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Kinetic modelling of formation of K^+ doped $BaTiO_3$ bones from barium titanyl oxalate *via* multi stage thermal decomposition

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ABSTRACT

The thermal decomposition kinetics of formation of bone shaped $BaTiO_3$ from barium titanyl oxalate (BTO) and the effect of doping of potassium titanyl oxalate (1×10^{-4} mol%) with BTO upon the reaction pathway and the mechanism were studied at four different heating rates: 2, 5, 7 and 10 K min^{-1} under linear non-isothermal heating program using DSC technique in an inert atmosphere (N_2). Kinetic deconvolution procedure was applied to perform the overall kinetics of the formation of doped and undoped $BaTiO_3$. The prepared samples and their decomposed products were identified and characterized by means of FT-IR, FT-Raman, XRD, SEM, TEM and SAED pattern. Activation energy needed for each resolved stage of the thermal decomposition was calculated by the KAS method in the temperature range 303–873 K. XRD pattern at different stages of thermal decomposition indicates that cubic $BaTiO_3$ is transformed into tetragonal phase. The introduction of K^+ −ion into the lattice of BTO enhances the thermal stability of BTO and shows a high energy reaction pathway revealing the complex mechanism.

1. Introduction

Nano-materials which form the most challenging areas of the scientific and technological research are still being explored because of their tremendous possibilities in generating novel shapes, structures and unusual phenomena. Currently, researchers in chemistry, physics, biochemistry, and engineering are exploring a new class of nano sized materials for the applications in electronics, optics, catalysis and for solar light conversion, etc [1]. The chemical and catalytic reactivity of a solid state material depends on its method of preparation and the structural and electronic imperfections. 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 precursory solids. The processes of forming titanates, in crystalline mixtures have become very important in the ceramic industry and other technologies. The "*first ferroelectric ceramic*", barium titanate (BT) is a good candidate for various applications due to its excellent dielectric, ferroelectric and piezoelectric properties [2]. It is the one member of perovskite family having the general formula ABO_3. The crystalline size of BT determines the final crystal structure of $BaTiO_3$. It has rhombohedral, orthorhombic, cubic and tetragonal phases. The cubic structures are paraelectric while rhombohedral, orthorhombic and tetragonal phases are ferroelectric in nature [2]. Paraelectric cubic phase can be transformed into ferroelectric tetragonal phase at its Curie temperature (around 393 K). The ferroelectric and dielectric properties of BT are correlated with its size. Nano-sized BT possessed higher activity, potential for device miniaturization and enhanced dielectric properties. It is an important raw material for electronic devices such as multi layered ceramic capacitors and nonlinear resistors [3]. It finds vast applications in transducers, actuators, capacitors and memories [2]. Takin et al. [4] explored the applications of barium titanate core–gold shell nanoparticles for hyperthermia treatment against cancer cells. They proposed that this nano shells have suitable cytocompatibility at concentrations up to 50ηg/L. Recently, it has been extensively studied particularly for its application as a capacitor material in down- sized portable machines and dynamic random access memory (DRAM) devices. $BaTiO_3$-based ceramics have found their application in the design of microwave tunable devices [5,6].

Many methods such as so-gel [7], hydrothermal [8], combustion [9,10], crystal growth [11], thermal decomposition [12] and other different chemical routes [13] were used for the BT synthesis. Among these, thermal decomposition using oxalate precursor has been widely used due to its simplicity and the precise

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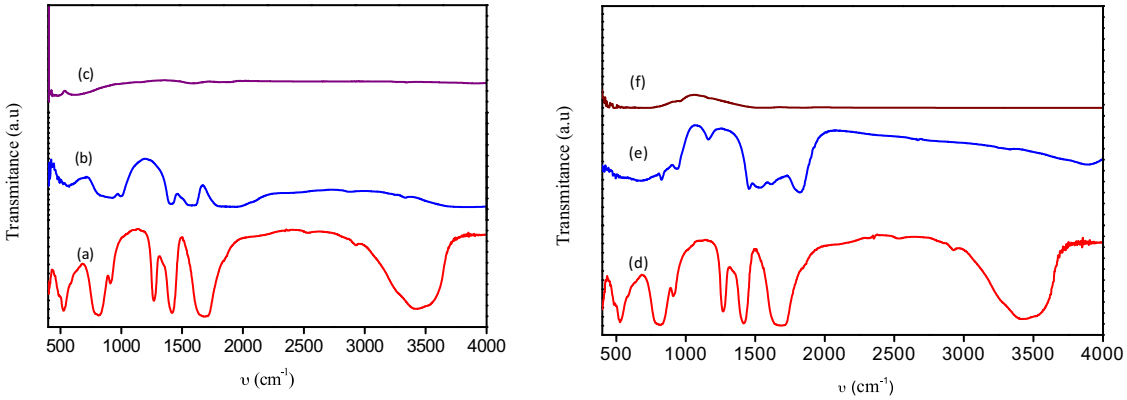

