

Quantum-Chemical and Experimental Study for Formation Interaction of Barium Titanate

Weaam Abdulkader Akkad¹ Ibrahim Ismaeel² Adnan Kodlaa³

1.Master degree student in Al-baath Univ.

2.Prof. Dr. in Inorganic Chemistry - Faculty of Science at Al-Baath University

3.Prof. Dr. in Quantum Chemistry- Faculty of Science at Al-Baath University

Department of Chemistry, Faculty of Science, Al-Baath University, Homs, Syria

Abstract

In this research we study the synthesis of Barium Titanate **BTO** by solid state method from 400 to 1100°C, under pressure about 5 ton.mm⁻² by using BaCO₃+TiO₂ as a reactants or BaO +TiO₂. By comparing the samples results we found that the optimum reaction is [BaCO₃+TiO₂ (1:1)] and the best temperature for the synthesis was 1100°C. We Study the manufactured samples with DFT/B3LYB(SDD) method and we confirmed that the compound is formed from XRD diffraction pattern and DTA curves.

Keywords: Barium Titanate, Solid State, DFT, XRD, DTA.

1. Introduction

The continuing drive towards greater miniaturization of electronic components has led to the development of thin film materials for a wide variety of applications, and among these are the thin film ferroelectrics^[1]. Barium titanate (**BaTiO₃** or **BTO**) based materials have been widely studied because of their fascinating properties like high dielectric, piezo-electric and pyro-electric coefficients^[2]. After the discovery of ferroelectricity in BTO, research from various laboratories all over the world start studies of solid solutions of BTO. This research field is of great basic and applied interest since the experimental results should facilitate developing of theory and fining of ferroelectric solid solutions with properties optimal for application. The phase development and dielectric behavior of various perovskite ferroelectric ceramics was reported, which may be applied to several micro- or nano-positioning devices such as deformable mirrors, microactuators, miniaturized transducers, multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers, and a variety of electro-optic devices^[3]. This perovskite cells are thin films which prepared easily in laboratories by mixing solid reactants together^{[4][5]}. Which is the optimum way to get them?

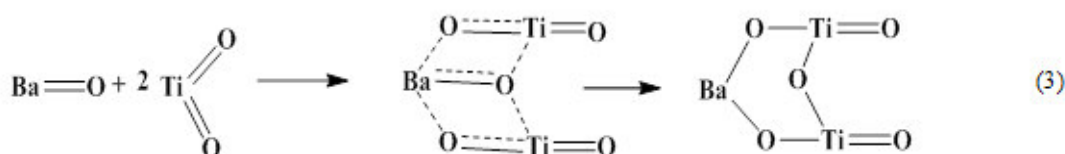
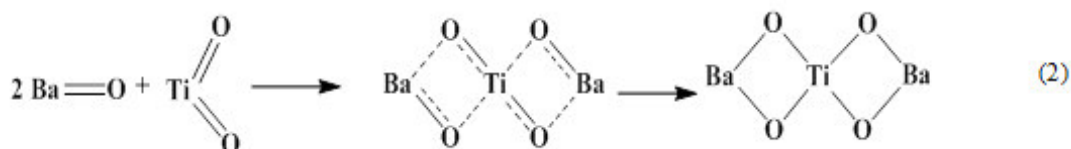
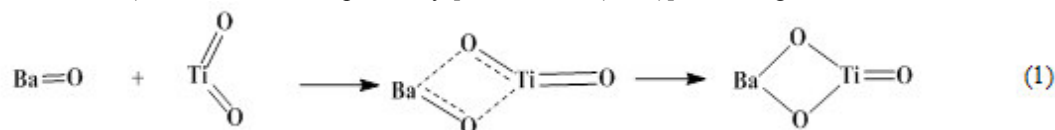
2. Materials and methods

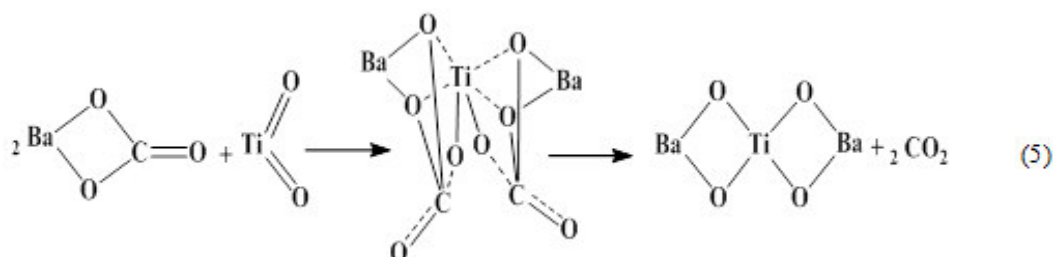
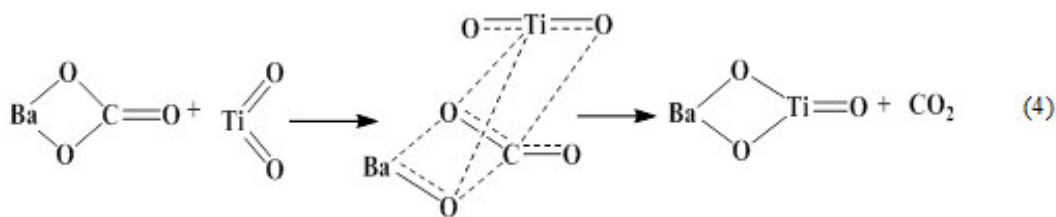
Barium Carbonate (TITAN BIOTECH 98.5%) , Barium Oxide (PROLABO 97%) , Titanium Oxide (Qualikems Fine Chemicals 99%) , Aceton (eurolab above 99.8%) .

