



Transparency enhancement for SrVO₃ by SrTiO₃ mixing: A first-principles study

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ABSTRACT

SrVO₃ was recently found to be a strong candidate for transparent conducting oxide (TCO) applications. However, there is still a noticeable range of the blue spectrum that is not part of the transparency window. In response to that, we have studied the mixing of SrVO₃ and SrTiO₃ with density functional theory, cluster expansion, Monte Carlo simulations and special quasi-random structures (SQS). We confirmed with thermodynamics modeling the feasibility of obtaining solid solutions SrTi_{1-x}V_xO₃ across the full composition range (0 ≤ x ≤ 1). A simple miscibility gap closes at consolute temperature T_c = 500 K. Phase boundaries show slight asymmetry skewing toward the larger cation SrTiO₃-side. Electronic density of states and optical properties, including complex dielectric function spectra and band structures of the random solid solutions were studied with SQS. Substitution of V with Ti reduces the electrical conductivity of SrTi_{1-x}V_xO₃, which goes through a composition-driven metal to insulator transition close to x = 0.67, but suppresses the optical absorption beyond 3.25 eV. It is likely that doping or vacancy creation would enhance the electrical conductivity and extend the conducting compositions, leaving room for property tuning to obtain optimal TCO materials.

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1. Introduction

The development of transparent conductors for solar cell, light emitting, and display technologies requires combining two seemingly contradicting material properties: high optical transparency and high electrical conductivity. Among them, transparent conducting oxides (TCO) have been widely researched [1–5]. Usually, a material that excels at one aspect does not do well at the other. Traditional approaches to fabricating 10 s–100 s nm thick transparent conducting layers include heavily doping wide-gap semiconductors, adding free carriers to a transparent base material, such as degenerately doped indium tin oxide (ITO) [3]. The added carriers turn the semiconductor base material into a conductor, but there are limits as to the concentration of dopants, self-compensation [2] as well as reduced total scattering time by impurities [1]. Recently a new approach was proposed [1], taking advantage of strong electron–electron interactions in highly correlated transition metal oxides [6–13], such as SrVO₃ and CaVO₃ [1]. These TCO materials have their Fermi energy levels in the conduction band edge and are therefore already conducting. The energies of interband optical transitions are primarily above 2.8 eV, extending

into and above the blue region of the visible spectrum near 3.25 eV. The strong electronic correlation in these materials flattens the conduction band and increases the carrier effective mass, therefore reducing the energy scale of intraband transitions, limiting absorption on the red end of the visible spectrum near 1.75 eV. The outcome is a window containing the visible spectrum with low absorption present. Conductivity is in turn negatively influenced relative to metals, but is better than that of degenerately doped wide band gap semiconductors like ITO with a magnitude of 10⁴ S cm⁻¹. The “correlated metal” approach potentially provides a better trade-off between optical transparency and electrical conductivity as well as alleviating the dependency on highly priced indium.

However, the optical absorption of SrVO₃ on the higher-energy part of the visible spectrum, starting from 2.8 eV, is not optimal. There is still a noticeable range of the blue spectrum that is not part of the transparency window. Improved transparent conductor performance would be obtained if absorption due to interband transitions can be blue-shifted to higher photon energies or suppressed in magnitude. One possible approach is mixing this material with a wide-gap semiconductor of similar structure and volume, such as SrTiO₃. Both compounds adopt the ideal perovskite structure. Ti is one group earlier than V, with an ionic radius [14] of Ti⁴⁺, 0.61 Å, very close to that of V⁴⁺, 0.58 Å. As a

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Table 1

Lattice parameters a , volumes per formula unit (V/f.u.), and bulk moduli (B) from EOS's of SrTiO₃ and SrVO₃.

	a (Å)	V/f.u. (Å ³)	B (GPa)
SrTiO ₃	3.94	61.3	168
expt. ^a	3.905	59.55	184
calc. ^c	3.946	61.42	172.8
SrVO ₃	3.89	58.8	175
expt. ^b	3.841	56.67	
calc. ^c	3.866	57.79	181.5

^a Ref. [94].

^b Ref. [95].

^c FP-LAPW-GGA [112].

result, their unit-cell volumes are close too, calculated to be 61.3 Å³ and 58.8 Å³ (Table 1). SrTiO₃ has a rather large band gap of 3.25 eV [15] with interband transitions above. Previously experimental results showed that synthesis of solid solutions of the two in the full composition range is feasible [16–18]. Tsuiki et al. first demonstrated it with heat treatment of powders of SrCO₃, TiO₂ and V₂O₅ at 900–1100 °C under a flowing H₂ atmosphere and hydrostatic pressing at 100 MPa [16]. They measured the temperature-dependent conductivity, metal-nonmetal transition composition and the depth of the donor level of V⁴⁺ in SrTiO₃ [17]. Hong et al. used a higher temperature, 1550 °C and obtained similar results. Gu et al. grew epitaxial thin films using a pulsed electron-beam deposition (PED) technique at 800 °C [18]. Although conductivity was studied, optical properties were not. We intend to computationally study if the solid solutions could tune the absorption behaviors.

