Thermoelectric properties of $CdGa_2O_4$ spinel

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Abstract. Thermolectric materials can convert heat into electricity and thermoelectric devices can play an important role in the efficient use of energy. In this study, we investigate the thermoelectric properties of the hard glassy spinel mineral $CdGa_2O_4$. The potential of a material to be a candidate as the active component of a thermoelectric device is given by the figure of merit (denoted by ZT), which includes information on the lattice and electronic transport properties. Given the difficulties of directly measuring ZT experimentally, we computed its value within density functional theory using linearised Boltzmann transport equations in a relaxation time approximation. From the determined ZT values, we find that $CdGa_2O_4$ is promising as a high temperature thermoelectric material.

1. Introduction

The world continues face a grand challenge in discovering sustainable and alternative energy sources. To help meet this challenge a significant scientific effort is needed in basic science related to clean energy generation, conservation and utilization. To this end we present results from ab-initio calculations on thermoelectric materials that show promise for application in this technological and societally valuable field. Thermoelectric materials can generate electricity from waste heat or be used as solid state Peltier coolers which in turn play a crucial role in finding a global sustainable energy solution. Although a number of materials have been studied as well as applied in thermoelectric applications such as Bi_2Te_3 [1], PbTe [2] and $MgIn_2X_4$ (X=S, Se) [3] just to mention a few; the attainable efficiency at the moment is very low for practical large scale energy production. In this study, we explore $CdGa_2O_4$ as a candidate for thermoelectric applications based on first principles study. $CdGa_2O_4$ belongs to a group of compounds called spinels. Generally, a spinel is a hard glassy mineral that occur either as octahedral or tetrahedral crystals of variable colour consisting mainly of magnesium and aluminium oxides having a general formula AB_2O_4 [4]. $CdGa_2O_4$ belong to space group Fd3m consisting of 8 formula units having a closed packed face-centered-cubic structure hence highly symmetric. To review what has been done on this compound, first principle studies on structural, electronic, optical and mechanical properties of $CdGa_2O_4$ has been reported by Bouhemadou *et al.* [5]. As per Nguyen and Koffyberg [6], this compound has a wide indirect experimental band gap of 3.07 eV. In addition, it has been explored as a sensor [7] as well as a phosphor when combined with $ZnGa_2O_4$ [8]. To the best of author's knowledge, lattice thermal conductivity, transport and thermoelectric

properties of $CdGa_2O_4$ spinel has never been reported before, which forms the basis of the present study.

2. Methodology

We report a computational study on the structural, vibrational, energetic, mechanical, electronic, thermal, transport and thermoelectric properties of $CdGa_2O_4$ done using density functional theory as implemented in Vienna *ab initio* simulation package (VASP) [9]. In order to test the reliability of our results, structural, energetic and mechanical studies were carried out using three functionals namely: local density approximation (LDA), generalized gradient approximation (GGA-PBE) as well as PBEsol (a functional intended for solid state and surface systems). The energy cut-off for the plane wave expansion was fixed at 520 eV. The atomic forces and energies were converged within 10^{-4} eV/$\mathring{A}$ and 10^{-8} eV respectively for structural calculations. For elastic constant calculations, stress-strain technique proposed by Shang *et al.* was applied [10]. Vibrational studies were carried out following the finite displacement approach as implemented in Phonopy [11] with a 2×2×2 supercell of the primitive unit cell consisting of 112 atoms with a Monkorst-Pack grid of size 3×3×3 used to sample the Brillouin zone in order to obtain the second and third order force constants from Phonopy and Phono3py [12] respectively. We computed the intrinsic lattice thermal conductivity of $CdGa_2O_4$ by solving Boltzmann transport equations based on first principle studies under the mode dependent relaxation time approximation. A mesh size of 20×20×20 was found sufficient for computing lattice thermal conductivity. All triplet displacements in the supercell were included.

3. Results and discussion

3.1. Structural and energetic properties

From Table 1, LDA functional is capable of reproducing the structural properties of $CdGa_2O_4$ better than PBE and PBEsol in comparison with the existing experimental information. Hence further in-depth study on phonon, electronic, thermal and transport properties of $CdGa_2O_4$ was conducted using LDA functional. Moreover, negative values of formation and cohesive energies obtained indicates that this material is energetically stable [13].