We use Quantum method (DFT/B3LYP(SDD))^{[6][7][8]} and Solid State^[9] method to prepare the samples.

3. Quantum-Chemical Study

Before we synthesis BTO, we study the reactants (BaO, BaCO₃, TiO₂), the resultants (BaTiO₃, Ba₂TiO₄, BaTi₂O₅, CO₂) and activated complexes by [DFT/B₃LYP(SDD)] according to the reactions:





3.1. Results and discussion:

3.1.1. the reaction between BaO+TiO₂:

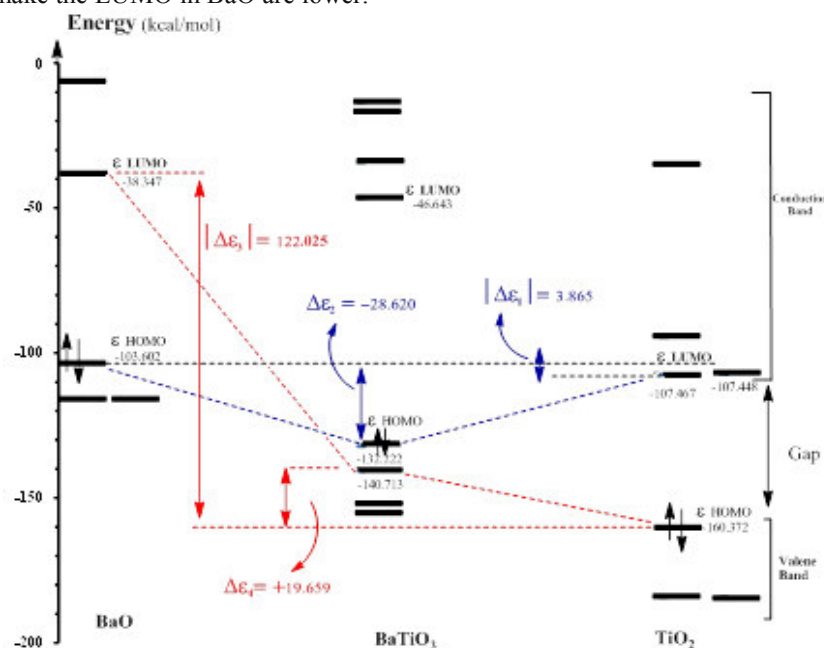
We calculated the activated energy and free gibbs energy for activated complexes, and ordered the results in table (1).

Table (1): shows the values of activated energy (ΔE_A) free gibbs energy (ΔG_A) for different stoichiometric ratio

The proportion of reaction	BaO + TiO ₂	
	$\frac{\Delta E_A}{\Delta E_A (1:1)}$	$\frac{\Delta G_A}{\Delta G_A (1:1)}$
1:1	1.00	1.00
2:1	0.21	0.32
1:2	2.17	2.17

Extrapolating the table values, we find that the stoichiometric ratio is 2:1 in the first stage.

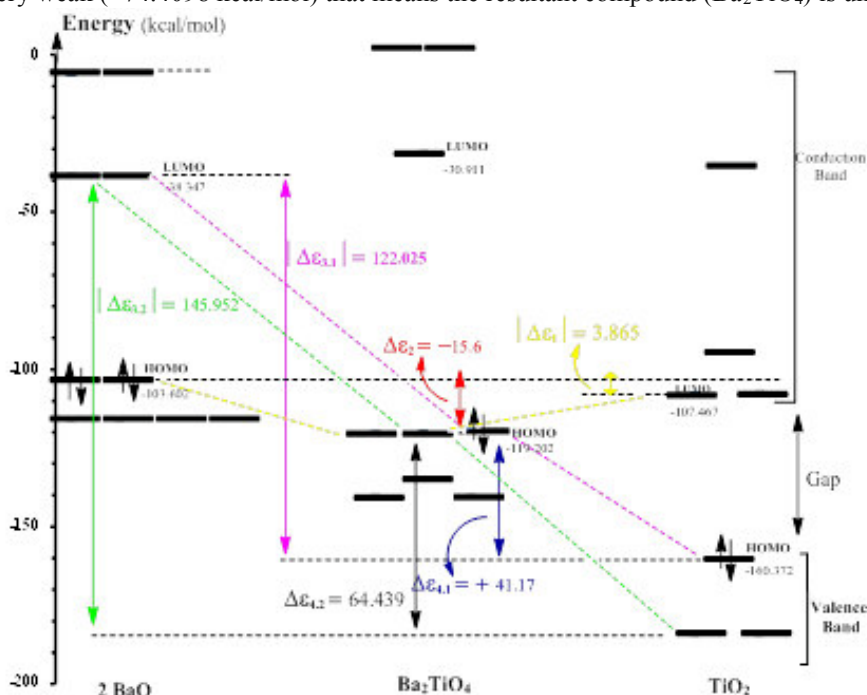
So we study the molecular orbitals energies specially LUMO, HOMO for reactants and resultants in reaction with (1:1) ratio, the average energy between reactants was (62.945 kcal/mol), and mutual influence was weak (-8.961 kcal/mol) that means the reaction between them is slow; so we need hard conditions(temperature and catalyze) to make the LUMO in BaO are lower.



