

X-ray Diffraction Study on Structural Characteristics of Pure and Doped Perovskite BaTiO₃

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Pure and doped barium titanate, BaMTiO₃, (where M = Cu, Cr, Fe and Gd) were prepared by solid state reaction (ceramic technique). Structural characteristics of the prepared samples were studied by X-ray diffraction analysis. The crystal structure has been refined by Rietveld method, from which accurate lattice parameters and cell volume as well as the ratio c/a were calculated. Winfit program was used in order to calculate the crystallite size and the residual strain. All the samples were single phase except that doped by Gd₂O₃, and they belong to the tetragonal system. Neither of the additives results in transformation from the tetragonal system and values of c/a ratio (1.0084 – 1.0095) are in agreement with the pure BaTiO₃ of perovskite structure. Changes in cell volume and distortion (internal strain) depend on both the ionic size and oxidation state of the additives. Combination of these two factors with the cell volume helps in the prediction of the type of formed lattice defects. By using Kroger-Vink notation, the possible formation of lattice defects to compensate for the electric neutrality can be easily formulated.

1. Introduction:

Barium titanate (BaTiO₃) is one of the best known Perovskite ferroelectric compounds (A²⁺B⁴⁺O₃) that have been extensively studied [1, 2] due to the simplicity of its crystal structure, which can accommodate different types of dopant. This has led to the possibility of tailoring the properties [3] of doped BaTiO₃ for specific technological applications, such as capacitors, sensors with positive temperature coefficients of resistivity, piezoelectric transducers and ferroelectric thin-film memories. Because of the intrinsic capability of the Perovskite structure to host ions of different size, a large

number of different dopants can be accommodated in the lattice [1, 4]. The mechanism of dopant incorporation into BaTiO₃ has been extensively investigated [5] and the behaviour of some transition metal ions as well as that of the larger rare earth ions has been well elucidated. The ionic radius is the main parameter that determines the substitution site [5].

The present work aims to study the effect of different additives (CuO, Cr₂O₃, Fe₂O₃ and Gd₂O₃) on the crystallographic structural properties of Perovskite BaTiO₃ using X-ray diffraction (XRD) analysis. Influence of both the ionic size and oxidation state will be considered.

2. Experimental:

2.1. Sample preparation:

Samples were prepared following the ceramic technique described in [6, 7]. The starting materials for the preparation of pure BaTiO₃ (BTO) were BaCO₃ and TiO₂ (Merck). In case of doped sample (BTO-MO), additives (MO) of 5 mole % of CuO, Cr₂O₃, Fe₂O₃ and Gd₂O₃ were mixed with BaCO₃ and TiO₂ in the appropriate amounts. The materials were mixed by dry method and the mixture was calcined at 1000 °C for 3 hours.

2.2. X-ray diffraction study:

A computer controlled X-ray diffractometer (Diano-8000, USA) was used with a filtered CoK α radiation ($\lambda = 1.7903 \text{ \AA}$). The scanning range was 20° – 110° (2 θ) with step size of 0.02° (2 θ) and counting time of 3 s/step. Quartz was used as the standard material to correct for the instrumental broadening. Refinement by Fullprof program [8] was used for lattice parameter determination and Winfit program [9] for size/strain analysis.

3. Results and Discussion:

3.1. Phase characterization:

The structure characteristics of the prepared samples were investigated by the X-ray diffraction technique. X-ray diffractograms of the prepared samples of BTO-MO (M = Cu, Cr, Fe and Gd) are shown in Fig. (1). The XRD patterns confirm that BTO of Perovskite structure has been formed under the preparation conditions mentioned above for the solid state method. No evidence for the presence of the starting materials (BaCO₃ and TiO₂ or CuO, Cr₂O₃ and Fe₂O₃) in the diffractograms except the case of Gd₂O₃ where diffraction lines of the free oxide were observed (JCPDS file #: 88-2165). The samples were identified as tetragonal phase (JCPDS file #: 89-1428) and no structure changes

to the cubic one. This point was clearly depicted in Fig. (1) where (002) and (200) lines at $2\theta \approx 53^\circ$ are well resolved. Other pairs of (hkl) and (h \bar{l} k) or (lkh) lines are also resolved.

