I. Introduction

The performance of a thermoelectric (TE) material depends on the dimensionless figure of merit, $ZT$, given by $ZT = \frac{S^2T}{\kappa}$, where $S$, $\sigma$, $T$ and $\kappa$ are the Seebeck coefficient, electrical conductivity, absolute temperature and the thermal conductivity (which includes both electronic $\kappa_e$ and lattice contribution $\kappa_l$, i.e. $\kappa = \kappa_e + \kappa_l$) respectively, the efficiency of a thermoelectric device increasing with $ZT$. The best of the commonly available TE materials have a value of $ZT$ in the order of unity.$^3$ From the above expression for $ZT$, it is evident that finding materials with high $ZT$ (more than unity) still remains an open challenge, as it needs to satisfy the conflicting requirement of high thermopower like an insulator and behave as a good conductor like a metal. Also, it implies the need for materials with good electrical conductivity and poor thermal conductivity resulting in weak electron scattering and strong phonon scattering. In the last few years efforts have been made for identifying strategies to improve the value of the $ZT$. Several reports have been published by different research groups with focus on band structure engineering to enhance $S$ and $\sigma$ and usage of nanostructure technology for reducing the lattice thermal conductivity. Recently, Shi et al.$^7$ reported that the multiple-filled skutterudites show an improved figure of merit of 1.7 at 850 K, which is the highest value reported in skutterudites. Biswas et al.$^8$ reported that PbTe–SrTe doped with Na shows a $ZT$ of 2.2 at 923 K due to the hierarchical structure which maximises the phonon scattering.

There are well known constraints in developing good TE materials, like toxicity and scarcity of the elements which prevent the usage of the above materials in large scale industrial applications. Nevertheless, the search for such new TE materials still continues despite the above mentioned restrictions. Recently, the natural minerals of the tetrahedrite (Cu$_{12}$Se$_x$Sb$_{5}$S$_{13}$) and tennantite (Cu$_{12}$M$_x$As$_2$S$_{13}$), where M is a transition metal element such as Zn, Fe, Mn, or Ni, have shown potential thermoelectric application due to their intrinsic low lattice thermal conductivity.$^{1,4}$ Such studies have motivated us to explore thermoelectric properties of other families of minerals such as FeSe$_2$ and FeTe$_2$. The reasons behind selecting the transition metal chalcogenides family are their excellent optical and magnetic properties,$^7$ and the potential for widespread applications. Recently, the polymorphic phases of FeSe$_2$ have been shown to be good for solar cell absorber application.$^9$ Several experimental reports are available attempting to understand the electrical resistivity, Hall coefficient and thermoelectric power of these compounds. The electrical resistivity and Hall coefficient of FeSe$_2$ have been measured in sintered poly-crystals.$^{10-11}$ Dudkin et. al.$^1$ have measured the electronic resistivity of FeTe$_2$. The same authors have also reported the thermoelectric properties of FeSe$_2$ and FeTe$_2$, measured at ambient temperature and the high temperature results have been reported by Harada.$^{12}$ The thermoelectric properties of pyrite-type FeSe$_2$ and FeTe$_2$ prepared at...
The properties like thermopower ($S$), electrical conductivity ($\sigma$), and the constant scattering time ($\tau$) approximation (CSTA). According to CSTA, the scattering time of the electron is taken to be independent of energy and depends only on concentration and temperature. The detailed explanation about the CSTA is given in ref. 30–32 and the references cited therein. It is evident that CSTA has been quite successful in the past in predicting the thermoelectric properties of many materials.31,33–36

