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Crystallographic X-ray Diffraction Study on Thermal Phase Transformation of Barium Titanate

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Abstract

$BaTiO_3$ exhibits several phases. Due to its exceptional ferroelectric and dielectric characteristics, Barium titanate ($BaTiO_3$) has received a lot of interest. In the current study, X-ray diffraction method was used to investigate the phase transition and structural stability of $BaTiO_3$ in temperature range of 30-700 ºC. The behaviour of phase transformation and lattice parameters of the $BaTiO_3$ were established by Rietveld refinement. At 100 ºC, transformation to cubic phase starts and remains cubic up to 700 ºC. Additionally, tetragonal to cubic transformation was accomplished by a decrease of tetragonality at 125 ºC.

Keywords: Barium titanate; High temperature X-ray diffraction; Phase transition; Rietveld refinement.

1. Introduction

Phase transformation is a fundamental chemical and physical property of materials. Thus, study of materials response to variation of temperature is of great importance from both the scientific and the technological points of view. Barium titanate is the first discovered ferroelectric perovskite. Its ferroelectric properties are connected with a series of three structural phase transitions[1]. In bulk form, BTO assumes four crystallographic phases. Below −90 °C (183 K), the ground-state crystal structure is rhombohedral (R3m); it is ferroelectric with Ti displacements aligned along a body diagonal ⟨111⟩. Between −90°C and 5 °C, BTO is orthorhombic (Amm2) and is again ferroelectric but with net polarization along a face diagonal ⟨011⟩. Between 5 °C and 120 °C, it is tetragonal (P4mm) and remains ferroelec- tric with polarization now along the z axis ⟨001⟩. Above 120 °C, BaTiO3 becomes paraelectric, exhibits long- range cubic order, and is generally assigned a cubic ($Pm\bar{3}m$) crystal structure [2].

$BaTiO_3$ is one of the most widely used electroceramics and has been used in thermistors, multilayer ceramic capacitors, electro-optic devices, actuators, transducers, field-effect transistors, dynamic random-access memory, and electromechanical devices [3-8]. Barium titanate can exist in one of different polymorphs depending on temperature. The bulk form of BaTiO3 predominantly exists in four different crystal phases, i.e., tetragonal, cubic, rhombohedral, and orthorhombic [9]. The present work aims at the study of the effect of heating above room temperature on the crystallographic structure of Barium titanate (BaTiO3) as lead free perovskite. Crystallographic characteristics (unit cell type and dimensions) will be studied using X-ray powder diffraction and Rietveld refinement.

2. Experimental

X-ray diffraction patterns of the sample were collected with Bruker D8-Advance diffractometer (Bragg-Brentano geometry). Using Step scanning with step $\Delta 2\theta = 0.05829^o$ the data were collected at different temperatures from 30 ºC up to 700 ºC using Cu-Kα radiation (1.5406 Å). The 2θ-range from 20 to 70º was chosen to cover the main diffraction patterns of the sample. Rietveld analysis was used for the refinement of the diffraction data as well as for quantitative phase analysis (QPA)to calculate the lattice parameters. The programme TOPAS 6.0 [10] was used for Rietveld refinement [11-12].

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3. Results and discussion

3.1. Phase Analysis

The X-ray diffractograms of $BaTiO_3$ at different temperatures from 30 to 700 ºC are depicted in Figure (1). Tetragonal phase (JCPDS#83_1880) was identified as the predominant one up to 75 ºC. Phase transformation begins at T = 100 ºC to cubic phase (JCPDS#79_2263) and increases up to 700 ºC. $BaTiO_3$ often exhibits numerous phase structure transitions, such as the transition from cubic (Pm-3m) to tetragonal (P4mm) at 130 ºC [13-16]. Phase identification was difficult due to the overlapping of diffraction peaks, such as (200) of cubic phase as well as (002) and (200) of tetragonal one. In addition to the difficulty of the overlapping, the expansion of the unit cell at temperatures higher than the room temperature results in a shift of the 2θ-values from the standard ones given in JCPDS cards.

To illustrate the difficulty of peak overlapping. the diffractograms within specified 2θ- ranges (Zoom) at different temperatures from 30 to 175 ºC are depicted in Figure (2). The shift to a high 2θ-value is due to the thermal expansion. Phase transformation from tetragonal to the cubic system was observed clearly at 100 ºC. The two diffraction peaks of the tetragonal phase (002) and (200) at 2θ ≈ 44.9 and 45.4º, respectively, are overlapped with (200) of the cubic phase at 2θ ≈ 45.2º. Also, the two diffraction peaks of the tetragonal phase (112) and (211) at 2θ ≈ 56.1 and 56.3º, respectively, are overlapped with the one of the cubic phases (211) at 2θ ≈ 56.1º.

