Supplementary Information

Doping Effect of Antimony on $BaFeO_3$ Perovskite Oxide: Optical, Electronic, Magnetic and Thermoelectric Properties

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Supplementary Methods:

1.1. Volume Optimization: Calculation Methods

The equation presented is a form of the Birch-Murnaghan equation of state[1], which is commonly used to fit the energy vs volume (E vs V) data obtained from first-principles calculations. It provides valuable insights into the mechanical properties of materials under hydrostatic pressure. Hence the fitting Birch-Murnaghan equation equation given by,

$$E(V) = E_0 + \frac{B_0.V}{[B'_0.(B'_0 - 1)]}.\left[\left(\frac{V_0}{V}\right)^{(B'_0 - 1)} + (B'_0 - 1)\right] - \frac{B_0 V_0}{B'_0 - 1} \quad (1)$$

Where $E(V)$ denotes the total energy at a given volume V, E_0 represents the minimum energy corresponding to the equilibrium volume V_0, The parameter B_0 is the bulk modulus at equilibrium, reflecting the material's resistance to volume change under applied pressure. The term B'_0 is the first derivative of the bulk modulus with respect to pressure, indicating how the compressibility of the material evolves under increasing pressure. The ratio $\left(\frac{V_0}{V}\right)^{(B'_0 - 1)}$ describes the non-linear change in energy with respect to compression or expansion.

Volume optimization of Pure $BaFeO_3$

Volume (Bohr³)	ΔVol (%)	Total Energy (Ry)
401.43966	-5.00	-19276. 15450501
405.66542	-4.00	-19276. 15630557
409.89109	-3.00	-19276. 15743921
414.11668	-2.00	-19276. 15810981

418.34234	-1.00	-19276. 15832588
422.56810	0.00	-19276. 15806284
426.79382	1.00	-19276. 15756652
431.01954	2.00	-19276. 15668103
435.24516	3.00	-19276. 15535176
439.47090	4.00	-19276. 15355434
443.69651	5.00	-19276. 15164043

Where,
Volume = 418.34234 Bohr^3
Minimum energy = -19276.15832588 Ry
Change in volume = -1.00 %

Volume optimization of 12.5% Sb- doped $BaFeO_3$

Volume (Bohr³)	ΔVol (%)	Total Energy (Ry)
3211.517	-5	-164630. 75647872
3245.323	-4	-164630. 78031558
3279.129	-3	-164630. 80098508
3312.934	-2	-164630. 81692826
3346.739	-1	-164630. 82906511
3380.545	0	-164630. 83640005
3414.351	1	-164630. 84234781
3448.156	2	-164630. 84481484
3481.961	3	-164630. 84404520
3515.767	4	-164630. 83995004
3549.572	5	-164630. 83316549
3583.377	6	-164630. 82332920
3617.183	7	-164630. 81188272

Where,
Volume = 3448.15567 Bohr^3
Minimum energy = -164630.84481484 Ry
Change in volume = 2.00 %

Volume optimization of 25% Sb- doped $BaFeO_3$

Volume (Bohr³)	ΔVol (%)	Total Energy (Ry)
3199.9557	-5	-175052.26743460
3233.63938	-4	-175052.30382875
3267.32345	-3	-175052.33733845
3301.00717	-2	-175052.36504879
3334.69058	-1	-175052.38896332
3368.37449	0	-175052.40737160
3402.05849	1	-175052.42318450
3435.74226	2	-175052.43459231
3469.42555	3	-175052.44232088
3503.1096	4	-175052.44757688
3536.793	5	-175052.44960388

3570.47717	6	-175052.44816678
3604.16085	7	-175052.44449742
3637.84424	8	-175052.43789815
3671.52836	9	-175052.42944722
3705.21217	10	-175052.41856316

Where,
Volume = 3536.79300 Bohr^3
Minimum energy = -175052.44960388 Ry
Change in volume = 5.00 %

1.2. Optical Constants: Calculation Methods

The dielectric function's real and imaginary parts can be used to determine the optical behavior of a material. For crystalline solids, the complex dielectric function, dependent on frequency, is expressed as:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \tag{2}$$

where $\varepsilon_1(\omega)$ represents the material's dispersive properties (i.e. real part), and $\varepsilon_2(\omega)$ accounts for absorption effects (i.e. imaginary part). In cartesian coordinates,

$$\varepsilon(\omega) = \begin{pmatrix} \varepsilon_{xx}(\omega) & \varepsilon_{xy}(\omega) & \varepsilon_{xz}(\omega) \\ \varepsilon_{yx}(\omega) & \varepsilon_{yy}(\omega) & \varepsilon_{yz}(\omega) \\ \varepsilon_{zx}(\omega) & \varepsilon_{zy}(\omega) & \varepsilon_{zz}(\omega) \end{pmatrix} \tag{3}$$

