Study of thermoelectric properties of Sr0.92A0.08TiO3 (A=Yb/ Tm) perovskite oxide using density functional theory method

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Abstract. The first principle methods have been employed to investigate electronic and thermoelectric properties of Sr0.92Yb0.08TiO3 and Sr0.92Tm0.08TiO3 perovskite-oxide based molded samples. Generalized gradient approximation (GGA) with Hubbard U parameter is used by WIEN2k code for the calculations. The straight band line was observed in the band structure of both studied samples. This was generated from 4f-orbitals as shown in partial density of state diagrams. It is also noticed that Yb and Tm doped in SrTiO3 changed the perovskite-based oxide from a wideband insulator to metallic nature. A thermoelectric power factor of Sr0.92Tm0.08TiO3 sample is higher than that of Sr0.92Yb0.08TiO3, this is as a result of its huge electrical conductivity. The dependent of chemical potential to temperature was revealed in the study where high value of power factor was recorded for high temperature.

1 Introduction

Perovskite-based oxide compounds displayed similar crystal structure as the calcium titanate mineral (CaTiO3). Ideally, cubic perovskite's oxide crystal structure can be described as ABO3, where the A-site cation is 12-fold coordinate and the B site cation is 6-fold coordinate with oxygen which is anions, as present in Fig. 1[1]. Atom in A-site is typically alkaline or rare earth metal, and B-site is likely to be transition or non-transition metals [2–4]. These perovskite compounds have advantages of low toxicity and high abundance compared to the state-of-the-art materials; chalcogenides, telluride-base, etc. Nonetheless, the overall thermoelectric performance of oxide perovskites is relatively low as a result of its high thermal conductivity and low electrical conductivity. Various methods have been used to enhance oxide perovskite materials among them are doping, inducing oxygen vacancy, nanostructure, etc. These perovskite oxides have been used in many applications as well as in thermoelectric devices [5].

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Fig. 1. ABO$_3$ perovskite-oxide structure [1].

Thermoelectric (TE) materials are capable of converting heat directly into electricity through the Seebeck effect [6-8]. The performance of thermoelectric material can be determined by the dimensionless Fig. of merit (ZT) expressed by:

$$ZT = \frac{P_f T}{k}$$  \hspace{1cm} (1)

where $P_f$ is power factor, $k$ is thermal conductivity and $T$ is temperature. The $P_f$ is the product of electrical transport properties ($P_f = S^2\sigma$); Seebeck coefficient ($S$) and electrical conductivity($\sigma$). The thermoelectric material’s performance can be improved by enhancing $P_f$ and reducing thermal conductivity [9]. SrTiO$_3$ is one of the most promising n-type materials because it has unusual combinations (for an oxide) of good electrical conductivity and a high Seebeck coefficient, resulting in a power factor of 3.5 mW m$^{-1}$ K$^{-2}$ in single crystals and epitaxial films. Ytterbium and thulium are rare earth elements, lanthanides with oxidation state of 3. Yb$^{3+}$ and Tm$^{3+}$ ion can be used as a dopant in perovskite oxide, especially at A-site which is A$^{2+}$ ion. This will create the interaction between 4f orbitals in elements (Yb and Tm) and 3d-orbital in B-site [10]. Especially in SrTiO$_3$ when Yb$^{3+}$ or Tm$^{3+}$ is hosted into A-site, it can contribute an electron to Ti at its d state [11].

Hence an additional charge carrier would be induced and exchange interactions may cause improvement in electronic properties which will lead to enhancement of electronic transport properties. A current study exhibits the enhancement of thermoelectric properties in rare-earth-doped ABO$_3$ perovskite structured materials. Electronic and thermoelectric properties of SrTiO$_3$ doped by 8%Yb and 8%Tm were investigated by using first-principle methods. Band structure and density of state of Sr$_{0.92}$Yb$_{0.08}$TiO$_3$ samples are analysed for electronic properties. The thermoelectric parameter; Seebeck coefficient, electrical conductivity and power factor were studied with their dependence on temperature. Variation of power factor and chemical potential were also calculated for temperature of 300, 600, 900 and 1200 K.

