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— A₆B₃O₁₈ 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 (Ba₆Ti₅O₁₈) 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 \( \{\text{Ba(NO}_3\}_2\} \) (Sigma Aldrich) and Titanium Iso-propoxide \( \text{[Ti\{OCH(CH}_3\}_3\}_4\} \) (Sigma Aldrich) are used as starting chemicals. Nitric Acid (HNO₃) (Fisher Scientific), Citric Acid Monohydrate (\( \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O} \)) (CDH) and Ammonia (\( \text{NH}_3 \)) are used as solvents. The required amount of chemicals is calculated according to chemical equation given below:

\[
54\text{Ba(NO}_3\}_2 + 45\text{TiO(NO}_3\}_2 + 53\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O} \rightarrow \\
\text{Ba}_6\text{Ti}_5\text{O}_{18} + 99\text{N}_2 + 318\text{CO}_2 + 265\text{H}_2\text{O} \]

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 \( \text{[Ti\{OCH(CH}_3\}_3\}_4\} \) according to the following equation:

\[
\text{Ti(OCH}_3\}_3\text{H}_7\} + 3\text{H}_2\text{O} \rightarrow \text{TiO(OH)}_2 + 4\text{C}_3\text{H}_7\text{OH} \]

\[
\text{TiO(OH)}_2 + 2\text{HNO}_3 \rightarrow \text{TiO(NO}_3\}_2 + 2\text{H}_2\text{O} 
\]
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 TiO(OH)₂. The precipitates collected by filtration are dissolved in minimum amount of 1.4M nitric acid (HNO₃) under ice cold condition (4°C) with stirring. The available 15.55M Nitric acid is diluted using molarity equation (M₁V₁=M₂V₂) to 1.4 M. A clear solution of titanyl nitrate {TiO(NO₃)₂} is obtained.

**Synthesis of Citrate - Nitrate Solution**

An aqueous solution of Ba²⁺ cations is formed by dissolving weighed amount of Ba(NO₃)₂ in minimum amount of distilled water at 40°C by continuous stirring. The above obtained {TiO(NO₃)₂} solution and aqueous Ba²⁺ 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 NH₄OH 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 CuKα1 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 BaCO₃ 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 Ba(NO₃)₂ and its reaction with TiO₂ to form BaTiO₃ [8]. The following reaction represents the chemical change:

\[
\text{Ba(NO}_3\text{)}_2 + \text{TiO}_2 \rightarrow \text{BaTiO}_3 + 2\text{N}_2\text{O}_2 + 0.5\text{O}_2
\]

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 BaCO₃ and TiO₂ to form BaTiO₃ [9]. Similar trends are observed in XRD results, the decrease in amount of BaCO₃ and TiO₂ and increase in BaTiO₃ amount within temperature range of 600-900°C (table 1) suggests the following reaction:

\[
\text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2
\]

\[
\text{BaO} + \text{TiO}_2 \rightarrow \text{BaTiO}_3
\]
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 Ba₆Ti₅O₁₈-δ phase.

\[
\text{BaCO}_3 + 5\text{BaTiO}_3 \rightarrow \text{Ba}_6\text{Ti}_5\text{O}_{18-\delta} + \text{CO}_2 \quad \text{...vii}
\]

\[
2\text{BaCO}_3 + \text{TiO}_2 + 4\text{BaTiO}_3 \rightarrow \text{Ba}_6\text{Ti}_5\text{O}_{18-\delta} + 2\text{CO}_2 \quad \text{...viii}
\]

**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.

![Figure 2. XRD pattern for powders calcined at various temperature](image)

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.

| Temperature | Ba₆Ti₅O₁₈ | TiO₂ | BaC | BaN | BaTi |
|-------------|-----------|------|-----|-----|------|
| Uncalcined (225°C) | 0 | 8.23 | 19.9 | 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 |
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 Ba₆Ti₅O₁₈ calcined at 1100°C, 1200°C and 1250°C. These values are shown in the table 2 below.

| Temperature(°C) | a(Å)     | c(Å)     | c/a     |
|-----------------|----------|----------|---------|
| 1100            | 5.7145   | 0.0      | 7.344   |
| 1200            | 5.7145   | 0.0      | 7.348   |
| 1250            | 5.708    | 0.0      | 7.349   |

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

**Lattice Parameters**

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

**Figure 3. Amount of impurities and Ba₆Ti₅O₁₈ 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(NO₃)₂, BaCO₃, TiO₂, and BaTiO₃ decreases with temperature (figure 3 & figure 4) while that of required phase increases. The amount of intermediate phases BaCO₃, TiO₂ and BaTiO₃ increases up to temperature 900°C and after that it decreases as these undergo metallurgical reaction to synthesize Ba₆Ti₅O₁₈ phase which appears at 1100°C and increases up to 1250°C. The negligible amount of impurities at 1250°C confirms the formation of pure, single phase & well crystalline Ba₆Ti₅O₁₈. The intensity for few planes showed decrease above 1200°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 interplanar shift of atoms with rise of temperature.

**Figure 4. Percentage amount of impurities and Ba₆Ti₅O₁₈ phase**

| Temperature(°C) | a(Å)     | c(Å)     | c/a     |
|-----------------|----------|----------|---------|
| 1100            | 5.7145   | 0.0      | 7.344   |
| 1200            | 5.7145   | 0.0      | 7.348   |
| 1250            | 5.708    | 0.0      | 7.349   |

| Temperature(°C) | a(Å)     | c(Å)     | c/a     |
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| 1100            | 5.7145   | 0.0      | 7.344   |
| 1200            | 5.7145   | 0.0      | 7.348   |
| 1250            | 5.708    | 0.0      | 7.349   |

**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 Ba$_6$Ti$_5$O$_{18}$ phase shift toward higher $\Theta$ 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 serrer’s equation is:

$$d = \frac{k\lambda}{\beta \cos\Theta} \quad \ldots \ldots \text{(ix)}$$

Here $d$ is the crystallite size; $k$ is constant, equal to 0.9, as the particles are assumed to be spherical, $\lambda$ is the wavelength of x-ray (1.5406 Å), $\beta$ is the FWHM and $\Theta$ represents the angle of diffraction for the peak under consideration.

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

| Temperature (°C) | (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   |

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 Ba$_6$Ti$_5$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 Ba$_6$Ti$_5$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 pervoskites with $n=6$. The crystallite size exhibited a critical dependence on calcinations temperature.

**ACKNOWLEDGMENT**

One of the authors Ms. Karamveer Kaur highly acknowledges I.K. Gujral Punjab Technical University, Kapurthala, for its valuable inputs in course of this work. The authors are also very grateful to TEQIP, MHRD/World Bank Project for providing the necessary research facilities. Furthermore, authors appreciatively acknowledge IIC, I.I.T. Roorkee and SAIF Panjab University Chandigarh for support in characterization of the samples.

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