

Thermoanalytical and XRD Investigations on Ba₆Ti₅O₁₈ Ceramics Synthesized by Auto Combustion

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Abstract— The cation deficient perovskite (Ba₆Ti₅O₁₈) has been successfully synthesized using auto combustion technique. Thermal analysis of obtained powders is carried out to investigate the phase development and to optimize the preparation parameters. The evolution of the desired phase, its structure, lattice parameters and crystallite size variation as a function of calcinations/firing temperature have also been studied using XRD analysis.

Keywords— A₆B₅O₁₈ Cation Deficient Perovskite, Auto-Combustion, Crystallite Size, Thermoanalytical Investigations, XRD

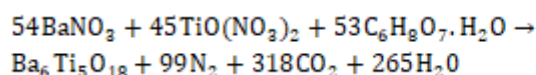
I. INTRODUCTION

Barium titanates have emerged as one of the leading option for Dielectric Resonator (DR) materials to be used in Microwave Communication Technology (MCT) because of their suitable values of dielectric constant, highest quality factors & low values of temperature coefficients of resonant frequency [1]. Major phases of these complex titanates include barium titanate BaTiO₃ (perovskite), barium tetra titanate (BaTi₄O₉), barium nona titanate (Ba₂Ti₉O₂₀) and cation deficient perovskite etc. These complex cubic perovskites have been extensively investigated in literature but very few reports are there on the relatively less popular hexagonal cation deficient perovskites, though they possess best suited dielectric properties for MCT as compared to simple perovskites [2-3]. A number of synthesis routes have been employed to synthesize these materials in literature but all of them suffers from one or the other problems but sol gel based internal combustion method offers a clean, contamination free and easy method for synthesizing these materials.

In the present work, we have synthesized Ba₆Ti₅O₁₈ dielectric ceramics using sol gel combustion method, an energy saving technique. The experimental work is described in section II. Thermal analysis and structural analysis of the synthesized compound have also been carried out in this work. In the section III, the results of these analyses and their discussion have been given. Section IV includes the conclusions of the research work described in the paper.

II. EXPERIMENTAL WORK

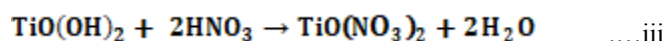
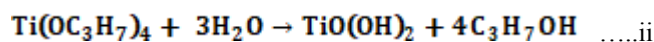
In the synthesis of Ba₆Ti₅O₁₈, Barium Nitrate {Ba(NO₃)₂} (Sigma Aldrich) and Titanium Iso-propoxide [Ti{OCH(CH₃)₂}₄] (Sigma Aldrich) are used as starting chemicals. Nitric Acid (HNO₃) (Fisher Scientific), Citric Acid Monohydrate (C₆H₈O₇·H₂O) (CDH) and Ammonia (NH₃) are used as solvents. The required amount of chemicals is calculated according to chemical equation given below:



According to above equation, for the synthesis of one mole of Ba₆Ti₅O₁₈, Ba(NO₃)₂, TiO(NO₃)₂ and citric acid should be combined in a molar proportion of 6:5:5.88 or we can say that total metal ion to citric acid molar ratio is 1:0.54.

Synthesis of TiO(NO₃)₂ Solution

Firstly TiO(NO₃)₂ is prepared using titanium isopropoxide [Ti{OCH(CH₃)₂}₄] according to the following equation:



Weighed amount of titanium isopropoxide is added drop wise to a beaker filled with distilled water kept at 4°C under ice cold conditions under vigorous stirring that resulted in instant formation of white precipitate of $\text{TiO}(\text{OH})_2$. The precipitates collected by filtration are dissolved in minimum amount of 1.4M nitric acid (HNO_3) under ice cold condition (4°C) with stirring. The available 15.55M Nitric acid is diluted using molarity equation ($M_1V_1=M_2V_2$) to 1.4 M. A clear solution of titanyl nitrate $\{\text{TiO}(\text{NO}_3)_2\}$ is obtained.

Synthesis of Citrate - Nitrate Solution

An aqueous solution of Ba^{2+} cations is formed by dissolving weighed amount of $\text{Ba}(\text{NO}_3)_2$ in minimum amount of distilled water at 40°C by continuous stirring. The above obtained $\{\text{TiO}(\text{NO}_3)_2\}$ solution and aqueous Ba^{2+} solution are mixed together under vigorous stirring to obtain clear solution. The citric acid solution is prepared by dissolving weighed amount of citric acid in distilled water. The citric acid solution is added to the above prepared solution under vigorous stirring to obtain transparent aqueous solution having citrate and nitrates [4]. The solution is named citrate - nitrate solution.