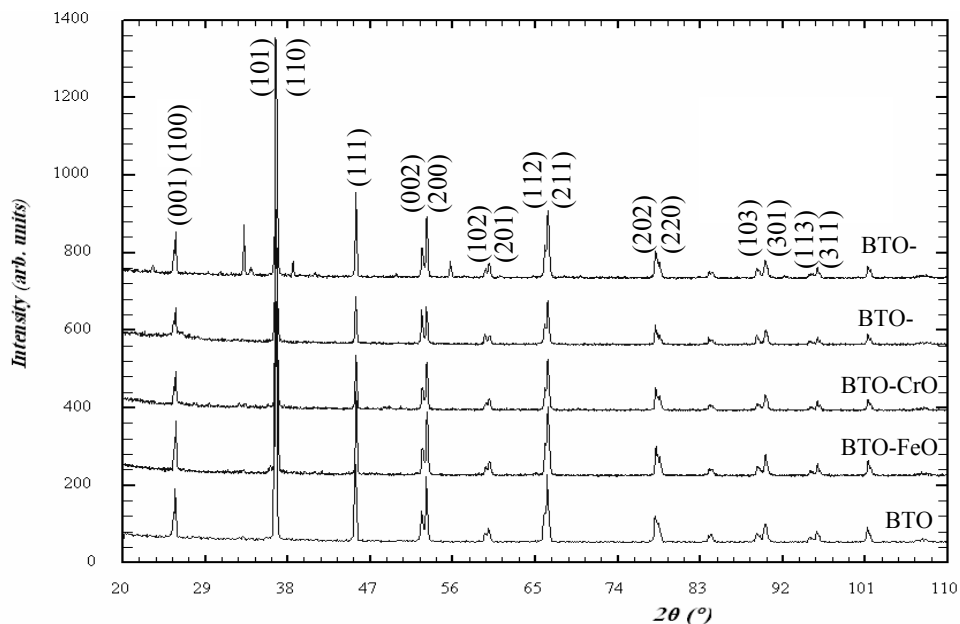


Fig. (1): X-ray diffractograms of pure and doped BaTiO₃ samples.

3. 2. Whole Pattern Refinement:

To calculate the accurate lattice parameters, a structure refinement was done using Rietveld whole-patterns fitting method [10]. The space group used is P4mm and, since the profile matching mode of LeBail [11] was used, the fractional coordinates of the atoms are not needed. In this mode, the full profile is fitted without prior knowledge of and independent on the structure model. The Rietveld plots for the observed and calculated pattern and their difference are shown in Fig. (2). Lattice dimensions of pure and doped BaTiO₃ (BTO) as well as the oxidation state and ionic size are given in Table (1). The cell volume of all the doped BTO-MO samples (64.427- 64.583 Å³) is smaller than that of the undoped BTO one (64.835 Å³). This is due to the small ionic size of the dopant (0.63-0.97 Å) relative to that of Ba⁺² (1.34 Å). The tetragonal structure has c/a values from 1.0084 to 1.0095 in good agreement with the data of JCPDS files.

