

Morphological Investigation, FTIR Analysis and Dielectric Measurement of Auto Ignition Synthesized Ba₆Ti₅O₁₈ Ceramics

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Abstract: Cation deficient perovskite Ba₆Ti₅O₁₈ is successfully synthesized by auto ignition method in this work. The morphological and elemental composition analysis of the obtained ceramics have been done using FESEM and EDS. FTIR analysis of the synthesized powders has been carried out to study the presence of various functional groups. The dielectric properties of the Ba₆Ti₅O₁₈ i.e. dielectric constant, quality factor and conductivity have been analyzed at room temperature with the help of Impedance Analyzer.

Index Terms - A₆B₅O₁₈, Cation Deficient Perovskites, Morphological Investigation, Auto Ignition, Dielectric Measurement.

1. INTRODUCTION

During the last decade, microwave communication technology (MCT) has developed at a rapid rate which consequently has enormously increased the demand of Dielectric resonators (DRs). DRs are generally very small in size, have very high temperature stability with low power losses. These are normally used to create, filter, and select frequencies in oscillators at microwave frequency range. The desirable characteristics of materials that are used to fabricate DRs are high dielectric constant, low dissipation factors and small temperature coefficients [1-2]. The ceramics belonging to simple and complex perovskite families have been widely employed for manufacturing DRs. Among the complex perovskites, cation deficient perovskites (A_nB_{n-1}O_{3n}) are the leading candidates to be used as DR materials owing to their best suited dielectric properties [3-4]. Despite the promising features, these cation deficient perovskites (A_nB_{n-1}O_{3n}) have not been investigated extensively [5-6]. These materials can be synthesized by almost any technique typically used to prepare advanced electroceramics but low temperature solution techniques have not been employed by any research group so far as per research reports available in literature.

Auto ignition which is a novel, energy efficient, easy, contamination free and clean low temperature solution technique has been used to synthesize Ba₆Ti₅O₁₈ ceramics in the present work. The structure, micro-structure, elemental composition, presence of various functional groups and dielectric properties of the synthesized materials have been thoroughly investigated using advanced characterization techniques.

2. EXPERIMENTAL WORK

2.1 Synthesis

Ba₆Ti₅O₁₈ ceramics are synthesized using Barium Nitrate, Titanium Iso-propoxide, Nitric Acid, Citric Acid and Ammonia as starting materials. The following chemical equation is used to synthesize Ba₆Ti₅O₁₈:



Firstly a clear solution of titanyl nitrate {TiO(NO₃)₂} is obtained from titanium isopropoxide [Ti{OCH(CH₃)₂}₄] under ice cold conditions. The aqueous solution of Ba²⁺ cations formed by dissolution of Ba(NO₃)₂ in distilled water is added to {TiO(NO₃)₂} solution under vigorous stirring to obtain clear solution. Citric acid is added to the above prepared solution under vigorous stirring to yield citrate - nitrate solution [7]. The pH of the solution is adjusted to ~6 using dilute ammonium hydroxide leading to formation of clear yellow transparent solution. The obtained solution is heated on a hot plate at ~90°C till the formation of gel. On raising the temperature, the gel swells up and gets ignited at around 240°C. The ignition occurs for approximately 5 seconds with evolution of large volume of gaseous products and results in formation of black voluminous powder with little carbon residue. The obtained powder was calcined at 600°C to eliminate carbon residue. For pellet formation few drops of PVA solution (3-5 wt%) are added to the obtained powders as binder. The pellets of mixture of binder and Ba₆Ti₅O₁₈ powders prepared using Hydraulic press are calcined at 600°C to expel the binder. The sintering of pellets is done at 1250°C for 2 hours at heating rate of 3°C/minute.

2.2 Characterization

X ray diffraction studies of sintered pellet are carried out using $\text{CuK}\alpha_1$ radiation with the help of Bruker D8 Advance diffractometer. SEM/EDS analysis of sintered pellet is done using FESEM QUANTA 200 FEG for morphological and elemental analysis. FTIR analysis of the powders obtained after calcination is carried out using FT-IR Spectrum 2 (Perkin Elmer). Dielectric properties are measured using impedance analyzer at SBSSTC, Ferozepur in frequency range 100Hz to 5MHz at room temperature.

3. RESULTS AND DISCUSSION

3.1 XRD Characterization

The XRD pattern for $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ pellet sintered at 1250°C using $\text{Cu-K}\alpha$ is shown in figure 1. The XRD pattern is almost similar to the XRD pattern of $\text{Ba}_6\text{Nb}_4\text{TiO}_{18}$ and is indexed accordingly [5, 8] on the basis of hexagonal symmetry of the structure. It can be depicted from the figure that all the XRD peaks are well defined; indexed and having negligible amount of impurities which confirms the formation of pure, single phase & well crystalline $\text{Ba}_6\text{Ti}_5\text{O}_{18}$. The lattice parameters ('a' & 'c') calculated for $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ sintered at 1250°C have values 5.67\AA and 41.62\AA respectively. The crystallite size is calculated for peak with maximum intensity i.e. (110) using Sherrer's equation [9] and it is found to be 37.5227 nm .