III. Results and discussion

A. Ground state properties

FeSe$_2$ and FeTe$_2$ crystallize in both the marcasite and the pyrite structures.27 The marcasite form of both the compounds are available in nature whereas pyrite structure is a synthetic mineral. The atomic arrangements of the marcasite phase can be considered within either of the two space groups $Pnm2$ or $Pnnm$. However, we did not find any significant energy difference between these two arrangements (see Fig. 1(b) for FeTe$_2$).38 In general, most marcasite type minerals are available in the space group $Pnnm$, and hence we have used this space group for detailed electronic structure calculations for both the compounds. In order to verify their structural relation between the marcasite and pyrite we have calculated the total energy under the application of the hydrostatic pressure from –8 to 8 GPa. The total energy variation with the pressure for both the compounds is shown in Fig. 1(a) and (b). We find an energy difference of 1.9 mRy per unit cell between the marcasite and pyrite structures of FeSe$_2$, whereas we found the energy difference between the marcasite and pyrite phases of FeTe$_2$ to be 3.5 mRy per unitcell (see Fig. 1(b)). The optimized structural parameters are shown in Table 1 along with available experimental results. The agreement between theory and experiment is quite good.

B. Band structure and density of states

The electronic properties of FeX$_2$ ($X$ = Se, Te) are calculated using the optimized parameters obtained from the PWscf calculations. Since LDA/GGA underestimate the band gaps in semiconductors and insulators, and as the studied compounds have partially filled Fe d-levels, we used GGA+U method and adjusted $U$ to get a reasonable value of the band gap. In our calculations we have used a value of $U_{\text{Fe}} = 0.52$ Ry (7.67 eV) for the Fe d electrons in both the structures and both the compounds. This value of $U$ is slightly on the higher side compared to values used in the literature (3–5 eV) for metals and semiconductors. The calculated band structures along high
symmetry directions in the Brillouin zone for both the compounds and both marcasite and pyrite structures are shown in Fig. 2–5, along with the density of states (DOS).

Both the compounds are indirect band gap semiconductors irrespective of their crystal structures. From the partial density of state (PDOS) analysis, we find that there is a strong hybridization between Fe-d and chalcogen p bands. The Fe-d bands are partially filled and Se p bands are partially empty. The top of the valence band is predominantly Fe-d whereas the bottom of the conduction band is predominately chalcogen p. However, a closer look at the PDOS shows that the states within an energy range 0.25 eV just below the valence band maxima (VBM) (responsible for charge and energy transport) are an equal mixture of Fe-d and chalcogen p states. In contrast, states near the bottom of the conduction band minima (CBM) are mostly of chalcogen p-character. In the marcasite phase of FeSe₂ (m-FeSe₂), the CBM and VBM are located along the Γ–Y and Γ–X directions respectively whereas for FeTe₂ (m-FeTe₂) they are along the Γ–Y and Γ–X directions, although there is another CBM along the Γ–Z direction nearby in energy. In contrast, in the pyrite phase both of them (p-FeSe₂ and p-FeTe₂) show similar behavior, CBM is at the Γ point and the VBM lies along the Γ–M direction. Quite interestingly, in p-FeTe₂, there are other nearly degenerate VBM along the Γ–X directions. The nature of CBM and VBM and states near their neighborhood will have significant effect on the thermoelectric properties of these two compounds, as discussed later in the paper.

The theoretical values of the band gaps are 1.23 eV for m-FeSe₂ and 0.69 eV for p-FeSe₂, in good agreement with earlier theoretical calculations by Ganga et al. However in m-FeTe₂ the discrepancy between theory (0.328 eV using GGA+) and experiment (0.92 eV) is quite large and in the wrong direction compared to m-FeSe₂. We expect experimental band gap in m-FeTe₂ to be smaller than that of m-FeSe₂. In view of this we are calling for more experiments on the optical properties on FeTe₂ to measure its band gap. To further understand the difference between the two compounds we have calculated the effective masses in the neighborhood of different VBM and CBM. The calculated results are shown in Table 3. The rapid increase in the DOS near the CBM in the marcasite phase for both the compounds suggests that these will be excellent n-type thermoelectric. In contrast, the pyrite structure is more favorable to p-type thermoelectric due to multiple valence band extreme close in energy. These qualitative ideas will be tested by explicit calculations of thermopower in the next section.

