EFFECT OF DOPANT ON THE MULTISTAGE THERMAL DECOMPOSITION KINETICS OF BARIUM TITANYL OXALATE
4.1 Introduction

Solid-state kinetic data are of practical interest for the large and growing number of technologically important processes, a number of reports regarding the kinetics mechanism of these processes [1–4]. The chemical and catalytic reactivity of a solid depends on its method of preparation, so that structural and electronic imperfections may have important effects on the behaviour of a solid state reaction. Chemical processes involving the chemical transformation of solids play an important role in research technology, as sophisticated solids can be produced by thermal decomposition reaction of precursor materials. The decomposition atmosphere, crystal shape, size, presence of defects and various pre-treatments such as irradiation, mechanical grinding, doping, etc., play an important role in the decomposition, especially in determining the kinetics of oxalate decomposition [5].

Normally, defects mainly refer to point defects, including vacancies, interstitial, electrons, and holes, which can be created easily by doping. Doping is a highly complex subject, as there are quantities of paper to explore the doping properties and several mechanisms to achieve charge balance [6–7]. Taking the perovskite BaTiO$_3$, doping with higher valence cations, the charge may be compensated by ionic mechanism by the creation of vacancies on either of the cation sublattices or of oxygen interstitials [8]. Moreover, electronic compensation is possible in which the valence of Ti reduces from 4$^+$ to 3$^+$. Conversely, on doping BaTiO$_3$ with lower valence cations, the dopants may substitute onto either of the cation sites or in some cases onto a mixture of both sites depending on dopants size. The charge
compensation mechanism involves primarily the creation of oxygen vacancies as ionic compensation [9–10]. Also, sintering at high temperatures can create point defects due to the reduced atmosphere in which the samples would lose a small amount of oxygen and thus oxygen vacancies would be created. [11].

The thermal decomposition processes of metal titanyl oxalates are relatively complicated because of the reduction property of \( \text{C}_2\text{O}_4^{2-} \); the thermal decomposition of metal oxalates involves the cleavage of the C-C bond, since the products are CO and CO\(_2\) which contain only one carbon atom each. In many cases the C-C bond cleavage is the rate determining step [8]. The cleavage may be heterolytic to produce CO\(_2\) and CO\(_2\)\(^{2-}\) or homolytic to produce two CO\(_2\)\(^{-}\) anions [9]. Decomposition of metal oxalate, a chemical change believed to involve a small number of relatively simple steps occurring in and between the components of the crystalline reactant and the product, both of known lattice structures. In metal oxalate, the transfer of an electron from the \( \text{C}_2\text{O}_4^{2-} \) to the cation is the first stage of the decomposition which leads to the rupture of the C-C bond [12]. Pre-treatment such as irradiation, mechanical grinding, doping, etc., affect the rate and temperature of decomposition of oxalates [13-15]. The first two factors generally increase the rate and decrease the decomposition and dehydration temperatures. In some cases even the treatment itself brings about dehydration and decomposition [16]. Doping with metal ions or other pre-treatment of samples may have important effects on the reactivity of solids and might alter the kinetics of a reaction and help to clarify the reaction mechanism [17]. It has been reported that the effect of
doping depends on the nature of dopants [18]. Gallagher et al. reported that the thermal decomposition of substituted barium titanyl oxalates and its effect on the semiconducting properties of the doped materials [19].

The effects of several pre-treatments on the kinetics and mechanism of the thermal decomposition of Na$_2$C$_2$O$_4$ have been studied [20–21]. A comparative differential thermal analysis (DTA) study of some oxalates in N$_2$ and O$_2$ atmosphere has been reported [22]. The onset temperatures of dehydration and decomposition reactions are reported and the influence of atmosphere upon the temperatures and products of decomposition is discussed. The activation energies of solid state reactions could vary between relatively large limits depending on the nature and the method of preparing the starting materials [23-24]. Guha et al. studied barium titanate doped with Nb impurities, the chemically processed material with high dielectric constant have become an important for the electronic industry [25].

Kotlyarchuk et al. synthesized calcium doped nanocrystalline barium titanate powder by oxalate route. Addition of Ca on the surface of the samples of semi decomposed barium titanyl oxalate reduces lattice parameter for samples that related with replacement of barium by calcium which is confirmed by characterization of the semi decomposed barium titanyl oxalate and doped barium titanate carried out by specific surface area measurements, TEM and XRD [26]. Yangsheng Liu et al. synthesized chromium doped barium titanyl oxalate particles via a facile chemical co-precipitation method and
their morphologies, structures as well as dielectric and electro rheological properties were studied [27]. The synthesis, characterisation and dielectric properties of Ni-doped BaTiO$_3$ and the effect of magnetic field on the dielectric properties studied by Yogeswar Kumar et al. [28]. Upon doping A$^+$ or B$^-$ sites in barium titanyl oxalate or their oxides, the catalytic activity, ionic and electronic conductivity and flexible physical and chemical properties can be altered, that lend a hand for utilization in various applications [29]. Different cations with different sizes and charges can be hosted in the A$^+$ and B$^-$ sites of these metal oxalates or their oxides; thus many studies can be performed to utilize doped perovskites in various applications.

In the present study, the peculiarity of K$^+$ ions to intrude into the BTO lattice due to its small size made us to consider K$^+$ ions as a promising candidate to study the effect of doping on the thermal decomposition kinetics of BTO.

4.2 Experimental

4.2.1 Materials

AnalaR grade barium nitrate (Ba(NO$_3$)$_2$) (Merck, India; assay $\geq$ 99.9 %) and potassium titanyl oxalate (K$_2$TiO(C$_2$O$_4$)$_2$) (BHO Laboratory England; assay $\geq$ 99.9 %) were used in the present investigation.
4.2.2 Preparation of doped BTO

$K^+$ doped samples of BTO were prepared as per the following procedure; 10 g of BTO was dissolved in 230 mL of distilled water at boiling temperature in a 500 mL beaker. 10mL of a solution containing the desired quantity of $K^+$ was added to the hot solution so as to achieve a total volume of 240 mL. The solution containing the desired quantity of dopant was then cooled slowly to room temperature. The beaker containing the solution was covered using a clean uniformly perforated paper and kept in an air oven at a temperature of 323 K over a period of 6–7 days to allow the slow crystallization of doped sample by evaporation. The resulting crystals were removed; air dried and powdered in an agate mortar. The samples prepared were sieved through the mesh and fixed the particle size in the range 45–53 $\mu$m and kept in a vacuum dessiccatior. The doped samples were prepared at different concentrations, viz., $10^0$, $10^{-2}$ and $10^{-4}$ mol % and are named as BTO$_1$, BTO$_2$ and BTO$_3$ respectively and control (pure) compound as BTO.