Gelation and Powder Formation

Dilute ammonium hydroxide NH_4OH is added drop wise to the solution to adjust the pH value at ~6. It leads to clear yellow transparent solution. The obtained solution is heated on a hot plate at ~90°C till the gel formation takes place. Actually on heating this solution undergoes thermal dehydration to form yellow transparent gel. On slowly raising the temperature of the hot plate, the gel swells up and gets ignited at around 240°C. The ignition takes place for approximately 5 seconds with evolution of large volume of gaseous products. This resulted in the formation of black voluminous powder with little carbon residue. The obtained powder is calcined at 600, 900, 1100, 1200 and 1250°C.

Characterization

DTA/TGA/DTG analysis of uncalcined powder is carried out under nitrogen atmosphere at heating rate 10°C/minute using EXSTAR TG/DTA 6300 instrument. X ray diffraction studies of powders obtained after calcinations at various temperatures are carried out using $\text{CuK}\alpha 1$ radiation with the help of XPERT-PRO X-RAY diffractometer.

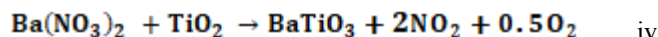
III. RESULTS AND DISCUSSION

Thermal Analysis

DTA/TG/DTG curve obtained for uncalcined powder is shown in figure 1. The curve can be divided mainly in four

parts. First part is a broad exotherm up to 500°C with weight loss of 6.52%. This weight loss may be due to dehydration processes, bond breaking of organic compounds and formation of Barium carbonate, Ti complex by oxidation and combustion of organic substance [5-7]. The increase in amount of BaCO_3 up to 600°C is also observed in XRD studies (table 1).

The second part is from 500-600°C with endothermic peaks at 568 and 586°C and weight loss of 5%. These peaks correspond to melting of $\text{Ba}(\text{NO}_3)_2$ and its reaction with TiO_2 to form BaTiO_3 [8]. The following reaction represents the chemical change:



XRD results also indicate that, $\text{Ba}(\text{NO}_3)_2$ which was present in uncalcined powder obtained after auto ignition, completely vanishes at 600°C and amount of BaTiO_3 has increased (table 1).

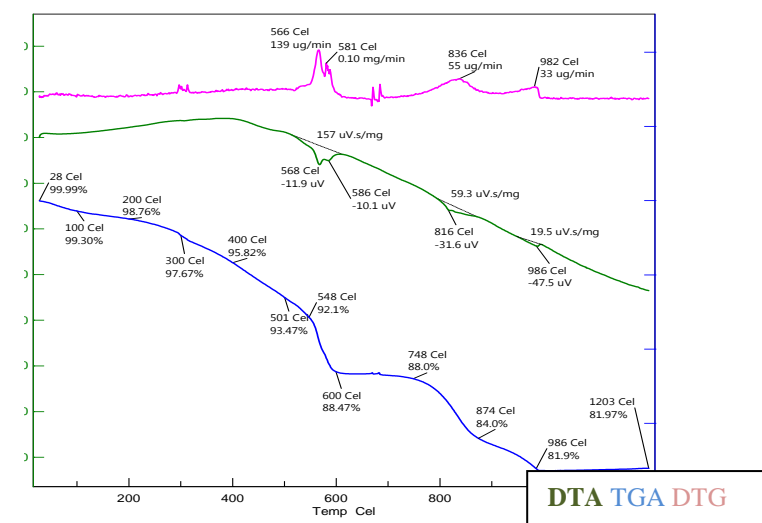
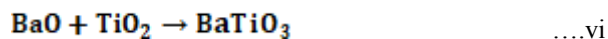
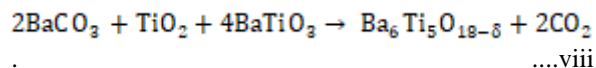
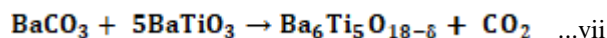


Figure 1. DTA/TGA/DTG curve for uncalcined powder

The third part of curve is from 750-875°C with endothermic peak at 816°C and weight loss of 4%. This corresponds to complex reaction between BaCO_3 and TiO_2 to form BaTiO_3 [9]. Similar trends are observed in XRD results, the decrease in amount of BaCO_3 and TiO_2 and increase in BaTiO_3 amount within temperature range of 600-900°C (table 1) suggests the following reaction:



Fourth part of curve is from 875 to 1000°C showing endothermic peak at 986°C with weight loss of 3%. The peak corresponds to reaction of BaTiO₃, BaCO₃ and TiO₂ to synthesize Ba₆Ti₅O₁₈. This is in accordance with XRD results (table 1) which indicate onset increase of Ba₆Ti₅O₁₈ from 1100°C and decrease in amount of BaTiO₃, BaCO₃ and TiO₂. The following metallurgical reaction can be suggested from above discussion for the development of the Ba₆Ti₅O_{18-δ} phase.



