

# Mechanical Properties, Born Effective Charge Tensors and High Frequency Dielectric Constants of the Eight Phases of BaTiO<sub>3</sub><sup>1</sup>

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**Abstract**—We have performed the first-principles calculations for the mechanical properties, Born effective charge tensors and high frequency dielectric constants of the eight phases of BaTiO<sub>3</sub>. The independent elastic constants, bulk modulus, shear modulus, Young's modulus and Poisson's ratio were obtained, which were consistent with the available theoretical and experimental values. The mechanical stability and brittle/ductile behaviors of the eight phases of BaTiO<sub>3</sub> have been discussed. The calculated results indicated that the eight phases were all mechanically stable and behaved in a brittle manner. The calculated Born effective charge tensors shown the covalent Ti–O bond and ionic Ba–O bond. Moreover, the high frequency dielectric constants have been given.

**Keywords:** BaTiO<sub>3</sub>, mechanical properties, dielectric constant, first-principles.

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## 1. INTRODUCTION

BaTiO<sub>3</sub> has been extensively investigated over the last decades due to its wide applications as ferroelectric devices [1–10], nonlinear optic devices [11, 12], electronic devices [13–20], etc. As a fundamental ferroelectric oxide, BaTiO<sub>3</sub> ceramic capacitors are widely used due to their high dielectric constants, low loss characteristics and positive temperature coefficients.

BaTiO<sub>3</sub> is paraelectric with a cubic  $Pm\bar{3}m$  space group above 398 K [21] (393 K [22], 408 K [23]). When the temperature decreases, its cubic structure is transformed into a ferroelectric tetragonal phase with  $P4mm$  space group, then to orthorhombic  $Amm2$  phase at 281 K [21] (273 K [22], 278 K [23]), and to rhombohedral  $R3m$  phase at 202 K [21] (183 K [22]). The tetragonal, orthorhombic and rhombohedral phases are all ferroelectric [8]. Besides the above four phases, there are hexagonal  $P6_3/mmc$  phase [24–26], tetragonal  $P4/mmm$  phase [27–29], orthorhombic

$C22_1$  [30] and  $Pmm2$  phases [31]. However, the existence of these ground-state structures of high-temperature phases needs further investigations [5–7]. Ravel et al. [5] found that the Ti<sup>4+</sup> ions were shifted along the eight  $\langle 111 \rangle$  directions in all structural phases of BaTiO<sub>3</sub>, which induced a new structural model of the FE-AFE model [6]. The model leads to the  $R3m$ ,  $Pmn2_1$ ,  $I4cm$  and  $I-43m$  space groups for the rhombohedral, orthorhombic, tetragonal and cubic phases. Yoneda et al. [7] further verified this phenomenon using the X-ray diffraction. More and more works have proved that two contradictory models both coexist [2].

Considerable efforts have been devoted to investigate the physical properties of BaTiO<sub>3</sub> by experiments [32–34] and theoretical works [35–48]. Using different functionals of DFT with linear combination of atomic orbital approximation, Evarestov and Bandura [8] studied the structural, electronic properties and phonon frequencies of cubic, tetragonal, orthorhombic and rhombohedral phases of BaTiO<sub>3</sub>. Wang et al.

<sup>1</sup>The article is published in the original.

[12] investigated the lattice, elastic, polarization and electrostrictive properties of cubic, tetragonal, orthorhombic and rhombohedral BaTiO<sub>3</sub>. Recently, Goh et al. [45] reported the structural and response properties of BaTiO<sub>3</sub> using different exchange correlation functionals and PAW potentials with the projector-augmented wave methods. Although many researches and data on bulk BaTiO<sub>3</sub> have been shown, these results are mainly about  $Pm\bar{3}m$ ,  $P4mm$ ,  $Amm2$  and  $R3m$  phases. The reports of  $P6_3/mmc$ ,  $P4/mmm$ ,  $C22_1$  and  $Pmm2$  phases are not too much. In this paper, we want to systematically study the mechanical properties, Born effective charge tensors and high frequency dielectric constants of the eight phases (these phases with old model) of BaTiO<sub>3</sub> using the first-principles density functional theory.

