



SYNTHESIS, STRUCTURAL AND ELECTRICAL PROPERTIES OF PURE BaTiO_3 FERROELECTRIC CERAMICS

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Abstract: Single phase polycrystalline samples of barium titanate (BaTiO_3) with perovskite structure have been synthesized using solid-state reaction technique. The processing parameters have been optimized to obtain phase pure, dense, crack free and homogeneous samples. The sintering behavior of PT-powders has been investigated using X-ray diffraction patterns (XRD). The X-ray powder diffraction data have been analyzed to confirm the phase formation and phase purity, to obtain unit cell parameters and unit cell volume. The porosity of the samples has been obtained through X-ray density and bulk density. The average particle sizes of the phase pure samples were obtained from the X-ray peak width (FWHM) using Scherrer's formula. The influence of sintering temperature and time on the microstructure of samples has also been studied by carrying out SEM investigations. The notable feature of this microstructure study shows that the samples sintered at 900°C for 12 hrs possess a fairly uniform grain distribution.

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

1. Introduction

BaTiO_3 has been considered to be one of the most important members of this family. Above 120°C it is cubic and belongs to space group $\text{Fm}\bar{3}\text{m}$ (O_h^1). At room temperatures below 120°C it is ferroelectric and its structure is $\text{P}4\text{mm}$ (C_{4v}^1). If the temperature is lowered further the crystals of BaTiO_3 undergo new structural transitions at 5°C and -90°C , transformation to orthorhombic and tetragonal symmetries, respectively. A number of researchers have studied the temperature-dependent vibration spectra of this material [1-7] utilizing Raman and infrared spectroscopic techniques. There are however, conflicting reports with regard to the interpretation of their experimental observations in relation 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 BaTiO_3 , demand morphologically homogeneous samples of the material. The conventional ceramic process of synthesizing BaTiO_3 relies on the solid-state reaction between TiO_2 and BaCO_3 at high temperatures. The conventional solid-state reaction method has a tendency to produce a coarse BaTiO_3 powder with compositional inhomogeneity 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 of the effect of sintering temperature and sintering time on the structural phases and microstructural aspect present in the samples using X-ray powder

diffractometric and Scanning electron microscopic studies.

2. Experimental Procedures

Synthesis of BaTiO₃ (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°C is carried out to synthesize the BT compound before sintering at different temperatures.

Commercially available BaCO₃ (99.9% purity; Aldrich chemicals), and TiO₂ (99.9% purity; Loba Chemie.), were used as a starting materials. The polycrystalline samples of BaTiO₃ 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

X-ray diffraction patterns collected at room temperature for the samples sintered at 700°C, 750°C, 800°C, 900°C are shown in Fig.1 All the observed peaks/reflections are indexed in cubic crystal system on the basis of the best agreement between observed and calculated interplanar (d) values. The values of unit cell parameters (a, b, c) are given in Table 1. Gaussian FWHM and particle size for BaTiO₃ samples at different temperatures are given in Table 2.

The powder diffraction peaks from sample sintered at different temperatures showed that all the samples 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).

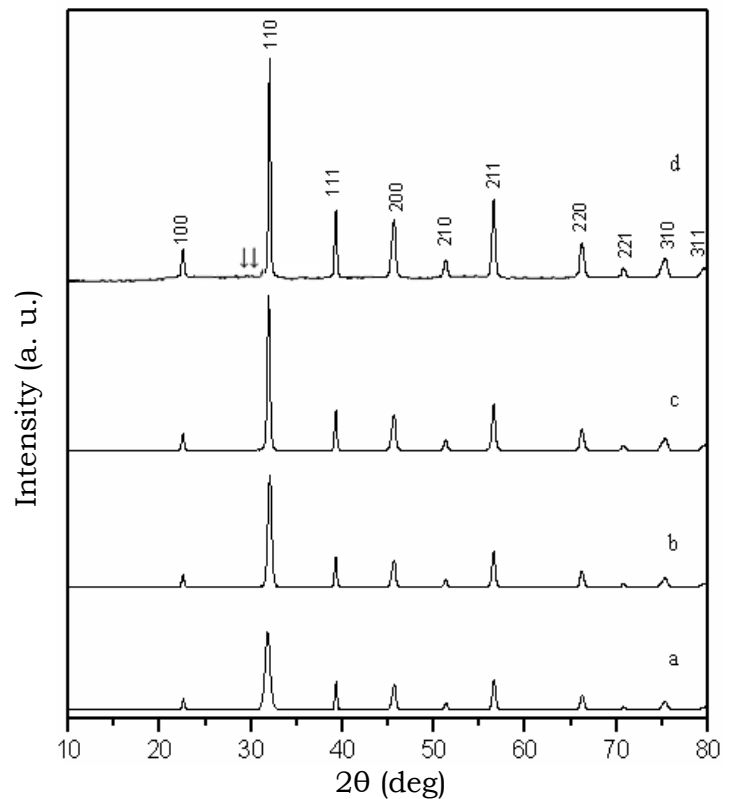
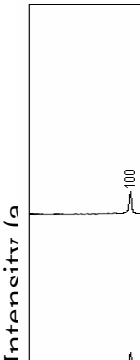