Table 1. Structural and energetic parameters.

	a (Å)	V_0 (Å^3)	E_{coh} (eV/atom)	E_{form} (eV/atom)
PBE	8.783	677.52	-4.078	-1.630
PBEsol	8.666	650.80	-4.535	-1.683
LDA	8.583	632.29	-4.974	-1.796
Expt.[14]	8.590	633.84	-	-

3.2. Mechanical properties

Table 2 gives a summary of the bulk (B), shear (G) and Young's modulus (E) as well as the independent elastic coefficients of cubic $CdGa_2O_4$. Its Zener anisotropy factor (A) and Fratserich's ratio (G/B) computed using three functionals in comparison with existing theoretical values. From the elastic coefficient values obtained, $C_{44} > 0$; $C_{11} > |C_{12}|$ and $(C_{11}+2C_{12})C_{33} > 2C_{13}^2$ fulfilling the requirement of mechanical stability in cubic crystals [15]. Computed values of Zener anisotropy factor is non-unity for all functionals, suggesting that $CdGa_2O_4$ possess mechanical anisotropy. Fratserich's ratio (G/B) [16] is less than 0.571 for all the three functionals used, indicating that $CdGa_2O_4$ is ductile in nature.

Table 2. Mechanical properties of $CdGa_2O_4$ spinel oxide.

	B (GPa)	G (GPa)	E (GPa)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	A	G/B
LDA	182.21	61.45	165.71	229.38	158.63	88.92	2.51	0.34
PBEsol	166.49	56.85	153.13	208.45	145.51	84.42	2.68	0.34
PBE	149.08	56.05	149.43	190.00	128.62	83.83	2.73	0.38
Theory [17]	154.00	-	102.00	203.00	130.00	91.00	-	-

3.3. Dynamical and electronic properties

Phonon dispersion curves had no soft phonon modes as provided in Figure 1 which indicates dynamical stability in $CdGa_2O_4$. The acoustic cut-off frequency which marks the maxima of acoustic phonon modes was determined to be 3.9 THz. From the partial phonon density of states, the primary element contributing to the acoustic phonon modes is Cadmium. To overcome the shortcoming of band gap underestimation at DFT level, we applied the scissor correction technique [18] to open the indirect band gap of $CdGa_2O_4$ from its 1.805 eV DFT value to its reported experimental gap of 3.07 eV [6] as shown in Figure 2. This was attained by upshifting the conduction band energies. The resultant energies were then used as input for BoltzTrap code [19] in order to explore transport properties of $CdGa_2O_4$. In addition, our computed DFT value of the indirect band gap (1.805 eV) is comparable to that reported by Bouhemadou *et al.* [5] (1.899 eV) along the K-Γ point in the Brillouin zone.

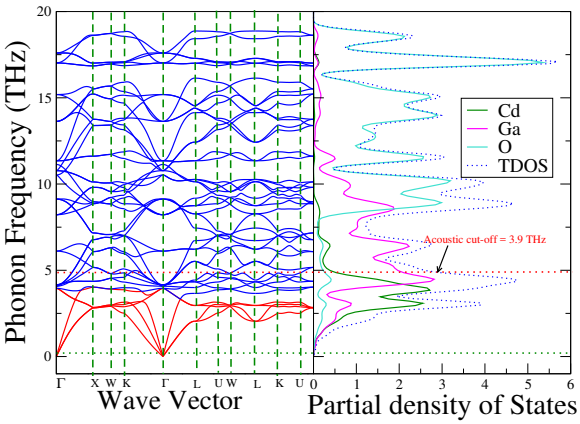

Figure 1. Phonon dispersion.

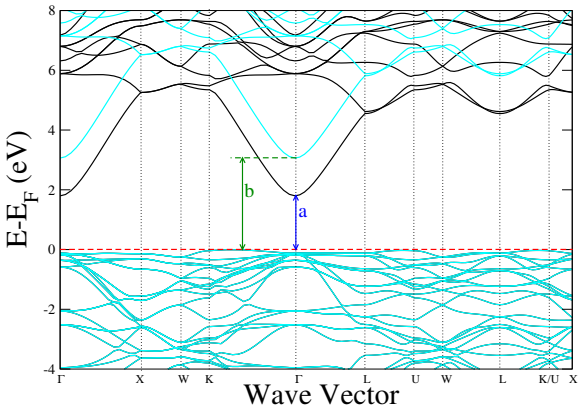

Figure 2. Electronic bands with (cyan) and without (black) scissor correction at DFT level.