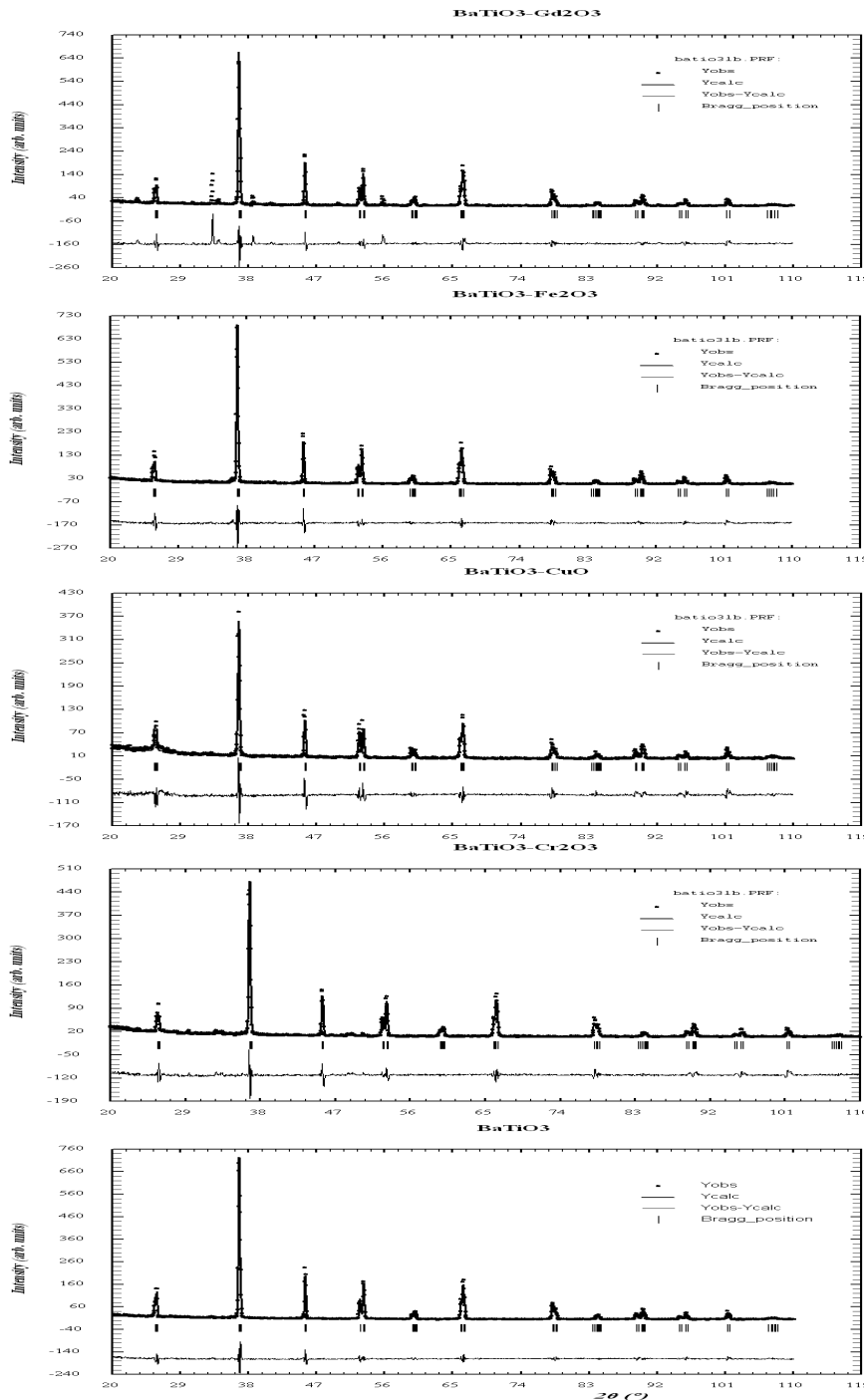


Fig. (2): Rietveld plots (observed and calculated pattern and their difference; Bragg peaks are marked by vertical lines). The free Gd₂O₃ is clearly observed.

Table (1): Lattice parameters and cell volume from Rietveld refinement.

Sample	Ion		Unit cell dimensions			
	Type	Size (Å)	a (Å)	c (Å)	c/a	Volume (Å ³)
BTO	Ba ⁺²	1.34	4.0049	4.0423	1.0093	64.835
	Ti ⁺³	0.76				
	Ti ⁺⁴	0.68				
BTO-CuO	Cu ⁺²	0.72	3.9990	4.0370	1.0095	64.560
BTO-CrO	Cr ⁺³	0.63	4.0007	4.0350	1.0086	64.583
BTO-FeO	Fe ⁺²	0.74	3.9977	4.0313	1.0084	64.427
	Fe ⁺³	0.64				
BTO-GdO	Gd ⁺³	0.97	3.9983	4.0329	1.0086	64.472