scheme(1): shows the molecular orbital energies for BaO:TiO₂ by (1:1).

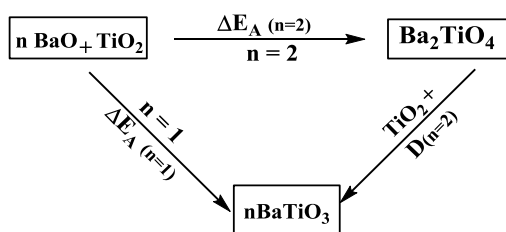
In BaO:TiO₂(2:1), we find that the average energy between reactants was (68.923 kcal/mol), and mutual

influence was very weak (+74.4098 kcal/mol) that means the resultant compound (Ba_2TiO_4) is unstable.



scheme(2): shows the molecular orbital energies for $BaO:TiO_2$ by (2:1).

Extrapolating the previous results, we find that the formation interaction of BTO is probably passed through Ba_2TiO_4 as an activated complex:



3.1.2. the reaction between $BaCO_3+TiO_2$:

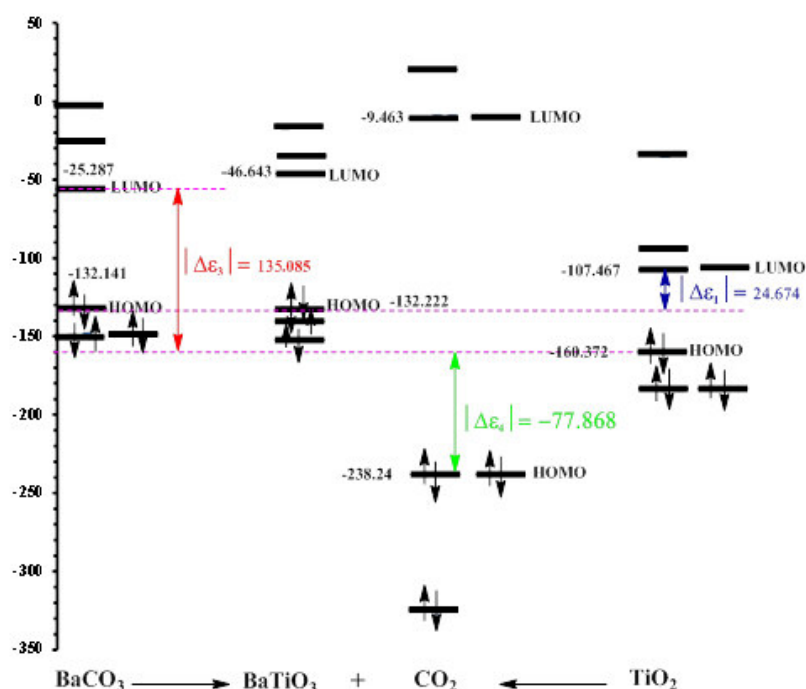
We calculated the activated energy and free gibbs energy for activated complexes, we ordered the results in table (2).

Table (2): shows the values of activated energy (ΔE_A) and free gibbs energy(ΔG_A) for different stoichiometric ratio.

The proportion of reaction	$BaCO_3 + TiO_2$	
	$\frac{\Delta E_A}{\Delta E_A (1:1)}$	$\frac{\Delta G_A}{\Delta G_A (1:1)}$
1:1	1.00	1.00
2:1	2.70	2.71

Extrapolating the table values, we find that the stoichiometric ratio is (1:1).

When we study the MO's energies (HOMO, LUMO) for reactants and resultants in reaction with (1:1) ratio, the average energy between reactants was large (79.8795 kcal/mol), but because of the disengage from CO_2 that make the mutual influence is large too (-78.030 kcal/mol) so they can combined to form BTO.