4.2.3 Methods

The Fourier Transform Infrared (FT-IR) spectrum of the samples in KBr pellet was recorded using a JASCO FT-IR-4100 instrument. The sample was first compressed with KBr into pellet and analyzed as KBr disk from 400 to 4000 cm$^{-1}$. The instrument offers high sensitivity, maximum resolution (0.9 cm$^{-1}$) and high signal-to-noise ratio (22,000:1). The X-ray diffraction (XRD) measurements of the samples were taken on a RIGAKU MINI FLEX-600 X-ray
diffraction spectrophotometer using Cu K\textsubscript{\alpha} (1.5418 Å) radiation. FT-Raman spectroscopy of the samples were taken on MultiRAM spectrometer, range 3600 to 50 cm\textsuperscript{-1}, laser excitation 1064 nm (standard) or 785 nm (optional). It is equipped with Rayleigh filters, primary filters, room temperature ‘InGaAs’ detector and ‘Si’ avalanche detector. The Scanning Electron Microscopic (SEM) analyses of all the samples studied were performed with SEM-EDS combination using JEOL Model JSM - 6390LV, JEOL Model JED - 2300. The instrument offers a resolution of 3 nm (Acc V 30 KV, WD 8 mm, SEI) , 8 nm(Acc V 3.0 KV, WD 6 mm, SEI) and magnification of 5 × to 300, 000 × (Both in high and low vacuum mode). For the present investigation, the imaging techniques employed was secondary electrons (SE), backscattered electrons (BSE) and energy-dispersive X-ray analysis (EDXA). The transmission electron microscopy (TEM) analysis of the particles was achieved by using a JEOL 2100 field emission transmission electron microscope operated at 200 kV with a 0.18 nm resolution. The thermo gravimetric (TG) analysis of the samples was made on a T.A. thermal analyzer, model: TGA Q50 v20.2 Build 27 at a heating rate 10 K min\textsuperscript{-1}. The operational characteristics of the TG system are as follows: atmosphere: flowing air, at a flow rate of 60 mL min\textsuperscript{-1}; sample mass: 5 mg; and sample pan: silica. Duplicate runs were made under similar conditions and found that the data overlap with each other, indicating satisfactory reproducibility. The differential scanning calorimetric (DSC) measurements of the samples were taken on a Mettler ToledoDSC822e. The operational characteristics of the DSC system are as follows: atmosphere: flowing N\textsubscript{2} at a flow rate of 50 mL min\textsuperscript{-1}; sample mass: 5 mg; and sample holder: aluminium.
4.3 Results and Discussion

4.3.1 Sample Characterization

Fig. 4.1 The FT-IR spectra of sample BTO (a), BTO calcined at 628 K for 1 h (b), BTO calcined at 1023 K for 1 h (c), sample BTO$_3$ (d), BTO$_3$ calcined at 628 K for 1 h (e) and BTO$_3$ calcined at 1023 K for 1 h (f).

Fig. 4.1 represents the FT-IR spectra of pure BTO, BTO calcined at 628 and 1023 K for 1 h, sample BTO$_3$ and BTO$_3$ calcined at 628 and 1023 K for 1 h. For the sample BTO (Fig. 4.1a), the principal band (\( \sqcap_{\text{as}}, -\text{C}=\text{O} \)) occurs at 1686 cm\(^{-1}\). The FTIR spectrum of the sample calcined at 628 K (Fig. 4.1b) in vacuum for 1 h shows the appearance of an intense band at 2339 cm\(^{-1}\) which can be attributed to the asymmetric stretching frequency of free CO$_2$. The FTIR spectra of the sample calcined at 1023 K was presented in Fig. 4.1c, which represents the pure BaTiO$_3$. The FT-IR absorption spectrum of K$^+$ doped BTO crystalline particle (sample BTO$_3$) is shown in Fig. 4.1d. The broad band extending from 2800 to 3600 cm\(^{-1}\) is assigned to the symmetric and asymmetric stretching modes of the water molecules. The strong band appearing in the IR spectrum around 1615 cm\(^{-1}\) can be identified as the asymmetric stretching vibrations of CO groups of
the C$_2$O$_4^{2-}$ ions together with the bending mode of water. Fig. 4.1e displays the FTIR spectrum for the doped sample, BTO$_3$ calcined at 628K. The strong peak around 1316 cm$^{-1}$ is also assigned to the asymmetric stretching of CO groups. The strong bands around 495 and 796 cm$^{-1}$ are due to the combined effect of the in-plane deformation mode of OCO and MO bond and the weak one around 582 cm$^{-1}$ observed in the spectrum represent the wagging mode [30-32]. The FTIR spectroscopic analysis of crystals of Ba$_{1-x}$K$_x$TiO(C$_2$O$_4$)$_2$.4H$_2$O confirms the presence of functional groups associated with the oxalate ligands and the metal–oxygen bond. Fig. 4.1f represents the FT-IR spectrum of K$^+$ doped BaTiO$_3$. FTIR spectra displays two strong absorption peaks at 441 and 563 cm$^{-1}$ for control (pure) BTO (Fig. 4.1c); and 430 and 557 cm$^{-1}$ in doped sample (Fig. 4.1f). The former peaks (441 and 430 cm$^{-1}$) were assigned to Ti-O bending vibrations along the polar axis whereas the latter peaks (563 and 557 cm$^{-1}$) were assigned to Ti-O stretching vibrations. These peaks suggest that both doped and control sample had pure tetragonal phase [33, 34]. Further, the peaks at 868 cm$^{-1}$ in control and doped sample were assigned to stretching vibrations of metal-oxygen. The peaks displayed at 1724 and 3429 cm$^{-1}$, in control and doped sample were attributed to moisture absorption by samples. All other doped samples have same FT-IR characteristics of BTO$_3$. 
Powder XRD was used for the phase identification and the relative percentage of different phases of the prepared samples. The diffraction patterns were recorded over the angular range $2\theta$ from 20 to 80°. Using the XRD data of the samples, particle size and lattice parameters were estimated. Fig. 4.2a exhibits the XRD pattern of sample BTO and sample BTO calcined at 773 and 1023 K (Figs. 4.2b & 4.2c respectively). Before the calcination of the sample BTO, slight amorphous phase was observed due to the presence of carbon atoms.
and water in the mixture. After calcination at 773 K, the crystalline phase with cubic structure \((a = 4.0073 \, \text{Å})\) was appeared (Fig. 4.2b). The calcinations of sample BTO at 1023 K for 1h tend to produce the crystalline phase with tetragonal phase \((a = b = 3.999 \, \text{Å}, c = 4.0053 \, \text{Å})\) (Fig. 4.2c).

