Investigation of doped Perovskite systems $RAlO_3$ using density functional theory based electronic structure and thermoelectric studies

Sandeep[1]*, D. P. Rai[2], A Shankar[3], M. P. Ghimire[1] and R. K. Thapa[1]

[1]Condensed Matter Theory Research Group, Physics Department, Mizoram University-796004, India
[2]Department of Physics, Pachhunga University College, Aizawl-796001, India
[3]Department of Physics, University of North Bengal, Darjeeling -734013

*Email: sndp.chettri@gmail.com

Abstract. Samarium doping effects on the thermoelectric properties in $Eu_{1-x}Sm_xAlO_3$ (x=0%, 50%, and 100%) were studied using first principles calculations based thermal transport property measurement. The result indicate that the compound is an intrinsic n-type material. Samarium doping has a positive effect on the overall thermoelectric performance of the $Eu_{1-x}Sm_xAlO_3$ system, with sharp increase in figure of merit (*ZT*) observed when x=0, 50 and 100% up to 150K. Compared to x=0 and 100%, the case of x=50% was found to have more positive increment in *ZT* value suggesting that the doing to have positive effect on figure of merit in $Eu_{1-x}Sm_xAlO_3$. Furthermore, all the samples show stable thermoelectric compatibility factors over a broad temperature range from 700 to 1000 K, which could have great benefits for their practical applications. It is concluded that the overall thermoelectric performance of the $Eu_{1-x}Sm_xAlO_3$ could be highly enhanced using doping techniques.

1. Introduction

Thermoelectric compounds have drawn renewed interest in the recent past due to their wide applicability in the field of device and high temperature components [1]. The perovskites have been known for their potential applications as electronic and thermoelectric devices [2-3] due to the rich exhibition of phase transformation with temperature and doping [4]. $EuAlO_3$ have been studied using mBJ and GGA+U based approximation to compute the electronic structures and were found to have high density of states at E_F supporting its candidature as thermoelectric device fabrication [5]. Thermoelectric power and electrical conductivity of $LaAl_{0.95}Mg_{0.05}O_{3-\delta}$ and $ErAl_{0.95}Mg_{0.05}O_{3-\delta}$ have been studied as a function of oxygen partial pressure [6]. The isobaric heat capacity of $SmAlO_3$ in the range 0-300 K has been measured with adiabatic calorimetry and its dependence on the electronic structures were reported with emphasis on 4*f* state electrons [7]. Thermo-electric efficient materials in pure or doped form have attracted the researchers in the last few decades, because of their striking features like easy synthesis, good conductance, price and stability [8]. Wilfried *et al.* studied the large Seebeck coefficient and its dependence on effective electron mass and suggested doping and increase of lattice constant [9]

2. Methodology

Seebeck coefficient (S), thermal conductivity (κ) and electrical conductivities (σ) for an isotropic electronic structure using BoltzTrap code [10]. Eq. (1) interprets electrical conductivity tensors [11]

$$\sigma_{\alpha,\beta} = e^2 \sum_{i,k} \left[\frac{-\partial f_0(T,\varepsilon,\mu)}{\partial \varepsilon}\right] \upsilon_\alpha \upsilon_\beta \tau_k \qquad (1)$$

where, α, β are the tensor indices, $\upsilon_\alpha \upsilon_\beta$ are the group velocities, e is the electron charge and τ_k is the relaxation time. The relaxation time τ is neglected for isotropic systems as the variation of τ is not known. The electrons contribution remain near the chemical potential (μ) in a narrow range of $\mu - k_B T < \varepsilon < \mu + k_B T$, where k_B is the Boltzmann constant [12]. The transport distribution is written as [13]

$$\Xi_{i,k} = e^2 \sum_{i,k} \upsilon_\alpha \upsilon_\beta \tau_k \qquad (2)$$

which is the kernel of all transport coefficients. From the rigid band approach, the electrical conductivity, thermal conductivity and Seebeck coefficient can be written as a function of temperature (T) and chemical potential (μ) by integrating the transport distribution [10, 14]

$$\sigma = \frac{1}{\Omega} \int \Xi_{i,k} \left[\frac{-\partial f_0(T,\varepsilon)}{\partial \varepsilon}\right] d\varepsilon \qquad (3)$$

$$\kappa = \frac{1}{e^2} k_B^2 T \int \Xi_{i,k} \left(\frac{\varepsilon-\mu}{k_B T}\right)^2 \left[\frac{-\partial f_0(T,\varepsilon)}{\partial \varepsilon}\right] d\varepsilon \qquad (4)$$

$$\upsilon_{\alpha\beta} = \frac{k_B}{e\Omega} \int \Xi_{i,k} \left(\frac{\varepsilon-\mu}{k_B T}\right) \left[\frac{-\partial f_0(T,\varepsilon)}{\partial \varepsilon}\right] d\varepsilon \qquad (5)$$