3.4. Thermal properties

Atoms constituting a crystal vibrate about their mean positions generating thermal energy arising from the vibrational motion. This thermal energy increases with an increase in temperature and dictates the thermal properties of a given material. For $CdGa_2O_4$, specific heat capacity at a constant volume (C_v), approaches constant value of about 340 J(mol K)$^{-1}$ at high temperature. This value is known as Dulong-Petit limit [20]. From Figure 3, we predict that at 300 K, entropy, Helmholtz free energy and specific heat capacity of $CdGa_2O_4$ are 50.3 kJmol^{-1}, 274.4 J(mol K)$^{-1}$ and 271.7 J(mol K)$^{-1}$ respectively. It is evident that the degree of

disorderness (entropy), increases with an increase in temperature whereas the reverse is true for free energy. $CdGa_2O_4$ shows isotropic thermal properties in that its lattice thermal conductivity is similar in all the directions. This could be attributed to the fact that this compound is highly symmetric having a cubic structure. At 300 K, the predicted K_l value is 9.38 W/mK as indicated in the inset plot of Figure 4. In addition, the cummulative lattice thermal conductivity (Cum K_l) and its derivative (dK_l) attest that the dominant contributor to K_l is acoustic phonon modes. This is reinforced by the fact that below 3.9 THz which is the acoustic cut-off limit (dotted), there is a sizable increase in Cum K_l and dK_l with an increase in frequency.

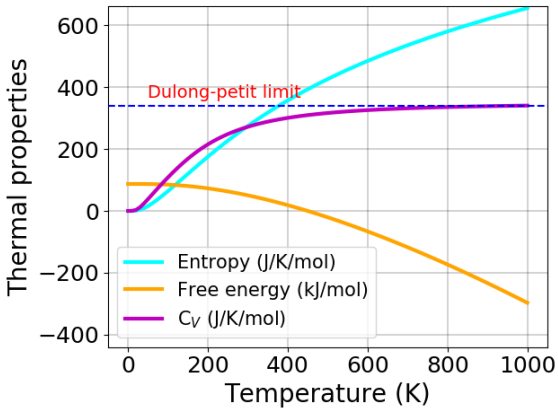

Figure 3. Calculated temperature dependence of free energy, entropy and C_v.

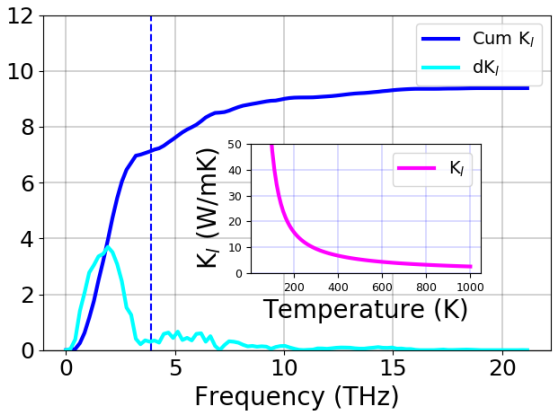

Figure 4. Calculated K_l, its cummulative and derivative.

3.5. Transport properties

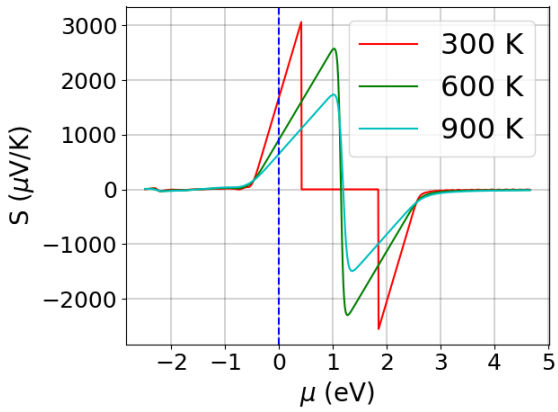

Figure 5. Seebeck coefficient vs chemical potential (μ).

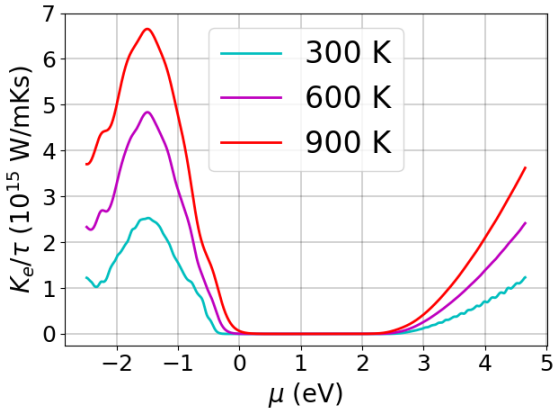

Figure 6. Electronic contribution to total thermal conductivity.

From Figure 5, it is visible that when $\mu = 0$ eV the value of Seebeck coefficient (S) is positive which indicates prior doping, $CdGa_2O_4$ is an intrinsic p-type semiconductor with a value of about 1700 μV/K at 300 K. Moreover, the magnitude of S increases with an increase in temperature at a constant μ value whereas the inverse is true for K_e/τ as substantiated by Figure 5 and 6.

