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Thermoelectric Properties of Binary *Ln*N (*Ln*=La and Lu): First Principles Study

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Abstract. First principles density functional calculations were carried out to study the electronic structure and thermoelectric properties of LnN (Ln = La and Lu) using the full potential linearized augmented plane wave (FP-LAPW) method. The thermoelectric properties were calculated by solving the Boltzmann transport equation within the constant relaxation time approximation. The obtained lattice parameters are in good agreement with the available experimental and other theoretical results. The calculated band gaps using the Tran-Blaha modified Becke-Johnson potential (TB-mBJ), of both compounds are in good agreement with the available experimental values. Thermoelectric properties like thermopower (S), electrical conductivity scaled by relaxation time (σ/τ) and power-factor ($S^2\sigma/\tau$) are calculated as functions of the carrier concentration and temperature for both compounds. The calculated thermoelectric properties are compared with the available experimental results of the similar material ScN.

Keywords: Electronic structure, Transport properties.
PACS: 71, 72

INTRODUCTION

Transition metal (TM) carbides and nitrides are well known as refractory materials. The nitride compounds possess very good properties like high hardness, high melting points and high corrosion resistance [1-4], and early TM nitrides such as ScN, YN, LaN and LuN possess many of these properties. The unclear semi-metallic/semiconducting nature of TM compounds has provoked new directions of research both experimentally and theoretically. Experimental reports claim that the early TM nitrides are narrow gap semiconductors [5]. For LaN, some of the measured data indicate a semi-metallic nature, while others indicate a semiconducting nature [5]. Previous studies on ScN [6] show this material to be a good candidate for thermoelectric (TE) applications and the present work explores further in this direction for the LaN and LuN compounds. TE materials play a major role in energy conversion and can be used to convert waste heat into electrical energy. The quality of the TE materials can be assessed from the dimensionless figure of merit $ZT=S^2\sigma T/\kappa$, where S, σ, κ, and T are thermopower, electrical conductivity, thermal conductivity, and absolute temperature respectively. κ includes both the electronic κ_e, and lattice contributions κ_l, i.e ,$\kappa=\kappa_e+\kappa_l$. Doped semiconductors are prospective materials for good TE performance. The present work finds both LaN and LuN to be semiconductors, which further motivates investigations into their thermoelectric properties.

COMPUTATIONAL DETAILS

The present study used the FP-LAPW method as implemented in the Wien2k package [7]. The TB-mBJ [8] functional was used to obtain the electronic properties since the more traditional exchange correlation functional severely underestimate the band gap of semi-conductors. Both LaN and LuN crystallize in the rock-salt structure at ambient condition. Total energy calculations were carried out for a k-grid of (22x22x22) which results in 328 k-points in the irreducible part of the Brillouin zone. The optimized

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theoretical lattice parameters are used to get the thermoelectric properties such as thermopower (S), electrical conductivity scaled by relaxation time (σ/τ) and power-factor($S^2\sigma/\tau$) using the BoltzTraP code[9].

RESULTS AND DISCUSSION

(a) Structural and Electronic properties

The optimised lattice parameters of LaN and LuN along with available experimental and other theoretical values are presented in TABLE 1. It is evident that the optimised parameters from the present study are in good agreement with the available reports. The calculated band structures along the high symmetry points of the Brillouin zone and the density of states (DOS) for both compounds are presented in Figure 1. In contrast to the earlier local density approximation (LDA) calculations which results in a metallic/semi-metallic nature, we find energy gaps of 0.814 eV for LaN and 1.173 eV for LuN. The band gaps are included in TABLE 1, along with the available experimental reports. In the screened exchange calculations by Stampfl et. al. [10] LaN has an indirect band gap, similar to ScN and YN, whereas the present study finds a direct band gap at the X-point for LaN. This feature was also confirmed by self-consistent GW calculations [11]. The gap of LuN is indirect. From the DOS of LaN it can be seen that the bands near the valence band maximum are dominated by the N p-states, whereas the conduction band dipping down at the X-point is a hybridized La s, d bands. For LuN a strong hybridization between the Lu f-states and the N p-states is seen. The Lu f-states are best considered as core-like, and the TB-mBJ functional might not describe their position properly. The GW calculations find them positioned considerably lower, below the N p valence band at about -7 eV and -8.5 eV with respect to the valence band top, for the j=7/2 and j=5/2 peaks, respectively.