Here f_0 is a Fermi-Dirac distribution function and Ω is the volume of a unit cell. The Seebeck coefficient (S) is determined as

$$S_{ij} = E_i \left(\nabla_j T\right)^{-1} = (\sigma^{-1}) \alpha_i \upsilon_{\alpha j} \qquad (6)$$

The thermoelectric efficiency is presented as

$$ZT = \frac{S^2 \sigma T}{\kappa} (7)$$

Thus the efficiency of thermoelectric materials (ZT) can be tuned by optimizing any of the three parameters *S*, σ and κ at defined temperature *T*.

3. Results and discussions

The electronic structure studies have been performed by Sandeep *et al.* [5] using both mBJ as well as GGA+U approximations. The contribution of density of states in the vicinity of Fermi level (E_F) motivated the thermoelectric studies of doped $EuAlO_3$. The negative value of *S* indicates *n*-type carriers (Fig. 1a). Since *S* depends on temperature, the sharp decrease of *S* at lowest temperature is due to the depopulation of phonon modes.

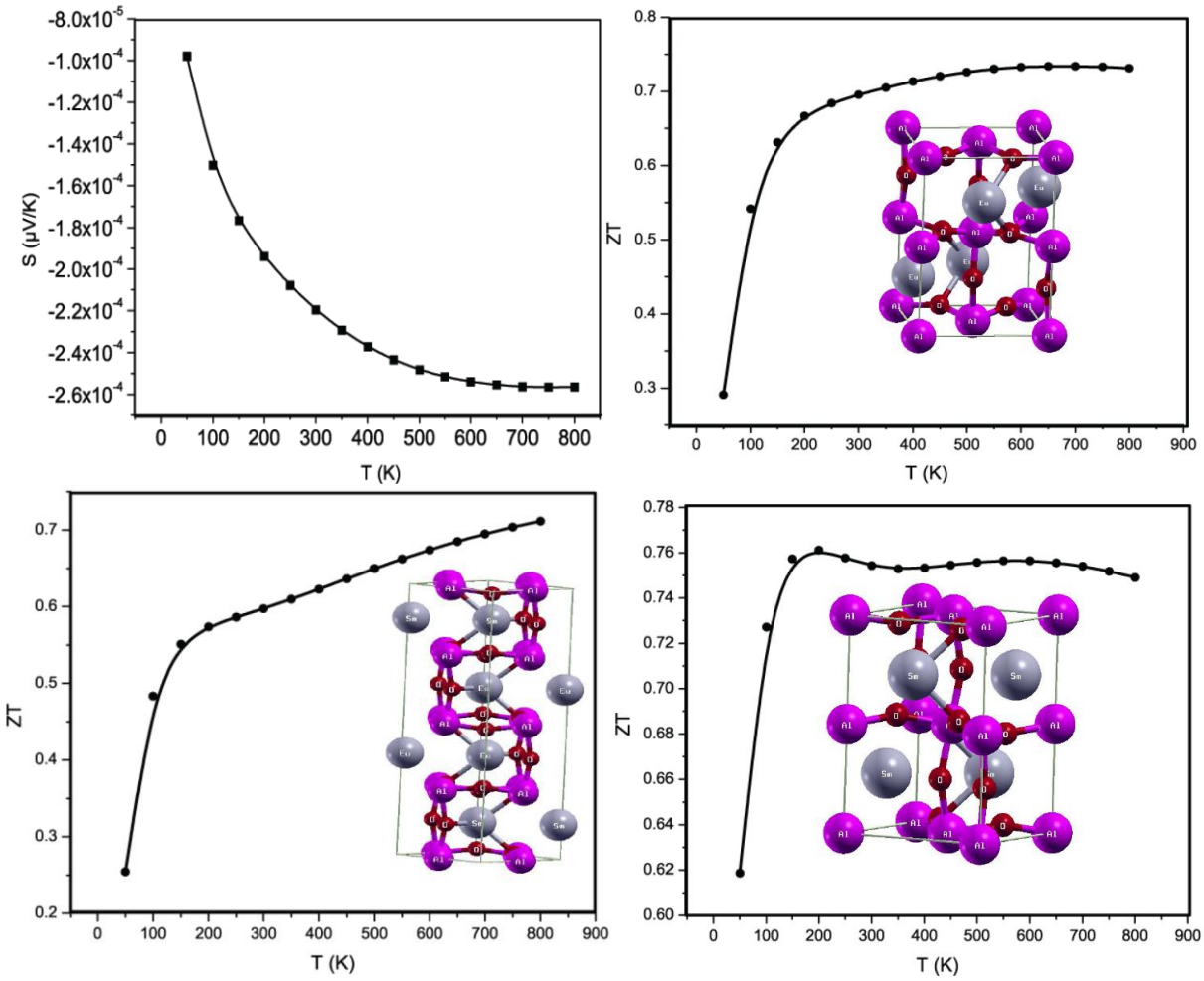

Fig 1. Temperature dependence of (a) Seebeck coefficient (S); Temperature dependence of figure of merit (ZT) calculated within GGA for $Eu_{1-x}Sm_xAlO_3$ with (b) x=0%, (c) x=50% and (d) x=100%.

Strongly correlated heavy Fermion compounds of Ce and Yb also show similar type of low temperature phenomena [15]. The value of S at room temperature was found to be -2.19 ×10 -4 μV/K. The figure of merits are shown in Fig 1(b-d) for three different doping concentrations along with their structures for x=0%, 50% and 100% respectively. It was found that below 150 K all the three ZT values for different doping states were of similar nature. They showed sharp increment with temperature below 200 K. x=50% doping configuration was found to have a more positive effect of temperature on it compared to x= 0% and 50% suggesting the presence of doped Sm in $EuAlO_3$ enhanced the thermoelectric efficiency of the material and is also indication that a doping of other such concentration may yield higher ZT values which may be useful for thermoelectric device fabrications.