Figs. 4.2 d, g, j displays the XRD pattern of \(\text{K}^+\) doped BTO (sample BTO_1, BTO_2 & BTO_3) and its decomposed products at 773 and 1023 K (Figs. 4.2 e, f, h, i, k, & l respectively). It was observed that the formation of BaTiO_3 from BTO completes at about 773 K. The products of the samples BTO and doped samples calcined at 773 K consist of pure cubic BaTiO_3 (Figs. 4.2 b, e, h & k respectively). The products of the samples BTO and doped samples calcined at 1023 K (Figs. 4.2 c, f, i & l) indicate that the cubic form possibly transforms to tetragonal structure. This was revealed by the asymmetry introduced in the peaks at the \(2\theta\) values corresponding to 45.26, 50.90, 56.14, 74.89 and 79.5^0 respectively, which confirms the transformation of the cubic phase to the tetragonal phase [35].

Figs. 4.3 a & b shows the FT-Raman spectra of the sample BTO and BTO_3 at room temperature. Sample BTO exhibits the tetragonal structure belonging to the space group \(C_{4v}\), symmetry [36].
Fig. 4.3 The FT Raman spectra of sample BTO (a), BTO$_3$ (b) BTO calcined at 1023 K (c), BTO$_3$ calcined at 1023 K (d) for 1 h

The peak observed at 305 cm$^{-1}$ corresponds to the E (TO$_2$) phonon mode of tetragonal BTO. The A$_1$ (TO$_1$), A$_1$ (TO$_2$), A$_1$ (TO$_3$) and A$_1$ (LO$_3$) modes were observed at about 180, 270, 516 and 720 cm$^{-1}$ respectively [36]. The FT-Raman spectra obtained for the sample BTO$_3$ did not show any remarkable shift in wavelength. This can be attributed to the effective doping of K$^+$ ion into the lattice structure of BTO. It was also seen that all Raman modes are weaker and broader with change in the concentration. Figs. 4.3b & d show the FT-Raman spectra of decomposed product (calcined at 1023 K) of both the sample BTO and doped samples. For the sample BTO, the spectrum consists of peaks at 52, 174, 260, 306, 547 & 717 cm$^{-1}$ and for the doped
samples BTO₁, BTO₂ and BTO₃ the spectrum made up of peaks at 185, 308, 515, 728 cm⁻¹. This confirms that all are characteristic bands of the tetragonal phase BaTiO₃. The strong peaks at 174 and 547 cm⁻¹ were due to the TO₂ and TO₄ phonons respectively and the weak peak at 260 cm⁻¹ to the silent TO₃ mode. The appearance of a peak at 305 cm⁻¹ [A₁ (TO₂) mode] indicates the asymmetry within the TiO₆ octahedra of barium titanate phase with the particle size of 50 nm [37, 38]. According to Kaiser et al. [39] the weak shoulder below 300 cm⁻¹ belongs to an A₁ (TO) phonon mode. The peak at ~307 cm⁻¹ corresponds to the E (TO+LO) phonon mode of tetragonal BaTiO₃ [40] and the strong band at ~515 cm⁻¹ can be attributed to the A₁ (TO) phonon mode of the tetragonal phase [41, 42]. The weak peak at ~718 cm⁻¹ has been associated with the highest-frequency longitudinal optical mode (LO) of A₁ symmetry.

4.3.2 Thermal decomposition behaviour

Fig. 4.4 shows the result of thermo gravimetric analysis of the samples BTO, BTO₁, BTO₂ & BTO₃ which confirms the mass change in the various stages upon heating up to 1373 K (Table 4.1). TG curve shows the sequence of five steps with different mass losses involving dehydration and decarboxylation.
Fig. 4.4 The TG curves for the thermal decomposition of samples (m₀ = 5.3 mg) at 10 K min⁻¹; sample BTO, BTO₁ (10⁰ mol %), BTO₂ (10⁻² mol %) and sample BTO₃ (10⁻⁴ mol %)

Table 4.1 Mass loss data of samples

<table>
<thead>
<tr>
<th>Decomposition steps</th>
<th>Temperature range (K)</th>
<th>Mass loss (%)</th>
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<td></td>
<td></td>
<td>BTO</td>
<td>BTO₃</td>
<td>BTO₂</td>
<td>BTO₁</td>
<td></td>
</tr>
<tr>
<td>1</td>
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<td>17.62</td>
<td>16.21</td>
<td>16.94</td>
<td>17.02</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>463-523</td>
<td>02.79</td>
<td>03.18</td>
<td>03.25</td>
<td>03.75</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>523-753</td>
<td>20.52</td>
<td>18.93</td>
<td>19.34</td>
<td>19.94</td>
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</tr>
<tr>
<td>4</td>
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<td>05.96</td>
<td>06.13</td>
<td>06.77</td>
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</tr>
<tr>
<td>5</td>
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<td>06.99</td>
<td>07.68</td>
<td>07.06</td>
<td>07.92</td>
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<tr>
<td></td>
<td>308-1053</td>
<td>53.05</td>
<td>52.46</td>
<td>52.72</td>
<td>55.40</td>
<td></td>
</tr>
</tbody>
</table>
For the sample BTO, the first major mass loss, of about 17.62 % is within the temperature range from room temperature to 463 K, which may be attributed to the dehydration of BaTiO(C₂O₄)₂.4H₂O to BaTiO(C₂O₄). The second stage of mass loss of about 2.79 % appearing in the temperature range 463-523 K, can be attributed to the initial low temperature decomposition of BTO. The third major mass loss of about 20.52 % observed in the temperature range 523-753 K is attributed to the complete decomposition of the oxalate groups, resulting in the formation of a carbonate with CO₂ and CO:

