Structural and thermoelectric properties of pure and La, Y doped HoMnO$_3$ for their use as alternative energy materials

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ABSTRACT

HoMnO$_3$ and its La and Y doped compounds Ho$_{0.67}$La$_{0.33}$MnO$_3$ and Ho$_{0.67}$Y$_{0.33}$MnO$_3$ are investigated for their structural and thermoelectric transport properties. Small bandgaps of these compounds, as investigated by first principles calculations, make them suitable for application in thermoelectric devices. It is found that the bandgap of pure HoMnO$_3$ increases with La and Y dopants. Thermoelectric parameters such as Seebeck coefficient, electric conductivity and thermal conductivity are calculated and their dependences on chemical potential are reported. Electrical conductivity is found to be of the order of $10^{20}$ $\Omega^{-1}$ m$^{-1}$ s and thermal conductivity of the order of $10^{15}$ W/mK for all these alloys. HoMnO$_3$ in pure form and in the presence of La and Y dopants is very suitable for thermoelectric devices and as alternative energy materials.

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1. Introduction

Energy has been one of the most common and critical issues across the globe for the last few decades. Scholars and researchers are in search of alternative energy sources and energy saving devices to overcome this issue. Therefore, search for alternative sources of energy instead of the conventional sources and different types of energy conversion technology are initiated significantly. One of the relevant technologies is the thermoelectric energy conversion which is receiving remarkable attention. In this technology, heat is directly converted into electricity and vice versa. The materials used in such technology are called thermoelectric materials [1]. Due to the high reliability and simple mechanism of converting heat into electricity thermoelectric materials are extensively used in space power generation. Broader use of thermoelectric materials is possible as these materials require only temperature gradient to operate and extract heat from waste heat energy stream [2]. Usually a figure of merit (ZT) value greater than 1 is suitable for practical applications of thermoelectric materials which is exhibited by a few non oxide materials like Bi$_2$Te$_3$ and Zn$_3$Sb$_2$. However, these materials have high toxicity and are unstable at high temperatures. Oxide materials, which do not have toxic elements and are stable at high temperature, are suitable to be investigated for thermoelectric applications [3]. Perovskite oxides display a rich variety of electronic properties as metals, ferroelectrics, ferromagnetics, and thermoelectrics. Due to their diverse range of properties, temperature stability, and robust chemistry, perovskite oxides have gained interest from the scientific community for potential application as thermoelectric materials [4,5]. Rare-earth cobalt perovskite oxides GdCoO$_3$ and NdCoO$_3$ show fairly high Seebeck coefficient at room temperature and were expected to have unique thermoelectric properties. Although, there have been a lot of studies on rare-earth oxides focused on electronic transport mechanism, but the study related to their applicability to thermoelectric materials is very rare [6]. Electron-doped SrMnO$_3$ having cubic structure can also be a good thermoelectric material because of its reported values of Seebeck coefficient. Its
value of Seebeck Coefficient is same as that of doped CaMnO$_3$ having similar electron concentration. It is pointed out that ferroelectric instability increases upon enlarging the A-site ionic radius in the perovskite compound A$^{2+}$Mn$^{3+}$O$_3$, and so an increase in the carrier mobility ($\mu$) is expected from the enhanced dielectric constant, which can screen well the impurity potential. Thus, enlarged thermoelectric capability can be achieved due to the higher $\mu$ in the electron-doped SrMnO$_3$ perovskite [7]. Heavily doping by Nb or La turns SrTiO$_3$ into a n-type semiconductor and rather large thermoelectric figure of merit of 0.34 at 1000 K is achieved which is so far more than any other oxide semiconductor. The thermal conductivity is reduced, when SrO-layers are periodically inserted in between SrTiO$_3$-layers [8].