## 2. TECHNICAL DETAILS

Our calculations were performed within the local density approximation (LDA) with the Ceperley-Alder-Perdew-Zunger functional (LDA-CAPZ) [49, 50] and the generalized gradient approximation (GGA) with the PW91 functional (GGA-PW91) [51], as implemented in the CASTEP code [52]. The O 2s<sup>2</sup>2p<sup>4</sup>, Ti 3s<sup>2</sup>3p<sup>6</sup>3d<sup>2</sup>4s<sup>2</sup> and Ba 5s<sup>2</sup>5p<sup>6</sup>6s<sup>2</sup> electrons were treated as valence states. A cutoff energy of 380 eV and the ultrasoft pseudopotential were used to calculate the mechanical properties. The calculations were stopped until the total energy convergence was  $<5.0 \times 10^{-6}$  eV/atom. The Born effective charge tensors and dielectric properties were obtained by using the density functional perturbation theory implemented in the CASTEP code [52], where a cutoff energy of 830 eV and the norm-conserving pseudopotential were used.

## 3. RESULTS AND DISCUSSION

### 3.1. Mechanical Properties

Structural properties of the eight phases at zero pressure have been calculated [48], which are in agreement with the experimental and theoretical values. According to our obtained structural parameters, we firstly calculate the independent elastic constants. The elastic constants  $C_{ij}$  are important parameters and show the response to stress, which are related with the solid state phenomena. For cubic  $Pm\bar{3}m$  phase tetragonal  $P4/mmm$  and  $P4mm$  phases, hexagonal  $P6_3/mmc$  phase trigonal  $R3m$  phase, orthorhombic  $C22_1$ ,  $Amm2$  and  $Pmm2$  phases, there are three, six, five, six and nine independent elastic constants. Our calculated independent elastic constants of the eight phases of BaTiO<sub>3</sub> along with the experimental [53–56] and theoretical values [12, 16, 18, 20, 37, 41] are shown in Table 1.

The cubic structure is presented by three independent elastic constants, namely  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ . Our calculated elastic constants of cubic phase are in agreement with the previous theoretical [12, 16, 18, 37, 41] and experimental results [53]. The  $C_{11}$  determines the unidirectional compression and the  $C_{44}$  means the resistance against the shear deformation. The relatively high  $C_{11}$  and the low  $C_{44}$  of cubic phase indicate that the resistances against the strain  $\epsilon_{11}$  and shear deformation are strong and weak, respectively. Moreover, the mechanical stability criteria for a cubic structure are [57]:  $(C_{11} - C_{12}) > 0$ ,  $C_{11} > 0$ ,  $C_{44} > 0$ ,  $(C_{11} + 2C_{12}) > 0$ . We can see that these criteria are all satisfied, showing that cubic BaTiO<sub>3</sub> is mechanically stable.

For tetragonal  $P4/mmm$  and  $P4mm$  phases, the six independent elastic constants are  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ ,  $C_{44}$  and  $C_{66}$ . The resistances against the strains  $\epsilon_{11}$  and  $\epsilon_{33}$  of tetragonal  $P4/mmm$  phase are almost the same, but the resistance against the strain  $\epsilon_{11}$  of tetragonal  $P4mm$  phase is stronger than the resistance against the strain  $\epsilon_{33}$ . The conclusion shows that the anisotropy of  $P4mm$  phase is bigger than that of  $P4/mmm$  phase. Two tetragonal phases both obey the mechanical stability criteria [57]:  $(C_{11} - C_{12}) > 0$ ,  $(C_{11} + C_{33} - 2C_{13}) > 0$ ,  $(2C_{11} + C_{33} + 2C_{12} + 4C_{13}) > 0$ ,  $C_{11} > 0$ ,  $C_{33} > 0$ ,  $C_{44} > 0$ ,  $C_{66} > 0$ , indicating that they are stable.

