

Structural, Optical and Ferroelectric Properties of BaTiO₃ Sintered at Different Temperatures

Anurag Gaur, Neha Sharma

Abstract—In this work, we have synthesized BaTiO₃ via sol gel method by sintering at different temperatures (600, 700, 800, 900, 1000°C) and studied their structural, optical and ferroelectric properties through X-ray diffraction (XRD), UV-Vis spectrophotometer and PE Loop Tracer. X-ray diffraction patterns of barium titanate samples show that the peaks of the diffractogram are successfully indexed with the tetragonal and cubic structure of BaTiO₃. The Optical band gap calculated through UV Visible spectrophotometer varies from 4.37 to 3.80 eV for the samples sintered at 600 to 1000°C, respectively. The particle size calculated through transmission electron microscopy varies from 20 to 40 nm for the samples sintered at 600 to 1000°C, respectively. Moreover, it has been observed that the ferroelectricity increases as we increase the sintering temperature.

Keywords—Nanostructures, Ferroelectricity, Sol-gel method.

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I. INTRODUCTION

THE barium titanate (BTO) compound is the most studied perovskite system and is being considered as a potential candidate in ceramic and electronic industry [1]. It finds application as a technologically important material, e.g. in high-capacitance capacitors, including multilayer ceramic capacitor, piezoelectric sensors, positive temperature coefficient devices, ferroelectric random access memories [2], printed circuit boards [3] and electro-optical devices [4]. Its optical properties have attracted considerable attention and many experimental and theoretical reports have been published about the luminescence properties of BaTiO₃ nanometer sized powder, bulk and thin films [5]-[7]. All these applications require BTO particles with good crystallinity, high purity, and narrow particle size distribution to fabricate reliable microelectronic devices. Barium titanate (BaTiO₃) is also a common dielectric material in multilayer ceramic capacitors (MLCCs) due to its high dielectric constant.

Recently, lead-free perovskite barium titanate (BaTiO₃) has attracted renewed interest because of its environmentally friendly feature compared with the currently used Pb(Zr_{1-x}Ti_x)O₃-based lead-containing dielectric, piezo- and ferroelectric materials [8]-[10]. As the scale of electronic components continues to be down-sized, the need for BaTiO₃-based materials of nanometer size has become more and more urgent. However, one of the biggest issues in the utilization of the dielectric properties of nanosize BaTiO₃ is the “size

effect,” i.e., the size-dependence of the dielectric and ferroelectric properties, which need to be understood both for fundamental research and for practical applications [11]-[18]. According to the theoretical calculation by Zhong et al. [19] the ferroelectricity of BaTiO₃ particles decreases significantly with decreasing grain size, and disappears when the grain size drops down to about 44 nm. More recent studies by Wada et al. [20], [21] show that the dielectric permittivity of BaTiO₃ nanopowders does not decrease with particle size monotonically, but exhibits a maximum at about 68 nm.

A large number of reports regarding the fabrication and size control aspects of micro and nanoscale BTO are available in the literature. The synthesis routes include hydrothermal and microwave-assisted hydrothermal methods [22]-[24], co-precipitation-cum-micro emulsion methods [25], [26], sol-gel processing [27], [28], spray pyrolysis [29] and polymeric precursor method [30]. These methods have their own advantages and shortcomings. It still remains a challenge for the scientific community to obtain quality BT particles while avoiding unwanted by-products. In all these methods, sol-gel route is one of the most feasible methods to fabricate monodispersed BT powders with particle size below 100nm [31].

In the present work, we have synthesized the BaTiO₃ nanoparticles via sol-gel method by sintering at different temperatures (600,700, 800, 900, 1000°C) and studied their structural, optical and ferroelectric properties.

II. EXPERIMENTAL

Barium acetate (2.5542mg) and Titanium isopropoxide (2.8421ml) were dissolved in deionized water (100ml) and then mixed under continuous stirring at room temperature (25°C) for 2 hours. In order to avoid precipitation, small amounts of acetic acid and acetyl acetone were added drop wise in to the solution. The solution was relatively stable and became a gel in 3 days. The BaTiO₃ gel was dried at 100°C for 24 hours and then sintered at different temperatures (600-1000°C) for 24 hours to obtain the final phase of BaTiO₃.