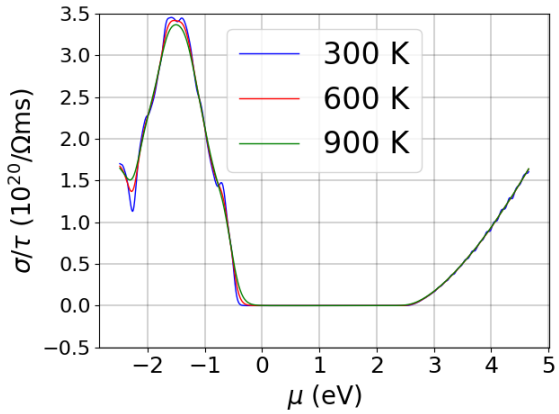

Figure 7. Electrical conductivity.

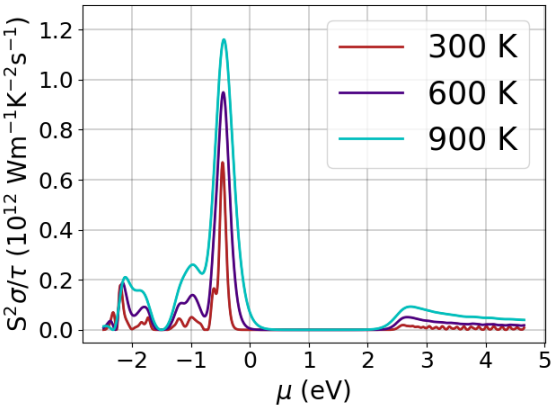

Figure 8. Power factor.

Within the rigid band-shift model, the chemical potential determines the carrier concentration of a compound. For p-type (n-type) doping, the Fermi-level shifts down (up) corresponding to a negative (positive) chemical potential [21]. The intensity of the peaks for σ/τ, K_e/τ and power factor are higher for p-type than n-type indicating that $CdGa_2O_4$ is more efficient when majority charge carriers are holes than electrons as backed by Figure 7 and 8. This is further verified by the magnitudes of ZT with respect to temperature at various doping levels as presented in Figure 9.

3.6. Thermoelectric properties

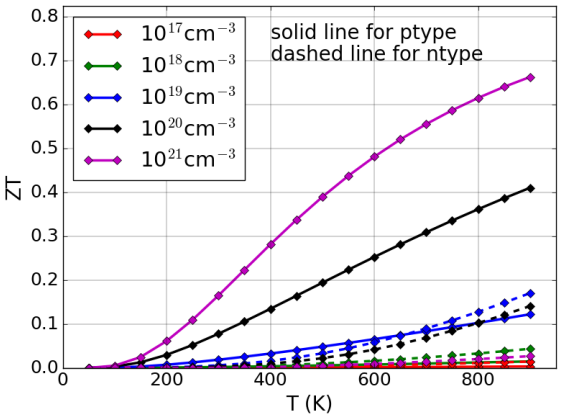

Figure 9. ZT for both holes and electrons.

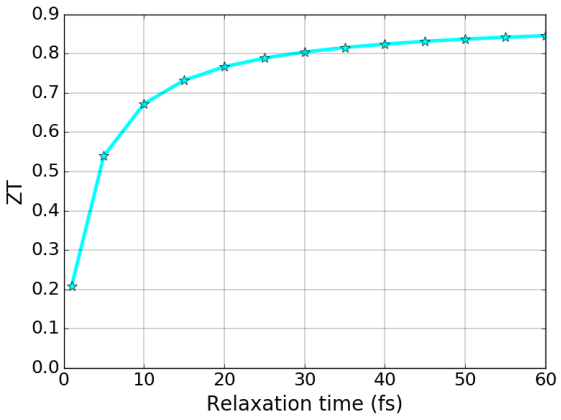

Figure 10. Variation of ZT with τ.

All the above transport and thermoelectric analysis was done at the constant relaxation time (τ) value of 10 *fs* as implemented in Boltztrap code. To further check the behaviour of ZT upon varying τ during data analysis, we performed ZT convergence with respect to τ as exhibited in Figure 10. Above 45 *fs*, the value of ZT becomes less dependent on τ. When τ is 45 *fs*, the optimum value of ZT attained at high temp of 900 K with hole concentration of 10^{21} cm^{-3} is 0.82 which is slightly higher than 0.66 attained when relaxation time is kept at its default value of 10 *fs*.

4. Summary and conclusion

We have computed structural, vibrational, energetic, mechanical, electronic, thermal, transport and thermoelectric properties of $CdGa_2O_4$ based on density functional theory. Besides being stable, $CdGa_2O_4$ is a promising high temperature thermoelectric material. The highest ZT value is attained when majority charge carriers are holes with a concentration of 10^{21} cm^{-3} at 900 K having an estimated ZT value of 0.66 and 0.82 when the constant relaxation time is 10 *fs* and 45 *fs* respectively.

Acknowledgments

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