2 Methods of calculation

In the present study solution of Kohn-Sham equation [12] was adopted in first-principles calculations based on the density functional theory in order to investigate the electronic and thermoelectric properties of SrTiO$_3$ doped by Yb/ Tm. This first principle was implemented
by WIEN2k package [13] by means of full-potential linearized augmented plane wave (FP-LAPW) [14] basis set. The exchange-correlation functional Perdew, Burke, and Ernzerhof (PBE) [15] in generalized gradient approximation with Hubbard model (GGA+U) was used in the calculation. The Hubbard U value of 0.8 used was selected using semi-empirical method [16] based on the result of band structure of un-doped SrTiO₃ as implemented in WIEN2K.

The self-consistent calculation were performed using 6×6×4 mesh Monkhorst-Pack in k-points, where the angular momentum Lmax = 12, RKmax = 7 and Gmax = 24 (a.u.)¹ were set. A mesh of 2000 k-points and the tetrahedral method [17] was used for the integration of the Brillouin zone. The thermoelectric properties are calculated within the basis of semiclassical Boltzmann theory using BoltzTraP software [18] and relaxation time τ = 5×10⁻¹¹s was adopted from Lemanov et al., (2004) work on dielectric relaxation in SrTiO₃: Mn[19].

3 Results and discussion

The electronic properties of un-doped SrTiO₃ were calculated in order to see the influence of dopant (Yb or Tm) on the SrTiO₃. These were analyzed via band structure and density of state results. The thermoelectric properties were determined through electrical transport properties; Seebeck coefficient and electrical conductivity. Variation of these transport properties and power factors with temperature at range of 300 to 1200 K were calculated.

3.1 Electronic structure properties

In electronic band structure, the possible energy ranges available for electrons to occupy and those regions energy which cannot be occupied; the two regions are named as energy band and forbidden or bandgap respectively. These regions are so important that the electronic properties of material can be analysed through them. They are used to illustrate the possible electronic transitions from valence band maximum (VBM) to conduction band minimum (CBM). In Fig. 2, the band structures of SrTiO₃, Sr₀.₉₂Tm₀.₀₈TiO₃, and Sr₀.₉₂Yb₀.₀₈TiO₃ samples were presented. The band energy was plotted against Brillouin zone; R, Γ, X, M, and Γ as shown in Fig. 2.

![Fig. 2. Electronic Band structure for SrTiO₃, Sr₀.₉₂Yb₀.₀₈TiO₃ and Sr₀.₉₂Tm₀.₀₈TiO₃ samples.](image)

In the process of determining the energy band gap of SrTiO₃ closed to experimental value, several Hubbard U are used [20] and at the end 0.8 of U give band energy that is in
good agreement. The direct bandgap of 3.26 eV was recorded at Γ-Γ point for SrTiO$_3$ sample (Fig. 2) similar to experimental report of indirect 3.25 eV [21]. Metallic nature in doping samples Sr$_{0.92}$Yb$_{0.08}$TiO$_3$ and Sr$_{0.92}$Tm$_{0.08}$TiO$_3$ were observed by the straight band line on the Fermi level ($E_F$), that originated from doped element Yb and Tm, as compared to un-doped SrTiO$_3$ in Fig. 2.

