



# INVESTIGATION OF $\text{BaTiO}_3$ FERROELECTRIC CERAMICS FOR STRUCTURAL AND ELECTRICAL PROPERTIES

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**Abstract:** Perovskite structure polycrystalline samples of barium titanate ( $\text{BaTiO}_3$ ) have been synthesized using solid-state reaction technique. Phase pure, dense, crack free and homogeneous samples have been optimized. X-ray diffraction patterns (XRD) of BT-powders has been investigated to understand the sintering behavior. The XRD data were analyzed to confirm the phase formation and purity, to obtain lattice parameters and unit cell volume. The porosity of the samples has been calculated through X-ray density and bulk density. The average particle sizes of the samples were obtained from the X-ray peak width (FWHM) using Scherrer's formula. The notable feature of sintering temperature and microstructure of samples has also been studied by SEM investigations. The microstructure study shows that the samples sintered at  $900^\circ\text{C}$  for 12 hrs possess a fairly uniform grain distribution.

Keywords: Crystals/Crystallization; Ferroelectric materials; Grain growth; Barium titanate; Particle size;

## 1. Introduction

$\text{BaTiO}_3$  has been accounted to be one of the most important members of this family. Above  $120^\circ\text{C}$  it is cubic and belongs to space group  $\text{Fm}\bar{3}\text{m}$  ( $O_h^1$ ). Its structure is  $\text{P}4\text{mm}$  ( $\text{C}_{4v}^1$ ) and at room temperatures below  $120^\circ\text{C}$  it is ferroelectric. If the temperature is lowered further the crystals of  $\text{BaTiO}_3$  undergo new structural transitions at  $5^\circ\text{C}$  and  $-90^\circ\text{C}$ , transformation to orthorhombic and tetragonal symmetries, respectively. The temperature-dependent vibration spectra of this material have studied by a number of researchers [1-7] utilizing Raman and infrared spectroscopic techniques. There are however, ambivalent reports regarding to the interpretation of their experimental observations related to the applicability of so-called "soft-mode theory" originally proposed by Cochran [8] and Anderson [9] independently in order to explain the anomalous dielectric behavior and the structural phase transition in ferroelectric materials. The wide range of electronic application exhibited by  $\text{BaTiO}_3$  demand morphologically homogeneous samples of the material. The conventional ceramic process of synthesizing  $\text{BaTiO}_3$  relies on the solid-state reaction

between  $\text{TiO}_2$  and  $\text{BaCO}_3$  at high temperatures. The tendency of conventional solid-state reaction method is to produce a bristly  $\text{BaTiO}_3$  powder with compositional in homogeneity and a degree of particle agglomeration. In order to limit the extent of grain growth and control particle size it is necessary to carry out a detail study of the effect of the particle size of the starting material, sintering temperature, sintering time are not optimized as to facilitate ionic diffusion and reaction in the solid state and to limit the grain growth which is a function of sintering temperature and sintering time.

In this section the results of the present study i.e. the effect of sintering temperature and sintering time on the structural phases and microstructural aspect using X-ray powder diffractometric and Scanning electron microscopic studies were recorded.

## 2. Experimental Procedures

Synthesis of  $\text{BaTiO}_3$  (BT) samples were prepared by solid state reaction processing using high purity oxide and carbonate as the starting materials, involving several steps such as mixing, calcinations and sintering along with intermediate grinding. Calcinations in temperatures range from  $500$ - $600^\circ\text{C}$  is synthesized the BT compound before sintering at different temperatures.

Commercially available BaCO<sub>3</sub> (99.9% purity; Aldrich chemicals), and TiO<sub>2</sub> (99.9% purity; Loba Chemie.), were used as a starting materials. The polycrystalline samples of BaTiO<sub>3</sub> were prepared using the above high purity ingredient materials in the required stoichiometry. The sieved fine powders were then calcined in the temperature range 500–600°C for 8 hr. in an air atmosphere and brought to room temperature under slow cooling. The calcined powders were again finely ground and sieved through a 75µm (200 mesh). The sieved powders were pressed in to pellets using polyvinyl alcohol (PVA) as a binder. The BT powders were then cold pressed into pellets of diameter 10 mm and thickness 1-2 mm at a pressure of 50 MPa using an isostatic hydraulic press. The pellets were sintered at four different temperatures 700°C, 750°C, 800°C, and 900°C for 12 hr. The heating program was carried out using Carbolite programmable high temperature furnace with Eurotherm temperature controller. The phase structure of sintered specimens was investigated with X-ray diffraction. The X-ray diffraction data was collected over the scattering angle range 10° ≤ 2θ ≤ 80° at 2θ step 0.02° using Cu Kα (λ = 1.5418 Å) radiations recorded at room temperature using X-ray powder diffractometer (Xpert Pro-PAN Philips). The morphological studies of all the sintered samples were carried out by using scanning electron microscopy (SEM). Samples were examined using a (JEOL JSM – 6360 A) analytical scanning electron microscopy operated at (15kv) for determining the average particle size from full width at half maximum (FWHM) the intensity of Bragg peaks (110) and (111) were used.