The crystallographic phases of the reactant species and various phases of the as-received BTO product were studied by X-ray diffraction (XRD) measurements using a X-ray diffractometer (Rigaku Mini Flex 200, Cu K α , $\lambda= 1.54\text{\AA}$) with a data scanning rate of 2° per minutes in the range of 2 θ from 20 to 80°. The microstructure of the substrate was investigated by using transmission electron microscope (TEM). The optical properties of the nanoparticles were studied by UV-Visible Spectrophotometer (Camspec M550 Double Beam Scanning). The ferroelectric properties of BaTiO₃ samples were

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investigated by using P-E loop tracer (Marine India automatic P-E loop tracer system).

III. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern of BaTiO₃ powder sintered at different temperatures (600, 700, 800, 900, 1000°C). The peaks of the diffractogram are successfully indexed with the tetragonal structure of BaTiO₃. The average crystallite size of BTO samples is being estimated by using

Scherrer formula, $D \approx K \lambda / (\beta - b) \cos \theta$ where, $k \sim 0.89$ is the shape factor, λ is wavelength of x-rays, β is full width at half maximum (FWHM), b is the instrumental broadening and θ is Bragg angle [32]. The crystallite size, calculated through this formula, corresponding to (100) peak, is found to be ~ 22 , ~ 23 , ~ 25 , ~ 26 , and ~ 27 nm for BTO samples sintered at 600- 1000 °C respectively.

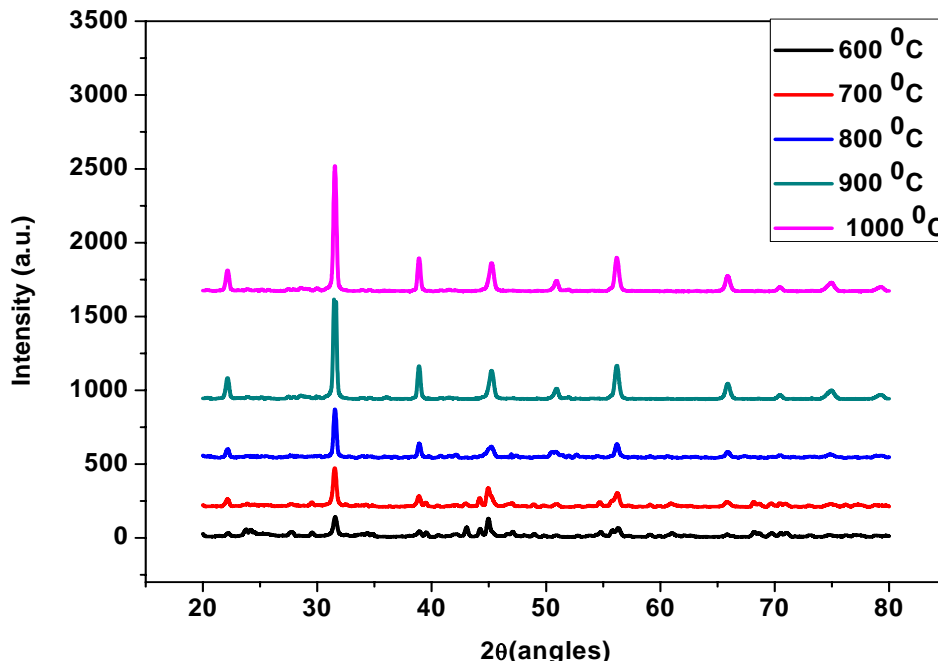


Fig. 1 XRD patterns of BaTiO₃ sintered at 600-1000 °C

The optical band gap of BTO nanoparticles was calculated via the direct allowed inter-band transition between valence and conduction bands using Tauc's Law [33] $(\alpha h\nu)^2 = A(h\nu - E_g)$ where A is a constant, α is the absorption coefficient ($\alpha = 4\pi k/\lambda$; k is the absorption index or absorbance, λ is the wavelength in nm), $h\nu$ is the photon energy and E_g is the optical band gap. As BaTiO₃ was a direct band gap semiconductor [34]-[37], its band gap E_g can be estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portion of the plot to $(\alpha h\nu)^2 = 0$ (shown in Fig. 2). We observed that have a band gap decreases from 4.37 to 3.80 eV BaTiO₃ powder sintered at different temperatures (600-1000°C), respectively.

