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Structural, Elastic and Thermal Properties of $BaTiO_3$

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Abstract

Extended Rigid Ion Model is developed and applied for the first time to study the structural, elastic and thermal properties of $BaTiO_3$ cubic perovskite material because of its advanced technological applications in microelectronics, substrates for superconducting materials and as non-linear optics detection devices. The dependency of lattice parameters, bulk moduli, heat capacities, Debye temperatures, volume expansion coefficients and the elastic constants on temperature is successfully predicted in the present study. The stability of $BaTiO_3$ is determined from the cohesive energy and the calculated values of cohesive energy show that $BaTiO_3$ is the stable compound. The results obtained in the present investigation are in good agreement with the corresponding available data.

Key words : Cubic perovskites, structural properties, elastic constants, thermal properties, heat capacity.

1. Introduction

ABO_3 perovskite materials have been investigated intensively because of their potential technological applications. In microelectronics, they are used as dielectrics, capacities for non-volatile ferroelectrics memory (FERAM), substrates for superconducting materials and as non-linear optics detection devices [1-3]. Especially, because of their simple crystalline structure with a large variety of low-symmetry phases, they are promising candidates that can give a better understanding of the ferroelelectric (FE) and anti-ferroelectroelctric phase transitions, including first and second order transitions. The first and the most studied perovskite is the $BaTiO_3$ oxide [4]. The perfect perovskite structure is an extremely simple one with the chemical formula ABO_3, where A is a monovalent, divalent or trivalent alkaline or rare-earth element and B is a pentavalent, tetravalent or trivalent transition-metal element such as Ti or Mn [5-7]. One of the advantages in studying this particular class of titanate lies in its relatively simple electronic and lattice features; namely in $BaTiO_3$, the material undergoes a succession of first order phase transitions from high to low temperatures characterized by a high symmetry cubic perovskite to slightly disordered ferroelectric structures with tetragonal, orthorhombic and rhombohedral symmetry. Orbital degrees of freedom, in addition to spin, charge, and lattice structure are gaining increasing interest in current solid state physics. The cubic unit cell of $BaTiO_3$ compound contains cations Ba at the cube corners, a cation Ti at the center of the cube, and oxygen atoms at the center of the cube faces, forming a regular octahedron [4, 8, 9]. In Section 2, we briefly described the computational techniques used in this study. The most relevant results obtained for the thermophysical properties such as structural, elastic, cohesive and thermal properties which include the temperature dependence of cohesive energy (ϕ), Reststrahlen frequency (υ_0), Debye temperature (θ_D), Grüneisen parameter (γ), Elastic constants (C_{11}, C_{12} and C_{44}), Lattice parameter (a), bulk modulus (B), volume expansion coefficient, α (T), and the heat capacity, C_V(T) of $BaTiO_3$ compound as a function of temperature are presented and discussed in Section 3. The concluding remarks are presented in Section 4.

2. Computational techniques of Extended Rigid Ion Model (ERIM)

The author has recently developed an Extended Rigid Ion Model (ERIM) by incorporating the long-range (LR) Coulomb attraction, the short-range (SR) Hafemeister-Flygare (HF) type overlap repulsion effective up to the second neighbour ions, the van der Waals (vdW) attraction due to the dipole-dipole (d-d) and dipole-quadrupole (d-q) interactions and zero point energy (ZPE) effects in the framework of Modified Rigid Ion Model (MRIM) developed earlier by the authors [10, 11].

The framework of ERIM is derived from the following interionic interaction potential:

$$\phi_{ERIM} = \phi_{MRIM} + \phi_{ZPE} \quad (1)$$

where, ϕMRIM potential is given by Renu Choithrani *et al* [10].

$$\phi_{MRIM} = -\frac{e^2}{2}\sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1} + \left[nb_1\beta_{kk'}\exp\{(r_k - r_{kk'})/\rho_1\} + \frac{n'}{2} b_2[\beta_{kk}\exp\{(2r_k - r_{kk})/\rho_2\} + \beta_{k'k'}\exp\{(2r_{k'} - r_{k'k'})/\rho_2\}] \right] - \sum_{kk'} C_{kk'} r_{kk'}^{-6} - \sum_{kk'} d_{kk'} r_{kk'}^{-8}$$

and $$\phi_{ZPE} = (9/8)\, N\, K_B\, \theta_D \quad (2)$$

The symbols involved in Eqs. (1) and (2) are the same as those defined in our earlier investigations [10, 11]. Here, k (k′) denote the positive (negative) ions and the sum is taken over all the ions (kk′). βkk′ are the Pauling coefficients expressed as:

