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Preparation and study the structure of pure and impure barium titanate with Mg^{2+} ion

Mojahid Mohammed Najim and Wasan Abd Alsatar Hekmt

Applied Science Department, University of Technology, Baghdad

E-mail: sosooeze@yahoo.com

Abstract

Pure and doped barium titanate with Mg^{2+} ion at two molar ratios x= (5%, 10%) mol. has been synthesized by solid state reaction technique. The powders sintered at two temperatures (1000 $^{\circ}$C and 1400 $^{\circ}$C). An XRD technique was used in order to study the crystal structure of pure and doped barium titanate, which confirmed the formation of the tetragonal phase of $BaTiO_3$, and then calculate the lattice parameters of pure and doped barium titanate, the addition of magnesium ion Mg^{2+} can lead to decreases lattice parameters.

Key words

Barium titanate, ferroelectric, piezoelectric, X-ray diffraction.

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تحضير ودراسة تركيب الباريوم تيتانيت النقي والمشوب بايون المغنيسيوم (Mg^{2+})

مجاهد محمد نجم و وسن عبد الستار حكمت

قسم العلوم التطبيقية، الجامعة التكنولوجية، بغداد

الخلاصة

تم تحضير ودراسة التركيب البلوري للباريوم تيتانيت النقي و المشوب بايون المغنيسيوم Mg^{2+} والمضاف بنسبة مولارية (5%, 10%) =x والتي حضرت بتقنية تفاعل الحالة الصلبة. تم تلبيد المساحيق المحضرة عند درجتي حرارة (1000 $^{\circ}$C, 1400 $^{\circ}$C) و أجريت فحوصات XRD لدراسة التركيب البلوري للباريوم تيتانيت النقي والمشوب حيث أظهرت النتائج تكون الطور الرباعي للباريوم تيتانيت، وتم حساب معاملات الشبيكة للباريوم تيتانيت النقي والمشوب حيث أظهرت النتائج إن إضافة ايون المغنيسيوم Mg^{2+} يؤدي إلى حدوث تناقص بمعاملات الشبيكة.

Introduction

Barium Titanate ($BaTiO_3$) has become more important in ceramic material because of its chemically and mechanically stable [1], have ferroelectric and piezoelectric properties, has high dielectric constant and can be easily prepared. Barium titanate has been used in wide application such as capacitors and multilayer ceramic capacitors (MLCS) [2,3], Positive Temperature Coefficient (PTC) thermistors, piezoelectric transducers, variety of electro-optic devices and integral capacitors in printed circuit boards (PCB) [4]. $BaTiO_3$ is also a semiconducting and non- linear optical material when doped with other elements, and therefore can be used for resistors with positive temperature coefficient of resistivity [5].

Barium titanate

Barium titanate $BaTiO_3$ has a perovskite structure with formula $A^{2+}B^{4+}O_3$, where A is the large cation which is located at eight corner, B is the small cation located in the body center and oxygen atoms in the face center [6] as shown in Fig. 1 [7].

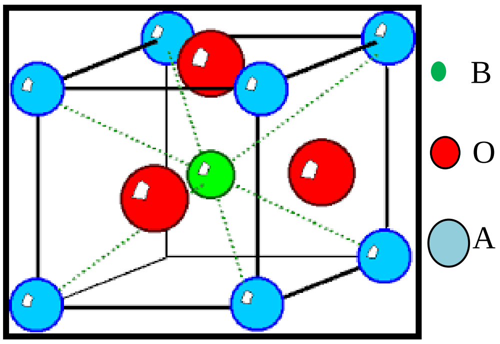

Fig. 1: Structure of Barium Titanate [7].

Phase transition of barium titanate

Barium titanate $BaTiO_3$ has four different phase 1- cubic, 2- tetragonal 3- Orthorhombic, 4- Rhombohedra [8-10]. The unique properties of perovskite material are due to the 1- Crystal structure 2- Phase transition as a function of temperature and 3-The size of ion present in the unit cell. Temperatures have a strong effect on the crystal structure of barium titanate $BaTiO_3$ [11].

Cubic phase, this phase occur above curie temperature (120 °C) and have a spontaneous random polarization. In this temperature range (120 °C) Ti^{4+} ion lies in the center of the structure. Tetragonal phase, it has a common uses, ferroelectric and stable phase between (5 °C < T < 120 °C) [12]. Orthorhombic phase, this phase occur at temperature (5 °C) which is stable between (-90 °C < T < 5° C). Rhombohedra phase, this phase occur at temperature below (-90 °C) [13]. As shown in Fig. 2.