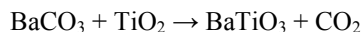


scheme(3): scheme shows the molecular orbital energies for BaCO₃:TiO₂ (1:1)

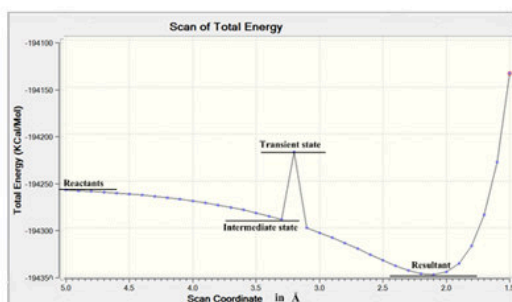
3.1.3. Choice of the best suited interaction to prepare BTO:

we depended on two main factors:

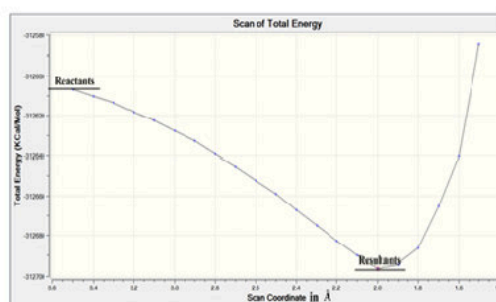
- **Molecular Orbitals Energies:** by comparing the schemes (1),(3) as we explained previously; we noticed that the free CO₂ reduced the gap between LUMO in TiO₂ and HOMO in BaCO₃, that due to increase the mutual influence between them; thus significantly reduced HOMO in CO₂. So the optimum reaction is:



- **Energy surfaces:** we have done a scan of energy for reactants and resultants by the distances between molecules of reactants in the previous probably reactions, we got the curves of energy scheme (4) and (5).



scheme (4): line chart for electric energy changes by the distances between molecules of reactants in the reaction between BaO+TiO₂



scheme (5): line chart for electric energy changes by the distances between molecules of reactants in the reaction between BaCO₃+TiO₂

In scheme (4) we find that the reaction need active energy about (72.163 kcal/mol) while in scheme (5) the interaction was semi-spontaneous.

3.2. Conclusion: We extract from previous studies that the optimum reaction to form BTO is from BaCO₃ and TiO₂. Table (3) shows some thermodynamics values for both reactions:

Table (3): shows the Reaction Energy ΔE_R , Entropy of reaction ΔS_R , enthalpy of reaction ΔH_R and free gibbs energy ΔG_R

Quantity	The reaction	
	$BaO + TiO_2 \longrightarrow BaTiO_3$	$BaCO_3 + TiO_2 \longrightarrow BaTiO_3 + CO_2$
ΔE_A (kcal/mol)	72.163	0.0
ΔE_R (kcal/mol)	-162.133	-116.404
ΔS_R (kcal/mol)	-28.407×10^{-3}	4.386×10^{-3}
ΔH_R (kcal/mol)	2.359	1.925
ΔG_R (kcal/mol)	10.829	0.617

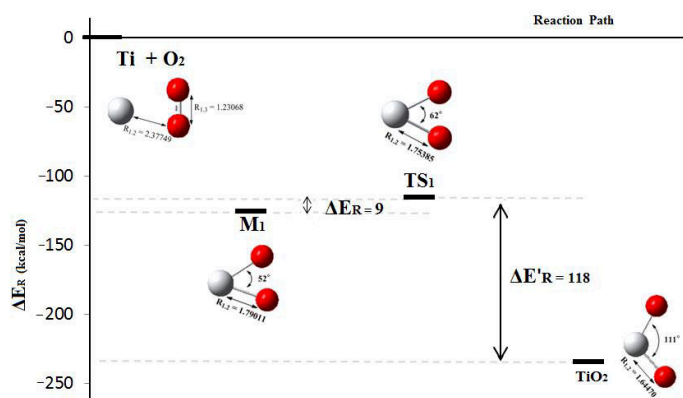
3.1.4. The mechanism of Crystal BTO formation reaction (perovskites) :

In the first stage both of BaO and TiO₂ molecules are forming, after that BTO molecules is composed too which combined together to form the unit cell of BTO crystal. The electronic energies for reactants, resultants, intermediate states and transient states were calculated and ordered in table(4)

table(4): electronic energies for reactants, resultants, intermediate states and transient states BTO crystal.

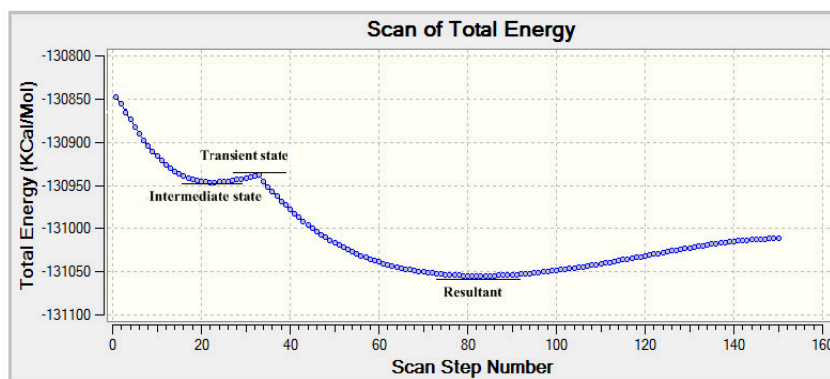
The Formation of Molecular TiO ₂		The Formation of Molecular BaO		The Formation of the BTO unit cell	
Particle	E_i (kcal/mol)	Particle	E_i (kcal/mol)	Particle	E_i (kcal/mol)
Ti	-36 533.937	Ba	-15 964.752	M2	-194 291
O	-47 114.643	C	-23 753.552	TS2	-194 219
O ₂	-94 285.110	CO ₂	-118 305.450	BaTiO ₃	-194 349
M1	-130 946	BaO	-63 195.966		
TS1	-130 937	BaCO ₃	-181 554.314		
TiO ₂	-131 055				