To the best of our knowledge, the elastic constants of hexagonal  $P6_3/mmc$  phase are firstly obtained. The obtained elastic constants of trigonal  $R3m$  phase agree with the previous theoretical data [12, 20]. The resistance against the strain  $\epsilon_{11}$  of hexagonal  $P6_3/mmc$  phase is smaller than the resistance against the strain  $\epsilon_{33}$ . However, for trigonal  $R3m$  phase, the result is opposite. The mechanical stability criteria of hexagonal and trigonal phases are [57, 58]:  $(C_{11} - C_{12}) > 0$ ,  $C_{11} > 0$ ,  $C_{33} > 0$ ,  $C_{44} > 0$ ,  $[(C_{11} + C_{12})C_{33} - 2C_{13}^2] > 0$  and  $(C_{11} - C_{12}) > 0$ ,  $C_{11} > 0$ ,  $C_{33} > 0$ ,  $C_{44} > 0$ ,  $[(C_{11} + C_{12})C_{33} - 2C_{13}^2] > 0$ ,  $[(C_{11} - C_{12})C_{44} - 2C_{14}^2] > 0$ , respectively. We can see that two phases are both stable due to that they obey these criteria.

For orthorhombic  $C22_1$ ,  $Amm2$  and  $Pmm2$  phases, the nine independent elastic constants are  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{22}$ ,  $C_{23}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{55}$  and  $C_{66}$ . The elastic constants of orthorhombic  $Amm2$  are consistent with the theoretical [20, 41] and experimental [56] results. The elastic constants of orthorhombic  $C22_1$  and  $Pmm2$  phases are firstly calculated. The resistances against the strains  $\epsilon_{11}$ ,  $\epsilon_{22}$  and  $\epsilon_{33}$  for  $Amm2$  and  $Pmm2$  phases are similar, which are better than those for  $C22_1$  phase. Moreover, the resistances against the shear deformation of three phases are not good, especially  $C22_1$  phase. The mechanical stability criteria of orthorhombic structure are [57]:  $C_{11} > 0$ ,  $C_{22} > 0$ ,  $C_{33} > 0$ ,  $C_{44} > 0$ ,  $C_{55} > 0$ ,  $C_{66} > 0$ ,  $(C_{11} + C_{22} - 2C_{12}) > 0$ ,

**Table 1.** Calculated independent elastic constants of the eight phases of BaTiO<sub>3</sub> along with the experimental [53–56] and theoretical values [12, 16, 18, 20, 37, 41]