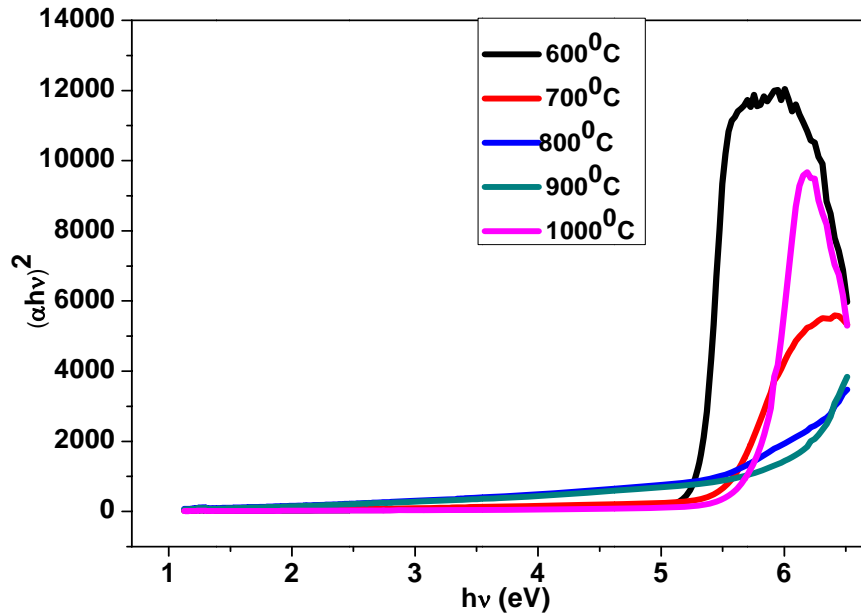


Fig. 2 $(\alpha h\nu)^2$ versus $h\nu$ curves of BaTiO_3 sintered at 600 - 1000 $^\circ\text{C}$

The structural morphology and size of the as synthesized BTO nanostructures were investigated by using transmission electron microscopy (TEM). Figs. 3(a)-(b) shows the TEM images of BTO nanostructures sintered at 600, 1000 $^\circ\text{C}$, respectively. It can be seen that the powder particles are submicrometer aggregates of nanocrystallites

20–30nm in size for the sample sintered at 600 $^\circ\text{C}$ while after sintering at 1000 $^\circ\text{C}$ the particles are agglomerated and had average particle size greater than 30nm. It is clear from these images that the particle size increases with increase in the sintering temperature.