3.1.4.1. TiO₂ Formation: Although we used pure TiO₂ (Qualikems Fine Chemicals 99%) in the synthesis, but we studied the formation mechanism of it starting from Ti and O₂ atoms; to compare our results by using DFT/B3LYP(SDD) method with other quantum method DMol/PW91^[8]. We calculated the energies of reactants (Ti and O₂), intermediate state M₁ and transient state TS₁ and ordered the values in table (4). We got energy diagram in scheme (6).



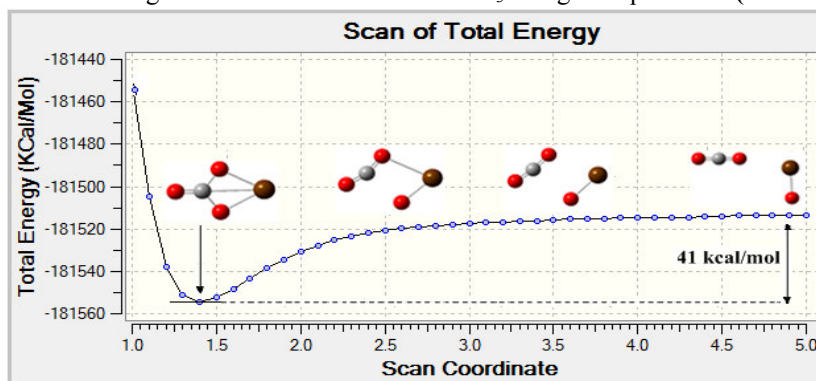
scheme (6): the formation energies for TiO₂ molecule.

Ti atom formed coordination bonds with two atoms of oxygen so they directly reacted to form M₁, due to the vibrated of O-O bond the TiO₂ molecule formed after passing through TS₁ as scheme (7) showed.



Scheme(7): the formation stages of TiO_2 molecule.

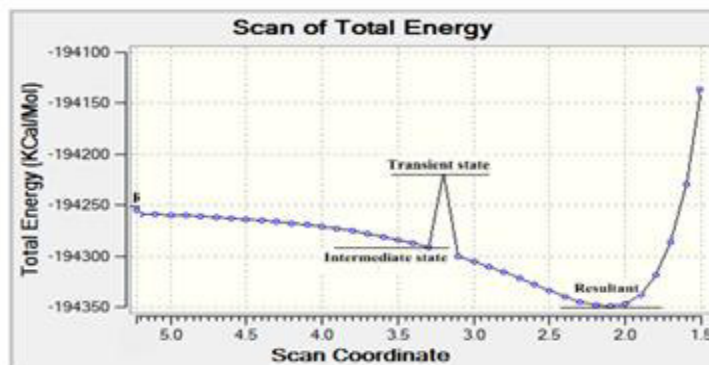
3.1.4.2. BaO Formation: we got it from dissociation of BaCO_3 in high temperatures (above of 885°C).



Scheme(8): the energies of BaCO_3 dissociation molecule to obtain BaO.

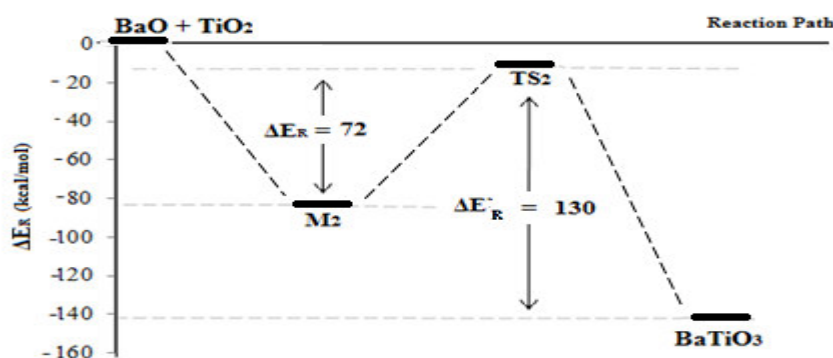
3.1.4.3. BTO Formation: TiO_2 molecule reacts with BaO which results from dissociation of BaCO_3 to get BTO molecule that react together to form BTO crystal.

