Optical and Thermodynamic Properties of Pure- and La-doped $SrTiO_3$

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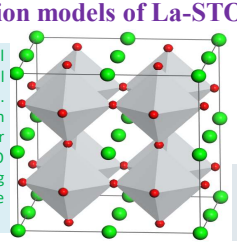
Motivation

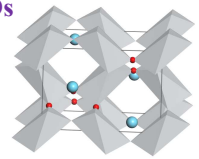
- Due to its unusual properties of large dielectric constant and non-linearity from Ti partially filled d orbitals, strontium titanate (STO) and its doped systems in perovskite structure attracts researchers' great attention and possesses a wide range of applications, for example, as a dielectric material in capacitor, as an oxygen ion conductor as in sensor and fuel cell, as a piezoelectric material in actuator, as a substrate for high Tc superconductor, and etc. Among those metal-doped STO systems, the substitution of La^{3+} for Sr^{2+} to form La-doped STO (La-STO) expresses significant interests due to many potential applications, such as serving as a thermoelectric material with low thermal conductivity and high electrical conductivity due to the enhanced electronic transport.
- Current studies mainly focused on ground state and at low-temperatures. High-temperature properties, such as phonon dispersion and thermodynamic properties, have not been fully investigated. Further detailed understanding of these properties at high temperature range for practical applications, such as fuel cell, sensor, *etc*., are highly desired.
- By combining first-principles density functional theory with lattice phonon dynamics calculations, this research is aimed a more complete fundamental understanding of the electronic structure, optical, and thermodynamic properties of different La-doping levels in STO versus temperatures.

Electronic Structural Properties

Construct simulation models of La-STOs

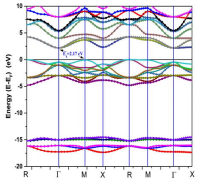
The 2x2x2 STO super cell ($Pm\bar{3}m$ (#221)). Red ball stands for oxygen atom. Green ball stands for Sr atom and the [TiO_6] forms a regular octahedron. To obtain La-STO with different La-doping levels, the 8 Sr atoms are gradually substituted by La.



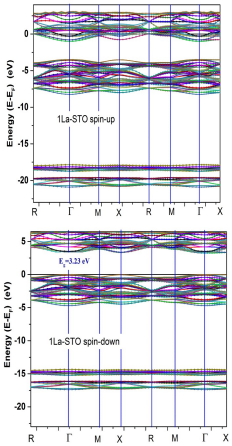


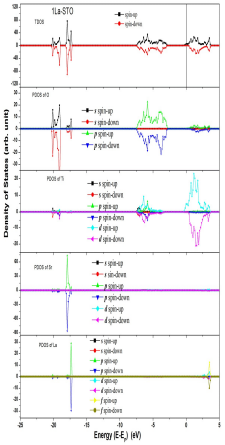
$LaTiO_3$ in $GdFeO_3$-type structure (Pnma (#62)). In this structure, the [TiO_6] octahedral are tilted and rotated. La atom is in light blue.

Band-structures and Density of States (DOS)