Fig. 1 X-ray diffraction patterns of BaTiO₃ sample sintered at different temperatures. (a = 700°C, b = 750°C, c = 800°C, d = 900°C).

Table 1 Unit cell parameters and phase and space group of BaTiO₃ samples sintered at different temperatures.

Sintering Temperature (°C)	Phase	Space Group	a (Å)	b (Å)	c (Å)
700	Perovskite	P63mc	3.91	3.91	3.91
750	Perovskite	P63mc	3.91	3.91	3.91
800	Perovskite	P63mc	3.91	3.91	3.91
900	Perovskite + Second Phase	P63mc	3.91	3.91	3.91



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 for the samples that have been sintered at 900°C for various time periods (4, 8, 12 hr). Fine perovskite BaTiO₃ 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 TiO₂ when the samples was subjected to for 4 hr. sintering.

Table 2 Gaussian FWHM and particle size for BaTiO₃ 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 X-ray diffraction patterns of BaTiO₃ 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 BaTiO₃ phase and at the same time; the peak broadening of TiO₂ implies that the first sintering has led to a significant refinement in the particle and crystallite sizes. The BaTiO₃ phase was observed further when the sintering was extended to 8 hr, which indicates that the formation of BaTiO₃ phase occurred at the expense of constituent oxides with increasing sintering time. BaTiO₃ 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.

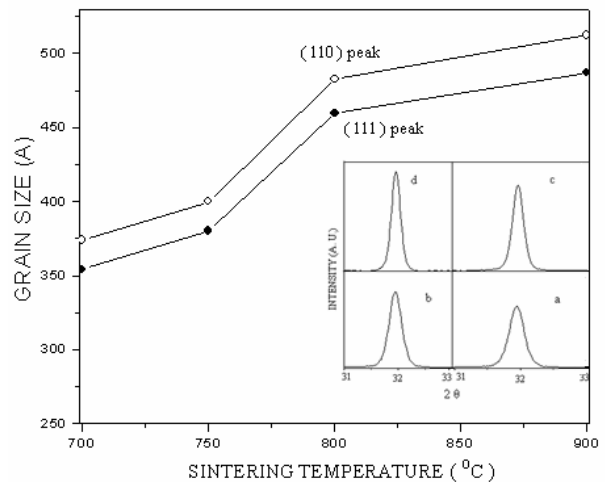


Fig. 3 Particle sizes as a function of sintering temperatures. Figure in the inset show (110) peak.

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 BaTiO₃ sample sintered at 900°C for 12 hr.

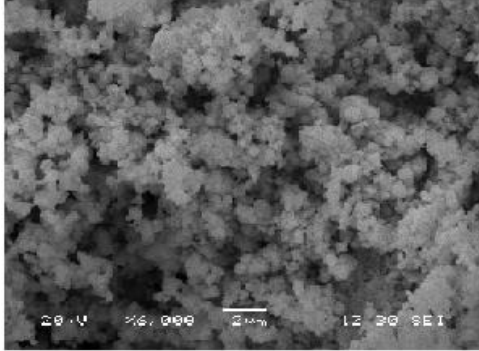


Fig. 4 SEM micrograph for sample sintered at 900°C for 12 hr.

The pattern shows that the BaTiO₃ 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. BaTiO₃ 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.

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