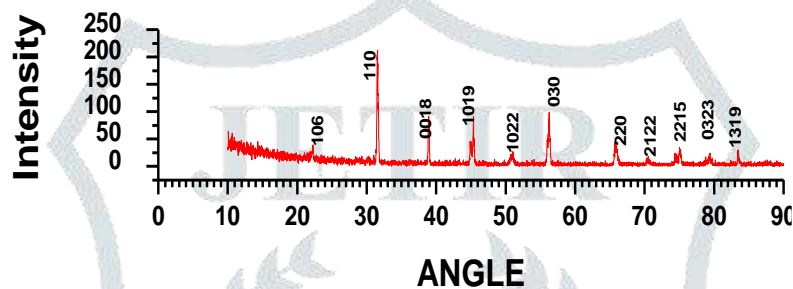


Figure1. XRD pattern of $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ sintered at 1250°C for 2 hours.

3.2 SEM Analysis

The experimental density of pellets is 3808.528 Kg/m^3 and theoretical value is 3877.279 Kg/m^3 thus density up to 98.22% has been achieved. The SEM images for $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ obtained after sintering at 1250°C for two hours are shown in figure 2. It can be observed from the FESEM images that $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ ceramics have homogeneous microstructure with clearly two different types i.e. smaller and larger grains. The grains have polyhedral shape with clear, well defined edges, corners, faces and grain boundaries. The ceramics have good sinterability with marginal inter-granular porosity. The grain size of ceramics ranges from 37.58 nm to 75.54 nm .

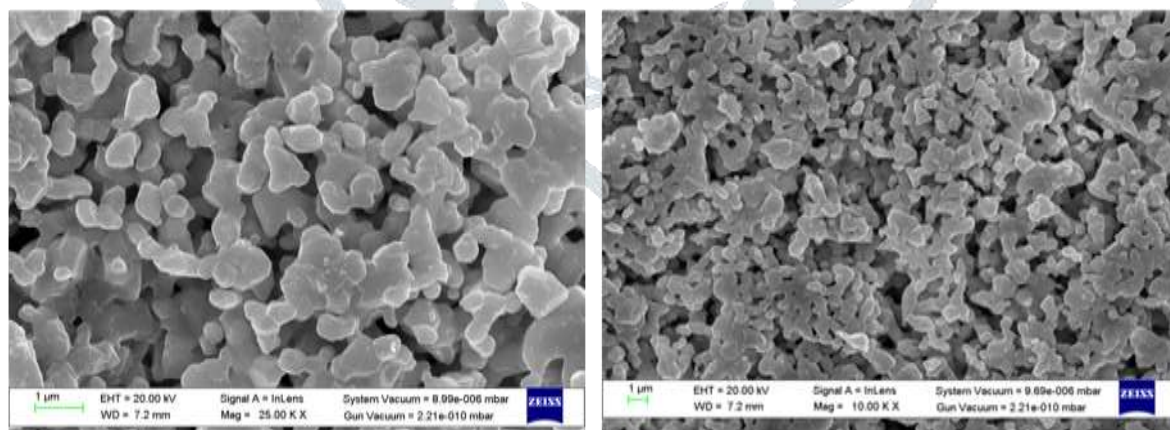


Figure 2. SEM image of $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ pellet sintered at 1250°C for 2 hours.