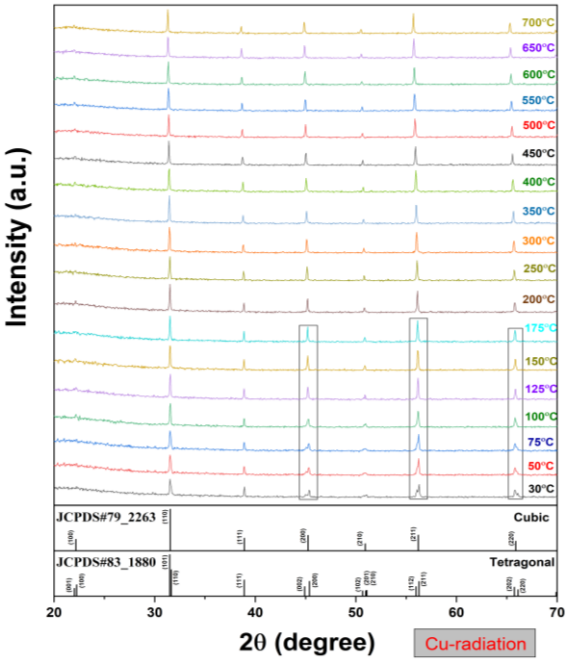


Figure 1. X-ray diffractograms of $BaTiO_3$ at different temperatures (using Cu-radiation).

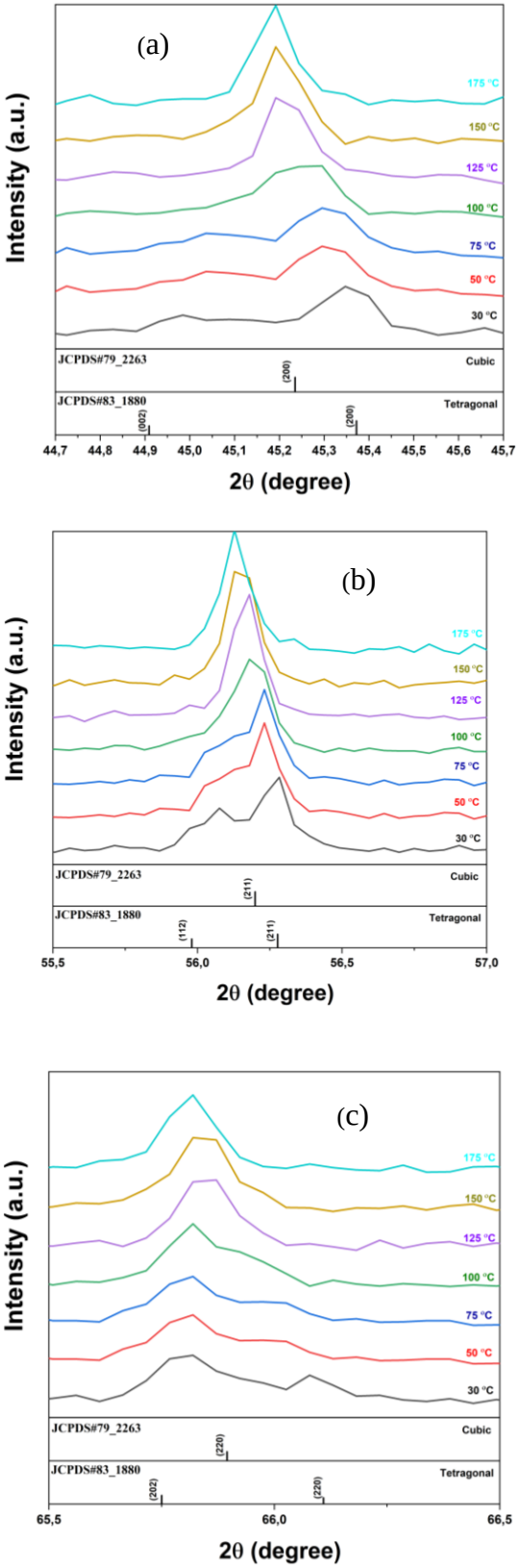


Figure 2. X-ray diffractograms of $BaTiO_3$ (Cu-radiation) in specific 2θ-ranges: (a) 2θ=44.7-45.7º, (b) 2θ=55.5-57º, and (c) 2θ=65.5-66.5º.