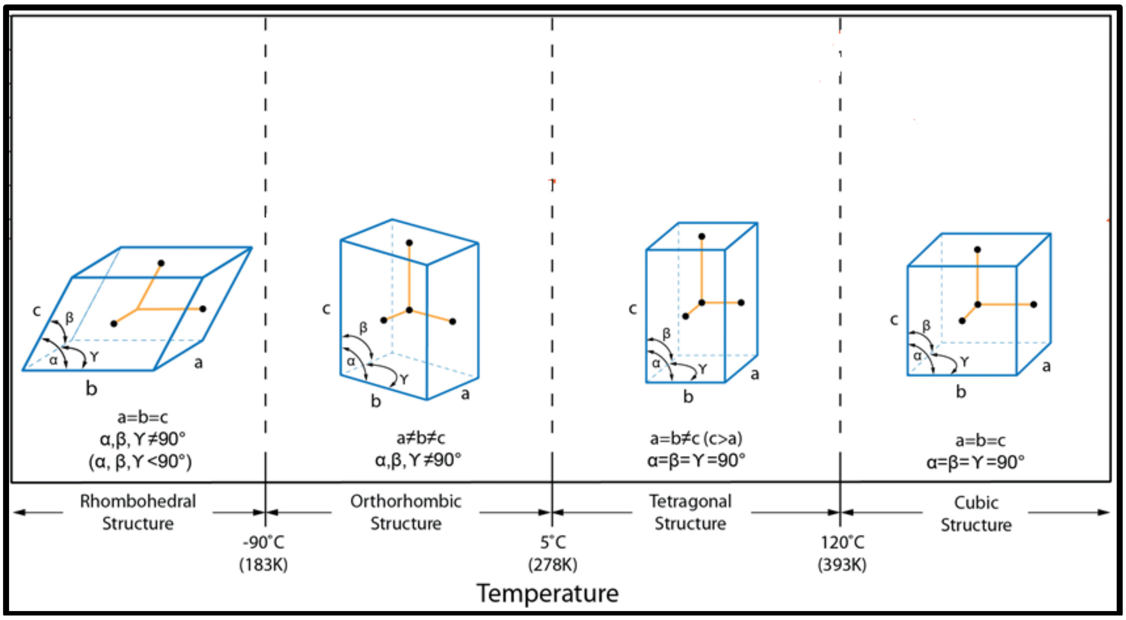

Fig. 2: Phase transformations of pure $BaTiO_3$ vs. temperature.

Experimental

Pure and doped barium titanate was synthesized via solid state reaction, pure barium titanate ($BaTiO_3$)(BT) was synthesized by mixing raw materials barium carbonate $BaCO_3$ with purity (98%) and titanium dioxide TiO_2 with purity (98%) of molar ratio [1:1], ethanol alcohol was added with purity (98%) in order to obtain good homogeneous, all mixtures were mixed in ball milling and grinding for 24 hrs., the mixture was dried at 80 °C for 15 hrs. to get rid of alcohol, the powder was sintered at two temperature (1000 °C and 1400 °C) for four hours.

Doped barium titanate (BMT), doped barium titanate synthesized by mixing raw materials $BaCO_3$ and TiO_2 and additive of (5 %, 10 %) mol. of magnesium carbonate $MgCO_3$ to prepare (BMT) ($Ba_{1-x}Mg_xTiO_3$) by substitution of Ba^{2+} ion instead Mg^{2+} ion, ethanol alcohol was added in order to obtain good homogeneous, all mixtures were mixed in ball milling and grinding for 24 hrs., mixture was dried at 80 °C for 15 hrs. to get rid of alcohol, the powder was sintered at two temperature (1000 °C and 1400 °C) for four hours.

$$(BaCO_3)_{1-x} + (Mg\,CO_3)_x + TiO_2 \longrightarrow Ba_{1-x}Mg_xTiO_3 + CO_2 \uparrow$$

Crystal structure was study to all powders were synthesized (BT) and (BMT) using X-ray diffraction with Cu target and wavelength 1.54 Å, operating at (40 kV), (30 mA) and the samples were scanned from (20-60 2θ°) with scan speed (8 deg/min).