$$\beta_{kk'} = 1 + (z_k / n_k) + (z_{k'} / n_{k'}) \quad (3)$$

with z_k (z_k') and n_k (n_k') as the valence and number of electrons in the outermost orbit of k (k′) ions and $r_{kk'}$ and r_{kk}(= $r_{k'k'}$) are the first and second neighbour ion separations respectively. In Eq. (2), the first term represents the long-range Coulomb attraction, the second and third terms are the short-range Hafemeister-Flygare type repulsion operating upto the second neighbour ions. The fourth and fifth terms in it are the vdW attraction energies due to the dipole-dipole (d-d) and dipole-quadrupole (d-q) interactions with $c_{kk'}$ and $d_{kk'}$ as the corresponding vdW coefficients.

The specific heat at constant volume (Cv) is calculated by using the following expression [11]:

$$Cv = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{e^x x^4}{e^x - 1} dx \quad (4)$$

at different temperature (T). Here, the notations involved have the same meaning as defined by us [11].

3. Results and Discussion

The input data for $BaTiO_3$ are taken from the data [4-9, 12, 13] and thermodynamic relations [10, 11, 14-17] for calculating the vdW coefficients ($c_{kk'}$ and $d_{kk'}$) and the model parameters (ρ_1, b_1 and ρ_2, b_2) for different temperatures (0 K ≤ T ≤ 1000 K) for $BaTiO_3$ and listed in Table 1. Using these model parameters, the cohesive energy (ϕ) in eV/cell for $BaTiO_3$ has been computed to test the validity of present model. It is found from Table 2 that the magnitude of the cohesive energy (ϕ) = -31.65 eV /cell at 300 K computed by ERIM is in good agreement with the previous computational results of cohesive energy = -32.87 eV /cell [4] for $BaTiO_3$ by Ab initio method. The negative values of the cohesive energy indicate the stability of the compound. The calculated values of Reststrahlen frequency (υ_0) by the ERIM shows conformity with the available data for other perovskites [10, 11, 14-17]. It is also noticed from Table 2 that the ERIM values of Debye temperature (θ_D) of $BaTiO_3$ decreases with increase of temperature and found closer to the values of θ_D by N. Iles et al [4]. It is well known that hard materials have higher Debye temperatures. The higher values of Debye temperature indicate the presence of higher phonon

Table 1
Model Parameters of $BaTiO_3$.

Model Parameters				
T (K)	Ba-O ρ_1 (Å)	Ba-O $b_1(10^{-12}$ erg)	Ti-O ρ_2 (Å)	Ti-O $b_2(10^{-12}$ erg)
0	0.4621	0.8514	0.6125	0.5105
300	0.4417	0.8328	0.6099	0.5078
600	0.4238	0.8297	0.6056	0.5054
900	0.4109	0.8185	0.6019	0.5016

Table 2
Comparison of the experimental data [12] and the first-principles calculations [4] with computed ERIM [10, 11, 14-17] thermophysical properties

Thermophysical Properties							
T (K)	ϕ (eV/cell)	υ_0 (THz)	θ_D (K)	γ	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
0	-31.47	9.01	435.63 [436.77][4]	2.86	267.5	154.3	121.3
300	-31.65	8.89	429.88 [429.88][4]	2.64	251.7	142.1	120.1
600	-31.86	8.61	416.45 [417.69][4]	2.57	249.6	139.2	112.5
900	-31.94	8.32	402.62 [403.84][4]	2.51	237.5	121.7	109.7
	[-32.87][4]			[2-3][18]	238.6][4]	[122.6][4]	[57.5][4]
					[206][12]	[140][12]	[126][12]

frequencies in $BaTiO_3$. The values of Grüneisen parameter (γ) are lying between 2 and 3 as reported by Dai *et al* [18]. The computed values of elastic constants (C_{11}, C_{12} and C_{44}), by ERIM are depicted in Table 2 and found to be comparable and in good agreement with the previous theoretical and experimental results [4, 12].

The temperature effects on the lattice parameters and bulk moduli computed by ERIM are presented in Figures 1(a) and (b) respectively and show similar trend of variations as displayed by N. Iles et al [4]. The lattice parameter of the compound increases with increasing temperature but the rate of increase is very moderate. However, the bulk moduli decrease with temperature. It means that $BaTiO_3$ is a hard material at high temperature.