3.2. Lattice Parameters

Rietveld plot of the sample at 30 ºC is given in Figure (3) including the observed and calculated data in addition to the difference between them. A good fit is observed. The quantitative change of the phases is illustrated in Figure (4). The effect of temperature on the lattice parameters of the two identified phases has been investigated. Effect of temperature on the lattice parameters is depicted in Figures (5) and (6) for the cubic and tetragonal phases, respectively. It was observed that a-axis of the cubic phase increases linearly with the temperature. On the other hand, the a-axis of the tetragonal phase also increases as the temperature ascends in the whole range of the temperature. However, the c-axis decreases up to about 150 ºC where it becomes nearly equal to the a-axis, then both axes gradually increase. First, anisotropic change in the lattice parameters take place, where a-axis increases and b-axis decreases. As the two axes become nearly equal, both increases up to 700 ºC. Thus, the observed effect of temperature on the lattice parameters during phase transformation of $BaTiO_3$ shows anomaly or irregularity.

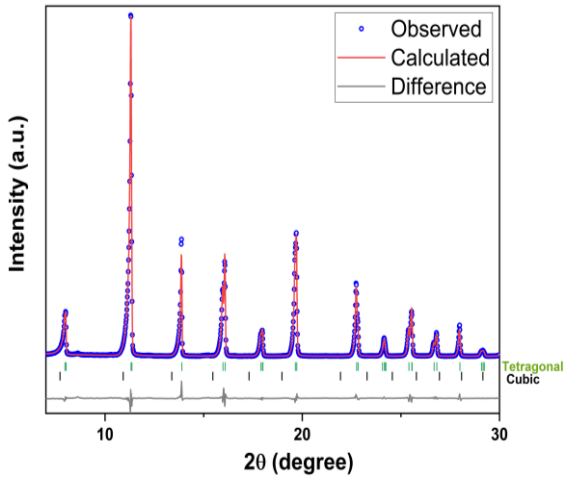


Figure 3. Rietveld refinement of BaTiO3 at 30 ºC (Rexp = 1.685, Rwp = 5.202, Rp = 3.863, GOF = 3.088, tetragonal phase = 99.97% [r_bragg = 1.789], cubic phase = 0.03% [r_bragg = 3.049]).

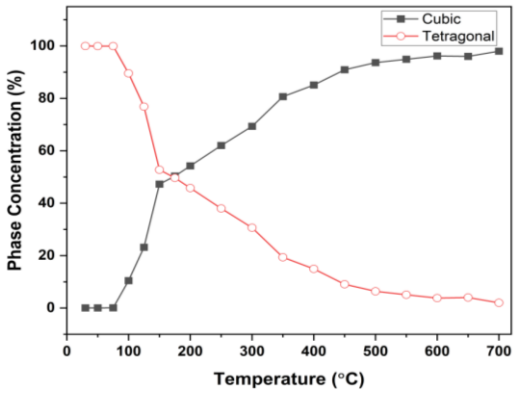


Figure 4. Phases percentage at different temperatures.

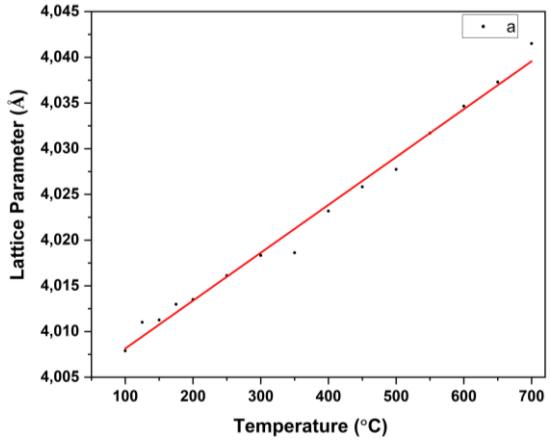


Figure 5. Effect of temperature on the lattice parameter a of the cubic phase.