Doped oxide thermoelectric materials are getting enormous attention to increase the thermopower and thermoelectric performance. It is pointed out that high thermoelectric figure of merit for half-metallic SrTi$_{1-x}$Co$_x$O$_3$ in a superlattice with SrTiO$_3$, the maximum value of Z hardly depends on the doping, while the temperature, at which the maximum occurs, increases with the Co concentration [9]. For a trial product of an oxide thermoelectric module using the perovskite at the room temperature thermopower is set to be larger than 200 $\mu$V/K. When temperature difference is 399 K, it generates a substantial power of 40 mW, and the generated energy density is comparable with that of commercial solar cells [10]. Enhancement of the Seebeck coefficient ($S$) without reducing the electrical conductivity is essential to realize practical thermoelectric materials exhibiting a dimensionless figure of merit $ZT$ exceeding 2, where $T$ is the absolute temperature. It is confirmed that high-density two-dimensional electron gas (2DEG) confined within a unit cell layer thickness in SrTiO$_3$ yields unusually large $S$, approximately five times larger than that of SrTiO$_3$ bulks, while maintaining a high $\sigma_{2DEG}$ [11]. To study the thermoelectric properties of SrTiO$_3$ doped with lanthanum and dysprosium, ceramic samples were prepared using the conventional solid-state reaction method. The total doping amount was fixed at 20 mol% with different amounts of lanthanum and dysprosium contents. The X-ray diffraction pattern suggests that the main crystal structure is cubic perovskite with a small amount of the second phase of Dy$_2$Ti$_3$O$_7$. The electrical conduction of the samples as a function of temperature had similar behavior to that of metallic conductivity. The negative value of Seebeck coefficient indicates that electrons are the dominant carriers. As the dysprosium content increased, both the electrical conductivity and thermal conductivity decreased whereas absolute value of the Seebeck coefficient increased. The power factor reached 1318 $\mu$W/K$^2$ m at 570 K having 12% dysprosium and 8% lanthanum doping in SrTiO$_3$. The lowest thermal conductivity was 2.3 W/mKs for the sample with 20% dysprosium as a dopant. The maximum figure of merit ($ZT$) of 0.36 at 1076 K was obtained for SrTiO$_3$ doped with 12% dysprosium and 8% lanthanum, which is a result of the high power factor combined with low thermal conductivity [12]. Mqabool and Ahmad have already investigated experimentally and reported the suitability of Ho [13] and other rare-earth elements [14] for their use in energy saving optical devices.

In this article an effort is made to investigate the thermoelectric properties of HoMnO$_3$ and its doped Ho$_{0.67}$Y$_{0.33}$MnO$_3$ and Ho$_{0.67}$La$_{0.33}$MnO$_3$, to use these compounds for their application in thermoelectric devices. As most of the good thermoelectric compounds, are toxic and unstable at high temperature. Perovskite oxides HoMnO$_3$ and its doped Ho$_{0.67}$Y$_{0.33}$MnO$_3$ and Ho$_{0.67}$La$_{0.33}$MnO$_3$ have the capability to replace them.

2. Method of calculations

Electronic structure calculations are performed through full potential linearized augmented plane waves (FP-LAPW) method based on the density functional theory implemented in the WIEN2k code [15]. For the exchange–correlation functionals, the generalized gradient approximation (GGA) [16] and generalized gradient approximation plus Hubbard potential GGA+U [17,18] are used in these calculations for ground state parameters and electronic states. Hubbard potential ($U$) value is optimized and the optimized value 3 eV is used for the calculations.

In order to calculate the electronic properties by GGA+U, we assumed that the density matrix is diagonal and $U$ is the same for all Coulomb interactions ($U_{ij} \equiv U$) and $J$ is also the same for all exchange interactions ($J_{ij} \equiv J$). There are several methods to incorporate the $U$-term [19,20], but here we used the self-interaction correction (SIC) introduced by Anisimov and co-workers [17] as implemented in the WIEN2k package. In the GGA + U $^{3C}$ method, the total energy may be written as

$$E = E_0 + E_{\text{GGA} + U^{3C}}$$

where

$$E_{\text{GGA} + U^{3C}} = \frac{U}{2} \left( N - \sum_{m} n_{\ell m}^2 \right)$$

in which $N$ is the total number of electrons and $n_{\ell m,\sigma}$ is the orbital occupancy of the $\ell$-orbital in question (i.e. s, p or d orbital) with spin $\sigma$. With an approximated correction value of $U - J$ for the SIC, this is probably best for a strongly correlated system and for a full potential method.

For the calculation of the $U_{\text{eff}}$, there are two approaches. The first approach is the method of Madsen et al. [21] as implemented in WIEN2k code. The second method is if the uncorrected GGA functional is used ($U_{\text{eff}} = 0$ eV), then the Mn 3d band in the density of states is located at significantly lower binding energies as compared to experiments. The increase in $U_{\text{eff}}$ affects the position of the Mn 3d band most prominently, which is shifted to more binding energies. The Hubbard potential used in this work was $U_{\text{eff}} = U - J \sim 3$ eV. We used this value of $U$ in order to adjust the first main peak of Mn 3d orbital level with the experimental value of about 1.7 eV [22]. This method is also used by Erhart et al. [23] for the calculation of Hubbard potential for Indium oxide.