	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>	C <sub>22</sub>	C <sub>23</sub>	C <sub>33</sub>	C <sub>44</sub>	C <sub>55</sub>	C <sub>66</sub>	B	G	E	v	B/G	
<i>Pm</i> $\bar{3}$ <i>m</i>	282.8	104.1						118.3			163.7	105.7	260.9	0.258	1.549	CASTEP-GGA
	261.6	88.7						117.3			146.3	103.8	251.8	0.213	1.409	CASTEP-LDA
	305	106						128								ABINIT-LDA [12]
	265.18	91.310						118.64			155.11	106.0				CASTEP-GGA [16]
	450	76						833			718	1522				VASP-GGA [18]
	305.4	111.8						118.6			176.3	109.4	271.9	0.243	1.613	VASP-LDA [37]
	357	123						137								VASP-GGA [37]
	303	111						125								CASTEP-GGA [41]
318.2	111.2						126.7			180.2	116.8					Expt. [53]
255	82						108									
<i>P6</i> <sub>3</sub> / <i>m</i> <i>m</i> <i>c</i>	251.9	77.3	71.2				286.3	66.9			136.5	81.1	203.1	0.252	1.683	CASTEP-GGA
	250.8	81.7	70.0				295.2	59.0			137.6	76.8	194.3	0.265	1.792	CASTEP-LDA
<i>P4</i> / <i>m</i> <i>m</i> <i>m</i>	283.1	104.8	104.8				283.5	118.0		118.1	164.3	105.5	260.7	0.236	1.557	CASTEP-GGA
	281.3	94.4	91.0				270.1	120.5		123.1	153.9	109.0	264.5	0.214	1.412	CASTEP-LDA
	317.96	111.07	111.11				318.4	126.7		126.72	180.10	116.8				CASTEP-GGA [41]
							3	4				7				
<i>C222</i> <sub>1</sub>	178.5	57.6	28.5		230.9	49.6	216.7	57.7	62.0	60.4	98.7	67.7	165.3	0.221	1.458	CASTEP-GGA
	195.5	67.4	41.5		246.4	64.2	268.3	61.8	64.2	61.4	116.2	71.8	178.6	0.244	1.618	CASTEP-LDA
<i>P4</i> <i>m</i> <i>m</i>	296.2	122.6	117.4				259.2	104.6		125.1	173.6	98.4	248.3	0.262	1.764	CASTEP-GGA
	270.0	103.7	99.0				224.5	98.6		121.6	151.3	93.0	231.6	0.245	1.627	CASTEP-LDA
	300	109	90				149	124		128						ABINIT-LDA [12]
	306.11	112.00	92.20				141.1	114.70		124.95	138.14	94.45				CASTEP-GGA [41]
	275	179	152				165	54		113						Expt. [54]
	222	108	111				151	61		134						Expt. [55]
<i>Amm</i> <sub>2</sub>	301.3	121.8	119.8		299.5	49.2	277.9	49.5	111.6	122.4	160.5	90.2	227.9	0.263	1.779	CASTEP-GGA
	275.6	106.0	102.0		268.2	27.2	244.7	39.0	105.3	119.3	137.3	82.0	205.2	0.251	1.674	CASTEP-LDA
	150	100	102		312	100	150	135	118	134						ABINIT-LDA [12]
	296	100	96		260	14	217	35	118	125	119.2	78.1	192.3	0.231	1.526	CASTEP-GGA [20]
	304.0	78.5	99.9		266.6	20.4	231.7	26.5	92.0	121.2	129.9	76.1				CASTEP-GGA [41]
	218	154	109		270	154	218	84.0	33.1	73.5						Expt. [56]
<i>Pmm</i> <sub>2</sub>	302.3	123.2	116.7		296.6	111.3	270.2	104.8	107.6	125.6	174.3	101.0	253.9	0.257	1.726	CASTEP-GGA
	275.9	104.2	98.4		269.8	93.6	235.7	98.9	101.7	122.1	152.1	95.6	237.1	0.240	1.591	CASTEP-LDA
<i>R3m</i>	256.2	68.0	41.1	−29.1			231.8	55.6			115.6	72.4	179.7	0.241	1.597	CASTEP-GGA
	249.9	58.2	27.2	−34.2			228.2	48.1			105.5	66.6	165.1	0.239	1.584	CASTEP-LDA
	276	79	41	45			263	47								ABINIT-LDA [12]
	264	71	41	39			258	53			118.6	74.6	185	0.24	1.59	CASTEP-GGA [20]
	169.1	102.4	102.4	1.1			142.7	107.5			121.2	51.5				CASTEP-GGA [41]

**Table 2.** Calculated Born effective charge tensors of the eight phases of BaTiO<sub>3</sub>. The occupied sites for Ba and Ti atoms are as follows: Ba 1a and Ti 1b (*Pm* $\bar{3}$ *m*), Ba1 2b, Ba2 4f, Ti1 2a and Ti2 4f (*P6*<sub>3</sub>/*mmc*), Ba 1a and Ti 1d (*P4*/*mmm*), Ba1 4b, Ba2 8c, Ti1 4a and Ti2 8c (*C222*<sub>1</sub>), Ba 1a and Ti 1b (*P4mm*), Ba 2a and Ti 2b (*Amm2*), Ba 1a and Ti 2h (*Pmm2*), Ba 1a and Ti 1a (*R3m*)