Characterization Using XRD

Phase Development

The XRD patterns for Ba₆Ti₅O₁₈ using Cu-Kα are shown in figure 2. The XRD peaks have been shown for uncalcined Ba₆Ti₅O₁₈ and calcined Ba₆Ti₅O₁₈ at different temperatures 600, 900, 1100, 1200 and 1250°C. The XRD pattern is almost similar to the XRD pattern of Ba₆Nb₄TiO₁₈ and is indexed accordingly [2,10]. The pattern is indexed on the basis of hexagonal symmetry of the structure. It can be depicted from the figure that XRD peaks are well defined and indexed. BaCO₃, TiO₂ and BaTiO₃ are present as impurity and intermediate phases at lower temperatures whereas XRD peak pattern at 1250°C contains only peaks corresponding to Ba₆Ti₅O₁₈.

The various inferences that can be drawn from the XRD pattern are shown graphically. The variation in amount of impurities and required phase with temperature is given in figure 3. The graph has been plotted using normalized intensities. The intensity for impure phases has been normalized by 790.92 (BaCO₃ 132), the maximum value of intensity for impure phase whereas the intensity of (110) reflection of required compound Ba₆Ti₅O₁₈ has been normalized by its own intensity i.e. 5926 and intensities of all other peaks of the desired compound have been normalized by 1532, the intensity of (1,0,19) reflection, the second maximum in Ba₆Ti₅O₁₈ XRD pattern.

The percentage amount of impurities i.e. Ba(NO₃)₂, BaCO₃, TiO₂ and BaTiO₃ and that of required Ba₆Ti₅O₁₈ phase has been calculated at various temperatures and is given in table 1. The graphical variation of percentage amount with temperature has been shown in figure 4.

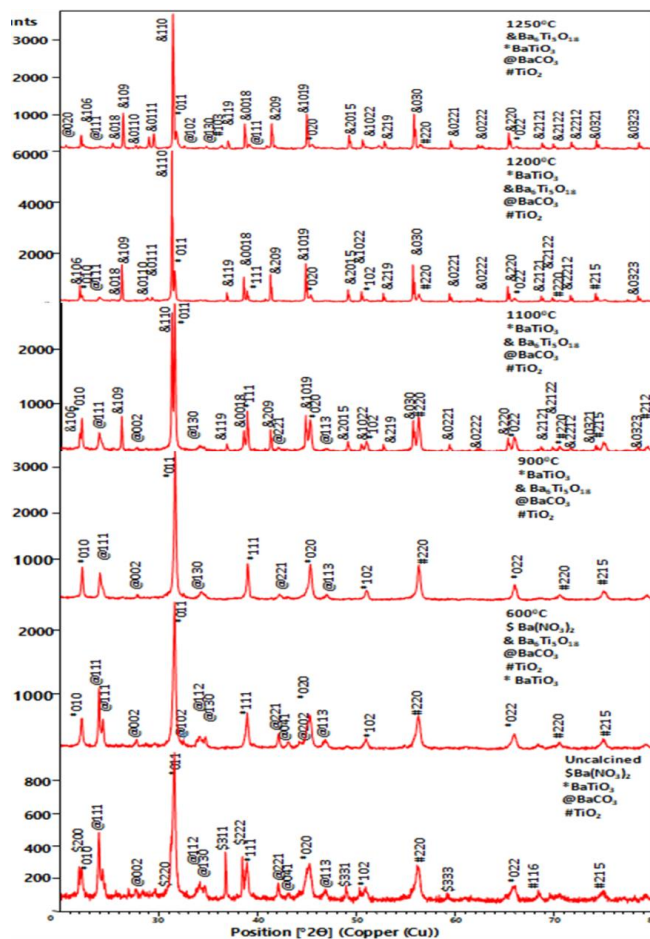
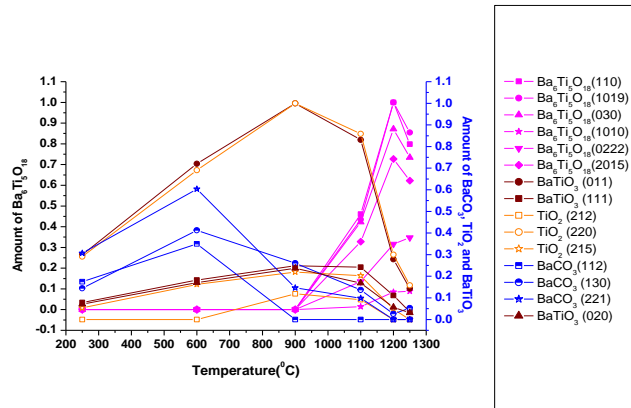