Fig. 3 refers to the XRD pattern of raw materials $BaCO_3$ and TiO_2 before sintering this pattern matched with the standard pattern of barium carbonate JCPDS-ICDD No. (00-005-0378) and standard of titanium dioxide TiO_2 JCPDS-ICDD No. (00-021-1272).

Fig. 4 shows the flow chart of synthesized pure and doped barium titanate.

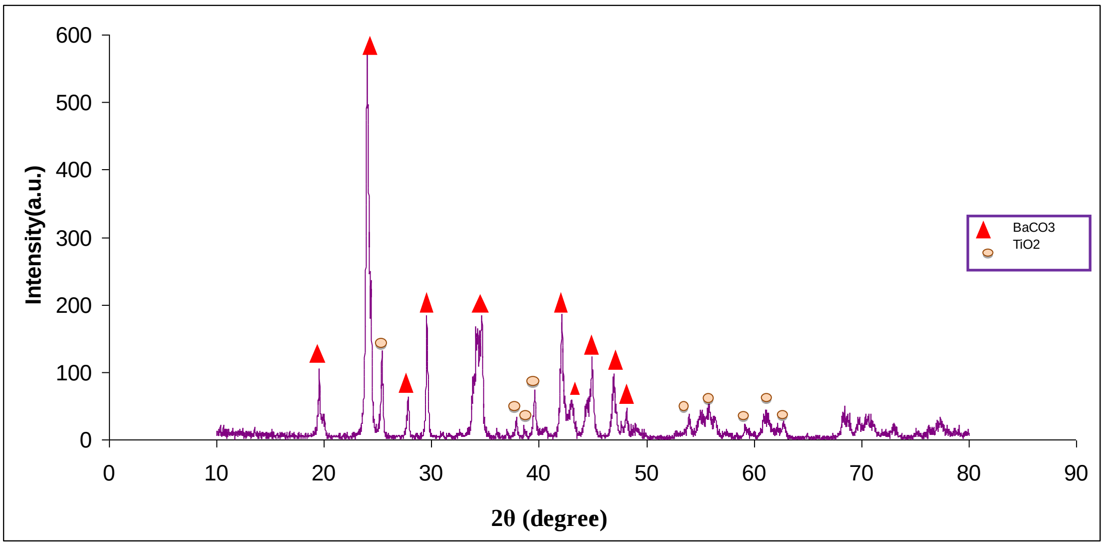

Fig. 3: XRD patterns for Barium Carbonate $BaCO_3$ and Titanium oxide TiO_2 before sintering.