3.3 EDS Analysis

Figure 3. XRD peak pattern for powders calcined at various temperatures

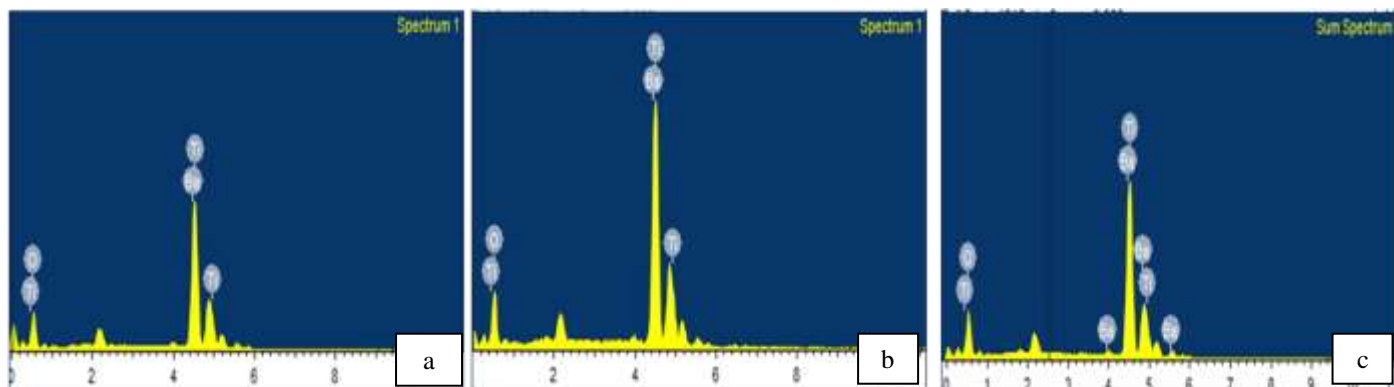


Figure 3. EDS spectrum of different grains (a, b) and sum spectrum of the two(c).

EDS spectra obtained for different grains (a,b) and the sum spectrum of the two spectras (c) are shown in figure 3. It can be observed from the above spectra that the elements titanium, barium and oxygen are present in $Ba_6Ti_5O_{18}$. There is no evidence for any other element indicating the purity of the phase. The weight composition and atomic composition of various elements for two different grains was calculated and is given in table 1.

Table 1: Weight and atomic composition of different elements

Weight and atomic composition of different elements			
Element	Weight% for one grain	Atomic% for one grain	Weight% for second grain
Oxygen	19.82	59.67	19.11
Titanium	18.66	18.76	20.65
Barium	61.52	21.57	60.24

The theoretical ratio of barium, titanium and oxygen atoms in $Ba_6Ti_5O_{18}$ is

$$Ba:Ti:O = 6:5:18 = 1 : 0.833 : 3$$

The ratio of these atoms as given by EDS analysis of different grains is given below:

$$Ba:Ti:O = 21.57:18.76:59.67 = 1:0.8697:2.766$$

$$Ba:Ti:O = 21.25:20.88:57.87 = 1:0.98 : 2.7232$$

It can be observed from above comparison that amount of barium and titanium match well with theoretical ratio.

3.4 FTIR Analysis

FTIR absorption spectrum for $Ba_6Ti_5O_{18}$ has been shown in the figure 4. In the spectrum of $Ba_6Ti_5O_{18}$, the absorption peaks at 3460.50cm^{-1} and 2823.21cm^{-1} have been assigned to stretching vibration of hydrogen bonded OH (hydroxyl) group of water (H_2O) absorbed on the surface. The absorption peak at 1428.37cm^{-1} corresponds to OH bond of water molecule [10-12]. The absorption peak at 858.25cm^{-1} may be due to stretching vibration mode of distorted TiO_6 octahedral [13]. The highly intense absorption peak at 540.07cm^{-1} corresponds to stretching vibration of TiO_6 octahedral connected to Barium ion [11, 14]. The absorption peak at 436.55cm^{-1} has been assigned to bending vibration of Ti-O bonds [15, 16].

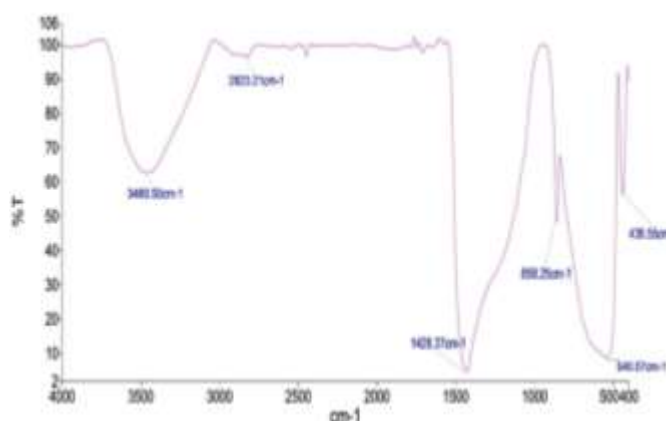


Figure 4. FTIR spectrum for $Ba_6Ti_5O_{18}$ ceramics

It is evident from figure 4 that FTIR spectra of the synthesized materials exhibit peaks corresponding to various vibration modes of water molecule. The presence of water can be due to absorption of moisture from the environment. The presence of highly intense peaks corresponding to stretching vibration of TiO_6 octahedral and Ti-O bending vibration confirms the presence of TiO_6 octahedral which is the main part of structure of cation deficient perovskites. The face sharing of these TiO_6 octahedral leads to formation of hexagonal closed pack structures.