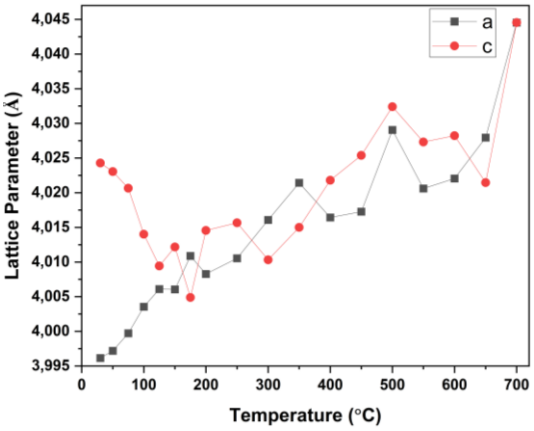


Figure 6. Effect of temperature on the lattice parameter a and c of the tetragonal.

The change of tetragonality with temperature is illustrated in Figure (7). Unit cell of Perovskite-type Barium titanate ($BaTiO_3$) in the symmetric cubic state above T_c and tetragonally distorted unit cell below T_c as depicted in Figure (8). Effect of temperature on the observed lattice parameter during phase transformation can be discussed according to polarization of the structure shown in Figure (9). As temperature ascends the polarization diminishing, so the c-axis decreases to value equals to a-axis then both axes start to increase with temperature due to the normal thermal expansion.

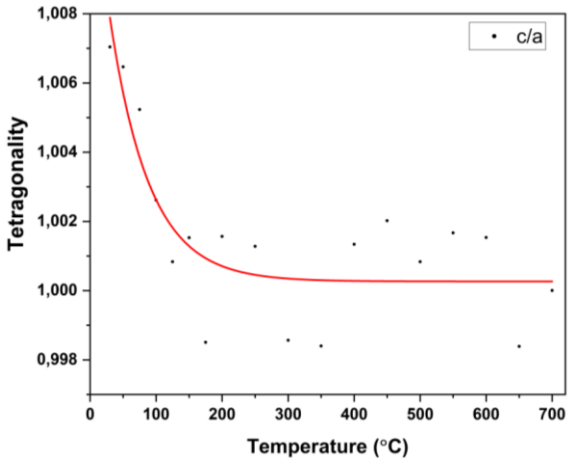
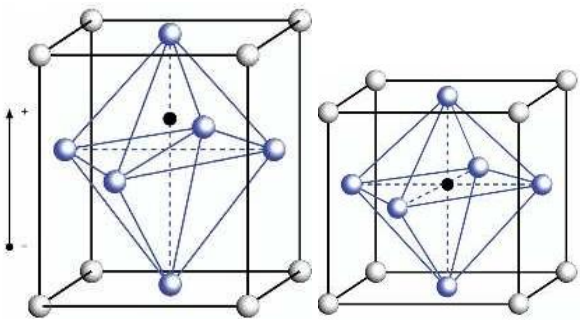


Figure 7. Effect of temperature on the tetragonality (c/a) of BaTiO3.



(a) (b)

Figure 8. Unit cell of Perovskite-type Barium titanate ($BaTiO_3$):

a) Tetragonally distorted unit cell below T_c and
b) Symmetric cubic state above T_c.

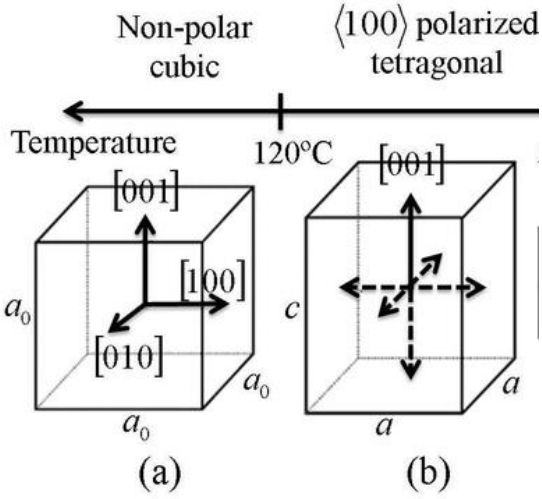


Figure 9. Effect of polarization on crystal system.

4. Conclusion

Barium titanate transforms crystalographically from tetragonal system to cubic one at 100 °C. For crystallographic investigation of a mixture of cubic and tetragonal phases of the same composition, care should be taken especially when a- and c-parameters are nearly equal (3.995 – 4.025 Å). Lattice parameters increase with temperature, however, c- of tetragonal phase decreases up to 100 °C then both a- and c- increase with temperature. Decrease of c-axis is due to the effect (diminution) of polarization, while increase (elongation) of both a- and c-parameter is due to the expansion as the temperature ascends.

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