Fig. 1. The FT-IR spectra of sample A_1 (a), A_1 calcined at 628 K for 1 h (b), A_1 calcined at 1023 K for 1 h (c), sample A_2 (d), A_2 calcined at 628 K for 1 h (e) and A_2 calcined at 1023 K for 1 h (f).

stoichiometry of the produced BT phase. Thermal decomposition of alkaline earth metal titanyl oxalate yield nano titanate particles. The decomposition proceeded through five steps and was not affected much by surrounding gaseous atmosphere. The first step is the dehydration of the tetra hydrate which was followed by low temperature decomposition of the oxalate groups. In the temperature range of 393–453 K, carbon monoxide is evolved with the formation of a transient intermediate substance containing both carbonate and oxalate groups. The oxalate groups were completely destroyed in the range of 453–523 K, resulting in the formation of a carbonate which retains free CO_2 in the matrix. The trapped CO_2 was released in the temperature range of 523–723 K. The final decomposition of carbonate takes place between 873 and 1023 K and yield barium titanate. Gopalakrishnamurthy et al. [14] investigated the evolution of water and CO_2 vapours during the thermal decomposition of BTO and the effect of doping and mixing conditions of the reactant molecules on the reactivity of the system. Doping with the metal ions and other pre-treatments of samples has important effects on the structural, chemical and physical properties of the solids, which might alter the kinetics of the reaction mechanism. 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 [15–17]. Ni^{2+} and Fe^{2+} doped $BaTiO_3$ showed enhanced dielectric permittivity than undoped $BaTiO_3$ [18]. This can be ascribed due to the change in the lattice parameters of the specimen.

There are several studies concerning the determination of kinetic parameters and possible physicochemical or physico-geometrical reaction models through the formal kinetic analysis of thermal decomposition process [19–21]. The kinetics of thermal decomposition of solids are restrained by interactions between concurrent and consecutive processes related with different physicochemical events, including surface nucleation, destruction of reactant crystals, crystal growth of the product solid and diffusional removal of gaseous product[19]. The knowledge of understanding the possible physicochemical events occurring during thermal decomposition of BTO is essential for the tuning of $BaTiO_3$ nanoparticle.

This study focus on the elucidation of the kinetics and mechanism of thermal decomposition of barium titanyl oxalates, and K^+ – doped barium titanyl oxalates by the DSC technique flowing N_2 atmosphere. The kinetic deconvolution procedure was used to yield the dependency of the E_a on the extent of conversion and the most probable kinetic model.

2. Experimental

2.1. Materials

AnalaR grade barium nitrate ($Ba(NO_3)_2$) (Merck, India; assay $\geq$ 99.9%) and potassium titanyl oxalate ($K_2TiO(C_2O_4)_2$) (BHO Laboratory England; assay $\geq$ 99.9%) were used in the present investigation.

2.2. Preparation of doped and undoped BTO

Sample A_1, barium titanyl oxalate (BTO) was synthesized by the precipitation reaction of equi molar aqueous solution of barium

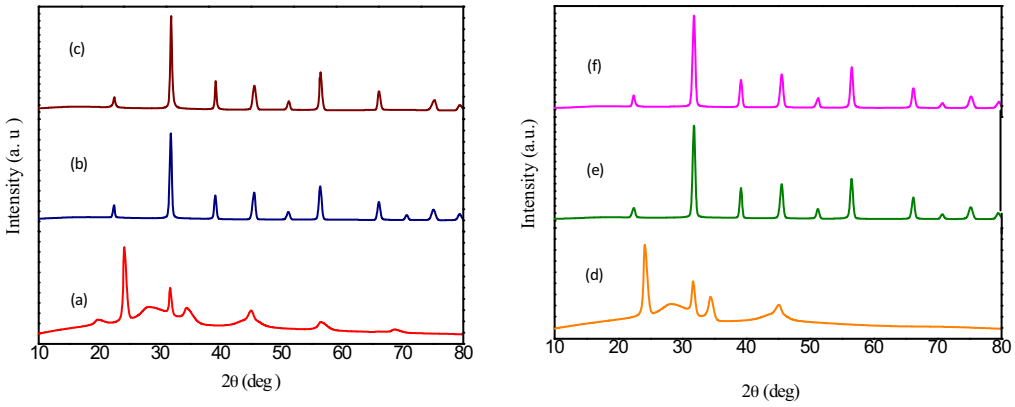

Fig. 2. The XRD pattern of sample A_1 (a), A_1 calcined at 773 K (b), A_1 calcined at 1023 K for 1 h (c), sample A_2 (d), A_2 calcined at 773 K (e) and A_2 calcined at 1023 K for 1 h (f).