The results are in agreement with the results reported in our last paper [17]. In that study it was concluded by thermal investigations and XRD analysis that metallurgical reaction of intermediate phases lead to formation of $\text{Ba}_6\text{Ti}_5\text{O}_{18-\delta}$. Here the FESEM/EDS and FTIR analysis also confirm the formation of $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ with required structure but with deficiency of oxygen.

3.5 Dielectric Measurement

The variation of dielectric constant with frequency is shown in figure 5. The dielectric constant values show decrease with increase of frequency. The conductivity values (Siemen m^{-1}) have been plotted against $\log(\text{frequency})$ (figure 6) which shows an increase with increase of frequency.

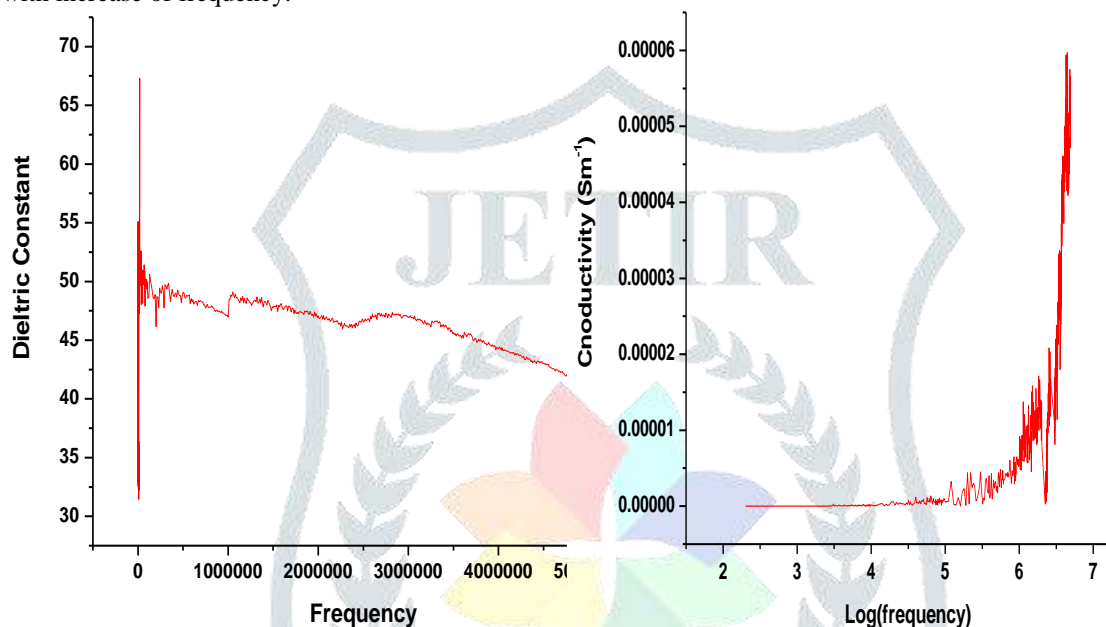


Figure 5 & 6. Variation of dielectric constant conductivity with frequency

The values of dielectric constant are 52.732, 46.97 and 39.93 at 1 KHz, 1 MHz and 5 MHz respectively. The maximum values of quality factor and conductivity are 12500 (2.15 MHz) and 5.66×10^{-5} (4.93MHz) respectively. The dielectric constant, quality factor and conductivity (S/m) values for cation deficient perovskites ($\text{A}_6\text{B}_5\text{O}_{18}$) has been reported to 26-44, 488-25000 and 8.65×10^{-8} to 4.07×10^{-6} respectively [5]. It can be observed from above discussion of microwave properties that $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ synthesized in this work possess reasonably good and comparable values of dielectric constant, quality factors and conductivity to that of the ceramics belonging to this family i. e. cation deficient perovskites ($\text{A}_6\text{B}_5\text{O}_{18}$) and thus a suitable candidate as dielectric material for DRs in MCT technology.

4. CONCLUSION

XRD pattern of $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ ceramics obtained after calcination at 1250°C is well defined, having all the peaks indexed and negligible amount of impurities indicating the formation of phase pure and well crystalline $\text{Ba}_6\text{Ti}_5\text{O}_{18}$. FESEM/EDS and FTIR studies indicate the formation of cation deficient perovskite $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ ceramics with required structure but with deficiency of oxygen. The dielectric constant values of $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ are determined to be 52.732, 46.97 and 39.93 at 1 KHz, 1 MHz and 5 MHz respectively. The maximum values of quality factor and conductivity are 12500 (2.15 MHz) and 5.66×10^{-5} (4.93MHz) respectively. Thus $\text{Ba}_6\text{Ti}_5\text{O}_{18}$ ceramics synthesized in this work qualify as a good candidate to be used as DRs in MCT applications because of owing high dielectric constants, high quality factors and good values of conductivity.

5. ACKNOWLEDGMENT

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