The selected muffin-tin radii are given in Table 1. These radii for Ho, Mn and O in HoMnO$_3$ are 2.27, 1.83 and 1.62 a.u. respectively; while for Ho, Mn, O, La in Ho$_{0.67}$La$_{0.33}$MnO$_3$ are 2.28, 1.83, 1.62, 2.27 a.u. respectively. In Ho$_{0.67}$La$_{0.33}$MnO$_3$, the selected muffin-tin radii for Ho, Mn, O, Y are 2.27, 1.85, 1.62 and 2.26 a.u. respectively. A maximum number of 24 000 k points is used for the thermoelectric transport calculations. Density of states are calculated for spin up and spin down states while for thermoelectric calculations, no spin polarization is taken into consideration. BoltzTraP code [24] with interface to WIEN2k is used to calculate the Seebeck coefficient, electrical conductivity and thermal conductivity of the compounds.

3. Results and discussion

3.1. Structural optimization analysis

In optimization, lattice parameters are relaxed to the ground state to have minimum energy state of a compound. To get that state of the system, structural optimization of the compound HoMnO$_3$ and its doped compounds Ho$_{0.67}$Y$_{0.33}$MnO$_3$ and Ho$_{0.67}$La$_{0.33}$MnO$_3$ in the hexagonal structure are performed. Ground state structural lattice parameters for the compounds are given in Table 1 and the hexagonal structure of HoMnO$_3$ is given in Fig. 1. It is clear that the doping affects the crystal symmetry of HoMnO$_3$. By doping Yttrium (Y) into compound the parameters
and $b$ change from 6.14 to 6.10 Å showing decrease in these parameter, whereas $c$ parameter is decreased to 11.56 Å from 11.45 Å. Similarly, by doping La structural geometry of the unit cell is also changed and an increase is observed and $a$ and $b$ are changed to 6.15 Å and $c$ to 11.49 Å. This indicates that doping as usual changes the symmetry of the crystal.

3.2. Density of states

The electronic structure of a material is important because the properties concerned to the electrical, magnetic, optical and thermoelectric behaviors are dependent on it. It is well known from electronic point of view that materials can be simply classified into metals, semiconductors, and insulators. These three different classes of materials can be characterized by zero, small and large bandgaps respectively. Therefore the question about the potential thermoelectric material arises. It is understood that metals have very good electrical conductivity however they have low Seebeck coefficient and large thermal conductivity which do not make them the most suitable materials for thermoelectric applications [27]. Insulators have large bandgap with large Seebeck coefficient, however their extremely low electrical conductivity estimates small value of $S^2\sigma$, and thus a small $Z$ ($\sim 5 \times 10^{-17} \text{ K}^{-1}$), which is far smaller than metal materials ($\sim 3 \times 10^{-8} \text{ K}^{-1}$). The optimal thermoelectric material with a large value of $S^2\sigma$ is located in the region near the crossover between semiconductor and metal, with optimized carrier concentration of about $1 \times 10^{15}$ cm$^{-3}$. Thus the narrow bandgap and dense states of a material around the Fermi level are extremely important for good thermoelectric properties [28,29]. Electronic structure of hexagonal HoMnO$_3$ is difficult to explain as it exists in nature with limited rare earth ion (Ho), so a systematic study in terms of the different ions has been lacking bandgap of HoMnO$_3$ [24]. GGA calculations result in the bandgap value of 1.4 eV (Fig. 2) and GGA+U calculations yield bandgap value 1.58 eV (0.72 eV) for spin-up (spin-down) state. When doped with Yttrium, the bandgap increases. GGA results give bandgap of 1.5 eV, while GGA+U for spin-up states gives bandgap of 1.8 eV and for spin-down states gives 0.88 eV. Similarly, doping of lanthanum affects the bandgap and also causes increase when GGA calculations are performed its value is 1.44 eV and when calculations are by GGA+U in spin up state bandgap is 1.69 eV and in spin down state is 0.76 eV. In partial density of states, as shown in Figs. 2 and 3, it is clear that major contributor to valence band at the Fermi level is 4f states of Ho 1st and 2nd atoms and in the conduction band there is little contribution of 5d states of the same atoms. Around the Fermi level in the conduction band major contributor is Mn 3d state. The bottom of the valence band and core states is because of 2s and 2p states of O$_1$, O$_2$, O$_3$, and O$_4$. Figs. 4 and 5 give a clear look into localization of total DOS and partial DOS for the spin up and spin down states of the pristine HoMnO$_3$ as calculated by GGA+U method. Similarly when HoMnO$_3$ is doped with 33% of La and Y then existence of the contributing states of La and Y in the material is indicated in Fig. 6. The doping with 33% of Yttrium by replacing Holmium in HoMnO$_3$ the compound Yttrium 4d state exists in the conduction band as shown in Fig. 7. Lanthanum doping shows same behavior as Yttrium doping in HoMnO$_3$ depicted in Fig. 8 but the difference is that in lanthanum atom 4f state contributes to conduction band.
3.3. Seebeck coefficient