At long-wavelength infrared (LWIR) wavelengths, intra-band transitions play a crucial role. Therefore, the overall dielectric function can be represented by the combined effect of inter-band ($\varepsilon^{inter}(\omega)$) and intra-band transitions ($\varepsilon^{intra}(\omega)$), respectively. And this is represented by the following expression,

$$\varepsilon(\omega) = \varepsilon^{inter}(\omega) + \varepsilon^{intra}(\omega) \tag{4}$$

First-order time-dependent perturbation theory allows for the derivation of the inter-band component of the dielectric function [4]. It is given by the following expression:

$$\varepsilon^{inter}_{\alpha\beta}(\omega) = 1 - \frac{8\pi e^2}{\Omega} \sum_{k,v,c} \frac{\left\langle \psi_{k+qe_\alpha}^{c} \middle| e^{iq.r} \middle| \psi_k^v \right\rangle \left\langle \psi_k^v \middle| e^{-iq.r} \middle| \psi_{k+qe_\beta}^{c} \right\rangle}{(E_{k+q}^{c} - E_k^v - \hbar\omega - i\hbar\alpha)} + CC \tag{5}$$

In this formulation, ω symbolizes the phonon frequency, while Ω represents the volume of a single unit cell. The elementary charge of an electron is represented by e and r defines the position vector. The parameter q captures the photon momentum. Furthermore, E_k^v and E_{k+q}^{c} correspond to the wavefunctions of electrons in the valence and conduction bands at a specific wavevector k. In computational approaches, the dielectric function's imaginary part is typically

evaluated through numerical methods, and the real component is subsequently determined using the Kramers-Kronig relation, as shown below,

$$\varepsilon_1^{inter}(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \varepsilon_2^{inter}(\omega') d\omega'}{\omega'^2 - \omega^2}. \quad (6)$$

In addition, the intra-band contributions to the dielectric function are analyzed with the help of the free-electron plasma model, which is represented by,

$$\varepsilon^{inter}(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}, \quad (7)$$

Here, the plasma frequency (ω_p) is determined using Density Functional Theory (DFT) calculations. Herein, The inverse lifetime (γ) may vary from 0 to 1 eV [5] and the complex optical conductivity (ω) is established based on the following relation:

$$\sigma(\omega) = -i\frac{\omega}{4\pi}[\varepsilon(\omega) - 1]. \quad (8)$$

However, the extinction coefficient $K(\omega)$, The absorbance coefficient $I(\omega)$, the energy loss function $L(\omega)$, refractive index $n(\omega)$, the reflectivity coefficient $r(\omega)$, and the dielectric function $\varepsilon(\omega)$, including its real $\varepsilon_1(\omega)$, and imaginary $\varepsilon_2(\omega)$ parts can be determined with the help of the following equations [6]:

$$K(\omega) = \frac{I(\omega)}{2\omega} \quad (9)$$

$$I(\omega) = \sqrt{2}\omega \left(\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)\right)^{1/2} \quad (10)$$

$$L(\omega) = \frac{E}{(\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2)} \quad (11)$$

$$r(\omega) = \frac{n + iK - 1}{n + iK + 1} \quad (12)$$

$$n(\omega) = \left(\frac{1}{\sqrt{2}}\right)\left(\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)\right)^{1/2} \quad (13)$$

$$\varepsilon_1(\omega) = n^2 - K^2 \quad (14)$$

$$\varepsilon_2(\omega) = 2nK \quad (15)$$

$$\sqrt{\varepsilon(\omega)} = n(\omega) + iK_{(\omega)} \quad (16)$$

1.3. Magnetic moments: Calculation Methods

The total magnetic moment given by the following equation[7],

$$M_{tol} = \sum_i M_i^{\uparrow} - M_i^{\downarrow} + M_{interstitial} \quad (17)$$

Where,

$M_i^{\uparrow}$ and $M_i^{\uparrow}$ are the spin-up and spin-down electron populations inside the muffin- tin sphere of atom i.

$M_{interstitial}$ is the spin density contribution from the interstitial region.

1.4. Thermoelectric properties: Calculation Methods

The performance of thermoelectric materials is commonly evaluated using the dimensionless figure of merit [7],

$$ZT = \frac{S^2\sigma T}{\kappa} \quad \frac{S^2\sigma T}{=\kappa_e + \kappa_L} \quad (18)$$

where T is the absolute temperature, σ is the electrical conductivity, S is the Seebeck coefficient, and $S^2\sigma$ is the power factor (PF). Also, k_e represents the thermal conductivity contributed by electrons and holes, while k_L denotes the thermal conductivity arising from phonons propagating through the crystal lattice [8].

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