Acknowledgment
SD acknowledges DST-SERB(India) FAST Track project project.

References

[1] Di Salvo F J 1999 *Science* **285** 703-706
[2] Sandeep, Rai D P, Shankar A, Ghimire M P, Khenata R and Thapa R K 2016 *Mod. Phys. Lett. B*, 2883-2887
[3] Hashimoto H, Kusunose T and Sekino T 2011 *Journal of Ceramic Processing Research* **12,** 223-227

[4] Karvonen L, Tomes P and Weidenkaff A 2011 *Material Matters* **6** 92–99
[5] Sandeep, Rai D P, Shankar A, Ghimire M P, Khenata R and Thapa R K 2015 *Phys. Scr.* **90** 065803-065810
[6] Ahlgren E O, Ranlov J and Poulsen F W 1995 *J. Electrochem. Soc.* **142** 4230-4234
[7] Kopan A R, Gorbachuk M. P, Lakiza S. M. and Tishchenko Ya S 2012 *Powder Metallurgy and Metal Ceramics* **51** 209-216
[8] Hochbaum A I, Chen R, Delgado R D, Liang W, Garnett E C, Najarian M, Majumdar A and Yang P, 2008 *Nature* **451** 163-167
[9] Wunderlich W, Ohta S, Ohta H, Koumoto K, "Effective mass and thermoelectric properties of $SrTiO_3$-based natural superlattices evaluated by ab-initio calculations" in 24th International Conference On Thermoelectrics, (ICT 2005 IEEE Proceedings) pp. 237-240
[10] Madsen G K H, Singh D 2006 *Comput. Phys. Commun* **175** 67-71
[11] Yamamoto A, Miyazaki H, Takeuchi T 2014 *J. Appl. Phys.* **115** 023708-023717
[12] Takeuchi T 2009 *Materials Transactions* **50** 2359-2365
[13] Mahan G D and Sofo J O 1996 Proc. Natl. Acad. Sci. USA **93** 7436-7439
[14] Scheidementel T J, Draxl C A, Thoonhauser T, Badding J V, Sofo J O 2003 *Phys. Rev. B* **68** 1252101-1252106
[15] Dilley N R, Bauer E D, Maple M B, Dordevic S, Basov D N, Freibert F, Darling T W, Migliori A,.C. Chakoumakos B, Sales B C 2000 *Phys. Rev. B* **61** 4608-4614