### C. Thermoelectric properties

From the analysis of the DOS, the sharp increase in the DOS at the band edge suggests that the investigated compounds may

---

**Table 1** Ground state properties of FeX₂ (X = Se, Te) with GGA functional along with the available experimental results

|             | FeSe₂          | FeTe₂          |
|-------------|----------------|----------------|
|             | Marcasite      | Pyrite         | Marcasite      | Pyrite         |
|             | This work      | Exp.ᵃ          | This work      | Exp.ᵇ          | This work      | Exp.ᵇ          |
| a (Å)       | 4.7627         | 4.8002         | 5.746          | 5.7859         | 5.2845         | 5.275          |
| b (Å)       | 5.7439         | 5.7823         | 6.2865         | 6.269          | 6.3083         | 6.2937         |
| c (Å)       | 3.5872         | 3.5834         | 3.9058         | 3.872          |
| V (Å³)      | 98.13          | 99.46          | 189.71         | 193.70         | 129.75         | 128.04         |

³ Ref. 39, ᵇ Ref. 13, ᶜ Ref. 40.
have good thermoelectric properties, particularly large thermopower. To further explore this, we have studied the thermoelectric properties of both the marcasite and pyrite FeX₂ using the Boltzmann transport equation as implemented in BOLTZTRAP code. All the properties are calculated using the Rigid Band Approximation (RBA) and the relaxation time $\tau$ is assumed to be independent of energy. In Table 3 we see that the effective masses change with symmetry directions for both m and p structures. Since most of the experiments are done in poly-crystalline samples, we have calculated the average of thermopower and conductivity over three orthogonal axes. The calculated thermoelectric properties such as thermopower ($S$ in $\mu$V K$^{-1}$), electrical conductivity ($\sigma/\tau$ in $\Omega^{-1}$ m$^{-1}$ s$^{-1}$) and power factor scaled by $S^2/\tau$ for both the electron ($n_e$) and hole ($n_h$) doping are given in Fig. 6–9. The melting temperatures of the marcasite phase of both the compounds are around 850 K, so we have calculated these properties up to 800 K for this structure. The pyrite structure on the other hand is found to be stable up to 1300 K, and we have calculated $S$ and $S^2/\tau$ up to 1200 K.

The observed reduction in the absolute value of the thermopower with the decrease in the concentration is a peculiar feature of bipolar conduction (both electrons and holes contribute significantly to transport) at fixed temperature which we have seen in the case of p-FeSe₂ (Fig. 7), m- and p-FeTe₂ (Fig. 8 and 9) which is due to the small band gaps of these compounds (see Table 2). From Fig. 6, we find that in m-FeSe₂ the thermopower values are almost similar for both electron and hole doping, whereas the electrical conductivity is higher in the case of hole doping in comparison with the electron doping. A similar behaviour is also seen in the power factor values. For p-FeSe₂, we have seen that up to $\sim$600 K all the thermoelectric
quantities are better in the hole doping case which is also consistent with the results of DOS, but at high temperatures (800 K and 1000 K) we find evidence of bipolar conduction. So p-FeSe₂ can be a good thermoelectric up to 600 K. In the case of m-FeTe₂ we find that electron doping is more favourable compared to the hole doping, whereas in p-FeTe₂ hole doping is favourable compared to electron doping. We find evidence of bipolar conduction in m-FeTe₂ above at 600 K and p-FeTe₂ above 800 K. So both m- and p-FeTe₂ can be used as thermoelectric material below 600 K.