\[ \text{Ba}_2 \text{Ti}_2 \text{O}_4 \left( \text{C}_2 \text{O}_4 \right)_3 \cdot \text{CO}_3 \rightarrow \text{Ba}_2 \text{Ti}_2 \text{O}_5 \text{CO}_3 \left( \text{CO}_2 \right) + 2\text{CO}_2 + 3\text{CO} \] (4.1)

The fourth mass loss of about 5.13 %, observed in the temperature range 753-823 K, is due to the evolution of entrapped CO₂, the final decomposition of carbonate takes place between 893-1023 K with a mass loss of about 6.9 %, which is due to the formation of BaTiO₃ [43, 44]. From Table 4.1 it is clear that the mass loss percentage of each step is increased with increase in the concentration of the dopant.
Fig. 4.5 The DSC curves for the thermal decomposition of sample BTO (m= 5.01 ± 0.01 mg) (a), sample BTO₁ (m₁= 5.01 ± 0.02 mg) (b), sample BTO₂ (m₂= 5.01 ± 0.01 mg) (c), sample BTO₃ (m₃= 5.01 ± 0.02 mg) (d) at different β in N₂ (50 mL min⁻¹).

DSC technique was used for the elucidation of kinetics of thermal decomposition of doped and undoped sample. Each sample of ~5 mg was weighed in an aluminium pan (6 mm in diameter and 2.5 mm in depth). A reference sample was made under the similar conditions. This method measures the difference in the amount of heat supplied to the examined sample and reference sample when both are subjected to the controlled changes of temperature. Figs. 4.5a, b, c & d respectively show the DSC curves for the thermal decomposition of BTO from RT–873 K and K⁺ doped BTO samples (sample BTO₁,
BTO₂ & BTO₃) in an atmosphere of N₂ (with a flow rate of 50 mL min⁻¹) at a heating rates of 2, 5, 7, and 10 K min⁻¹. These calorimetric investigations indicate that many endothermic transformations takes place in both doped and undoped samples. The DSC curves of both the samples were separated into five reaction process. The reaction below 500 K corresponds to the dehydration of four moles of water associated with BTO. Low temperature decomposition of sample BTO and doped samples occur within the temperature region 550-650 K, third stage of decomposition, i.e., complete decomposition of oxalate occurs within the temperature range of 523-753 K. The evolution of entrapped CO₂ occurs within the temperature range 753-873 K. Finally the formation of BaTiO₃ occurs in the temperature range 893-1023 K. It was noticed from the DSC curves that the curves are shifted towards right with increasing the value of β. At a β value of 2 K min⁻¹ the DSC curves for both the sample depicts the intermediate stages. The α-T curve (Fig. 4.6) shows the multistep thermal decomposition reaction for both pure and doped barium titanyl oxalates. The α-T curve for BTO (Fig. 4.6a) shows five steps while the α-T curves for BTO₁, BTO₂ and BTO₃ show six steps goes through more complex reaction pathways during the decomposition reaction. The physico-geometrical kinetic behavior and the complex multistage reaction mechanism under linear and non-isothermal condition were illustrated through kinetic analysis using the kinetic deconvolution method.
Fig. 4.6 $\alpha$–$T$ curve for the thermal decomposition of BTO (a), BTO$_1$ (b), BTO$_2$ (c) and BTO$_3$ (d) at different $\beta$ in N$_2$ (50 mL min$^{-1}$).

4.3.3 Kinetic behavior

The kinetic analysis of solid state decomposition is described by two functions, one of the reaction temperature and another of the extent of conversions i.e. $k(T)$ and $f(\alpha)$ respectively. The mathematical equations used to model kinetic reactions generally take the form of

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (4.2)$$

Where $t$ is the time and $T$ the temperature and $\alpha$ is the extent of conversion, which can be determined from the DSC as a fractional heat release. In general $k(T)$ is described by an Arrhenius equation:
\[ k(T) = Ae^{-\frac{E_a}{RT}} \]  
(4.3)

\[ \frac{d\alpha}{dt} = Ae^{(-\frac{E_a}{RT})} f(\alpha) \]  
(4.4)

Where \( \alpha, A, E_a, \) and \( R \) are the fractional reaction, Arrhenius pre-exponential factor, apparent activation energy, and the gas constant respectively. The kinetic model function \( f(\alpha) \) proposed is the physico-geometrical reaction mechanism of the reaction.

Kinetic analysis of thermal decomposition of BTO and doped BTO was executed with DSC data taken under linear non-isothermal heating program at different values of \( \beta: \) 2, 5, 7 and 10 K min\(^{-1}\). Heat flow (dQ/dt) by the reaction and overall heat of reaction obtained from the experimentally resolved DSC curve after subtracting the baseline. The overall reaction rate can be expressed as

\[ \frac{d\alpha}{dt} = \left( \frac{dQ}{dt} \right) \frac{1}{Q} \]  
(4.5)

DSC curves for the thermal decomposition of BTO and doped BTO are resulted through five component processes such as dehydration, formation of carbonate, decomposition of oxalate ligand, evolution of entrapped CO\(_2\) and formation of barium titanate. The direct application of the kinetic equation and the optimization of the composition of the reactant mixtures and the kinetic parameters of the respective reaction steps known as kinetic deconvolution, is a simple and rapid mathematical procedure of peak fitting for the deconvolution.
of partially overlapped thermal decomposition processes of solids. The deconvolution of the kinetic rate data determined via DSC into the initial and established reaction stages should enable the discussion of the kinetics of the reaction stages from the physico-geometrical reaction mechanism, the different reaction stages were approximately treated as kinetically independent. Thus, the different partially overlapping reaction stages were separated through the mathematical deconvolution in order to elicit the kinetic behaviour of the respective reaction. The overall process of the thermal decomposition is composed of \( n \) independent kinetic processes, is expressed by the summation of the respective kinetic processes \( i \) by considering their contribution \( c_i \), the following cumulative kinetic equation can be applied [45-52].

