nm from the samples BMT(1) and BMT(2), respectively (Fig. 2), which behavior is in accordance with that observed on XRD patterns.

3.3. Dielectric properties

Variation of the dielectric permittivity (ε_r) as function of the temperature, for different frequencies, are presented in figure 3, which shows that the relative permittivity ε_r increases when the temperature increases and passes through a maximum ε_{rmax} diffused at the temperature T_m, then decreases. The shape of the variation of ε_r at temperature T_m is independent of the frequency, this suggests that it is a classic transition.

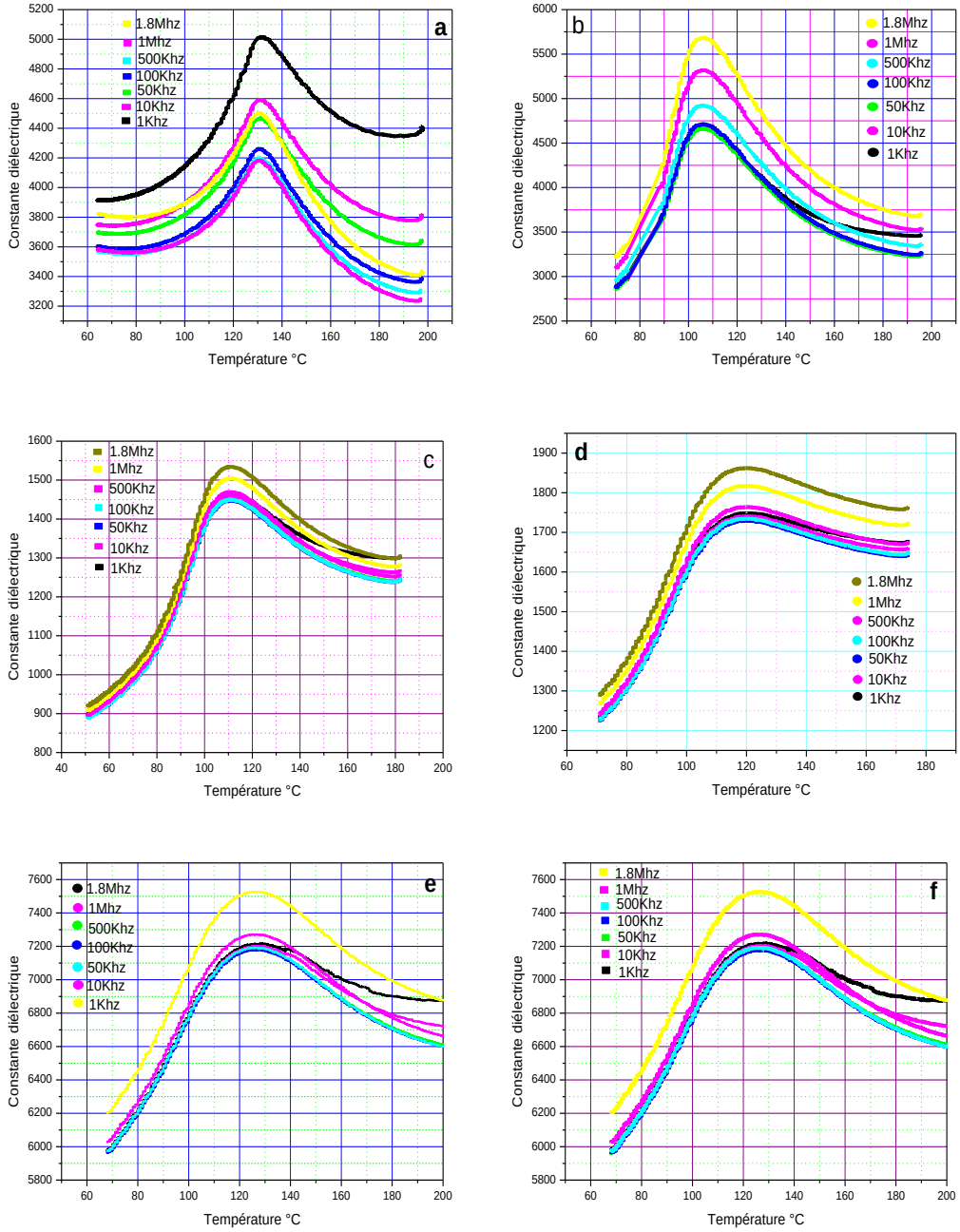

Figure. 3. Thermal variations of the relative permittivity, ε_r of BMxT (x=0, 0.1, 0.2, 0.3, 0.4, 0.5) heat treated at 1100°C/8H

It is observed (Table 1), that the insertion of Mg causes a decrease in the temperature T_m. From the value 130°C for $BaTiO_3$ (x = 0) up to 105°C for a rate of 10%. On the other hand, the permittivity E_{max} undergoes a slight increase (from 5000 for x = 0 to 5300 for x = 0.1).
Above 10% Mg, there is a gradual increase in temperature T_m up to 125 ° C. On the other hand, the value of the dielectric permittivity ε_r max undergoes a rapid fall for x = 0.2. (E_{max} = 1700), Then, the maximum dielectric permittivity ε_r max increases and reaches higher values (7300).