As per the earlier study, the optimum value of the magnitude of S usually falls in the region of 200–300 μV K⁻¹ to get a figure of merit (ZT) to be ~1. In our study the hole concentration is between 2.10 × 10¹⁹ to 7.96 × 10¹⁹ cm⁻³, 1.78 × 10²⁰ to 5.56 × 10²⁰ cm⁻³ for m- and p-FeSe₂ respectively. In case of FeTe₂ the optimum value in the marcasite phase is found in the electron concentration range of 1.46 × 10¹⁹ to 5.40 × 10²⁰ cm⁻³ and for the pyrite phase it is found for the hole concentration range 1.36 × 10²⁰ to 5.31 × 10²⁰ cm⁻³ at 600 K.

Table 2  Band gaps of marcasite and pyrite FeX₂ (X = Se, Te) along with available experimental results in eV

|                | FeSe₂                  | FeTe₂                  |
|----------------|------------------------|------------------------|
| Marcasite      | This work: 1.234        | 0.328                  |
| Pyrite         | Exp/other: 0.95−1.03    | 0.92                   |
|                | Other calculation: 0.86 | 0.67                   |

*Ref. 39*  *Ref. 8*  *Ref. 41*

Our theoretical results for S are compared with the earlier experimental work of Harada,* and can be compared with the thermopower values at room and high temperature for the m-FeSe₂ structures. For marcasite the hole and electron concentrations are found to be 5.8 × 10¹⁸ cm⁻³ and 8.5 × 10¹⁹ cm⁻³ for a thermopower of +320 μV K⁻¹ and −120 μV K⁻¹ at 300 and 600 K, respectively. Similarly, for m-FeTe₂ we find the
hole and electron concentration to be $9.2 \times 10^{19} \text{ cm}^{-3}$ and $1.4 \times 10^{21} \text{ cm}^{-3}$ for the thermopower values of 96 $\mu \text{V K}^{-1}$ and $-74$ $\mu \text{V K}^{-1}$ at 300 and 600 K. The experimental data on thermoelectric power and electrical conductivity is used to obtain an estimation of the relaxation time $\tau$. We find $\tau$ to be $1.01 \times 10^{-13}$ s and $2.38 \times 10^{-15}$ s for FeSe$_2$ at 300 and 600 K, respectively. Similarly, for m-FeTe$_2$ $\tau$ is found to be $2.3 \times 10^{-14}$ s and $3.1 \times 10^{-14}$ s, respectively. We can clearly see that the relaxation time of m-FeTe$_2$ is lower than that of m-FeSe$_2$, and hence one could expect that FeSe$_2$ shows better TE properties than FeTe$_2$. Overall, both marcasite and pyrite phases of the investigated compounds are good candidates for thermoelectric properties, and marcasite FeSe$_2$ is found to be the best thermoelectric material among all the compounds studied. In order to evaluate these compounds’ figure of merit $ZT$, one should have the experimental measurements of their thermal conductivities.

IV. Conclusion

The structural and electronic transport properties of marcasite and pyrite phases of FeX$_2$ are studied using density functional theory. We did not find any structural transition between the marcasite and pyrite, and we found that the marcasite structure of both the compounds is energetically more stable than the pyrite structure. The calculated ground state properties of FeX$_2$ ($X = \text{Se, Te}$) agree quite well with the available experiments. Electronic structure calculations show that all the investigated compounds are indirect band gap semiconductors, in good agreement with earlier reports. We further calculated the thermoelectric properties of these compounds and compared them with those obtained from available experimental reports. The calculations show all the investigated compounds to be very good thermoelectric materials for p-type doping, except marcasite FeTe$_2$ which favours electron doping. Among all the

### Table 3

| Marcasite | FeSe$_2$ | FeTe$_2$ |
|-----------|---------|---------|
| Direction | Valence band | Conduction band | Valence band | Conduction band |
| $\Gamma-Z$ | 0.048 | 0.451 | 0.019 | 0.038 |
| $\Gamma-Y$ | 0.042 | 0.041 | 0.018 | 0.021 |
| $\Gamma-X$ | 0.024 | 0.066 | 0.017 | 0.014 |
| Pyrite | | | | |
| $\Gamma-X$ | 0.012 | 0.028 | 0.010 | 0.027 |
| $\Gamma-M$ | 0.028 | 0.055 | 0.019 | 0.046 |
| $\Gamma-R$ | 0.032 | 0.036 | 0.028 | 0.025 |

Fig. 6 Thermoelectric properties such as thermopower ($S$), electrical conductivity scaled by relaxation time ($\sigma/\tau$) and power factor scaled by relaxation time ($S^2\sigma/\tau$) for both electron (left) and hole (right) doping of marcasite FeSe$_2$.