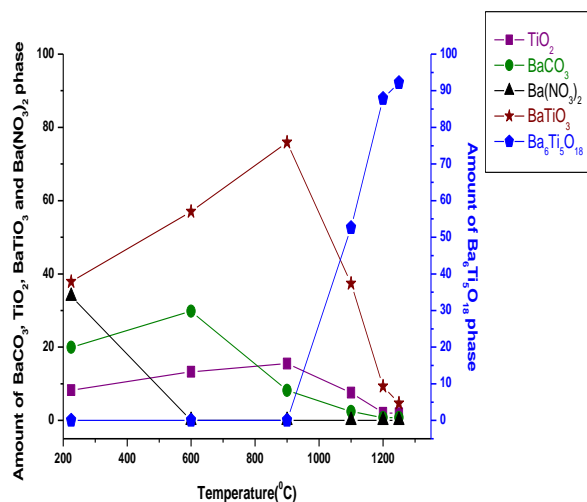
Figure 2. XRD pattern for powders calcined at various temperature

Table 1: Percentage amount of various phases at different temperatures

Percentage amount of various phases at different temperatures					
Temperature	Ba ₆ Ti ₅ O ₁₈	TiO ₂	BaCO ₃	Ba(NO ₃) ₂	BaTiO ₃
Uncalcined (225°C)	0	8.23	19.98	33.88	37.88
600°C	0	13.3	29.8	0	57
900°C	0	15.5	8.2	0	75.9
1100°C	52.6	7.59	2.43	0	37.35
1200°C	87.85	2.04	0.75	0	9.34
1250°C	92.21	1.94	0.78	0	4.67

Figure 3. Amount of impurities and $Ba_6Ti_5O_{18}$ phase vs temperature

It can be easily interpreted from the graphs (figure 3 & figure 4) and XRD peak patterns that the amounts of impurities i.e. $Ba(NO_3)_2$, $BaCO_3$, TiO_2 and $BaTiO_3$ decreases with temperature (figure 3 & figure 4) while that of required phase increases. The amount of intermediate phases $BaCO_3$, TiO_2 and $BaTiO_3$ increases up to temperature $900^\circ C$ and after that it decreases as these undergo metallurgical reaction to synthesize $Ba_6Ti_5O_{18}$ phase which appears at $1100^\circ C$ and increases up to $1250^\circ C$. The negligible amount of impurities at $1250^\circ C$ confirms the formation of pure, single phase & well crystalline $Ba_6Ti_5O_{18}$. The intensity for few planes showed decrease above $1200^\circ C$ (figure 3) while few planes show increase but overall intensity increases (figure 4). The decrease in intensity for few planes may be due to inter-planar shift of atoms with rise of temperature.

Figure 4. Percentage amount of impurities and $Ba_6Ti_5O_{18}$ phase

Lattice Parameters

The indexing of peaks and calculation of lattice parameters were done using analytical method for non-cubic crystals.

The lattice parameters ('a' & 'c') are calculated for $Ba_6Ti_5O_{18}$ calcined at $1100^\circ C$, $1200^\circ C$ and $1250^\circ C$. These values are shown in the table 2 below.

Table 2: Lattice parameters for $Ba_6Ti_5O_{18}$ at various calcination temperatures

Lattice parameters for $Ba_6Ti_5O_{18}$			
Temperature($^\circ C$)	a(\AA)	c(\AA)	c/a
1100	5.714579901	42.00559	7.35060047
1200	5.714538352	41.99268	7.34839412
1250	5.701862594	41.87503	7.34409617

The variation of lattice parameters ('a' & 'c') with temperature is shown in figure 5 and 6.