	$Z_{ij,Ba1}^*$			$Z_{ij,Ba2}^*$			$Z_{ij,Ti1}^*$			$Z_{ij,Ti2}^*$		
	$Z_{11,Ba1}^*$	$Z_{22,Ba1}^*$	$Z_{33,Ba1}^*$	$Z_{11,Ba2}^*$	$Z_{22,Ba2}^*$	$Z_{33,Ba2}^*$	$Z_{11,Ti1}^*$	$Z_{22,Ti1}^*$	$Z_{33,Ti1}^*$	$Z_{11,Ti2}^*$	$Z_{22,Ti2}^*$	$Z_{33,Ti2}^*$
<i>Pm</i> $\bar{3}$ <i>m</i>	2.7383	2.7383	2.7383				7.0571	7.0571	7.0571			
<i>P6</i> <sub>3</sub> / <i>mmc</i>	2.8076	2.8076	2.6934	3.0074	3.0074	2.7148	7.5735	7.5735	7.1577	5.4717	5.4717	7.1176
<i>P4</i> / <i>mmm</i>	2.7415	2.7415	2.7381				7.0416	7.0416	7.0573			
<i>C222</i> <sub>1</sub>	2.8002	2.8382	2.7143	2.9887	3.0064	2.7566	5.7217	6.8305	6.4925	4.3846	5.0387	6.4421
<i>P4mm</i>	2.7367	2.7367	2.9090				6.7173	6.7173	4.9135			
<i>Amm2</i>	2.7445	2.9415	2.8320				6.7529	5.9268	4.6035			
<i>Pmm2</i>	2.8817	2.7466	2.8950				5.3376	6.7422	5.2326			
<i>R3m</i>	2.8339	2.8339	2.7501				6.1718	6.1718	4.9086			

$(C_{11} + C_{33} - 2C_{13}) > 0$ ,  $(C_{22} + C_{33} - 2C_{23}) > 0$ ,  $(C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) > 0$ . Hence three phases are all stable.

Next we apply the Voigt–Reuss–Hill [59–61] approximation to analyze the mechanical properties of the eight phases of BaTiO<sub>3</sub>. Table 1 shows the calculated bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio ( $\nu$ ) and B/G. The bulk modulus represents the resistance of a material to the volume change. The shear modulus reflects the resistance of a material to the shape change. The Young's modulus describes the resistance of a material to the uniaxial tension. According the obtained results (the arithmetic mean value based on the GGA and LDA values), we can see that the orders of the resistances to the volume change, shape change and uniaxial tension are: *Pmm2* (163.2 GPa) > *P4mm* (162.5 GPa) > *P4*/*mmm* (159.1 GPa) > *Pm* $\bar{3}$ *m* (155.0 GPa) > *Amm2* (148.9 GPa) > *P6*<sub>3</sub>/*mmc* (137.1 GPa) > *R3m* (110.6 GPa) > *C222*<sub>1</sub> (107.5 GPa), *P4*/*mmm* (107.3 GPa) > *Pm* $\bar{3}$ *m* (104.8 GPa) > *Pmm2* (98.3 GPa) > *P4mm* (95.7 GPa) > *Amm2* (86.1 GPa) > *P6*<sub>3</sub>/*mmc* (79.0 GPa) > *C222*<sub>1</sub> (69.8 GPa) > *R3m* (69.5 GPa), *P4*/*mmm* (262.6 GPa) > *Pm* $\bar{3}$ *m* (256.4 GPa) > *Pmm2* (245.5 GPa) > *P4mm* (240.0 GPa) > *Amm2* (216.6 GPa) > *P6*<sub>3</sub>/*mmc* (198.7 GPa) > *R3m* (172.4 GPa) > *C222*<sub>1</sub> (172.0 GPa). Then the ductile and brittle behaviors are important to the applications of materials. The bulk modulus and shear modulus are associated with the resistances of fracture and plastic deformation, respectively, which are used to judge the ductile and brittle behaviors of materials. The ratio of bulk modulus to shear modulus (B/G) was proposed by Pugh [62]: the material behaves in a brittle manner if B/G < 1.75, otherwise it is ductile. According to the calculated results, the eight phases of BaTiO<sub>3</sub> are classified as brittle materials. The order of brittle behavior

is *Pm* $\bar{3}$ *m* (1.479) > *P4*/*mmm* (1.485) > *C222*<sub>1</sub> (1.538) > *R3m* (1.591) > *Pmm2* (1.659) > *P4mm* (1.696) > *Amm2* (1.727) > *P6*<sub>3</sub>/*mmc* (1.738).