Fig. 7 Thermoelectric properties such as thermopower ($S$), electrical conductivity scaled by relaxation time ($\sigma/\tau$) and power factor scaled by relaxation time ($S^2\sigma/\tau$) for both electron (left) and hole (right) doping of pyrite FeSe$_2$.

Fig. 8 Thermoelectric properties such as thermopower ($S$), electrical conductivity scaled by relaxation time ($\sigma/\tau$) and power factor scaled by relaxation time ($S^2\sigma/\tau$) for both electron (left) and hole (right) doping of marcasite FeTe$_2$. 

This journal is © The Royal Society of Chemistry 2014

RSC Adv., 2014, 4, 9424–9431 | 9429
studied compounds we find marcasite FeSe₂ to be a good p-type thermoelectric material.

Acknowledgements

V. K. G. and V. K. would like to acknowledge IIT-Hyderabad for the computational facility. V. K. G. would like to thank MHRD for the fellowship. V. K. thanks NSFC awarded Research Fellowship for International Young Scientists under Grant no. 11250110051. One of us (S. D. M.) would like to acknowledge support by the Department of Energy (DOE)-Energy Frontier Research Center (EFRC) at Michigan State University on Revolutionary Materials for Solid State Energy Conversion.

References

1 D. M. Rowe, CRC Handbook of Thermoelectrics, CRC, Boca Raton, 1995.
2 X. Shi, J. Yang, J. R. Salvador, M. Chi, J. Y. Cho, H. Wang, S. Bai, J. Yang, W. Zhang and L. Chen, J. Am. Chem. Soc., 2011, 133, 7837.
3 K. Biswas, J. He, I. D. Blum, C.-I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid and M. G. Kanatzidis, Nature, 2012, 489, 414.
4 G. A. Slack, Solid State Physics, ed. H. Ehrenreich, F. Seitz and D. Turnbull, Academic Press, New York, 1979, p. 171.
5 X. Lu and D. T. Morelli, Phys. Chem. Chem. Phys., 2013, 15, 5762.
6 X. Lu, D. T. Morelli, Y. Xia, F. Zhou, V. Ozolins, H. Chi, X. Zhou and C. Uber, Adv. Energy Mater., 2013, 3, 342.
7 C. N. R. Rao, F. L. Deepak, G. Gundiah and A. Govindaraj, Prog. Solid State Chem., 2003, 31, 5.
8 B. G. Ganga, C. Ganeshraj, A. Gopal Krishna and P. N. Santhosh, http://arxiv.org/abs/1303.1381, 2013.
9 G. Fischer, Can. J. Phys., 1958, 36, 1435.
10 L. D. Dudkin and V. I. Vaidanich, Soviet Physics – Solid State, 1961, 2, 1384.
11 F. Hulliger, Helv. Phys. Acta, 1962, 35, 535.
12 T. Harada, J. Phys. Soc. Jpn., 1998, 67, 1352–1358.
13 T. A. Bither, R. J. Bouchard, W. H. Cloud, P. C. Donohue and W. J. Siemens, Inorg. Chem., 1968, 7, 2208.
14 S. Baroni, S. D. Gironcoli and A. dal Corso et al., http://www.pwscf.org, 2008.
15 P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka and J. Luitz, WIEN2K, An augmented plane wave + local orbitals program for calculating crystal properties, Karlheinz Schwarz, Techn. Universität Wien, Austria, 2001, http://www.wien2k.at/.