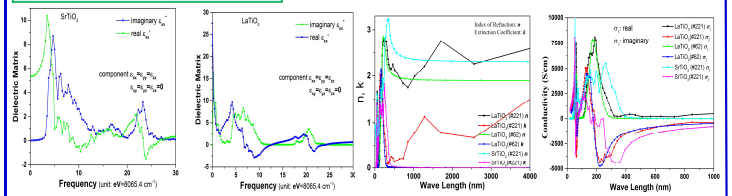
Pure STO



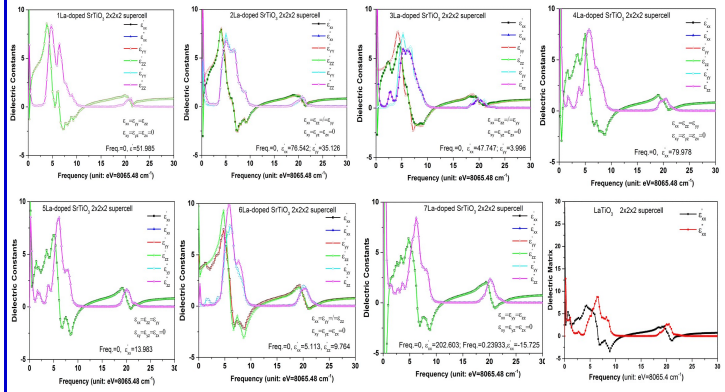


Optical Properties

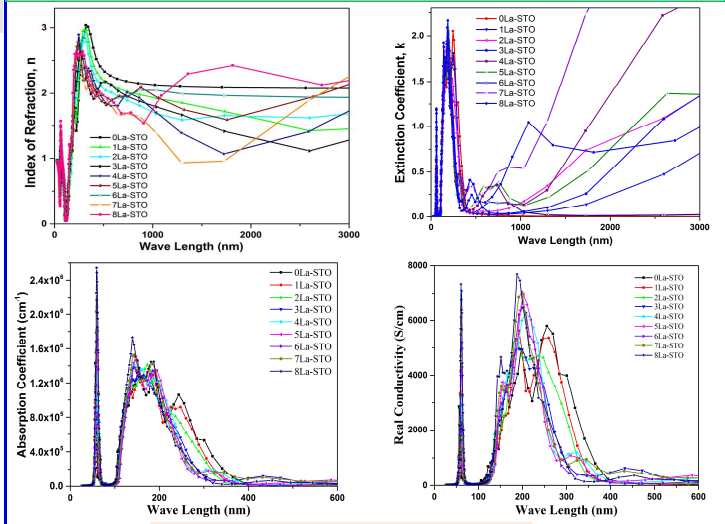
Pure STO and $LaTiO_3$



Dielectric Constant Matrix of La-STOs



Index of Refraction, Extinction Coefficient, Absorption Coefficient, Conductivity



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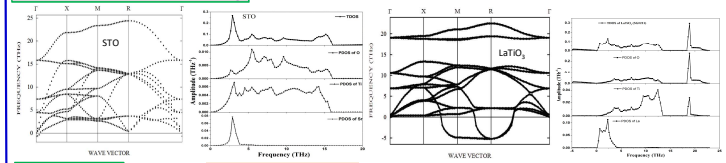
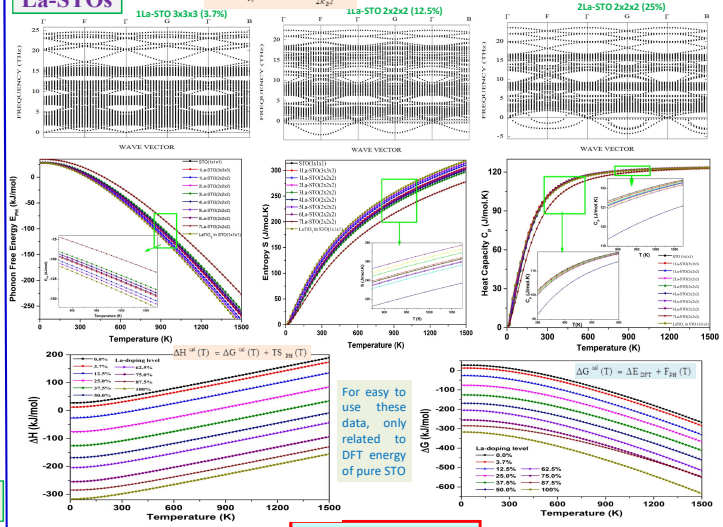
Phonon Lattice Dynamics

Pure STO and $LaTiO_3$



La-STOs



For easy to use these data, only related to DFT energy of pure STO

Conclusions

- When La is doped into STO, the extra electron goes to one conduction band of STO which results one spin has a band gap while another spin does not have band gap. Hence, overall, the La-doped STO does not possess a band gap and is predicted to be an n-type degenerate semiconductor consistent with experimentally derived results.
- The off-diagonal elements of STO dielectric tensor are zero and along the principle axes (x, y, z), they have equal values of ε_1 and ε_2 with frequency change. For all La-STOs with different La-doping levels, we found that in three cases (2La-STO, 3La-STO, 6La-STO) their diagonal elements are not equal, which means these crystal structures are uniaxial and anisotropic. Our results indicate that doping La into STO could alter the optical properties of pure STO to be birefringent.
- For La-STOs with different La-doping levels, their phonon dynamic data indicate that with increasing La-doping level, the corresponding La-STO structures possess more soft modes and become unstable, especially, when the La-doping level is greater than 25%.
- With increasing La-doping levels, related to DFT energy of STO, the $\Delta H(T)$ and $\Delta G(T)$ of La-STOs decrease at given temperature. With increasing temperature, the $\Delta H(T)$ of each La-STO increases while its $\Delta G(T)$ decreases because of the effects of $T\Delta S(T)$ term.