(b) Thermoelectric properties

The TE properties of LaN and LuN are calculated using the BoltzTrap code. The thermopower (S in μV/K), the electrical conductivity scaled by relaxation time (σ/τ in $\Omega^{-1}m^{-1}s^{-1}$) and the power-factor ($S^2\sigma/\tau$ in $Wm^{-1}K^{-2}s^{-1}$) are calculated as functions of carrier concentrations for both electrons and holes at different temperatures. The calculated TE properties of LaN and LuN are presented in Figure 2. All the thermoelectric properties are calculated up to 900 K. The absolute value of the thermopower is found to decrease with increasing concentration for both LaN and LuN. The cross-over of the thermopower of LaN at 900 K and low carrier concentrations is a signature of bipolar conduction setting in. A similar effect is not seen for LuN due to the larger gap. The thermopower of LaN is found to behave similarly as function of carrier concentration and temperature for e- and h-type carriers, albeit marginally higher for hole doping. The electrical conductivities scaled by relaxation time of both LaN and LuN are largely temperature independent and linear in carrier concentration. The power-factor of LaN is very similar for e- and h-type carriers, but turns out to be slightly larger for holes due to the thermopower being slightly higher for holes. A similar behaviour in the thermoelectric properties is also observed in LuN, however the asymmetry between electrons and holes is larger at large concentrations, which can be traced to the effect of the Lu f-bands, which might be incorrect, as discussed above.

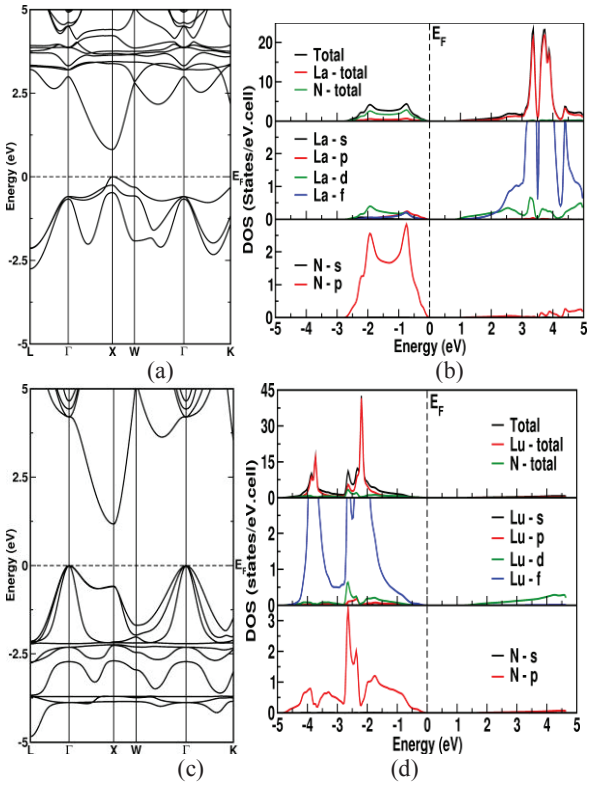


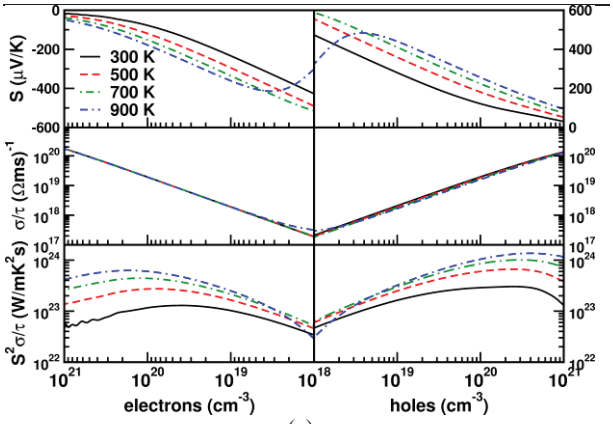
FIGURE 1. (a) Band structure and (b) Density of states of LaN, (c) Band structure and (d) Density of states of LuN.

In Figure 3, our result for the thermopower are compared with iso-structural ScN. At each temperature the maximum power-factor has been determined and the thermopower corresponding to that carrier concentration is plotted and compared with the experimental thermopower of ScN [6]. The thermopower increases with temperature in all cases, except for LaN with electron doping, where the thermopower is found to be high at room temperature, even exceeding that of the h-type carrier. Thus electron doped LaN might find use for low temperature application. For LaN, the thermopower is higher for h-type than for e-type carriers (for T>300 K), while for LuN it is opposite. The calculated

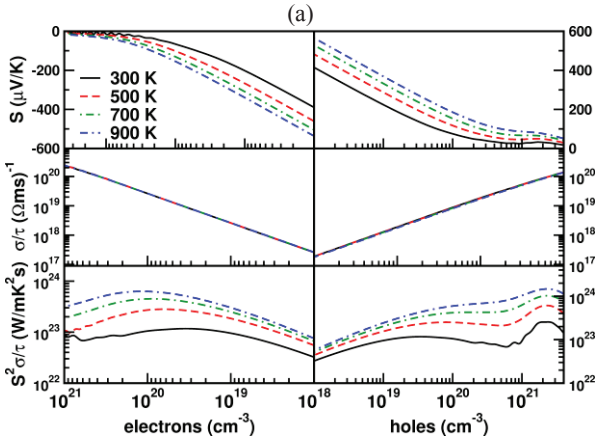
thermopowers of LaN (holes) and LuN (electrons) are higher in comparison with the values measured for ScN. LaN and LuN therefore hold great promise for good thermoelectric applications in line with that of iso-structural ScN.

