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# Thermal Properties of EuO, DyO and GdO Compounds

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In this study, the thermal properties of EuO, DyO, and GdO compounds were investigated. The calculations were performed by using an ab initio approach based on the density functional theory (DFT) and exchange-correlation functional taken as generalized gradient approximation (GGA) and GGA + *U* (Hubbard Coulomb onsite correction) as implemented in the Quantum Espresso suite of codes. Results indicate that the Seebeck coefficient of the rare earth oxide is high at low temperatures, and it decreases with increasing temperature. The figure of merit (ZT) increases with temperature up to the studied temperature range and also shows the higher figure-of-merit obtained by DyO compound as compared with EuO and GdO, respectively. We obtained a maximum value of 0.008 of ZT at 800 K of DyO.

**Keywords:** Rare earth oxides, Thermal properties, Density functional theory (DFT), Seebeck coefficient.

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## 1. INTRODUCTION

In the present scenario, lanthanide-based materials have been strongly developed for their technical application [1]. The rare earth oxides are presently the subject of significant and growing interest because of their probable use in the scientific field [2]. Due to the open valence layers 4*f*, 5*d*, relativistic influences, and near degeneration of the states of lanthanide compounds in these molecules, the spectra are extremely complex [3].

In the present work, the thermal properties of rare earth oxides such as the Seebeck coefficient, figure of merit, and thermal conductivity were calculated. The quality of materials for TE application is described by a dimensionless parameter $zT$ [4], which is defined as the following:

$$zT = \frac{S^2\sigma}{K}T\,,$$

where the Seebeck coefficient is denoted by $S$, electrical conductivity is denoted by $\sigma$, and thermal conductivity is denoted by $K$. The power factor (PF) is referred by $S^2\sigma$, which indicates the output power of thermoelectric power generator. The Seebeck coefficient ($S$, in V/K) can be expressed as the following:

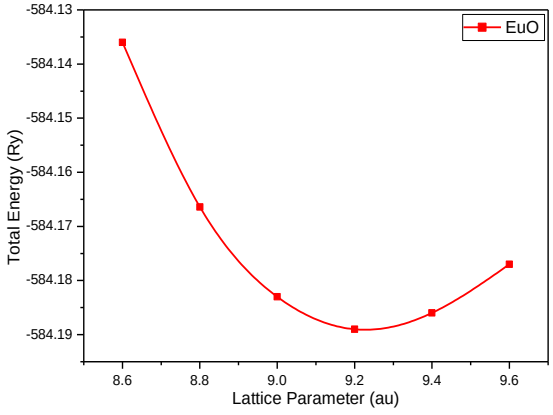
$$S_{\alpha\beta}(T,\mu) = \frac{1}{eT\sigma_{\alpha\beta}(T,\mu)}\int\sigma_{\alpha\beta}(\varepsilon)(\varepsilon-\mu)\left[-\frac{\partial f_\mu(T,\varepsilon,\mu)}{\partial E}\right]d\varepsilon\,.$$

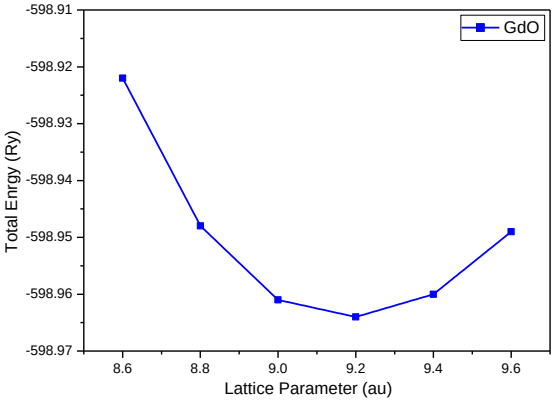
The electrical conductivity ($\sigma$) is defined as:

$$\sigma_{\alpha\beta}(T,\mu) = \frac{1}{\Omega}\int\sigma_{\alpha\beta}(\varepsilon)\left[-\frac{\partial f_\mu(T,\varepsilon)}{\partial E}\right]d\varepsilon\,.$$

The thermal conductivity ($k$) is given as:

$$\kappa_{\alpha\beta}(T,\mu) = \frac{1}{e^2T\Omega}\int\sigma_{\alpha\beta}(\varepsilon)(\varepsilon-\mu)^2\left[-\frac{\partial f_\mu(T,\varepsilon)}{\partial E}\right]d\varepsilon\,.$$