In order to visualize the orbital presence in the band structure, density of state calculation were performed. In Fig. 3 the partial density of state for Sr$_{0.92}$Yb$_{0.08}$TiO$_3$ and Sr$_{0.92}$Tm$_{0.08}$TiO$_3$ were presented. Fig. 3a and 3b are for Sr$_{0.92}$Yb$_{0.08}$TiO$_3$ sample while Fig. 3c is for Sr$_{0.92}$Tm$_{0.08}$TiO$_3$. It is clearly shown that 4f-orbital from dopant element (Yb and Tm) with 3d-orbital from Ti caused SrTiO$_3$ to become metallic in nature for both studied samples. Likewise, it is confirmed that this 4f-orbital formed a straight band line in the band structure diagram. Fig. 3b is displayed from scale of 10 to -10 DOS in order to see the participation of low DOS orbital in Sr$_{0.92}$Yb$_{0.08}$TiO$_3$ sample. The conduction band is composed of 3d-orbital of Ti, 4d-orbital of Yb/Tm, and 3d-orbital of Sr. The 4d and 3d from Yb/Tm and Sr atoms have little or contribution in the electronic influence of the material since the position is far from $E_F$. The valence band composed of 4f-orbital of Yb/Tm and 2p-orbital of O atom are as shown in Fig. 3b and Fig. 3c.

**Fig. 3.** Partial density of states for the study samples.
3.2 Thermoelectric properties

The thermoelectric transport properties are calculated via; Seebeck coefficient (S), electrical conductivity and power factor at the temperature of 300 to 1200 K as presented in Fig. 4. The Seebeck coefficients for both doped samples are negative; which indicate the n-type nature of the SrTiO$_3$ at these Yb and Tm doping levels. Absolute S value in Yb doped of SrTiO$_3$ is higher than that of Tm and this can be attributed to high DOS at the Fermi level in partial density of state diagram [22]. The electrical conductivity of Sr$_{0.92}$Yb$_{0.08}$TiO$_3$ and Sr$_{0.92}$Tm$_{0.08}$TiO$_3$ model sample increases with an increase in temperature which is general behaviour of semiconductors, despite the presence of doped in sample. The Tm doped model have higher electrical conductivity than the Yb doped model, as shown by the higher number of flat bands close to Fermi level in Fig. 2. It is clearly shows that the high power factor recorded for Sr$_{0.92}$Tm$_{0.08}$TiO$_3$ sample is due to large electrical conductivity compared to the Sr$_{0.92}$Yb$_{0.08}$TiO$_3$ sample. Performance of SrTiO$_3$ doped by Yb and Tm were plotted using power factor against chemical potential at range of 2 and -2 eV are displayed at constant temperature of 300 K, 600 K, 900 K and 1200 K in Fig. 5. In this Fig. 5, dependent on power factor on temperature are revealed, and both samples show high power factor at similar chemical potential value.

Fig. 4. Temperature-dependent of Seebeck coefficient, electrical conductivity and power factors for Sr$_{0.92}$Yb$_{0.08}$TiO$_3$ and Sr$_{0.92}$Tm$_{0.08}$TiO$_3$ samples.
4 Conclusion

Ab initio method in density functional theory is employed to investigate the electronic and thermoelectric properties of SrTiO$_3$ doped by 8% of Yb/Tm. It was noticed that present of Yb/Tm doped transforms SrTiO$_3$ from insulating oxide to metallic. A high density of state in doped sample is created by 4f-orbital from dopant Yb/Tm. By comparison, Yb doped sample has dense 4-f orbital at Fermi level than Tm doped sample, which leads to high Seebeck coefficient value record by Sr$_{0.92}$Yb$_{0.08}$TiO$_3$ sample. Electrical conductivity in SrTiO$_3$ doped by Tm is higher than Yb counterpart and this is a result of large number of flat band lines around Fermi level. The power factor value of Sr$_{0.92}$Tm$_{0.08}$TiO$_3$ is high than that of Sr$_{0.92}$Yb$_{0.08}$TiO$_3$, and that was attributed to its large electrical conductivity. Sr$_{0.92}$Yb$_{0.08}$TiO$_3$ and Sr$_{0.92}$Tm$_{0.08}$TiO$_3$ are excellent candidates for high temperature n-type thermoelectric devices have been recorded in variation of power factor and chemical potential.

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