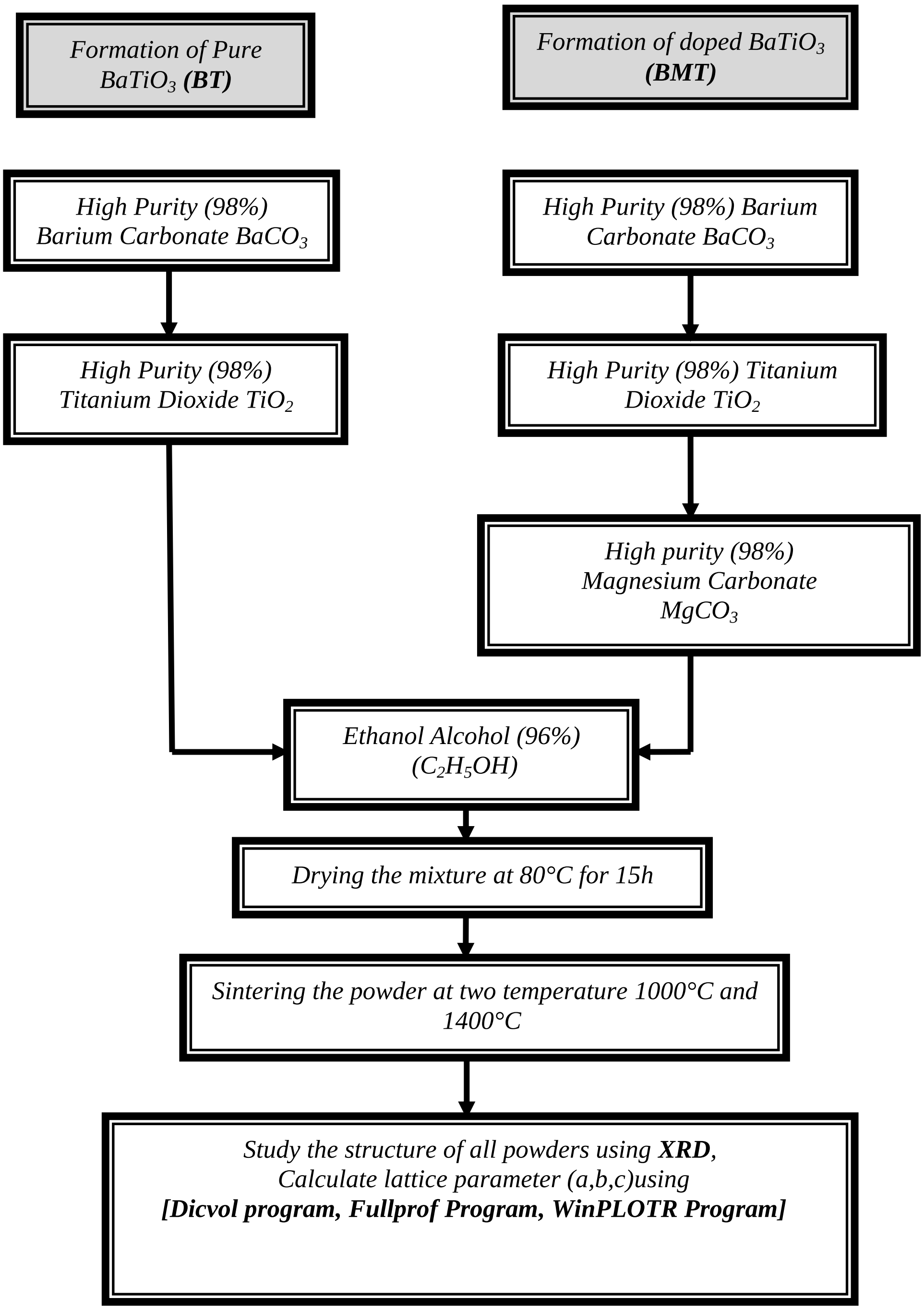

Fig. 4: Flow Chart of synthesized pure (BT) and doped (BMT).

Results and discussion

X-ray diffraction of pure Barium Titanate $BaTiO_3$ (BT).

In Fig. 5 X-ray diffraction pattern confirmed the existence of the barium titanate with tetragonal phase (the pattern matched with the standard pattern JCPDS no 05-0626). At 1000 °C temperature there was low intensity of TiO_2 (Titanium Dioxide) but there was no $BaCO_3$ (Barium Carbonate). The symbol * shows the peaks for the (TiO_2) titanium dioxide this mean not complete reaction of formation of barium titanate because of the present of another peak belong to TiO_2 [14].

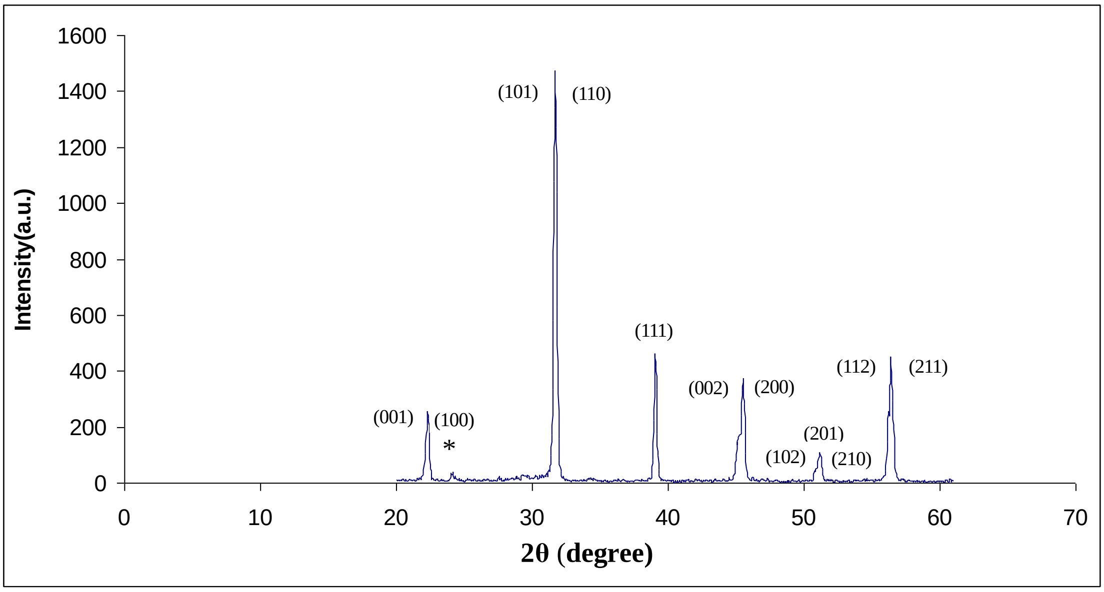

Fig. 5: XRD patterns for barium titanate at 1000 °C.