TABLE 1. Calculated lattice parameters and band gaps of LaN and LuN along with experiment and other theory.

a (in Å)	**$a_{present}$**	**a_{exp}**	**a_{theory}**
LaN	5.325	5.301[12]	5.307[13]
LuN	4.767	4.766[14]	4.77[15]
Eg(eV)	**Present**	**Exp**	**Other theory**
LaN	0.814	0.82[5]	0.75[10]
LuN	1.173	1.55[5]	



(a)



(b)

FIGURE 2. Variation of thermopower, electrical conductivity scaled by relaxation time, and power-factor with carrier concentrations for (a) LaN and (b) LuN.

CONCLUSIONS

The calculated ground state properties and band gaps of LaN and LuN are in good agreement with available experimental and other theoretical reports. The band structure of LaN reveals a direct band gap at the X-point of the Brillouin zone, while LuN has an indirect band gap similar to ScN. The thermopower of LaN suggests this as a favourable TE system especially with hole type doping, while for LuN electron doping is most favourable. Electron doped LaN might be useful for low temperature TE application. The thermopower at optimized doping levels are comparable to or higher than measured values for the well-known thermoelectric compound ScN.

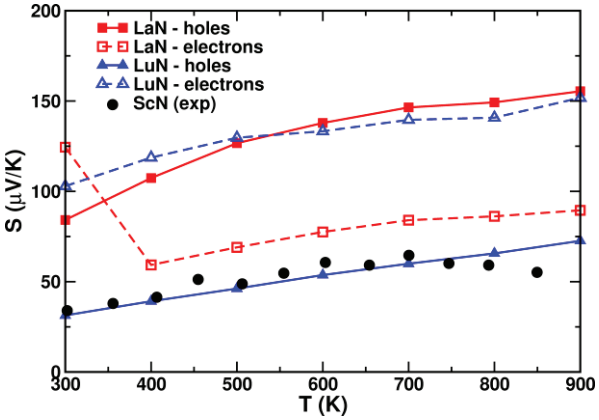


FIGURE 3. Thermopower of LaN and LuN at optimal carrier concentration in comparison with experimental result of ScN [6].

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REFERENCES

1. H. F. George and H. K. John, *Phys. Rev.* 93, 1004 (1954).
2. A. Nigro, G. Nobile, V. Palmieri, G. Rubino, and R. Vaglio, *Phys. Scr.* 38, 483 (1988).
3. K. Kawaguchi and M. Sohma, Jpn. J. Appl. Phys.30, 2088 (1991).
4. G. Vaitheeswaran, V. Kanchana and M. Rajagopalan, *Solid State Commun*. 124, 97 (2002).
5. F. Hulliger, *"Handbook of Physics and Chemistry of Rare Earths"*, Vol 4, edited by K.A. Gschneidner, L.R. Eyring (Elsevier, Amsterdam, 1979), pp 153-236.
6. M. Zebarjadi, Z. Bian, R. Singh, A. Shakouri, R. Wortman, V. Rawat and T.Sands, *J.Elec. Materials*, 38, 960 (2009).
7. P. Blaha, K. Schwarz, P. I. Sorantin and S. B. Tricky, *Comput. Phys. Commun*. 59, 399 (1990).
8. F. Tran and P. Blaha, *Phys. Rev. Lett.* 102, 226401(2009).
9. G. K. H. Madsen and D. J. Singh, *Comput. Phys. Commun,* 175, 67 (2006).
10. C. Stampfl, W. Mannstadt, R. Asahi, and A. J. Freman, *Phys. Rev. B* 63, 155106 (2001).
11. A. Svane, V. Kanchana, G. Vaitheeswaran and N. E. Christensen (Unpublished).
12. R. W. G. Wyckoff, *Crystal structures*, vol.1, second ed., Wiley, New York, 1963, p. 86.
13. Y. O. Ciftci, K. Colakoglu, E. Deligoz, and H. Ozisik, *Materials Chemistry and Physics* 108, 120 (2008).
14. C. G. Duan, R. F. Sabirianov, W. N. Mei, P. A. Dowben, S. S. Jaswal, and E. Y. Tsymbal, *J. Phys:. Condensed. Matter* 19, 315220 (2007).
15. D. C. Gupta and I. H. Bhat, *J. Mol. Model*, 19, 5343 (2013).