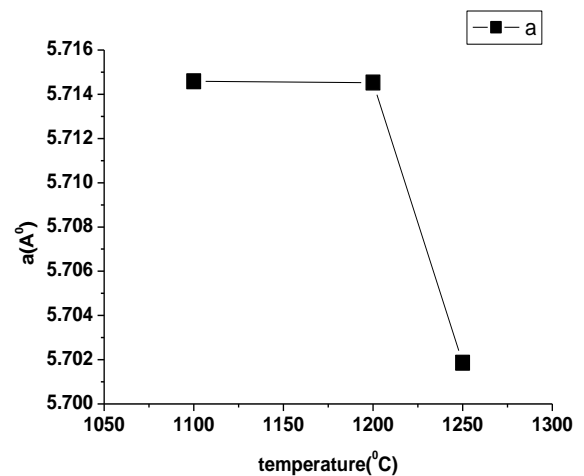


Figure 5. Variation of 'a' with temperature

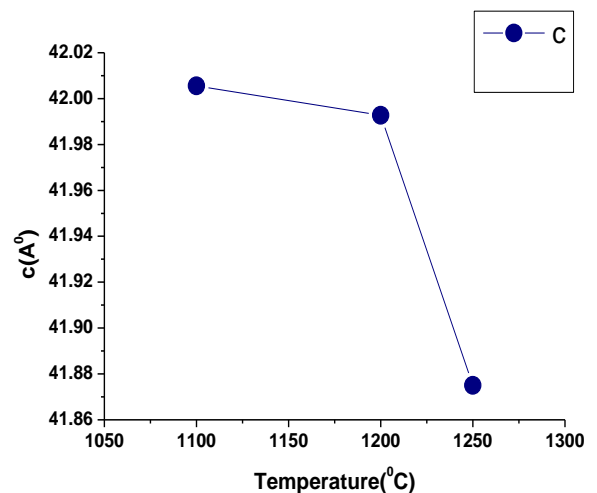


Figure 6. Variation of lattice parameter 'c' with temperature

As observed from above shown figures, the lattice parameters show decrease with rise in temperature. It can also be observed from XRD patterns that with increase in temperature, the peaks for $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ phase shift toward higher Θ value. This is due to decrease in lattice parameters.

Crystallite Size

The Sherrer's equation is used to calculate the crystallite size [11]. For this full width at half maximum (FWHM) was taken for peak with maximum intensity i.e. (110). The sherrer's equation is:

$$d = \frac{k\lambda}{\beta \cos \Theta} \quad \dots\dots ix$$

Here d is the crystallite size; k is constant, equal to 0.9, as the particles are assumed to be spherical, ' λ ' is the wavelength of x ray (1.5406 Å), β is the FWHM and Θ represents the angle of diffraction for the peak under consideration.

The crystallite sizes for various planes of $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ at different temperatures are calculated and are shown in the table (3) below:

$K=0.9$

$\lambda=1.5406 \text{ \AA}$

Table 3: Crystallite size (nm) for $\text{Ba}_6\text{Ti}_5\text{O}_{18}$

Crystallite size(nm) for $\text{Ba}_6\text{Ti}_5\text{O}_{18}$						
Temperature	(1 1 0)	(0 1 10)	(0 0 18)	(2 1 22)	(1 0 19)	(0 3 0)
1100	90.8	0	0	54.4	86.9	86.3
1200	124	68.7	24.2	99.8	141	122
1250	83.1	70.0	81.2	99.9	95.1	90.5

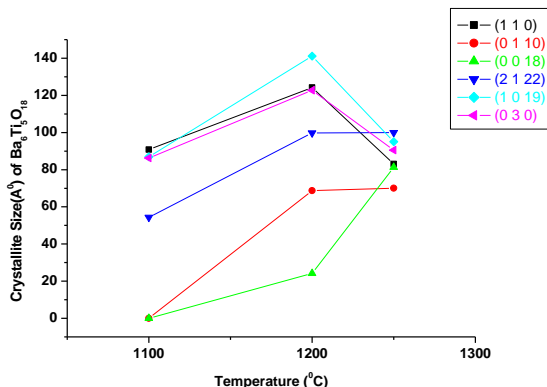


Figure 7. Variation of crystallite size with temperature

The variation of crystallite size with temperature is shown in figure 7. It is clear from figure that crystallite size for all the planes increases up to 1200°C and after that it increases for few planes whereas it showed decrease for some planes. The decrease in crystallite size for few planes may be due to inter-planar shift of atoms. This indicates that crystallization is ongoing up to temperature 1250°C.

IV. CONCLUSION

It can be concluded from above discussion that the impurities and intermediate phases diminish with increase of temperature and the required phase $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ is formed by metallurgical reaction of BaCO_3 , TiO_2 and BaTiO_3 but with deficiency of oxygen. A well defined XRD pattern of ceramics obtained after calcinations at 1250°C, having all the peaks indexed and with negligible amount of impurities indicates the formation of pure, single phase and well crystalline $\text{Ba}_6\text{Ti}_5\text{O}_{18}$. The values of lattice parameters ' a ' and ' c ' as determined from XRD, clearly showed that the synthesized materials have structure similar to the cation deficient perovskites with $n=6$. The crystallite size exhibited a critical dependence on calcinations temperature.

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