**3. Results and discussion**

Room temperature X-ray diffraction patterns samples sintered at 700°C, 750°C, 800°C, 900°C are shown in Fig.1. The best agreement between observed and calculated interplanar (d) values are indexed in cubic crystal system. The values of unit cell parameters (a, b, c) are given in Table 1. Gaussian FWHM and particle size for BaTiO<sub>3</sub> samples at different temperatures are given in Table 2.

All the samples of powder diffraction peaks were sintered at different temperatures possess single phase perovskite structure. The diffraction peaks have narrowed substantially with the increasing sintering temperature and the BT phase has persisted without evidence of second phase formation. Sintering at higher temperatures does not appear to substantially alter the nature of patterns. However the XRD pattern collected at the highest temperature 900°C Fig. 1(d) do show additional minor diffraction peaks, suggesting the beginning of the evolution of second phase (indicated by arrow).

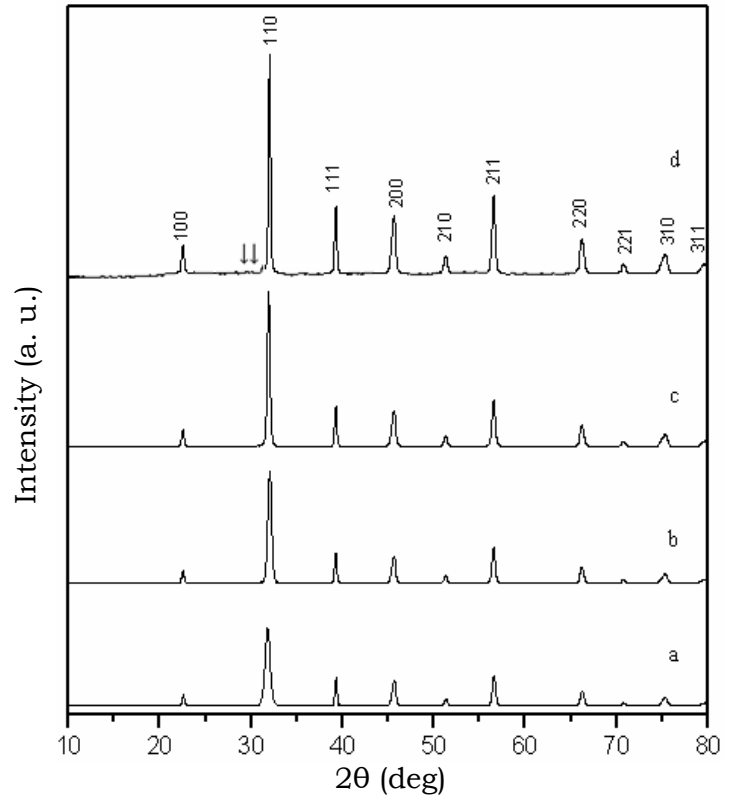


Fig. 1 XRD patterns of BaTiO<sub>3</sub> sample sintered at different temperatures. (a = 700°C, b = 750°C, c = 800°C, d = 900°C).

**Table 1 Lattice parameters and phase and space group of BaTiO<sub>3</sub> samples sintered at different temperatures.**

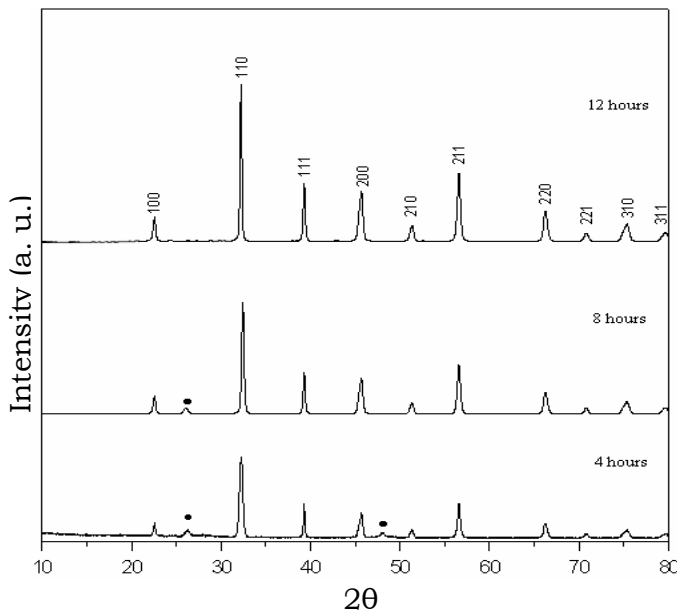
Sintering Temperature (°C)	a (Å)	b (Å)	c (Å)	Phase & Space Group
700	3.9923	3.9923	3.9923	C (Pm3m)
750	3.9946	3.9946	3.9946	C (Pm3m)
800	3.9952	3.9952	3.9952	C (Pm3m)
900	3.9976	3.9976	3.9976	C (Pm3m)

Fig. 2 shows the XRD patterns of BaTiO<sub>3</sub> that have been sintered at 900°C for various time periods (4, 8, 12 hr). Fine perovskite BaTiO<sub>3</sub> crystallites, as indicated by the peaks at 2θ angle of 22.0°, 31.4°,

38.7°, 45.0°, 55.9°, and 65.5°, were observed, together with much-weakened and broadened peaks of TiO<sub>2</sub> when the samples was subjected to for 4 hr. sintering.