Figures 2(a) and (b) represents the variation of the volume expansion coefficient, α (T), and the heat capacity, C_v(T) as function of the temperature respectively. These two quantities indicate a sharp increase up to ~ 300 K which is due to electronic contributions. Furthermore, the material displays roughly a similar behavior for the whole temperature range. The heat capacity of the material at sufficient high temperature does not depend much on temperature and tends to approach 125 J mol^{-1} K^{-1}. This beaviour is seen in both ERIM curves and the theoretical curves computed by Ab initio method [4] which increase linearly with temperature indicating the display of phononic contributions (~T^3) in $BaTiO_3$.

4. Conclusion

A detailed investigation of structural, elastic and

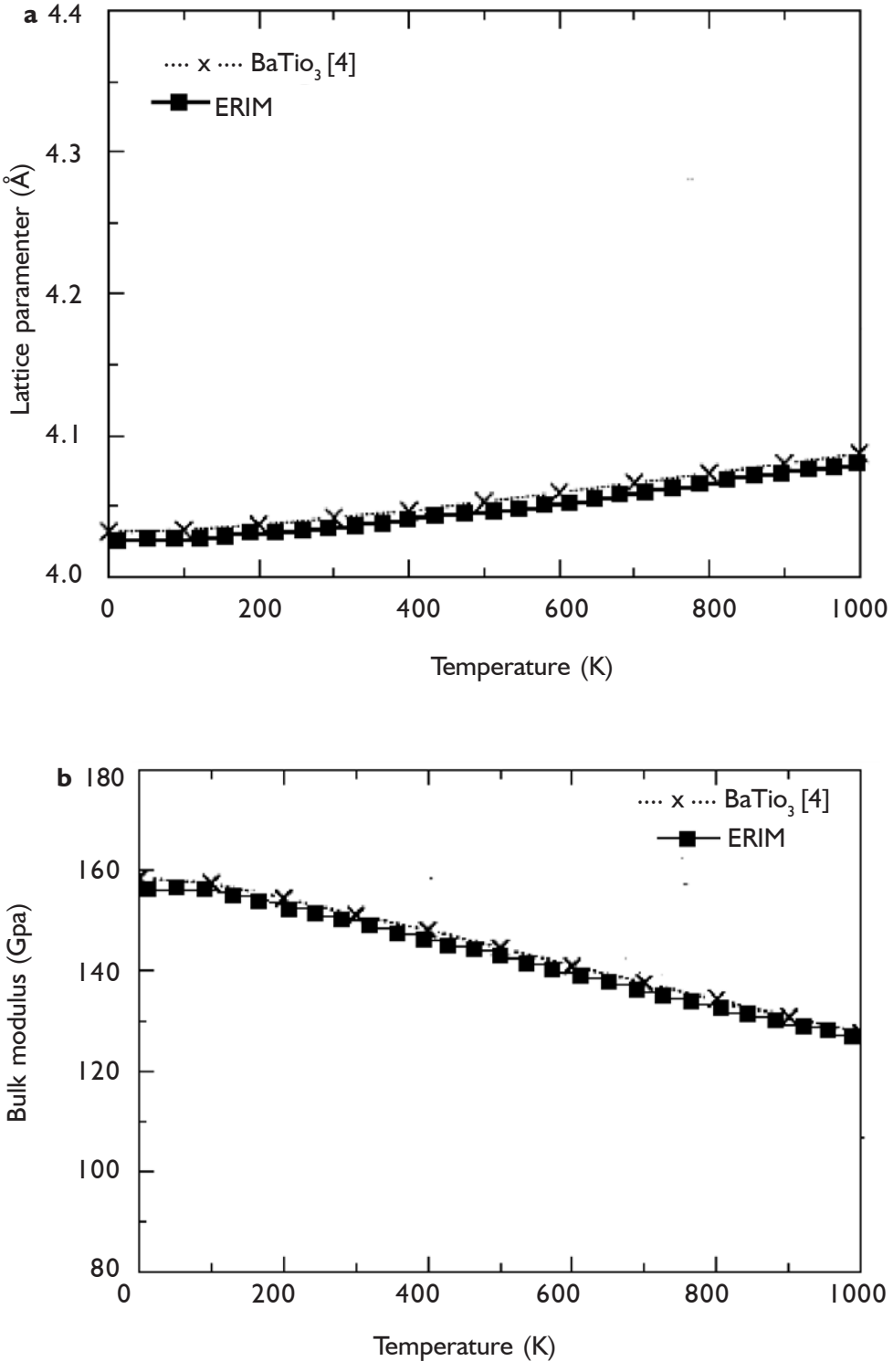

Fig. 1. Variation of (a) lattice parameter and (b) bulk modulus with temperature for $BaTiO_3$