This variation indicates that Mg is inserted into the crystallographic site A of coordination 12 of the perovskite $BaTiO_3$, by substituting the Ba. Indeed this phenomenon is comparable to that observed during the BT study doped with Strontium [14].

x (%) Magnésium	T_m (°C)	ε_{max}
0	130	5000
10	105	5300
20	110	1700
30	120	1850
40	125	7300
50	128	7300

Table1. Comparison of ε_r and T_m corresponding to samples of BMxT

3.4. Dielectric losses

Table 2 groups the dielectric losses of BMxT compounds as a function of the Mg rate for a frequency of 1.8 KHz.

It should be noted that the dielectric losses at ambient temperature are very low compared to that corresponding to pure BT (0.1272) to 0.0124 up to 0.0082 for x = 0.1 and 0.2.

This reduction in dielectric losses compared to that observed for the pure $BaTiO_3$ compound, may be due to the insertion of Mg, known by its effect of reducing dielectric losses, in the $BaTiO_3$ lattice [15].

Taux de Mg (%)	**BT (0%)**	**10%**	**20%**	**30%**	**40%**
Dielectric losses at T_m	0.1272	0.0124	0.0082	0.0142	0.0103

Table.2. Dielectric losses of BMxT

3.5. Diffuse transition

The diffuse phase transition is a transformation of the ferroelectric phase to the paraelectric phase around the maximum temperature (T_m), accompanied by a frequency dispersion above T_m [16].

Figure 3 shows the fitting simulation of ε_r by the modified Uchino' law, depending on the temperature of the different compounds BMxT at a frequency of 1.8 KHz.

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m}\left[1 + \frac{(T-T_m)^\gamma}{2\delta^\gamma}\right] \quad [17].$$

γ and **δ** are the relaxor and diffuse parameters respectively.

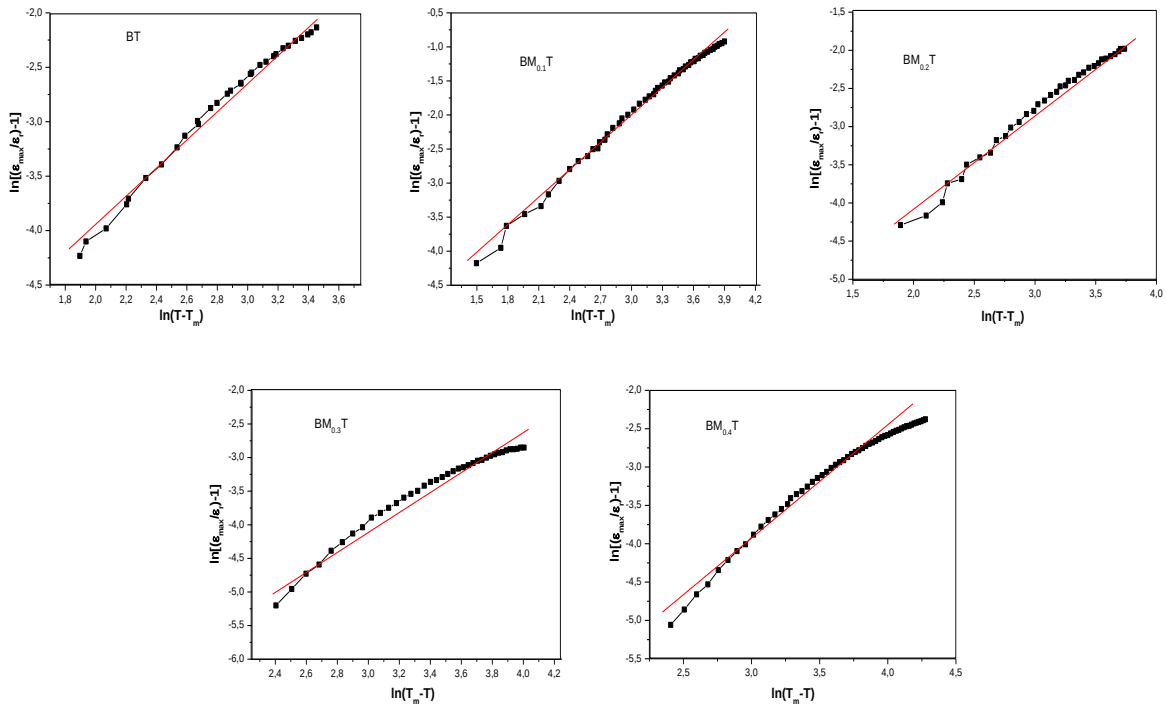

Figure.3. Plot of $\ln(\varepsilon_m/\varepsilon - 1)$ as a function $\ln(T_m-T)$

Magnesium (%)	**γ**	**Δ**
0	1,287	22.46
10	1,409	39,84
20	1,575	48,41
30	1,588	55,43
40	1,721	63,11

Table-3. Parameter values (γ, δ) for BMxT for frequency 1.8 KHz

The values γ and δ are given in Table-3. These values increase with increasing amounts of inserted magnesium. The evolution of these constants shows that transition a diffuse character ($1 < \gamma < 2$).
($1 < \gamma < 2$). The diffuse behaviour of the curie transition is considered to result from the inter-crystalline constraints that occur when the atomic order was absent within the material [16].