**Table 2 BaTiO<sub>3</sub> Gaussian FWHM and particle size at different temperatures.**

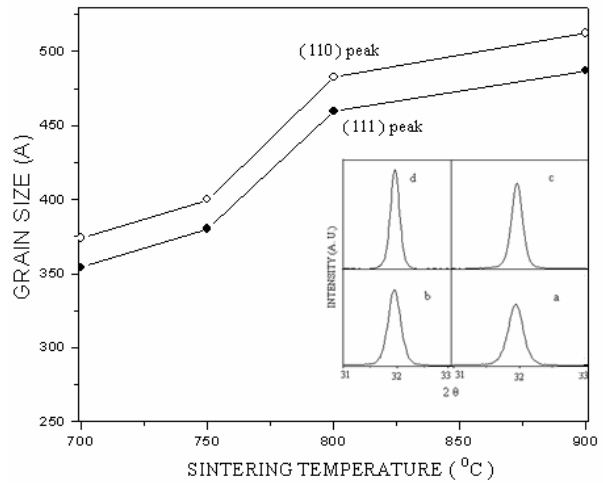
Sintering Temperature (°C)	(110) Gaussian FWHM (deg)	(110) Particle Size (nm)	(111) Gaussian FWHM (deg)	(111) Particle Size (nm)
700	0.21213	374	0.22413	354
750	0.19863	399	0.20894	380
800	0.16457	482	0.17273	459
900	0.15501	512	0.16310	487



**Fig. 2 XRD patterns of BaTiO<sub>3</sub> sample sintered at 900°C for various time duration (4, 8, 12 hr.).**

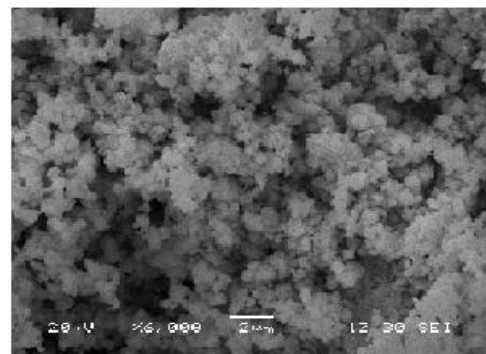
This observation indicates that sintering at 900°C for first 4 hr. triggers the formation of perovskites BaTiO<sub>3</sub> phase and at the same time; the peak broadening of TiO<sub>2</sub> implies that the first sintering has led to a significant refinement in the particle and crystallite sizes. The BaTiO<sub>3</sub> phase was observed further when the sintering was extended to 8 hr, which indicates that the formation of BaTiO<sub>3</sub> phase occurred at the expense of constituent oxides with increasing sintering time. BaTiO<sub>3</sub> was the only phase that was observed in the X-

ray diffraction pattern in the sample that was sintered for 12 hr. The average particle size has been determined from the full width at half maximum (FWHM) of 110 peak using Scherrer’s equation [10]. The value of FWHM includes errors from the apparatus conditions such as the slit width of the X-ray diffractometer and these errors were corrected. The results were supported by the SEM micrograph studies.



**Fig. 3 Particle sizes as a function of sintering temperatures. Figure in the inset show (110) peak. FWHM values were calculated from the Gaussian fits (solid lines).**

Fig. 3 shows the variation of average particle sizes as a function of sintering temperatures determine from the peaks in the inset figures. Fig.4 shows the typical SEM pattern of BaTiO<sub>3</sub> sample sintered at 900°C for 12 hr.



**Fig. 4 SEM micrograph for sample sintered at 900°C for 12 hr.**

The pattern shows that the BaTiO<sub>3</sub> particles have a more or less spherical morphology and consist of particle agglomerate of varying size and the sizes of the grains are in the range 200 to 350 nm.

#### 4. Conclusions

The unit cell dimensions are not significantly influenced by the sintering temperature. The Gaussian's FWHM values are all small suggesting that the interparticle strains may contribute little to the diffraction peak shapes in these samples. The SEM micrographs do not exhibit the fracture surfaces of sample sintered at 900°C and the sample has developed a relative uniform microstructure. BaTiO<sub>3</sub> powder can be synthesized directly from the constituent oxide using conventional ceramic technique by optimizing sintering temperature and time and by using starting oxides having fine uniform particle size. There is strong co-relation between the crystallite sizes on the sintering temperature and supporting to the notion that crystallite size determines the propensity of microcracking.

#### 5. Acknowledgments

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