To study the formation mechanism of BTO crystal we study the energies of reactants (BaO and TiO_2 molecules), resultants of reaction (BTO molecules), intermediate state M_2 and transient state TS_2 of compound



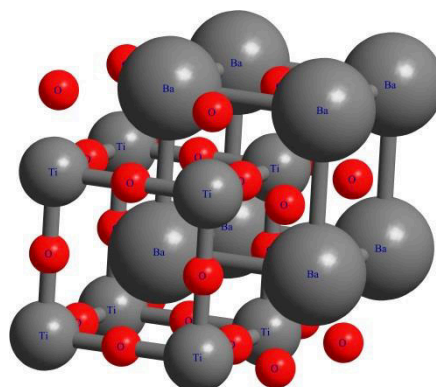
Scheme(8): the formation stages of BTO molecule.

In the first stage M_2 is formed due to the interfere between TiO_2 and BaO which obtained from BaCO_3 dissociation, after that Ba atoms directly moved to be in the middle of three oxygen atoms to form TS_2 as a result of single electrons allure power that belong to the three oxygen atoms.



Scheme(9): the reaction energies to form BTO.

We concluded that the first unit to build BTO crystal is made up from one cell which consists of five atoms in a cubic structure (Ba atom in one of cubic heads, Ti atom in the center of cubic and three oxygen atoms in three faces centers), while the second unit is included eight cells with forty atoms (Ba atoms in the cubic heads, Ti in the cubic centers which they formed cubic too and twenty four oxygen atoms in faces centers) scheme (10)



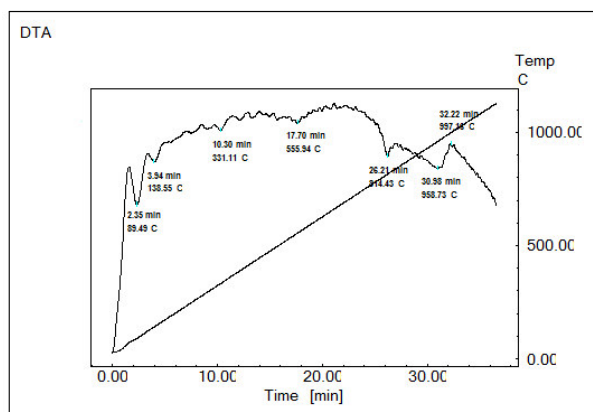
Scheme(10): the geometric distribution of unit cell for perovskite structure.

The total electronic energy is calculated for perovskite structure with cell constant ($a=b=c=4.00 \text{ \AA}$), it was (-1 555 297.657 kcal/mol) and the average of total electronic energy of BTO crystal was (-194 412.207 kcal/mol).

By comparing this energy with total electronic energy of BTO in the steady-state (-194 371.947 kcal/mol) we found that there is difference in values about (40.26 kcal/mol), which mean that the BTO crystal is more stable. So when BTO particles are formed they immediately united together to compose perovskite structure.

4. Samples preparation and method of synthesis:

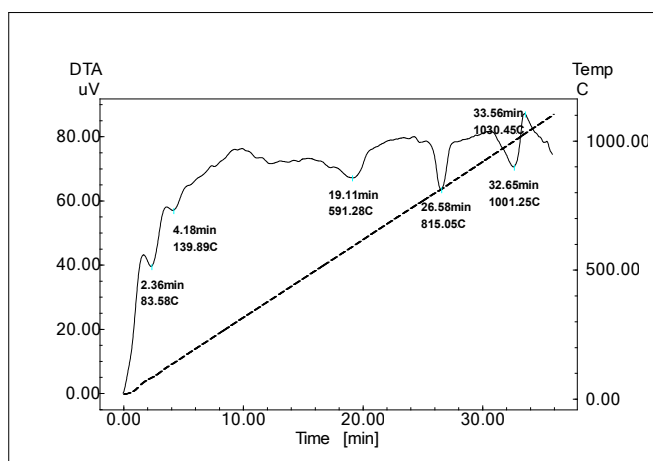
An equimolar mixture of reactants used to prepare the samples, they milled in agate mortar with acetone for three times. After milling the slurry was dried at 120°C for 2h in the drying Furnace (memert). The dried powder was milled in agate mortar again and we formed tables in size of 12 mm in diameter and 0.7mm thickness under a pressure of $5 \text{ ton}\cdot\text{mm}^{-2}$. These samples were sintered at different temperatures from $400\text{-}1100^\circ\text{C}$ for 3 h in a furnace (Carbolite Furnace, CWF 1200) and then cooled to room temperature^[6]. The structure and thermal analysis were studied using differential thermal analyzer (DTA-60 chimadzu), XRD diffractometer (XRD philips – PW– 1840).



Scheme(11): DTA curve for sample prepared from BaCO₃ , TiO₂

Table (5): determine types of peaks for DTA curve for BTO prepared from carbonate.