In this work, we study the thermodynamics of mixing SrVO₃ and SrTiO₃ with cluster expansion (CE) and Monte Carlo (MC) simulations to examine and validate the viability of obtaining SrTi_{1-x}V_xO₃ solid solutions across the full composition range (0 ≤ x ≤ 1). The cluster expansion formalism [19–24] is a first-principles approach to construct complete thermodynamic models to predict phase relations without resorting to experimental input. It fits the formation energies of a small number of structures (~50–100) calculated with density functional theory (DFT) to produce a set of effective cluster interactions (ECIs) for pairs, triplets, quadruplets, etc. This approach has been used to study a diverse set of material systems including alloys [25–32], semiconductors [33–36], ionic compounds [37–41], and minerals [42–46] yielding results that agree well with experiments. We then study electronic and optical properties, including complex dielectric function spectra, band structures, and electronic density of states (DOS) of the end members and random solid solutions with special quasi-random structures (SQS) [47,48]. SQS has also been used for a wide range of material systems and structures, both metal alloys [27,48–54] and ceramics [33,55–71], including peroxides [72,73]. We aim to explore the effects of mixing SrVO₃ with SrTiO₃ and whether it can suppress absorption near and beyond 2.8 eV, leaving the entire visible spectrum within the transparency window, and how much it adversely affects electrical conductivity.

2. Computational methods

We performed *ab initio* DFT computations with the Vienna Ab-initio Simulation Package (VASP) [74–77]. The projector-augmented wave method (PAW) [78,79] and Perdew–Burke–Ernzerhoff (PBE) generalized gradient approximation (GGA) [80,81] were used. Potentials of Sr_{sv}, Ti_{sv}, V_{sv} and O were selected, where “_{sv}” denotes that the semi-core s and p electrons are also included. Because transition metal oxides are correlated materials, the GGA + U correction scheme was used for the d orbitals of V

with U = 4 eV, a choice made by comparing the complex dielectric function spectra under different parameter sets (potentials, spin-polarization and U values) in Sec. A of the Supplemental Materials. We adjusted our choice of the U value to match the high-energy part of the visible spectra starting from 2.8 eV, which was well-modeled with FM/U = 0 in Ref. [1]. Spin-polarization was not considered due to the abrupt change of the V⁴⁺ magnetic moments, spin channel separation and non-matching visible spectra with the GGA + U scheme. The Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) did not improve the modeling of the visible spectra either, with or without spin-polarization. The GGA + U scheme for Ti however, was not used for the energy landscape calculations as per previous calibration work [82,83], but was used for electronic and optical calculations in Sections 3.4 and 3.5. A more detailed justification on our choice of a large U value is given in Section 3.3. The plane wave energy cutoff was chosen to be 400 eV for fixed cell volume & shape calculations and 520 eV for variable cell volume & shape relaxations. The k-point meshes were created with k-points per reciprocal atom (KPPRA) [84] of 1000 (Γ-centered 2 × 2 × 2) for relaxations and 4000 (Γ-centered 4 × 4 × 4) for electronic DOS and complex dielectric functions. Gaussian smearing was used with a σ value as small as 0.1 eV. For structural optimization, the atomic positions were allowed to relax until forces on any atom were below 0.02 eV/Å.

We first obtained equations of state (EOS's) for SrTiO₃ and SrVO₃. In each case, we picked 5 vol points, fitted the total energies to the Birch-Murnaghan EOS [85], and derived the equilibrium volumes (V₀) and bulk moduli (B) [86–89].

Next we used the Alloy Theoretic Automated Toolkit (ATAT) [90–93] to calculate the phase diagram of SrTi_{1-x}V_xO₃. Included in ATAT, the MIT Ab-initio Phase Stability (maps) [90,91] code was used to generate the energy landscape and CE. The Easy Monte Carlo Code (emc2 and phb) [92,93] was used to perform MC simulations to obtain the phase diagrams. Ground-state analysis was performed by using a well-converged CE to calculate formation energies (ΔE_f) for all 188,728 symmetrically inequivalent structures with 16 or fewer variable cation sites. In addition, we evaluated ΔE_f of the structures corresponding to random solid solution configurations at different compositions and fitted them to a smooth curve.

To obtain the phase diagram from CE, a box of 16 × 16 × 16 5-atom unit cells (4096 exchangeable sites) was chosen in the semi-grand canonical ensemble simulation. In such an ensemble chemical potential (μ) and temperature (T) can be given as external conditions. Chemical potential is defined as μ_i = (∂G/∂n_i)_{T,n_j≠i}, where G is the Gibbs free energy, n_i is the number of atoms of species i in the simulation cell. In a binary system A_{1-x}B_x, μ = μ_A - μ_B is used as the input. For each μ and T point, sufficient MC passes were used to make sure the composition (x) reached a precision of 0.01.

Electronic and optical properties were studied through energy/frequency-dependent complex dielectric function spectra from 0.4 to 6 eV. For random solid solution configurations of the mixed system SrTi_{1-x}V_xO₃, we employed SQS's, also used in other peroxides [72,73], at different compositions x = 1/9, 2/9, ..., 8/9. Each SQS is a supercell of 3 × 3 × 3 5-atom unit cells (27 exchangeable sites). Extensive testing suggested they are adequate, and necessarily large to model randomness. These structures were obtained from the Monte Carlo generator of Special Quasirandom Structures (mcsqs) [48] code in ATAT. The maximum pair cluster diameter was set to 7 Å and triplet to 6 Å. For each composition, four instances of stochastic searches were performed and sufficient time was allowed to obtain the same structure closest to a random configuration. These prototype structures are provided in the Supplemental Materials. For each composition, we obtained the EOS using the method described above for the end members, relaxing only the ionic positions at each volume point, and did another ionic

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