In Fig. 6 at (1400 °C) temperature there was no residual material detected by XRD technique indicated to complete reaction, this reaction appears high resolution in 2θ position for peaks indicated to a good crystallinity and formation of Pure Barium Titanate ($BaTiO_3$), diffraction peaks and miller indices at 2θ=44.950°, [002], 45.379°, [200], 50.704°, [102], 50.998°, [201], 51.096°, [210], 56.018°, [112] and 56.293°, [211], are widened gradually and lastly split during an increase in the calcinations temperature. This phenomenon refers to the (tetragonal structure) of barium titanate ($BaTiO_3$) phase was formed well with increases in calcinations temperature [15].

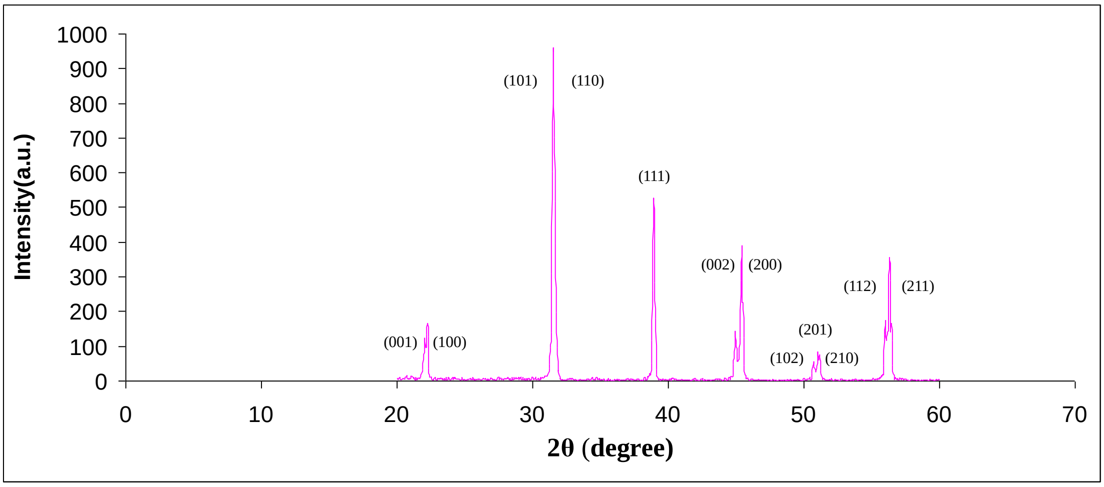

Fig. 6: XRD patterns for barium titanate at 1400 °C.

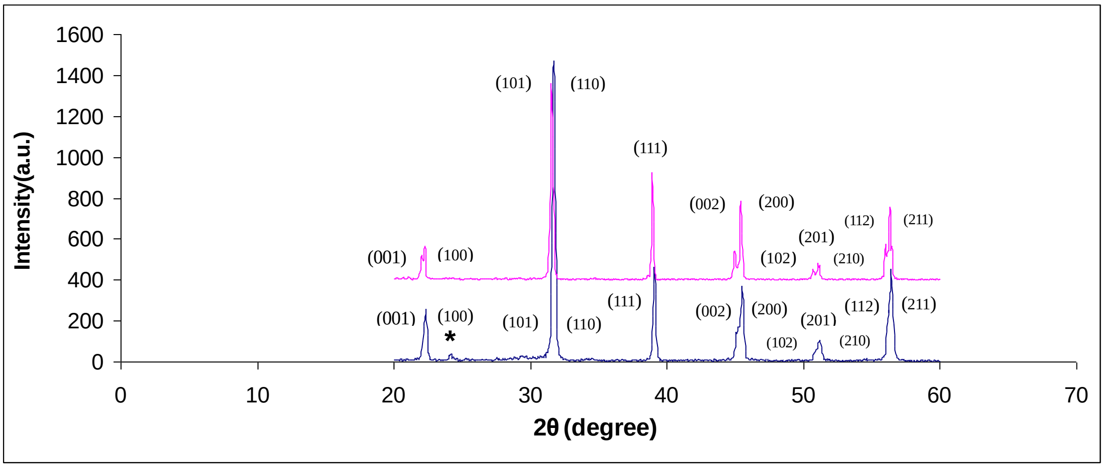

Fig. 7: XRD patterns for pure barium titanate (a) at 1000 °C and (b) at 1400 °C.