Reactants	DTA peaks (°C)	Type of peaks	Interpretation
BaCO₃ : TiO₂ 1:1	89.49	EXO	Remove acetone
	138.55	EXO	Remove water
	331.11	EXO	Switch to amorphous pattern
	555.94	EXO	Transition of TiO ₂ from Anatase to Rutile structure ^[10]
	914.43	EXO	Remove CO ₂ ^[11]
	958.73	EXO	Remove CO ₂ ^[11]
	997.16	Endo	BTO formation

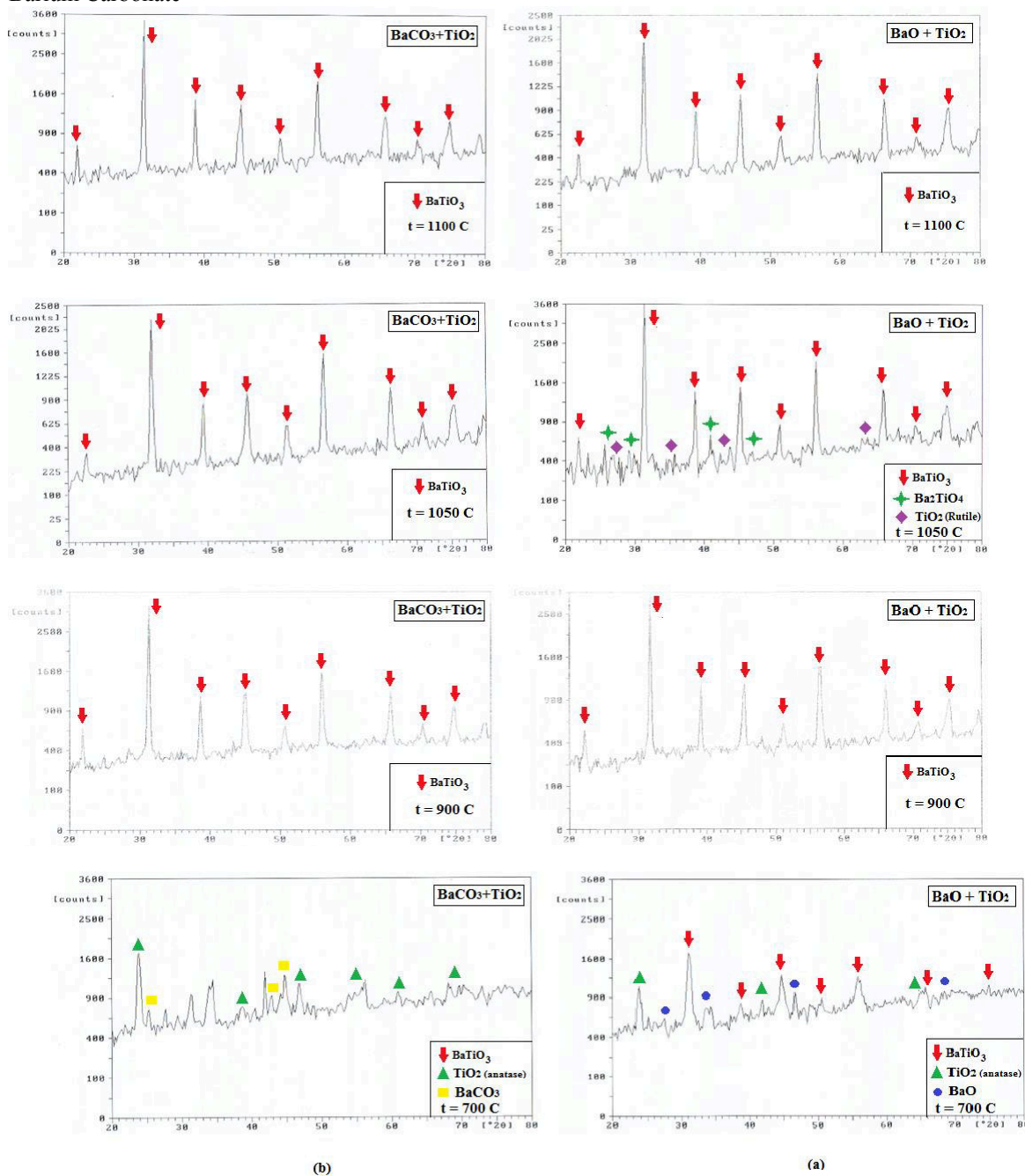


Scheme(12): DTA curve for sample prepared from BaO , TiO₂.

Table (6): determine types of peaks for DTA curve for BTO prepared from oxides.

Reactants	DTA peaks (°C)	Type of peaks	Interpretation
BaO : TiO₂ 1:1	83.58	EXO	Remove acetone
	139.89	EXO	Remove water
	331.11	EXO	Switch to amorphous pattern
	591.28	EXO	Transition of TiO ₂ from Anatase to Rutile structure ^[10]
	815.05	EXO	The disintegration of activated complex
	1001.25	EXO	Continued disintegration of activated complex
	1030.45	Endo	BTO formation

Scheme(13): XRD diffraction pattern of (a) BTO prepared from Barium Oxide, and (b) BTO prepared from Barium Carbonate



5. Results and discussion

We found that:

- i. Been confirmed that the accuracy of quantum method used in this work (DFT / B3LYP (SDD)) by comparing our results of studying the reaction mechanism form of titanium dioxide with the results of other method of quantum DMol / PW91, it has been described as very accurate; where the results were almost identical .
- ii. we didn't find any peaks due to BTO formation in scheme (8)(b) at 700°C, but these peaks clearly appeared when using barium oxide, the reason is due to the non-disintegration of barium carbonate into barium oxide that required for the synthesis.
 By increasing the temperature the BTO peaks are appeared because of liberalization BaO.
- iii. BTO formation from Barium Carbonate was at 885°C which agree with dissociation of BaCO₃ and getting-away of CO₂.
- iv. To prepare BTO from oxides we need active energy about (72.163 kcal/mol) while in the interaction

- from carbonate was semi-spontaneous.
- v. When we prepared BTO from oxides we noticed some disruption in spectrum 1050°C caused of activated complex Ba_2TiO_4 that disappear in parallel in BTO prepared from carbonate.
 - vi. The best reactants for synthesis are $BaCO_3:TiO_2(1:1)$ and the optimum conditions were $t=1100^\circ C - P=5 \text{ ton.mm}^{-2}$.

6. Conclusion

we extract from all previous studies that the optimum reaction to form BTO is from $BaCO_3$ and TiO_2 and free CO_2 was playing kinesthetic role to approximate reactants to each other and make the reaction easier and faster.

7. References

- [1] Kushwaha D, Ravikant, Singh K, Aggarwal M, *Fabrication and Characterization of Pulsed Laser Deposited Lead Free Thin Film Capacitors*, International Journal of Engineering and Advanced Technology (IJEAT), Volume 2, Issue 2, December (2012), p.1
- [2] Tang X.G., Chew K.-H., Chan H.L.W., *Diffuse phase transition and dielectric tunability of Ba(ZryTi_{1-y})O₃ relaxor ferroelectric ceramics*, Acta Materialia 52 (2004) 5177–5183
- [3] Huang H. H, Chiu H.H, Wu N.C. and Wang M.C. *Topics in Electric and Magnetic Ceramics*. Chapter 12, Costas Sikalidis, *Advanced In Ceramics – Electric And Magntic Ceramics, Bioceramics, Ceramics And Enviroment*. Croatia , Janeza Trdine , (2011)p. 293
- [4] Motta C. , El-Mellouhi F. , Kais S. , Tabet N. , Alharbi F. & Sanvito S. *Revealing the role of organic cations in hybrid halide perovskite CH₃NH₃PbI*, Nature Communications, Apr (2015)
- [5] Tvingstedt K. , Malinkiewicz O. , Baumann A. *Radiative efficiency of lead iodide based perovskite solar cells*. SCIENTIFIC REPORTS 4:6071 · August (2014)
- [6] Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Montgomery J. A., Vreven Jr., T., Kudin K. N., Burant J. C., Millam J. M., Iyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G. A, Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Knox X. Li, J. E, Hratchian H. P., Cross J. B., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Ayala P. Y., Morokuma K., Voth G. A., Salvador P., Dannenberg J. J., Zakrzewski V. G., Dapprich S., Daniels A. D., Strain M. C., Farkas O., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Ortiz J. V., Cui Q., Baboul A. G., Clifford S., Cioslowski J., Stefanov B. B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R. L., Fox D. J., Keith T., Al-Laham M. A., Peng C. Y., Nanayakkara A., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Gonzalez C., and Pople J. A., *Gaussian 03, Revision A.1, Gaussian, Inc., Pittsburgh PA, (2003)*.
- [7] Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Scalmani G., Barone V., Mennucci B., Petersson G. A., Nakatsuji H., Caricato M., Li X., Hratchian H. P., Izmaylov A. F., Bloino J., Zheng G., Sonnenberg J. L, Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J. A., Peralta Jr., J. E., Ogliaro F., Bearpark M., Heyd J. J., Brothers E., Kudin K. N., Staroverov V. N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J. C., Iyengar S. S., Tomasi J., Cossi M., Rega N., Millam J. M., Klene M., Knox J. E., Cross J. B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Martin R. L., Morokuma K., Zakrzewski V. G., Voth G. A., Salvador P., Dannenberg J. J., Dapprich S., Daniels A. D., Farkas O., Foresman J. B., Ortiz J. V., Cioslowski J., and Fox D. J., *Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT, (2009)*.
- [8] Yang C. , Liang X.-Q. , Huang P. , *Theoretical study of the reaction mechanism Ba, Ti, O, in the early growth of BTO thin films*, International Journal of Computational and Theoretical Chemistry: 2(5) (2014)41-45.
- [9] Othman K. I, Hassan A. A, Abdelal O. A. A, Elshazly E. S, Ali M. El-Sayed, El-Raghy S. M, El-Houte S, *Formation Mechanism of Barium Titanate by Solid-State Reactions*. International Journal of Scientific & Engineering Research, Volume 5, Issue 7,(2014) p. 1460-1463
- [10] Dorian A. H. H., Charles C. S., *Review of the anatase to rutile phase transformation*, J Mater Sci (2011) p.858
- [11] Maitra S, Chakrabart N, Pramanik J, *Decomposition kinetics of alkaline earth carbonates by integral approximation method*, Cerâmica 54 (2008) p.271