In thermoelectricity, the produced voltage depends on the temperature which can be well understood from Seebeck coefficient of the material. Mathematically, it is $S = \Delta V / \Delta T$ \[30\]. It is a fundamental parameter in the theory of thermoelectricity. Seebeck coefficient versus chemical potential is plotted for pure and doped HoMnO$_3$ in different directions in the materials shown in Fig. 9(a) and (b). It can be seen in the plots that for p-type materials an increase in the Seebeck coefficient starts at chemical potential $-0.4$ eV. The maximum Seebeck in the $x$ direction of the unit cell of the material is about 185 (10 $\mu$V/K) for pure and 165 (10 $\mu$V/K) for Lanthanum and 178 (10 $\mu$V/K) for Yttrium doped material. These peaks occur at $-0.1$ eV chemical potential. For the n-type HoMnO$_3$ the same peaks of Seebeck coefficient lie at 0.1 eV of chemical potential.
Fig. 7. $\text{Ho}_{0.67}\text{Y}_{0.33}\text{MnO}_3$ partial density of states by GGA potential.

Fig. 8. $\text{Ho}_{0.67}\text{La}_{0.33}\text{MnO}_3$ partial density of states by GGA potential.

Fig. 9. Seebeck coefficient of $\text{HoMnO}_3$ and $\text{Ho}_{0.67}\text{Y}_{0.33}\text{MnO}_3$ and $\text{Ho}_{0.67}\text{La}_{0.33}\text{MnO}_3$ at 300 K.

Fig. 10. Seebeck coefficient variation with respect to temperature.

potential. Decrease in Seebeck value is observed for higher values of chemical potential reaching to zero at $\mu = 0.6$ eV.

In the z-direction of the material relatively higher value of Seebeck coefficient is found for the pure $\text{HoMnO}_3$ as compared to its value in the x-direction for p-type. A peak corresponds to a maximum value of Seebeck coefficient of 220.04 (10 $\mu$V/K) for pure p-type material, while for Lanthanum and Yttrium doped materials it decreases to 186.50 (10 $\mu$V/K) and 206.01 (10 $\mu$V/K), respectively. These peaks are at $-0.1$ eV of chemical potential. Similarly in the z-direction, for the n-type materials, the Seebeck coefficient is not as big as for the p-type and the peak corresponds to the maximum value decreases to about $-160$ (10 $\mu$V/K) for $\text{HoMnO}_3$ and about $-150$ (10 $\mu$V/K) for La and Y dopants. The effect of temperature on the Seebeck coefficient of pure $\text{HoMnO}_3$ is given in Fig. 10. The value of Seebeck coefficient increases to a maximum value at 250 K followed by a decrease as temperature increases, reaching to zero with increase in temperature beyond 500 K.

3.4. Electrical conductivity

Another important parameter in reference to thermoelectricity is Electrical conductivity. Electrical conductivity depends on carrier concentration and its flow. Fig. 11(a) and (b) represents electrical conductivity along different directions for hexagonal pure
and doped HoMnO$_3$. Electrical conductivity of pure HoMnO$_3$ and doped in the p-type region is zero. Therefore, material is n-type and electrical conductivity starts to increase at 0.5 eV chemical potential. It is clear from the plot that in the x-direction maximum electrical conductivity of pure HoMnO$_3$ is about 1.4 (10$^{20}$ 1/mΩs). When doped with Lanthanum and Yttrium, electrical conductivity increases to 1.6 (10$^{20}$ 1/mΩs) at $\mu = 1$ eV for both dopants. Further increase in chemical potential again increases electrical conductivity with a maximum value of 1.7 (10$^{20}$ 1/mΩs) for Yttrium doping in the x-direction which is the maximum value among all values.