### 3.2. Born Effective Charge Tensors and High Frequency Dielectric Constants

The Born effective charge tensor relates polarization to atomic displacement, which can be used to discriminate ferroelectricity [45]. The  $j$  component is defined as [35, 63–65]:

$$Z_{ij,\tau}^* = \frac{V(\Delta\mathbf{P})_i}{|e|\Delta\mathbf{u}} \quad (1)$$

where  $i$  is the direction of polarization,  $V$  is the volume,  $\Delta\mathbf{P}$  is the total difference in polarization, and  $\Delta\mathbf{u}$  is the displacement of the  $\tau$  atom. The calculated Born effective charge tensors of the eight phases of BaTiO<sub>3</sub> are shown in Table 2. The unit sublattice displacement inducing the charge transfer can be estimated by the Born effective charge tensors [66]. For Ba and Ti atoms, their nominal ionic charges are  $+2e$  and  $+4e$ . We can see that the Born effective charges of Ba and Ti atoms are larger than their nominal ionic charges. For cubic phase, the ratios of Born effective charge to nominal ionic charge are 1.369 and 1.764 for Ba and Ti, respectively. The rate of deviation of Ti is larger than that of Ba. This is due to the hybridization between O-2p and Ti-3d states, which results in the covalent bonds. The more deviation of Born effective charge compared to nominal ionic charge is, the stronger covalency is. The calculated Mulliken bond populations of cubic phase are  $0.90e$  and  $0.04e$  for Ti–O and Ba–O bonds, indicating the covalent Ti–O bond and ionic Ba–O bond. The others phases show the similar bond character. Furthermore, due to the different symmetry of the others phases of BaTiO<sub>3</sub>, the Born effective charge tensors present anisotropy. The

**Table 3.** Calculated high frequency dielectric constants  $\epsilon_{\infty}$  of the eight phases of BaTiO<sub>3</sub> along with the experimental values [67–70]

				Experiments		
	$\epsilon_{\infty}^{xx}$	$\epsilon_{\infty}^{yy}$	$\epsilon_{\infty}^{zz}$	$\epsilon_{\infty}^{xx}$	$\epsilon_{\infty}^{yy}$	$\epsilon_{\infty}^{zz}$
<i>Pm</i> $\bar{3}$ <i>m</i>	6.25			5.40 [67]		
<i>P6</i> <sub>3</sub> / <i>mmc</i>	5.86		6.08			
<i>P4</i> / <i>mmm</i>	6.25		6.25			
<i>C222</i> <sub>1</sub>	5.06	5.45	5.66			
<i>P4mm</i>	6.04		5.01	5.93		5.60 [68]
				5.19		5.05 [70]
<i>Amm2</i>	5.97	5.60	5.03			
<i>Pmm2</i>	5.35	5.97	5.31			
<i>R3m</i>	5.67		5.05	6.19		5.88 [69]

calculated high frequency dielectric constants  $\epsilon_{\infty}$  of the eight phases of BaTiO<sub>3</sub> are given in Table 3. Our obtained results of *Pm* $\bar{3}$ *m*, *P4mm* and *R3m* are in agreement with the experimental results [67–70]. Moreover, the anisotropic dielectric constants for low-symmetry phases can be seen.

#### 4. CONCLUSIONS

In summary, the first-principles calculations have been performed to investigate the mechanical properties, Born effective charge tensors and high frequency dielectric constants of the eight phases of BaTiO<sub>3</sub>. Our calculated results suggest that the eight phases are all mechanical stability. Moreover, they are classified as brittle materials. The order of brittle behavior is *Pm* $\bar{3}$ *m* > *P4*/*mmm* > *C222*<sub>1</sub> > *R3m* > *Pmm2* > *P4mm* > *Amm2* > *P6*<sub>3</sub>/*mmc*. The bond character has been discussed according to the Born effective charge tensors: the covalent Ti–O bond and ionic Ba–O bond.

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