X-ray Diffraction of doped Barium Titanate (BMT)

Additive magnesium carbonate $MgCO_3$ to the barium titanate with two molar ratios (5 %, 10 %) mol. sintered at two temperature (1000 °C and 1400 °C) then study the structure of barium titanate using x-ray diffraction after this additive. X -ray technique show change in peak position as compared to pure barium titanate. So it can be seen that with (Mg^{2+}) substitution in barium titanate, the (2θ) peaks shifted towards higher angle side refers to decrease in lattice parameter, as shown in Figs. 8-11, this because of the substitute of (Mg^{2+}) ions instead of (Ba^{2+}) ions on the (A) sites of the $BaTiO_3$ lattice and the ionic radius of magnesium ion (Mg^{2+}) (0.065nm) [16] is smaller as compared to barium ion (Ba^{2+}) (0.2176 nm) [17].

The increase of the add ratio of Mg^{2+} ion from 5 % to 10% mol. leads to increase deviation to the higher angle as shown in Fig. 8.

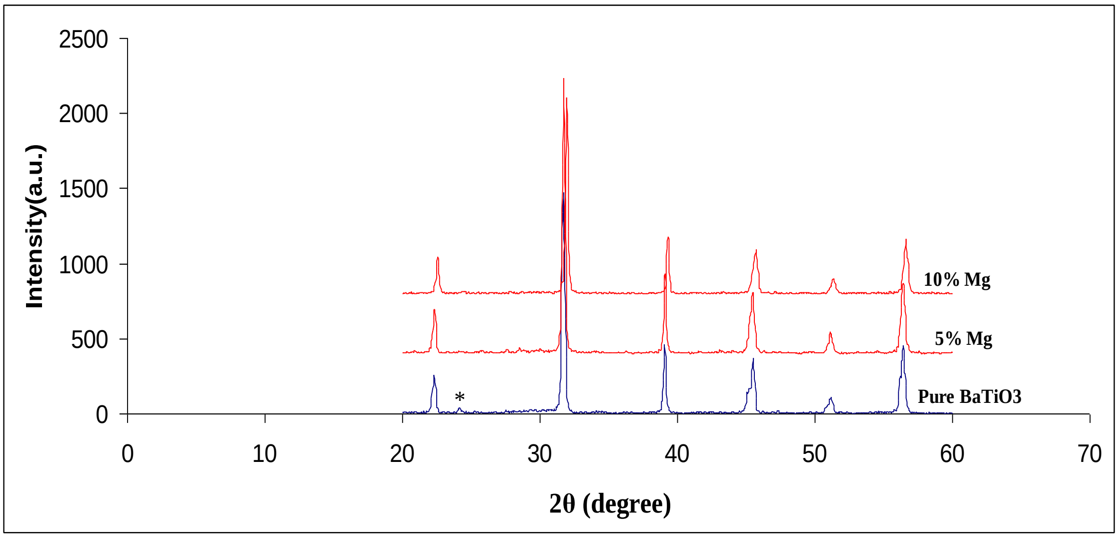

Fig. 8: XRD for $BaTiO_3$ with additives $MgCO_3$ (5 %, 10 %) mol. at 1000 °C.

Fig.9 refers to the magnification of the first three peaks from (20° to 40°) that appear shifted in peak position toward higher angle as increase in add ratio of Mg^{2+} ion at 1000 °C.