Conclusion

In summary, the study of the effect of substitution of Ba by Mg on the physicochemical and dielectric properties of the compounds $Ba_{1-x}Mg_xTiO_3$ produced by the sol-gel method for different concentrations (0, 0.1, 0.2, 0.3, 0.4 and 0.5) resulted in that Mg has an effect on both the transition temperature, the constant and the dielectric losses. Dielectric measurements revealed a diffuse ferro-to-paraelectric phase and confirmed by the modified Ushino's law. Note that when the Mg level increases, the temperature Tm decreases to the minimum value

of 105 ° C around a rate x of 15% in Magnesium. This decrease in temperature Tm indicates that Mg is inserted into the crystallographic site A of the perovskite $BaTiO_3$.
Using scanning electron microscopy on different samples of BMxT showed that magnesium affects grain shape and size, the more the Mg concentration increases, the more the grain sphericity increases. This reflects a new rearrangement at the level of the mesh.

REFERENCES

[1] K. Yang, X. Huang, Y. Huang, L. Xie, P. Jiang, Chem. Mater. 25 (2013) 2327.

[2] S. Roberts, Phys. Rev. 71 (1947) 890.

[3] A. von Hippel, Rev. Mod. Phys. 22 (1950) 221. [8] H. Xu, L. Gao, J. Am. Ceram. Soc. 86 (2003) 203.

[4] C.A. Miller, Br. J. Appl. Phys. 18 (1967) 1689.

[5] Z. Yu, R. Guo, A.S. Bhalla, J. Appl. Phys. 88 (2000) 410

[6] J. Qiu, T.T. Qiu, Fabrication and microwave absorption properties of magnetite nanoparticle carbon nanotube hollow carbon fiber composites, Carbon 81 (2015) 20e28

[7] P. Goel, K.L. Yadav, A.R. James, Double doping effect on the structural and dielectric properties of PZT ceramics J Phys D: Appl Phys, 2004, 37, 3174.

[8] - P. Goel, K.L. Yadav, Structural and optical properties of Ag-doped copper oxide thin films on polyethylene napthalate substrate prepared by low-temperature microwave annealing J Mater Sci, 2007, 42, 3928.

[9]- M. A Mohiddon, K.L. Yadav, Domain Reorientation Dynamics of Sol-Gel Derived Strontium Doped PLZT (8/65/35) J Sol-Gel Sci Technol, 2009, 49, 88.

[10] M. Kellati, S. Sayouri, N. Elmouden, M. Elaatmani, A. Kaal, and M. Taibi, , Structural and dielectric properties of La-doped lead titanate ceramics, Mater. Res. Bull. 39, 6 (2004).

[11] K. Bouayad, S. Sayouri, T. Lamcharfi, M. Ezzejari, D. Mezzane, L. Hajji, A. Elghazouali, M. Filali, P. Dieudonné, and M. Ghouta, Sol gel processing and dielectric properties of (Pb1-y Lay)(Zr0.52Ti0.48)O3, Physica A 358, 175 (2005)

[12] S. Komarneni, I. Abothu, A. Prasado Rao, ol-Gel processing of some Electroceramic powders. Sol-Gel Science and Technology 15, (1999), 263–270.

[13] O. El ghadraoui, International Journal of Current Research,Vol 8, Issue, 12, pp.42815-42820, December, 2016

[14] L. Zhang, W.L. Zhang, Y. G. Wang, C. L. Wang, and P.L. Zhang, "Fireter-size effet in ferroelectric solid solution BaxSr1-xTiO3" J. Phys. D: Appl.Phys. vol.32 pp 546-

551. (1999).

[15] Ultrafine Grinding of MgTiO3 Based Ceramic Influencing the Material Properties, Physical Chemistry & Biophysics, Hamieh et al. J Phys Chem Biophys, 3:3. (2013)

[16] Thése, M. Zouhairi, PROPRIETES PHYSICOCHIMIQUES DES PEROVSKITES DIELECTRIQUES $Pb(Fe_{1/2}\ Nb_{1/2})O_3$ (PFN) et $Pb_{1-x}La_xTi_{1-x/4}O_3$ ELABOREES PAR VOIE HYDROTHERMALE, P. 136.(2013)

[17] N.S. Echatoui, T. Lamcharfi, S. Sayouri, L. Hajji and A. Alimoussa, Phys. Chem. News, 26, 40 (2008).