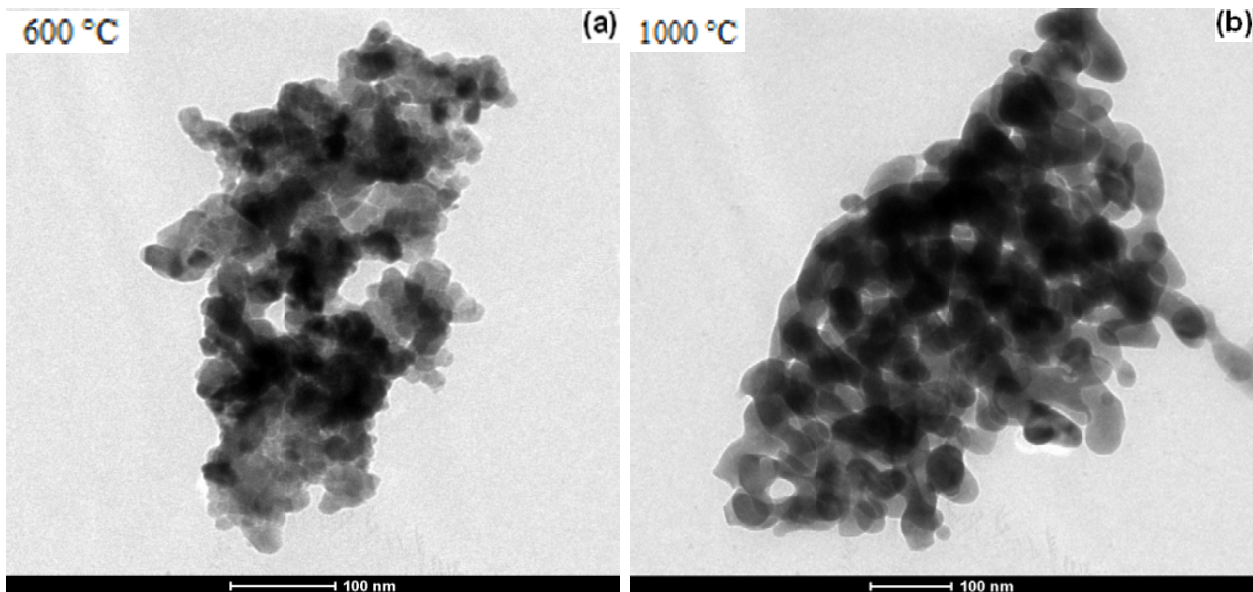


Fig. 3 (a)-(b) TEM image of BaTiO_3 sintered at 600 and 1000 $^\circ\text{C}$

P–E hysteresis loop was one of the most important properties for ferroelectric materials. The ferroelectric (P - E) hysteresis loops behavior of BaTiO_3 samples sintered at 600

and 1000 $^\circ\text{C}$ are shown in Figs. 4 (a)-(b). It can be observed that the sample sintered at 600 $^\circ\text{C}$ shows distorted ferroelectric loop which enhance for sample sintered at 1000 $^\circ\text{C}$.

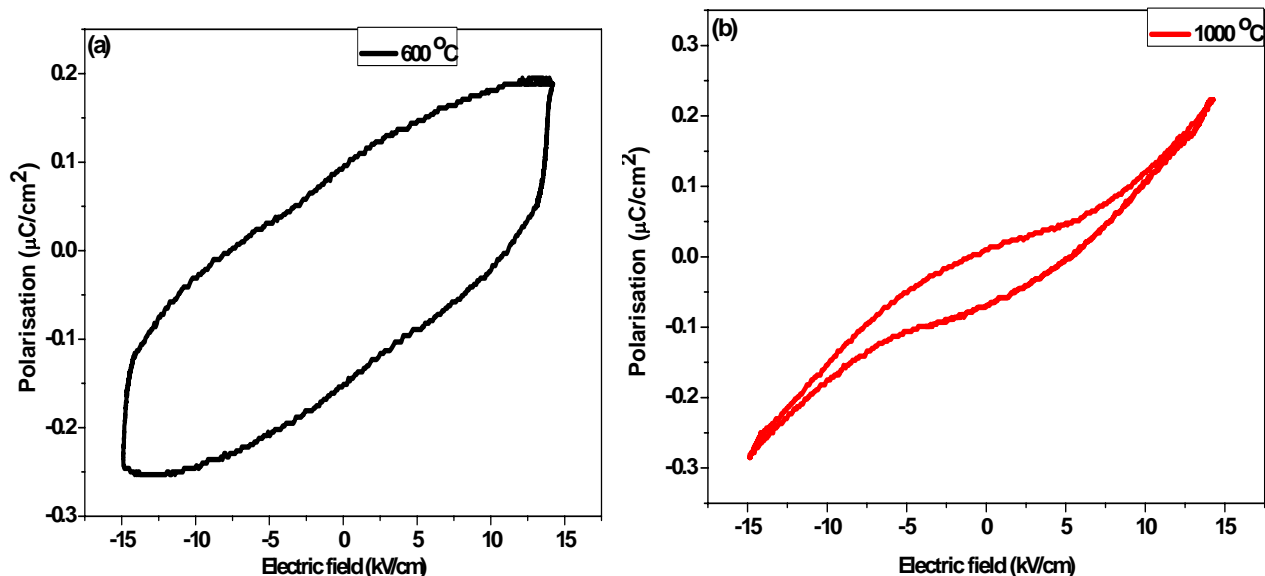


Fig. 4 (a)-(b) Ferroelectric behavior of BaTiO₃ sintered at 600 and 1000 °C

IV. CONCLUSIONS

We synthesized the BaTiO₃ samples via sol-gel method and studied their structural, optical and ferroelectric properties. XRD shows the pure phase formation in all the samples of BTO. It is observed that optical band gap varies from 4.37 to 3.80eV for the samples sintered at 600 to 1000°C, respectively. The particle size calculated through transmission electron microscopy varies from 20 to 40nm for the samples sintered at 600 to 1000°C, respectively. Furthermore, ferroelectricity enhances as we increase the sintering temperature from 600 to 1000°C.

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