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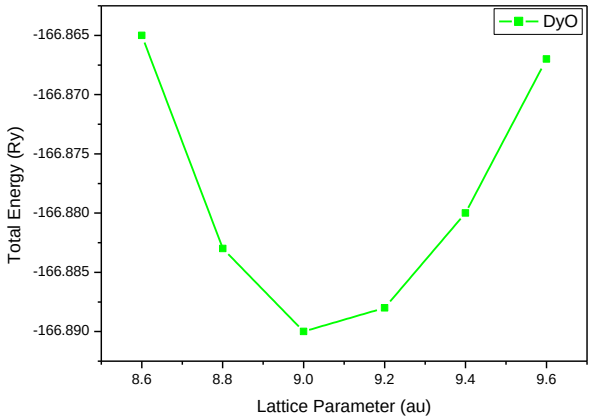


**Fig. 1** – Lattice parameters versus total energy plot of EuO, GdO and DyO compounds

To guide and understand the results of an experiment, computational calculations play a vital role. In this paper, thermoelectric properties such as the Seebeck coefficient, electrical conductivity, thermal conductivity, DOS, and hence the figure of merit of rare earth oxides were determined by an ab-initio approach.

## 2. COMPUTATIONAL DETAILS

The structural and thermal properties of rare earth oxides within rock salt structure have been investigated. As implemented in Quantum Espresso Code [5], all calculations were performed using the first-principles method of spin density-functional theory (DFT) and generalized gradient approximation (GGA) used for including exchange and correlation effects as implemented in Perdew-Burke-Ernzerhof (PBE) functional [6]. Ultra-soft pseudopotentials were employed [7]. On the basis of convergence, the energy cutoff of 250 Ryd was used in all calculations for the plane-wave basis functions, and Brillouin zone integration was performed using a $12 \times 12 \times 12$ special $k$-point mesh. The convergence for the energy was 0.001 Ry. BoltzTraP code [5] was used to find out the TE properties composed of $S$, $\sigma$, and $k$ of rare earth oxides.

## 3. RESULTS AND DISCUSSION

The ground-state properties of rare earth oxides were obtained using the energy-volume variation, equilibrium lattice constant, bulk modulus, and pressure derivative of the bulk modulus as implemented by the Murnaghan equation of state [8]. The lattice parameter versus total energy plot of the EuO, GdO, and DyO compounds is shown in Fig. 1, and the obtained results for all systems are presented in Table 1, along with some previous theoretical calculations and available experimental measurements. The obtained lattice parameters in our calculations are 4.88, 4.85, and 4.79 Å, for EuO, GdO, and DyO compounds, respectively. Our results are in good agreement with available theoretical and experimental results.

The valence band region of the EuO and DyO compounds is divided into three sets as low, medium, and high-energy bands as shown in the total DOS in Fig. 2. In which the contribution of anions and cations to each series of bands by decomposing the total DOS into con-