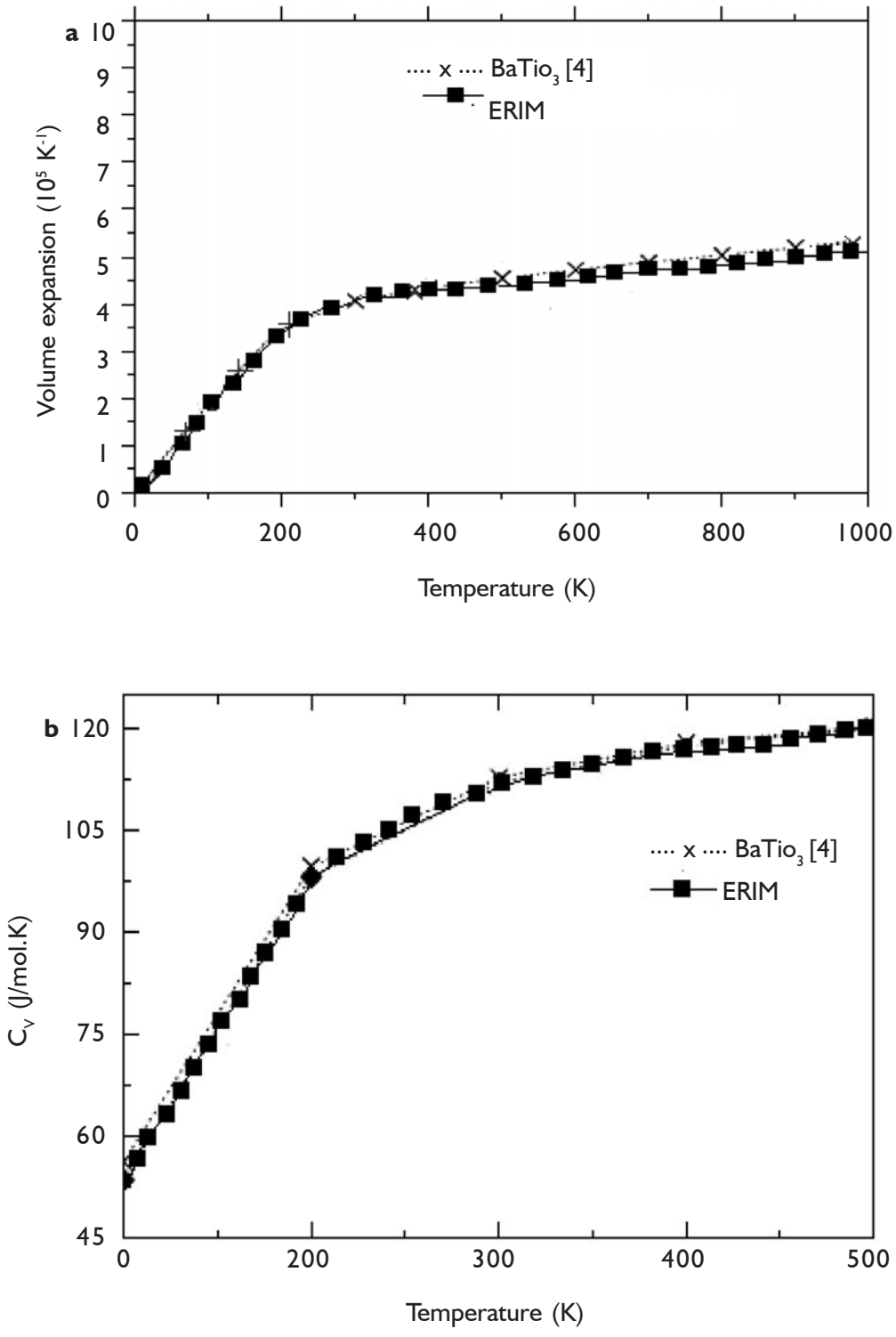

Fig. 2. Variation of (a) volume expansion and (b) heat capacity with temperature for $BaTiO_3$

thermal properties of $BaTiO_3$ at temperature 0 K ≤ T ≤ 1000 K has been presented in this study and are in closer agreement with the available experimental data and theoretically predicted results. This reveals the suitability and appropriateness of Extended Rigid Ion Model for the $BaTiO_3$ material. Some of the results are probably being reported for the first time and hence our comments on their reliability are restricted until the report of experimental data available. The dependency of lattice parameters, bulk moduli, heat capacities, and Debye temperatures on temperature is predicted as well as the elastic constants. Presently, these results are of academic interest and they can serve as a tool to the researchers in future. It may be concluded that ERIM is effectively useful model for the unified and comprehensive study of present system with same success [10, 11, 14-17] for the other perovskite materials.

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