\[
\frac{d\alpha}{dt} = \sum_{i=1}^{n} c_i A_i \exp\left(\frac{-E_{a,i}}{RT}\right) f_i(\alpha_i)
\]  

(4.6)

\[
\sum_{i=1}^{n} c_i = 1 \quad \text{and} \quad \sum_{i=1}^{n} c_i \alpha_i = \alpha
\]

where \( n \) and \( c \) are the number of component steps and the contribution ratio of each reaction step to the overall process, respectively and the subscript \( i \) denotes each component reaction step. The contribution \( c_{\text{endo}} \) and \( c_{\text{exo}} \) can be defined as

\[
c_{\text{endo}} = \frac{Q_{\text{endo}}}{Q} < 0 \quad \text{and} \quad c_{\text{exo}} = \frac{Q_{\text{exo}}}{Q} > 0
\]  

(4.7)
where $Q_{\text{endo}}$ and $Q_{\text{exo}}$ are the heats of endothermic and exothermic process respectively.

The kinetics of each component process of the overall reaction can be characterized by optimizing all the kinetic parameters in equation (4.6) using nonlinear least-squares analysis. In order to predict the physico-geometrical reaction mechanism, empirical kinetic model functions such as phase-boundary-controlled model, $RO(n)$ [53] and the nucleation and growth-type model, $JMA(m)$ were employed [54, 55].

\[ RO(n): f(\alpha) = n(1 - \alpha)^{1/n} \]  
\[ JMA(m): f(\alpha) = m(1 - \alpha) \left[ -\ln(1 - \alpha) \right]^{1/m} \]

(4.8)  
(4.9)

where $n$ and $m$ are the kinetic exponents.

By allowing the non-integral values for the kinetic exponents in both equations (4.8) & (4.9), possible reaction mechanisms for each component process can be found. For both the samples, BTO and doped samples, $RO(n)$ and $JMA(m)$ functions with $n \approx 1$ can be utilized.

The Kissinger-Akahira-Sunose (KAS) [56] method (Eq. 4.10) is a possible method to determine the apparent activation energy for the overall reaction from the DSC curves recorded at different $\beta$:

\[ \ln \left[ \frac{\beta}{T^2} \right] = \ln \left[ \frac{AR}{g(\alpha)Ea} \right] - \frac{Ea}{RT} \]

(4.10)
The plots of $\ln[\beta/T^2]$ versus $T^{-1}$, $E_a$ and $A$ can be obtained from the slope and intercept respectively. The isoconversional plots indicate a linear relationship irrespective of $\alpha$ and this was observed for samples with different $\beta$ values (Fig. 4.7).

**Fig. 4.7** Typical linear least-squares plot of KAS method for the samples, BTO (a), BTO$_1$ (b), BTO$_2$ (c) and BTO$_3$ (d).
The variation of the apparent $E_a$ values as a function of $\alpha$ was not almost similar for the prepared samples (Fig. 4.8). For the sample BTO, although a small deviation of the slope of the KAS plot was observed during the initial stage, the $E_a$ value was found to decrease from 055.83 to 039.80 kJ/mol ($0.05 \leq \alpha \leq 0.6$) approximately. In the decomposition part of the reaction, the average values of $E_a$ was found approximately 119.58 ($0.61 \leq \alpha \leq 0.92$), 179.97($0.92 \leq \alpha \leq 0.944$) and 041.34 kJ/mol ($0.95 \leq \alpha \leq 0.99$) respectively. While the apparent $E_a$ values for the sample BTO$_1$ was 111.37 kJ/mol ($0.05 \leq \alpha \leq 0.4$) which decreases to 062.21 kJ/mol ($0.485 \leq \alpha \leq 0.56$), 158.01 ($0.58 \leq \alpha \leq 0.78$), 266.12 ($0.785 \leq \alpha \leq 0.83$), 350.31 ($0.835 \leq \alpha \leq 0.945$) and 075.66 kJ/mol respectively. For the sample BTO$_2$ it was 094.00 kJ/mol
(0.05 ≤ α ≤ 0.4) which was found decreased to 054.80 kJ/mol (0.485 ≤ 
α ≤ 0.56, 131.30 (0.58 ≤ α ≤ 0.78), 253.00 (0.785 ≤ α ≤ 0.83), 335.00 
(0.835 ≤ α ≤ 0.945) and 067.08 kJ/mol respectively. For the sample 
BTO₃ it was 085.63 kJ/mol (0.05 ≤ α ≤ 0.4) which was found 
decreased to 043.31 kJ/mol (0.485 ≤ α ≤ 0.56, 114.92 (0.58 ≤ α ≤ 0.78), 
236.07(0.785 ≤ α ≤ 0.83), 325.68 (0.835 ≤ α ≤ 0.945) and 053.98 
kJ/mol respectively. This indicates that the doped samples BTO₁, 
BTO₂ and BTO₃ which made large deviation to the slope of the KAS 
plot and the contribution of doping to the overall kinetics is a plausible 
explanation for this variation in Ŕₐ.