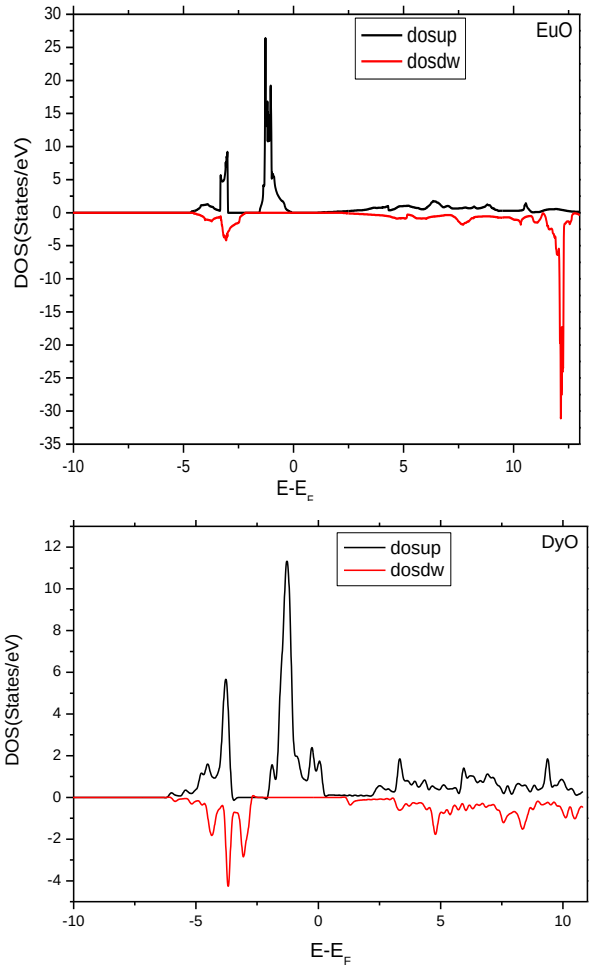


**Fig. 2** – Total DOS of EuO and DyO compounds

tributions of $s$, $p$, $d$, and $f$ orbitals were analyzed. It is clear that in the case of spin up, the valence band is between − 4.49 and − 2.98 eV and − 6.16 and − 3.14 eV, respectively, for EuO and DyO, has its origin from the O-$p$ orbitals, whereas the intermediate energy in the range of − 1.65-0 eV for EuO and − 2.18-0 eV for DyO comes from the $f$-orbitals of Eu and Dy atoms (zone close to the gap). In the high energy (conduction band) region, within 2.3-12.4 eV for EuO and 2.14-10.72 eV for DyO, orbitals of Eu and Dy atoms predominate.

In the case of spin down, at low energies (valence band) from − 4.49 to − 2.16 eV and − 6.16 to − 2.68 eV for EuO and DyO, respectively, O-$p$ orbitals predominate. In the valence band, close to the gap between − 0.92 and − 0.54 eV for DyO, Dy-$f$ predominate. The energies of the conduction band for DyO (between 1.13 and 10.72 eV) contribute significantly to the 4$d$ state of the Dy atom. Concerning the EuO compound, it is the Eu-4$d$ orbitals that are dominant for the conduction energies from 2.3 up to 12.78 eV.

It is clear from the figure that at low temperatures, the Seebeck coefficient of the rare earth oxide is high and with increasing temperature, it decreases. The reason for decreasing the Seebeck coefficient with increasing temperature is due to the band gap shift, hence the Fermi level shifts towards the middle of the band gap, and the intrinsic activation energy increases with temperature up to the bandgap energy.

**Table 1** – Lattice parameter, bulk modulus and their derivative of the EuO, GdO, and DyO compounds

| Material | | Lattice parameters ($a_0$) Å | Bulk modulus ($K_0$) GPa | Derivative ($dK_0$) | Volume (in ang$^3$) |
|---|---|---|---|---|---|
| EuO | Present work | 4.88 | 140.6 | 4.56 | 197.10 |
| | Experimental | 5.14 [9] | 110±5 [9] | – | – |
| | Theoretical | 4.8499 [10], 3.63 [11] | 118 [2], 136.899 [10] | 4.7931 [10], 3.3 [12] | – |
| GdO | Present work | 4.85 | 140.7 | 4.72 | 193.07 |
| | Experimental | – | – | – | – |
| | Theoretical | – | – | – | – |
| DyO | Present work | 4.79 | 141.4 | 4.95 | 185.59 |
| | Experimental | – | – | – | – |
| | Theoretical | 4.8403 [10] | 130.2469 [10] | 4.7579 [10] | – |