In the z-direction, the response of the electrical conductivity of materials is the same as in the x-direction up to 0.5 eV chemical potential. A variation in response starts in both directions for the chemical potential above 0.5 eV. At $\mu = 1.2$ eV a sudden increase occurs in electrical conductivity to a value of 2 (10$^{19}$ 1/mΩs) for La doped HoMnO$_3$ and 1.8 (10$^{19}$ 1/mΩs) for pure and Y doped materials. Fall and again increase at $\mu = 1.5$ eV, reaches to maximum value 6.7 (10$^{19}$ 1/mΩs) for pure HoMnO$_3$, 6.3 (10$^{19}$ 1/mΩs) for La doped material and 6 (10$^{19}$ 1/mΩs) for Y doped material when $\mu = 1.9$ eV.

3.5. Thermal conductivity

Thermal conductivity for HoMnO$_3$ and its doped compounds, calculated at 300 K, are plotted in Fig. 12(a) and (b). In the x-direction, there is no response and the thermal conductivity is zero for the p-type HoMnO$_3$, Ho$_{0.67}$La$_{0.33}$MnO$_3$ and Ho$_{0.67}$Y$_{0.33}$MnO$_3$. Along the x-direction, for the n-type materials, thermal conductivity starts getting value at 0.4 eV and exponentially increases to 0.96 (10$^{15}$ W/mKs) for pure and 1.05 (10$^{15}$ W/mKs) for doped HoMnO$_3$ with La and Y at $\mu = 1.1$ eV. As chemical potential increases, a sudden fall in the thermal conductivity occurs till 1.6 eV. Then an increase starts in thermal conductivity, reaching to maximum values with highest value of 1.19 (10$^{15}$ W/mKs) for Yttrium doped HoMnO$_3$. For Lanthanum doped thermal conductivity maximum value is approximately 1.1 (10$^{15}$ W/mKs) for pure HoMnO$_3$ it is 1.04 (10$^{15}$ W/mKs).

Along the z-direction, the thermal conductivity response is zero for the p-type materials and negligible for the n-type materials, below 1 eV chemical potential. An increase in thermal conductivity started above 1 eV chemical potential and reaches to maximum value around $\mu = 2$ eV. The maximum value of thermal conductivity attained for the pure HoMnO$_3$ is 4.3 (10$^{14}$ W/mKs). The compound Ho$_{0.67}$La$_{0.33}$MnO$_3$ has peak value of about 4.0 (10$^{14}$ W/mKs) and for Ho$_{0.67}$Y$_{0.33}$MnO$_3$ peak value is 3.7 (10$^{14}$ W/mKs). After it an exponential decrease in thermal conductivity occurs for all compounds.

4. Conclusions

Structural, electronic, and thermoelectric properties are calculated for the pristine HoMnO$_3$ and its La and Y doped compounds...
in the hexagonal structure for their use as alternative energy materials. The structural and electronic calculations are performed within the density functional theory using the full potential linearized augmented plane waves plus local orbital (FP-LAPW+lo) method employing GGA and GGA+U as embodied in the WIEN2k code, while the thermoelectric properties calculations are carried out applying the semiclassical Boltzmann transport theory utilizing the BoltzTraP package. The thermoelectric properties are obtained from the calculated band structures by performing additional postprocessing calculations applying the BoltzTraP package. The pristine and doped compounds are predicted to behave as narrow bandgap semiconductors in the scope of our used approximations. On the basis of the narrow bandgap nature, thermoelectric transport properties of these compounds are investigated. It is predicted that maximum (minimum) Seebeck coefficients for HoMnO$_3$, Ho$_{0.67}$Y$_{0.33}$MnO$_3$, and Ho$_{0.67}$La$_{0.33}$MnO$_3$ are 220.04 (−194.94), 206.01 (−184.94), and 186.50 (−173.37) in the unit of $10^\mu V/K$, respectively. Electrical conductivity for HoMnO$_3$, Ho$_{0.67}$La$_{0.33}$MnO$_3$ and Ho$_{0.67}$Y$_{0.33}$MnO$_3$ has maximum values of 1.4, 1.6, and 1.7 ($10^6$ 1/m Ω s), for x direction, respectively. Thermal conductivity has maximum values of 1.04, 1.19 and 1.1 ($10^15$ W/mKs) for HoMnO$_3$, Ho$_{0.67}$Y$_{0.33}$MnO$_3$ and Ho$_{0.67}$La$_{0.33}$MnO$_3$, respectively. These values of the thermoelectric characteristic properties show that HoMnO$_3$ and its La and Y doped compounds are good candidates for their potential use in thermoelectric devices.

References