The initial values of the kinetic parameters were determined 
through a formal kinetic analysis of the kinetic data, first subjected to a 
statistical deconvolution [57, 58] using Weibull function. The number 
of component steps for both samples are obtained through kinetic 
deconvolution of DSC peaks. After setting all initial values of kinetic 
parameters (Table 4.2) for each reaction stage, a parameter 
optimization was performed to minimize F (Eq. 4.11), defined as the 
squared sum of the difference between the experimental kinetic data 
(da/dt)ₑxp versus time and calculated kinetic data (da/dt)ₜₑₘₜ versus time 
[59-62].

\[
F = \sum_{j=1}^{n} \left[ \left( \frac{d\alpha}{dt} \right)_{\text{exp},j} - \left( \frac{d\alpha}{dt} \right)_{\text{cal},j} \right]^2
\]

(4.11)

where \( n \) is the number of data points
Table 4.2 Initial kinetic parameters used for the thermal decomposition of samples under linear non-isothermal conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>i</th>
<th>$C_i$</th>
<th>$E_{ai}$(kJ/ mol)</th>
<th>$A_i$(s$^{-1}$)</th>
<th>$f_i(\alpha)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTO</td>
<td>1</td>
<td>0.560</td>
<td>055.83</td>
<td>$6.34 \times 10^{21}$</td>
<td>R (n);n=1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.113</td>
<td>039.80</td>
<td>$2.33 \times 10^{6}$</td>
<td>R (n);n=0.99</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.250</td>
<td>119.58</td>
<td>$1.78 \times 10^{16}$</td>
<td>R (n);n=1.1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.022</td>
<td>179.97</td>
<td>$1.15 \times 10^{25}$</td>
<td>JMA (m);m=1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.055</td>
<td>041.34</td>
<td>$5.71 \times 10^{14}$</td>
<td>JMA (m);m=1.2</td>
</tr>
<tr>
<td>BTO$_1$</td>
<td>1</td>
<td>0.350</td>
<td>111.37</td>
<td>$1.05 \times 10^{28}$</td>
<td>R (n);n=1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.090</td>
<td>062.21</td>
<td>$1.15 \times 10^{3}$</td>
<td>R (n);n=0.98</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.060</td>
<td>158.01</td>
<td>$1.50 \times 10^{4}$</td>
<td>R (n);n=1.01</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.240</td>
<td>266.12</td>
<td>$4.60 \times 10^{15}$</td>
<td>JMA (m);m=1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.050</td>
<td>350.31</td>
<td>$1.01 \times 10^{19}$</td>
<td>JMA (m);m=1.02</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.210</td>
<td>075.66</td>
<td>$2.49 \times 10^{15}$</td>
<td>JMA (m);m=0.9</td>
</tr>
<tr>
<td>BTO$_2$</td>
<td>1</td>
<td>0.400</td>
<td>094.00</td>
<td>$9.40 \times 10^{24}$</td>
<td>R (n);n=1.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.080</td>
<td>054.80</td>
<td>$6.60 \times 10^{3}$</td>
<td>R (n);n=0.99</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.078</td>
<td>131.30</td>
<td>$4.10 \times 10^{3}$</td>
<td>R (n);n=1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.230</td>
<td>253.00</td>
<td>$6.09 \times 10^{13}$</td>
<td>JMA (m);m=1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.052</td>
<td>335.00</td>
<td>$1.92 \times 10^{18}$</td>
<td>JMA (m);m=1.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.160</td>
<td>067.08</td>
<td>$7.40 \times 10^{21}$</td>
<td>JMA (m);m=0.9</td>
</tr>
<tr>
<td>BTO$_3$</td>
<td>1</td>
<td><strong>0.400</strong></td>
<td><strong>085.63</strong></td>
<td><strong>$1.85 \times 10^{28}$</strong></td>
<td>R (n);n=1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.085</td>
<td>043.31</td>
<td>$2.70 \times 10^{3}$</td>
<td>R (n);n=0.995</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.075</td>
<td>114.92</td>
<td>$1.70 \times 10^{3}$</td>
<td>R (n);n=1.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.220</td>
<td>236.07</td>
<td>$1.52 \times 10^{15}$</td>
<td>JMA (m);m=1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.060</td>
<td>325.68</td>
<td>$9.64 \times 10^{18}$</td>
<td>JMA (m);m=1.3</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.160</td>
<td>053.98</td>
<td>$5.30 \times 10^{20}$</td>
<td>JMA (m);m=0.98</td>
</tr>
</tbody>
</table>
Fig. 4.9 Typical results of kinetic deconvolution of the thermal decomposition of the samples BTO (a), BTO$_3$ (b), BTO$_2$ (c) and BTO$_1$ (d) under linear non-isothermal condition at $\beta = 5 \text{ K min}^{-1}$
Formation of barium titanate from barium titanyl oxalate via thermal decomposition reaction can be brought through the following scheme (Eq. 4.12-4.16):

\[
\begin{align*}
BaTiO(C_2O_4)_2 \cdot 4H_2O & \xrightarrow{393-453K} BaTiO(C_2O_4)_2 + 4H_2O \quad (4.12) \\
BaTiO(C_2O_4)_2 & \xrightarrow{453-523K} Ba_2Ti_2O_2(C_2O_4)_3 \cdot CO_3 + CO \quad (4.13) \\
Ba_2Ti_2O_2(C_2O_4)_3 \cdot CO_3 & \xrightarrow{523-723K} Ba_2Ti_2O_3CO_3(CO_2) + 2CO_2 + 3CO \quad (4.14) \\
Ba_2Ti_2O_3CO_3(CO_2) & \xrightarrow{723-873K} Ba_2Ti_2O_3CO_3 + CO_2 \quad (4.15) \\
Ba_2Ti_2O_3CO_3 & \xrightarrow{873-1023K} 2BaTiO_3 + CO_2 \quad (4.16)
\end{align*}
\]

Barium titanate is formed from BTO through the evolution of \(H_2O\), CO and \(CO_2\). Initial low temperature reaction is known as the dehydration and low temperature decomposition occurs and forming the carbonate intermediate. Succeeding steps involves the decomposition of carbonate intermediate with the evolution of CO and \(CO_2\).

Fig. 4.9 shows the result of the kinetic deconvolution analysis of the thermal decomposition of the samples BTO and doped samples BTO₁, BTO₂ and BTO₃ on the basis of equation (4.6) after establishing the initial values of the kinetic parameters through mathematical deconvolution and the subsequent formal kinetic analysis of each resolved reaction step [63]. Under linear non isothermal conditions, for the sample BTO the overall reaction was resolved into five steps (Fig.
4.9a) and that of doped samples into six overlapping reaction steps (Fig. 4.9b, c & d). The first low temperature reaction observed is considered as the dehydration reaction [64, 65]. Both undoped and doped samples take one independent step for the removal of water molecules, whereas in the high temperature reaction, both go through more complex pathways.