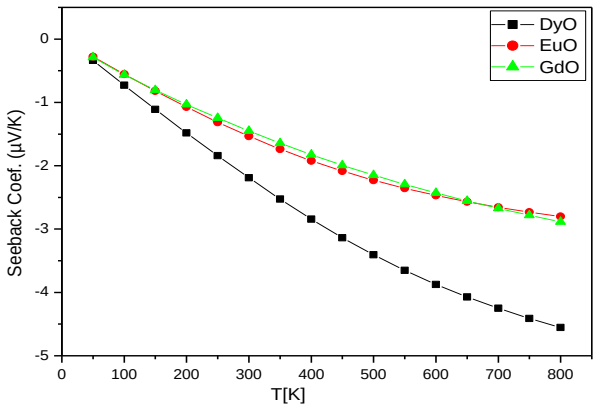


Fig. 3 – Seebeck coefficient as a function of temperature

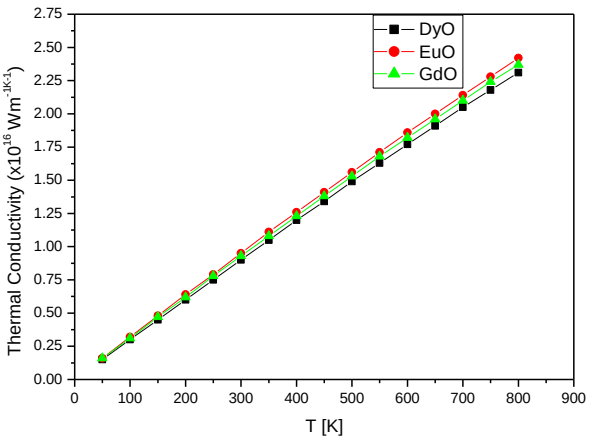


**Fig. 4** – Thermal conductivity of the EuO, DyO and GdO compounds as a function of temperature

The thermal conductivity ($k$) of EuO, DyO, and GdO compounds are shown in Fig. 4. The thermal conductivity has increased by increasing temperature and it has a very high maximum at 800 K due to the 3-phonon scattering [13]. At higher temperatures above 800 K, the thermal conductivity remains unchanged which does not show bipolar contribution.

As shown in Fig 5, the figure of merit (ZT) as a function of temperature was calculated to divulge its applicability in thermoelectric devices. It is clear that ZT increases with temperature up to the studied temperature range, and also Fig. 5 broadly illustrates that the DyO compound obtains more ZT as compared to EuO and GdO compounds. Whereas ZT of EuO and GdO at temperatures more than 800 K remains unchanged and ZT of DyO shows an increasing trend in ZT even at higher temperatures. We obtain a maximum ZT value of 0.008 at 800 K of DyO.

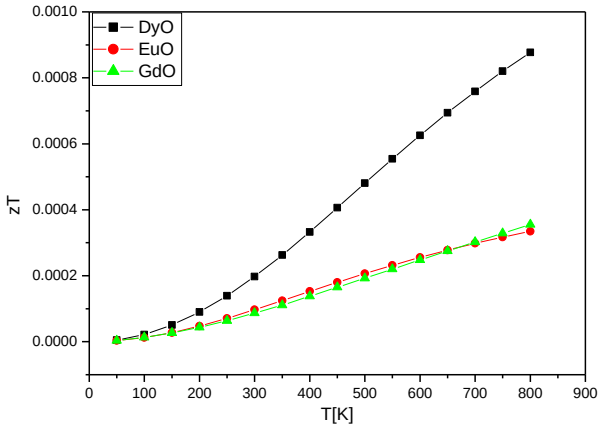


**Fig. 5** – Figure of merit (ZT) as a function of temperature

Therefore, our study shows that DyO is suitable for thermoelectric device applications if we can increase the figure of merit further by alloying or nanostructuring mechanism because the thermal conductivity can reduce drastically improvement of scattering of electrons and phonons [14-19]. To improve the value of the figure of merit, this study will inspire experimentalists to synthesize EuO, DyO and GdO compounds to improve thermoelectric performance by alloying with a suitable element.

## 4. CONCLUSIONS

After calculating the TE properties of EuO, DyO, and GdO compounds by DFT and Boltzmann transport theory, these rare earth oxides were observed as TE generator elements at a low temperature of 300 K. Due to their low cost and easy operation, EuO, DyO and GdO compounds will be very beneficial in situations, where the low-temperature conditions are required for energy conversion. Yet, as required these may also be fabricated in nanoscale. The ultimate thermal properties of these materials are important even for devices or electronic systems, and at the same time can be useful in energy conversion characteristics. As a result, the research paper concludes by introducing new materials for energy generation.

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## Теплові властивості сполук EuO, DyO та GdO


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У дослідженні вивчено теплові властивості сполук EuO, DyO та GdO. Розрахунки були виконані з використанням підходу ab initio, заснованого на теорії функціонала щільності (DFT) та обмінно-кореляційного функціонала, взятого як наближення узагальненого градієнта (GGA) і GGA + *U* (корекція Хаббарда-Кулона), як реалізовано в наборі кодів Quantum Espresso. Результати показують, що коефіцієнт Зеебека рідкісноземельного оксиду високий при низьких температурах і зменшується з підвищенням температури. Коефіцієнт якості (ZT) зростає з підвищенням температури до досліджуваного діапазону температур, сполука DyO показує вищий коефіцієнт якості порівняно з EuO та GdO. Ми отримали максимальне значення ZT 0,008 при 800 K DyO.



**Ключові слова:** Рідкоземельні оксиди, Теплові властивості, Теорія функціонала щільності (DFT), Коефіцієнт Зеебека.