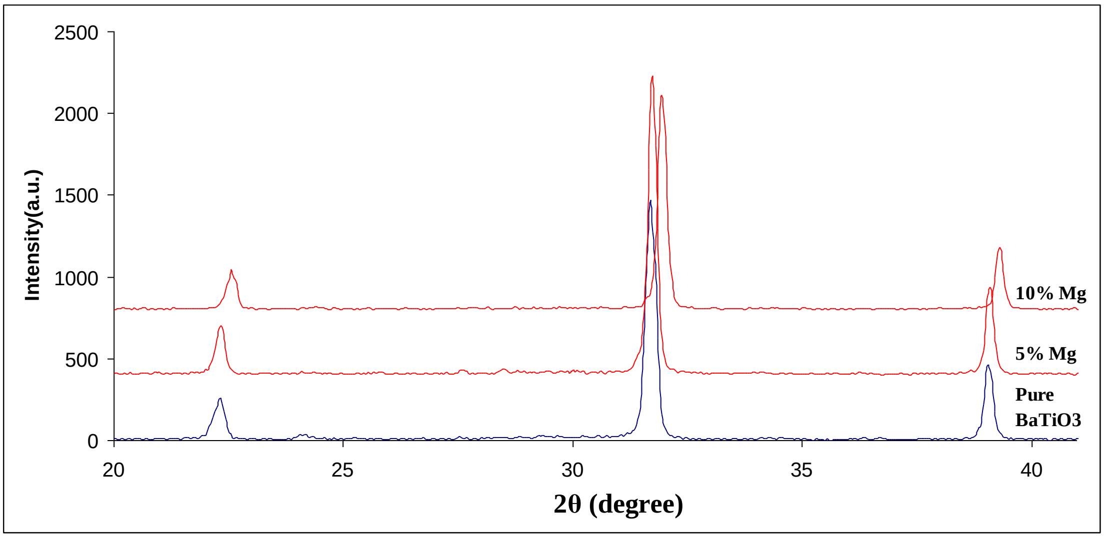

Fig. 9: The shifted of the first three peaks of (BMT) at 1000 °C.

At temperature (1400 °C), the addition of (5 %, 10 %) mol. of Mg^{2+} ion the lattice parameter value is decrease as compared with lattice parameter of pure barium titanate. And the divination to the higher angle is observed as increase in the add ratio of Mg^{2+} ion as shown in Fig. 10.

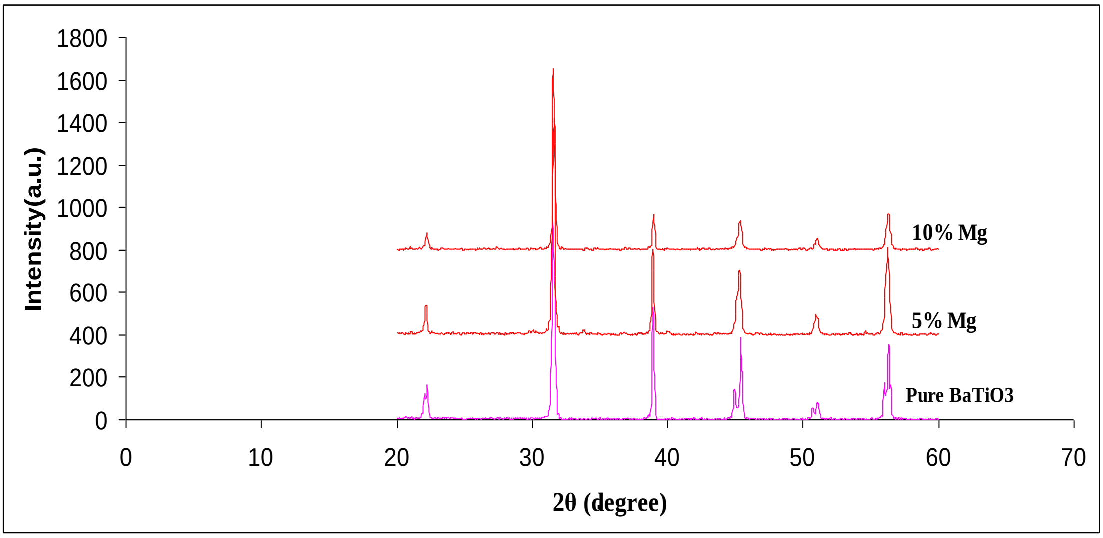

Fig. 10: XRD for $BaTiO_3$ with additives $MgCO_3$ (5 %, 10 %) mol. at 1400 °C.

Fig.11 refers to the magnification of the first three peaks from 20° to 40° that appear shifted in peak position toward higher angle as increase in add ratio of Mg^{2+} ion at 1400 °C.