The average values of the kinetic parameters optimized for each reaction stage at different $\beta$ values are summarized in Table 4.3. For each resolved reaction steps, the value of $E_a$ calculated for each reaction step are nearly in agreement with the respective corresponding values estimated by the KAS plots for the overall reaction under non isothermal conditions [66]. The data from thermal analysis curves in the decomposition range $0.05<\alpha<1$ were used to determine the kinetic parameters of the process, the integral method of a linear form of modified Coats and Redfern equation

$$
\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E_a}{RT} 
$$

(4.17)

The $g(\alpha)$, the integral form of the conversion function which depends on the kinetic model of the decomposition reaction. If the correct form of $g(\alpha)$ is used, the plot of $\ln(g(\alpha)/T^2$ against $1/T$ should give a straight line. For the sample BTO, the straight line plot with suitable model and regression values are represented in Figs. 4.10, 4.11, 4.12 & 4.13 represents typical model fitting least-squares plots for the samples BTO$_1$, BTO$_2$ & BTO$_3$. 

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For BTO the required average values of $E_a$ for each resolved steps are 56.30 ± 0.01 ($i=1$), 40.1 ± 0.2 ($i=2$), 120.5 ± 0.1 ($i=3$), 180.21 ± 0.09 ($i=4$) and 40.92 ± 0.01 kJ/mol ($i=5$) respectively.

Fig. 4.10 Typical model fitting least-squares plot for the different steps of thermal decomposition of BTO
For the sample BTO₁, thermal decomposition occurs via more complex reaction strategies i.e., through six overlapping stages. The average values of energy needed for the respective stages are 111.37 ± 0.11 (i=1), 62.21 ± 0.04 (i=2), 158.01 ± 0.21 (i=3), 266.12 ± 0.08 (i=4), 350.31 ± 0.03 (i=5) and 76.66 ± 0.31 kJ/mol (i=6) respectively.

**Fig. 4.11** Typical model fitting least-squares plot for the different steps of BTO₁
For BTO$_2$, the average values of energy needed for the respective steps are 94.01 ± 0.02 ($i=1$), 54.80 ± 0.01 ($i=2$), 131.30 ± 0.02 ($i=3$), 253.01 ± 0.03 ($i=4$), 335.02 ± 0.03 ($i=5$) and 67.08 ± 0.02 kJ/mol ($i=6$) respectively.

**Fig. 4.12** Typical model fitting least-squares plot for the different steps of BTO$_2$

For BTO$_3$, the average values of energy needed for the respective steps are 85.71 ± 0.02 ($i=1$), 44.12 ± 0.05 ($i=2$), 115.23 ±
0.02 \((i=3)\), \(236.81 \pm 0.04 \((i=4)\), \(326.43 \pm 0.03 \((i=5)\) and \(55.14 \pm 0.44 \)kJ/mol \((i=6)\) respectively

Fig. 4.13 Typical model fitting least-squares plot for the different steps of BTO

The physico-geometrical behaviour of each sample was best described empirically by the \(RO\) \((n)\) and \(JMA\) \((m)\) kinetic model functions as shown in the Table 4.3.
Table 4.3 Average kinetic parameters optimized for each reaction step of the thermal decomposition of samples under linear non-isothermal conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>i</th>
<th>$C_i$</th>
<th>$E_{ai}$ (kJ mol$^{-1}$)</th>
<th>$A_i$ (s$^{-1}$)</th>
<th>$f_i(\alpha)$; RO(n)</th>
<th>JMA(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>0.57±0.04</td>
<td>56.30 ± 0.01</td>
<td>6.34±0.09 x 10$^{21}$</td>
<td>n=1.0± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.13±0.02</td>
<td>40.10 ± 0.20</td>
<td>2.33±0.05 x 10$^{6}$</td>
<td>n=0.99±0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.22±0.23</td>
<td>120.50 ± 0.10</td>
<td>1.78 ±0.04 x 10$^{16}$</td>
<td>n=1.1± 0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.02±0.12</td>
<td>180.21±0.09</td>
<td>1.15±0.08 x 10$^{25}$</td>
<td>m=1.00±0.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.06±0.01</td>
<td>40.92 ± 0.01</td>
<td>5.71 ±0.02 x 10$^{14}$</td>
<td>m=1.2±0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.35±0.02</td>
<td>111.37±0.11</td>
<td>1.05±0.21 x 10$^{28}$</td>
<td>n=1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.09±0.11</td>
<td>062.21±0.04</td>
<td>1.15±0.11 x 10$^{3}$</td>
<td>n=1.10±0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.06±0.07</td>
<td>158.01±0.21</td>
<td>1.50±0.09 x 10$^{4}$</td>
<td>n=0.99±0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.24±0.01</td>
<td>266.12±0.08</td>
<td>4.60±0.05 x 10$^{15}$</td>
<td>m=1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.05±0.04</td>
<td>350.31±0.05</td>
<td>1.01±0.01 x 10$^{19}$</td>
<td>m=0.98±0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.21±0.41</td>
<td>075.66±0.31</td>
<td>2.49±0.02 x 10$^{15}$</td>
<td>m=1.1±0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.40±0.21</td>
<td>094.01±0.02</td>
<td>9.40±0.31 x 10$^{24}$</td>
<td>n=0.98±0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.08±0.11</td>
<td>054.80±0.01</td>
<td>6.60±0.08 x 10$^{3}$</td>
<td>n=1.20±0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.08±0.05</td>
<td>131.30±0.02</td>
<td>4.10±0.41 x 10$^{3}$</td>
<td>n=1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.23±0.31</td>
<td>253.01±0.03</td>
<td>6.09±0.11 x 10$^{13}$</td>
<td>m=1.0±0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.05±0.09</td>
<td>335.02±0.01</td>
<td>1.92±0.08 x 10$^{18}$</td>
<td>m=0.99±0.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.16±0.01</td>
<td>075.66±0.04</td>
<td>7.40±0.02 x 10$^{21}$</td>
<td>m=1.2±0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.36±0.00</td>
<td>085.71±0.02</td>
<td>1.85±0.05 x 10$^{28}$</td>
<td>n=1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.08±0.02</td>
<td>044.12±0.05</td>
<td>2.71±0.01 x 10$^{5}$</td>
<td>n=0.99±0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.07±0.05</td>
<td>115.23±0.02</td>
<td>1.73±0.02 x 10$^{3}$</td>
<td>n=1.20±0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.23±0.07</td>
<td>236.81±0.04</td>
<td>1.52±0.03 x 10$^{15}$</td>
<td>m=1.0±0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.04±0.03</td>
<td>326.43±0.03</td>
<td>9.64±0.07 x 10$^{18}$</td>
<td>m=1.3±0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.22±0.92</td>
<td>055.14±0.44</td>
<td>5.31±0.04 x 10$^{20}$</td>
<td>m=0.98±0.42</td>
<td></td>
</tr>
</tbody>
</table>