In case of Cu⁺², the ionic size is the factor that reduce the cell volume while the other dopants, both the size and oxidation state has to be considered. Combination of these two factors with the variation of cell volume helps in the prediction of the present type of lattice defects. Although, the ionic size of Cr⁺³ is less than the others, the cell volume is the largest one in the doped samples. Comparing with the case of Cu and Fe, this can be discussed considering the electric neutrality requirement. Formation of interstitial O⁻² is probably needed to compensate for the electrical neutrality. Using Kroger-Vink notation [12], this possibility can be formulated as:

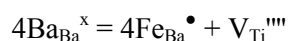


Another possibility is to consider also the oxidation state; formation of Ti⁺³ of larger ionic radius (0.76 Å) than Ti⁺⁴ (0.68 Å) is also probable for the electrical neutrality. These two possibilities or one of them results in the observed higher value of the cell volume relative to the other dopants.

Although, Fe⁺² is larger than Cu⁺² and Cr⁺³, the cell volume in case of Fe-doping is smaller. This may be due to the possibility of the presence of some Fe⁺³ of small ionic size (0.64 Å) which also results in the presence of Ba⁺² or Ti vacancies to compensate for the electric neutrality. Thus, following Kroger-Vink notation, this formula can be considered:



or



Gd^{+3} substitution has ionic radius larger than the other dopants and at the same time its oxidation state differ from that of Ba^{+2} . Thus, it is not easy to imbedded in the BTO lattice. Consequently free Gd_2O_3 oxide is present and the lattice volume is less than the case of Cu and Cr of smaller ionic radius. Thus, in case of Gd^{+3} , the difference in the ionic size, which is less than the case of the other dopants in addition to its oxidation state result in the presence of free Gd that is observed in the X-ray diffractogram. This means that, not all the added Gd_2O_3 is impeded in the BTO lattice. Also, formation of Ba- or Ti-vacancies is expected to compensate the electric neutrality. Consequently, the lattice volume is less than the case of Cr and Cu of smaller ionic radius.

2.1.3. Profile analysis:

True profile of the (111) reflection at $2\theta = 45^\circ$, corrected for the instrumental broadening, was used for the determination of crystallite size and lattice strain, especially because no overlapping with other reflections. Any smoothing procedure may lead to distortion of the original peak profile and may introduce significant errors into the data [13]. The crystallite size and internal residual strain were determined by the one-order (single line) method. The profile fitting of the (111) Bragg reflection of undoprd BTO is given in Fig. (3) as an example. The normalized Fourier coefficients $A(n)$ are plotted in Fig. (4) versus the domain size $L (= n d_{111})$. From the intercept of the straight part of the curve with the x-axis, an average value of the crystallite size was estimated while the strain was obtained according to Dehlez *et al.* [14] approach that implemented in WinFit. Size and strain from profile analysis are given in Table (2).

Table (2): Structure characteristics from profile analysis.

Sample	BTO	BTO-CrO	BTO-CuO	BTO- Fe ₂ O ₃	BTO- Gd ₂ O ₃
Integral breadth ($^\circ$, 2θ)	0.210	0.216	0.205	0.202	0.207
Crystallite size (nm)	41	40	44	44	43
Internal strain (%)	0.18	0.21	0.21	0.20	0.18

Distortion in case of Cr-doping, as discussed above, results in the highest values of internal strain. On the other hand, this distortion causes a low diffusion of ions and finally the smallest grain size and also implies the crystallization because more difficult as proved by the highest value of integral breadth.