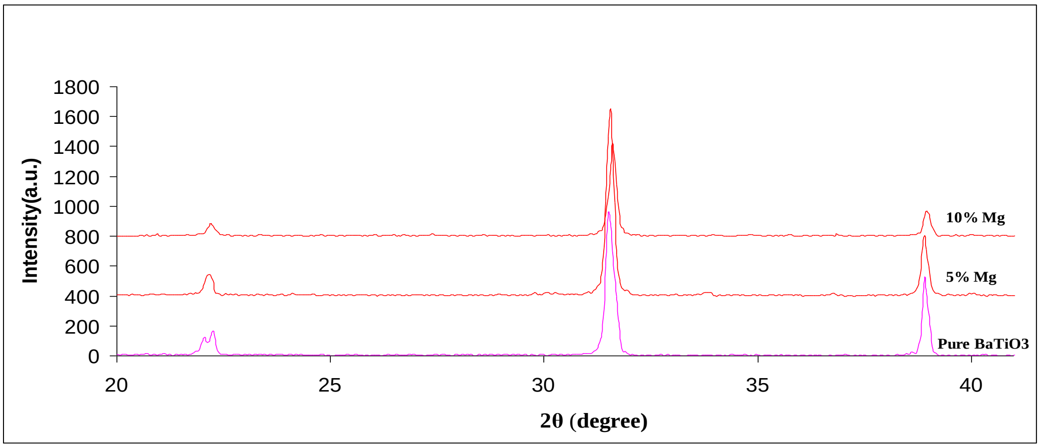

Fig. 11: The shifted of the first three peaks of (BMT) at 1400 °C.

Lattice parameters

Calculation the lattice parameters using (Dicvol Program, Fullprof Program, WinPLOTR Program) for pure and doped barium titanate with two molar ratio x= (5 %, 10 %) mol., sintered at two temperature 1000 °C and 1400 °C. Table 1 and 2 show the lattice parameters of pure and doped barium titanate.

Lattice parameter of pure $BaTiO_3$ at 1000 °C and 1400 °C.

Table 1 shows lattice parameter and volume of the tetragonal phase of pure (BT) sintered at 1000 °C and 1400 °C respectively.

Table 1: Lattice parameter of Pure $BaTiO_3$ (BT) in angstrom.

Pure BaTiO3(BT)	*a=b(Å)*	*c(Å)*	*Volume(Å)^3*
1000 °C	3.9911	4.0167	63.98
1400 °C	3.99392	4.02998	64.28

Lattice parameter of doped $Ba_{1-x}Mg_xTiO_3$ (BMT) at 1000 °C and 1400 °C.

Table 2 shows lattice parameter and volume of the tetragonal phase at 1000 °C when Mg^{2+} content (5 %) mol., at increase molar ratio to (10 %) mol., there are two tetragonal phase for (BMT).

At 1400 °C with (5 % and 10 %) mol. of Mg^{2+} ion there is multiple phase (cubic phase and tetragonal phase) respectively for (BMT).

Table 2: Lattice parameter of doped (BMT) in angstrom.

doped $BaTiO_3$(BMT)	*a=b(Å)*	*c(Å)*	*Volume(Å)^3*
1000 °C with 5% Mg^{2+}	3.98529	19.64812	312.06
1000 °C with 10% Mg^{2+}	3.98438	3.99062	63.35
	3.99361	4.00045	63.80
1400 °C with 5% Mg^{2+}	4.00014	4.00014	64.01
	2.82876	4.00109	32.02
1400 °C with 10% Mg^{2+}	3.99920	3.9992	63.96
	2.82802	4.00027	31.99

Lattice parameter for pure and doped barium titanate at two molar ratio x= (5 %, 10 %) mol., sintered at two temperature 1000°C and 1400°C,was calculated using (Dicvol Program, Fullprof Program, WinPLOTR Program), and can be calculated using the equation below:

$$\frac{1}{\mathrm{d}^2} = \frac{h^2+k^2+l^2}{a^2} \quad \text{for cubic phase}$$

$$\frac{1}{\mathrm{d}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad \text{for tetragonal phase}$$

Conclusions

In this study we observed pure barium titanate with tetragonal phase has been found at (1400 °C), the additives of $MgCO_3$ to barium titanate lead to decrease in lattice constant. Diffraction peaks undergo shifted toward higher angle because of the doped of (Mg^{2+}) ion (0.065 nm) which is smaller than (Ba^{2+}) ion (0.2176 nm) in the (A) sites of $BaTiO_3$ and this refers to decreases in lattice parameters, calculation of lattice parameter appears matched with X-ray diffraction.

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