It should also be noted that difference in the values of $A$ for the initial and final steps were larger for each of the samples indicating the larger lags of reaction time and temperature.
4.3.4 Morphological Analysis

Fig. 4.14 The SEM micrographs showing the surface microstructure of the sample BTO at 10 μm (a), 5 μm (b), 2 μm (c) and 1 μm (d).

Figs. 4.14, 4.15, 4.16 and 4.17 show the SEM images of the BTO and doped BTO, which confirm the bone shaped morphology of BTO having smooth surfaces. Figs. 4.18 & 4.19 exhibit the SEM images of BaTiO$_3$ which was formed by the multistage thermal decomposition of BTO. Bone like morphology of BTO was retained in the decomposed product. Doping with K$^+$ ion brought slight variation in the bone like morphology of BTO and decomposed product. Doping found to destroy the smoothness of the surfaces. Presence of pores and holes, created by the increased internal gaseous pressure during the process of thermal decomposition of doped BTO depicts the complexity of the reaction upon doping. These holes and pores act as diffusion channels for the removal of CO$_2$ and water.
Fig. 4.15 The SEM micrographs showing the surface microstructure of the sample BTO$_1$ at 10 μm (a), 5 μm (b), 2 μm (c) and 1 μm (d).

Fig. 4.16 The SEM micrographs showing the surface microstructure of the sample BTO$_2$ at 10 μm (a), 5 μm (b), 2 μm (c) and 1 μm (d).
Fig. 4.17 The SEM micrographs showing the surface microstructure of the sample BTO$_3$ at 10 μm (a), 5 μm (b), 2 μm (c) and 1μm (d).

Fig. 4.18 The SEM micrographs showing the surface microstructure of the sample BTO calcined at 1023 K for 1 h at 10 μm (a), 5 μm (b), 2 μm (c) and 1 μm (d).
Fig. 4.19 The SEM micrographs showing the surface microstructure of the sample BTO$_3$ calcined at 1023 K for 1 h; 10 μm (a), 5 μm (b), 2 μm (c) and 1 μm (d).

Figs. 4.20 & 4.21 show the TEM images of the BaTiO$_3$ and doped BaTiO$_3$ calcined at 1023 K for 1h. The estimated particle size of the both doped and undoped BT from the TEM image is in the range of 5-170 nm. The TEM image reveals that the particle exhibits as nano sphere having uniform grain size distribution and these nano spheres were underwent oriented growth to form the bone shaped morphology of barium titanate as shown in Figs. 4.18 and 4.19.

TEM image of K$^+$ doped BaTiO$_3$ shows a small depression in the nano spheres, which points out the complexity of formation of final product upon doping. Formation of cracks and holes in the surface of the product indicates the formation of surface product layer during the early stages of the reaction. As the temperature increases, there occurs change in the reaction condition at the reaction interface, leading to the
complexity of the process. The cracks and holes act as the channels for the diffusional removal of gaseous products such as $H_2O$, $CO_2$, $CO$, etc. Thus the synthesized $BaTiO_3$ nanoparticles can be used for the wide range of applications in the electronic as well as opto-electronic field.

**Fig. 4.20** The TEM images of the sample BTO calcined at 1023 K for 1 h at 100 nm (a), 50 nm (b) and 10 nm (c).

**Fig. 4.21** The TEM images of the sample $BTO_3$ calcined at 1023 K for 1 h at 100 nm (a), 20 nm (b) and 5 nm (c)

Figs. 4.22a & b displays the SEAD pattern of BTO and $BTO_3$. These images confirm the nano semi crystalline nature of the synthesized barium titanate. Doping does not affect the semi crystalline properties of the synthesised $BaTiO_3$. 

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4.4 Conclusion

The effect of $K^+$ ion doping on the thermal decomposition kinetics of the BTO was investigated using kinetic deconvolution method. The kinetic parameters and reaction model were revealed under linear non isothermal condition using the DSC technique in $N_2$ atmosphere. Both the samples went through multistage reaction pathways. BTO takes five steps for the formation of barium titanate, whereas $K^+$ doped BTO samples go through six steps. Doping of $K^+$ increases the complexity as well as activation energy of the decomposition reaction and hence enhances the thermal stability of BTO. The physico-geometrical reaction behaviours of both the samples were best described empirically by $RO \ (n)$ and $JMA \ (m)$ models. Morphological analysis disclosed that the synthesized nano spheres undergo oriented crystal growth forming the micro dimensional bone shaped $\text{BaTiO}_3$. The estimated size of the spheres is in the range 5-170 nm. The SAED pattern of both samples of doped and undoped BTO exposed the nano semi crystalline nature. The XRD pattern reveals the transformation of cubic phase of barium titanate in to tetragonal structure with increase in temperature.
4.5 References


Ornran ZA, Mousa MA, Abdel-Fattah AA. Kinetic analysis of thermal decomposition reactions Part IV: Kinetics of formation of


33. Deb N. Some heterobimetallic oxalate coordination precursors of lanthanum(III) of the type M₃[La(C₂O₄)₃(H₂O)m]₂.nH₂O (M=Mn(II), Co(II), Ni(II) and Cu(II)) an investigation on the solidstatepyrolytic decomposition. J. Therm. Anal. Calorim. 2012;107:561–71.


35. Hammer M, Monty C, Endriss A, Hoffmann MJ. Correlation between surface texture and chemical composition in undoped, hard


47 Koga N, Kasahara D, Kimura T. Aragonite crystal growth and solid-state aragonite-calcite transformation: a physico-geometrical