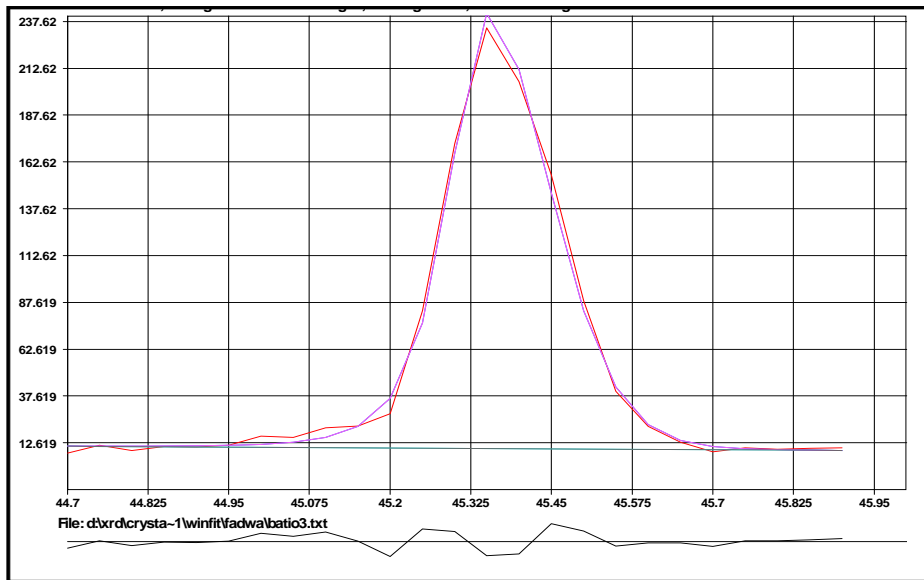


Fig. (3): Profile fitting of (111) reflection.

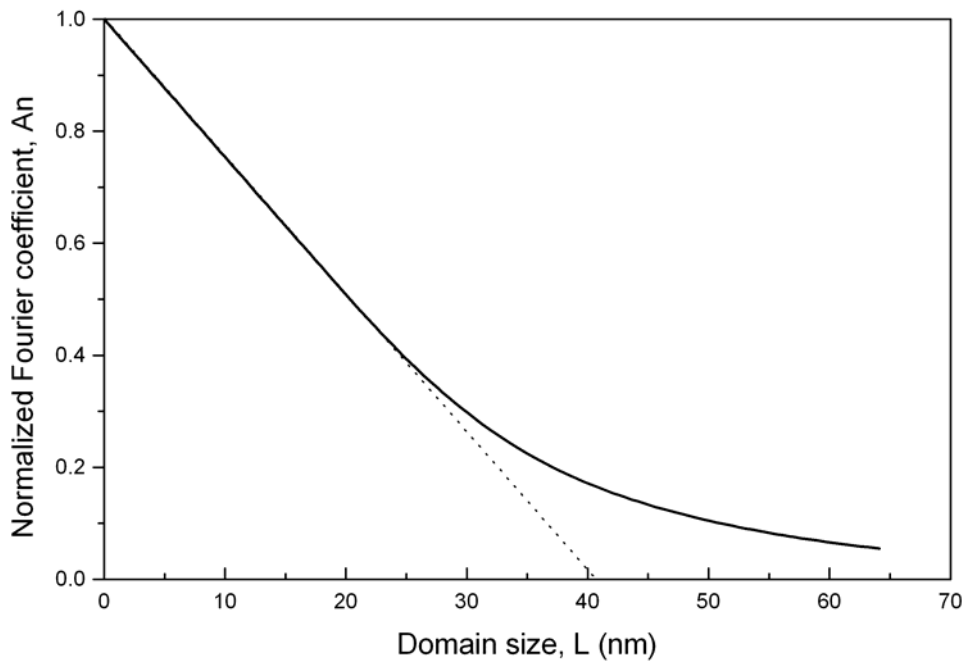


Fig. (4): Plot of normalized Fourier coefficients versus domain Size (dotted strain line is tangent to the straight part of the curve).

Conclusions:

Neither of the additives (Cu, Cr, Fe and Gd) results in transformation from the tetragonal to cubic system and values of tetragonality ($c/a = 1.0084 - 1.0095$) are in agreement with that of the pure BaTiO₃ of perovskite structure. Variations in cell volume and internal residual strain depend on both the ionic size and the oxidation state of the additives. Combination of these two factors with the cell volume may help in the prediction of the type of formed lattice defects. Gd is not recommended as additive to get single phase of doped barium titanate.

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