16 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.
17 H. J. Monkhorst and J. D. Pack, Phys. Rev. B: Solid State, 1976, 13, 5188.
18 D. Vanderbilt, Phys. Rev. B: Condens. Matter, 1990, 41, 7892.
19 R. M. Nieminen, Topics in Applied Physics: Theory of defects in semiconductors, Springer, Berlin, 2006, vol. 104, p. 3640.
20 G. K. H. Madsen and D. J. Singh, Comput. Phys. Commun., 2006, 175, 67.
21 T. J. Scheidemann, C. Ambrosch-Draxl, T. Thonhauser, J. V. Badding and J. O. Sofo, Phys. Rev. B: Condens. Matter, 2003, 68, 125210.
22 L. Jodin, J. Tobola, P. Pécheur, H. Scherrer and S. Kaprzyk, Phys. Rev. B: Condens. Matter Mater. Phys., 2004, 70, 184207.
23 L. Chaput, P. Pécheur, J. Tobola and H. Scherrer, Phys. Rev. B: Condens. Matter Mater. Phys., 2005, 72, 085126.
24 D. I. Bile, S. D. Mahanti and M. G. Kanatzidis, Phys. Rev. B: Condens. Matter Mater. Phys., 2006, 74, 125202.
25 J. M. Ziman, Electrons and Phonons: Theory of Transport Phenomena in Solids, Oxford University Press, London, UK, 1960.
26 B. R. Nag, Electron Transport in Compound Semiconductors, Springer-Verlag, Berlin, 1980.
27 D. Bile, S. D. Mahanti, E. Quarez, K.-F. Hsu, R. Peconie and M. G. Kanatzidis, Phys. Rev. Lett., 2004, 93, 146403.
28 S. Ahmad, K. Hoang and S. D. Mahanti, Phys. Rev. Lett., 2006, 96, 056403.
29 M.-S. Lee and S. D. Mahanti, Phys. Rev. B: Condens. Matter Mater. Phys., 2012, 85, 165149.
30 D. J. Singh, Funct. Mater. Lett., 2010, 3, 223.
31 K. P. Ong, D. J. Singh and P. Wu, Phys. Rev. B: Condens. Matter Mater. Phys., 2011, 83, 115110.
32 D. Parker and D. J. Singh, Phys. Rev. B: Condens. Matter Mater. Phys., 2012, 85, 125209.
33 D. J. Singh and I. I. Mazin, Phys. Rev. B: Condens. Matter, 1997, 56, R1650.
34 D. Parker and D. J. Singh, Phys. Rev. B: Condens. Matter Mater. Phys., 2010, 82, 035204.
35 G. K. H. Madsen, K. Schwarz, P. Blaha and D. J. Singh, Phys. Rev. B: Condens. Matter, 2003, 68, 125212.
36 L. Zhang, M.-H. Du and D. J. Singh, Phys. Rev. B: Condens. Matter Mater. Phys., 2010, 81, 075117.
37 T. A. Bither, C. T. Prewitt, J. L. Gillson, P. E. Bierstedt, R. B. Flippen and H. S. Young, *Solid State Commun.*, 1966, 4, 533.

38 G. Brostigen and A. Kjekshus, *Acta Chem. Scand.*, 1970, 24, 1925.

39 A. Kjekshus, T. Rakke and A. F. Andresen, *Acta Chem. Scand.*, Ser. A, 1974, 28a, 996.

40 G. Yamaguchi, M. Shimada and M. Koizumi, *Solid State Commun.*, 1976, 9, 63.

41 *Landolt-Börnstein (New Series)*, ed. K. H. Hellwege, Springer Verlag, Berlin, Heidelberg, New York, 1971, vol. III/6.

42 A. I. Liechtenstein, V. I. Anisimov and J. Zaanen, *Phys. Rev. B: Condens. Matter*, 1995, 52, R5467.