A new half metallic quaternary Heusler alloys for spin polarized device application and waste heat recovery treatment: Material computation

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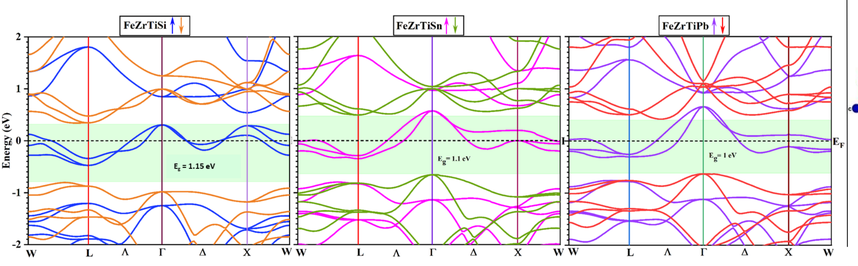
Abstract

- In this article, we have studied the structural, electronic, magnetic, mechanical and thermoelectric properties of new quaternary Heusler alloys FeZrTiZ (Z=Si, Sn, Pb), using ab-initio simulation methods.
- Our structural phase stability studies show that all these compounds stabilize in Y1-type structure and showing ferromagnetic ground state.
- From the calculation based on Generalized Gradient Approximation method, we found that all these alloys having half metallic behavior with the band gap in one of the spin channels.
- These alloys also satisfy the Slater-Pauling rule with magnetic moment of $M_T = N_V - 18$ for half metallicity and as a result they have a total magnetic moment of 2μB.
- The highest Seebeck coecient value for FeZrTiZ (Z = Si, Sn, Pb) is 110.5 μV/K, 121.8 μV/K and 100.6 μV/K respectively at the temperature 900K, 600K and 750K and the corresponding gure of merit is 0.85, 0.9 and 0.59.
- The observation of half metallicity indicate that these materials can be used in spintronic devices and the observation of substantial thermoelectric gure of merit suggest that these materials can be used in waste heat recovery.



Methodology

- In our work the calculations have been done using density functional theory (DFT) method which is implemented in WIEN2k package.
- The WIEN2k package is a computer program written in Fortran which performs quantum mechanical calculations on periodic solids. It uses the full-potential linearized augmented plane-wave [FPLA-PW] basis set to solve the Kohn–Sham equations of density functional theory..
- WIEN2k was originally developed by Peter Blaha and Karlheinz Schwarz from the Institute of Materials Chemistry of the Vienna University of Technology.
- In order to investigate the thermoelectric properties of Heusler material, Boltzmann theory as applied in Boltz-Trap code is used and it is depend on the data provided by WIEN2k code.
- The lattice dynamical calculations were done using finite difference method to calculate the phonon spectrum using the Vienna of Ab initio simulation package (VASP) with PAW potential along with the Phonopy code

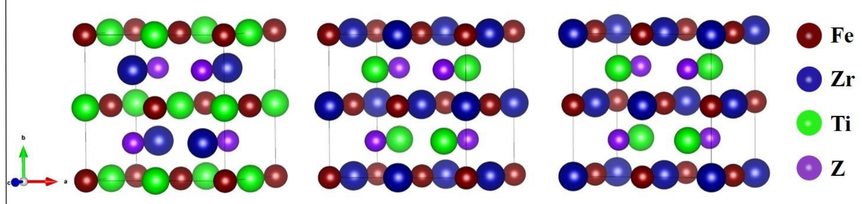


Fig. 1. The optimized crystal structure of FeZrTiZ in Y1-type (Leftmost), Y2 -type (middle) and Y3-type (rightmost) structure.

Results

Alloy	Type	E_0(Ry) FM	E_0(Ry) NM	a_0(Å)	V(a.u.)3
FeZrTiSi	Y1	-12031.8135	-12031.8036	6.2059	403.2354
	Y2	-12031.7791	-12031.7774	6.2227	406.5086
	Y3	-12031.7785	-12031.7773	6.2196	405.8953
FeZrTiSn	Y1	-23809.9415	-23809.9246	6.5143	466.3802
	Y2	-23809.8856	-23809.8822	6.5632	476.9620
	Y3	-23809.8857	-23809.8818	6.5645	477.2349
FeZrTiPb	Y1	-53308.9127	-53308.8932	6.5983	484.6630
	Y2	-53308.8561	-53308.8527	6.6597	498.3081
	Y3	-53308.8540	-53308.8518	6.6665	499.8387

Table 1. The equilibrium energy and lattice constant of FeZrTiZ

Structural stability

- The structural formula of quaternary HA is XX'YZ, where X, X' and Y belongs to transition elements and Z is the main group (sp-group) element and it belongs to F-43m space group..
- The equilibrium structural parameters are obtained by fitting the total energy vs volume curve with the help of Murnaghan equation of states
- Y-1 type structure is X = (0, 0, 0), X' = (0.25, 0.25, 0.25), Y = (0.5, 0.5, 0.5), Z = (0.75, 075, 0.75).
- Y-2 - X = (0, 0, 0), X' = (0.5, 0.5, 0.5), Y = (0.25, 0.25, 0.25), Z = (0.75, 075, 0.75) and
- Y-3 - X = (0.5, 0.5, 0.5), X' = (0, 0, 0), Y = (0.25, 0.25, 0.25), Z = (0.75, 075, 0.75).

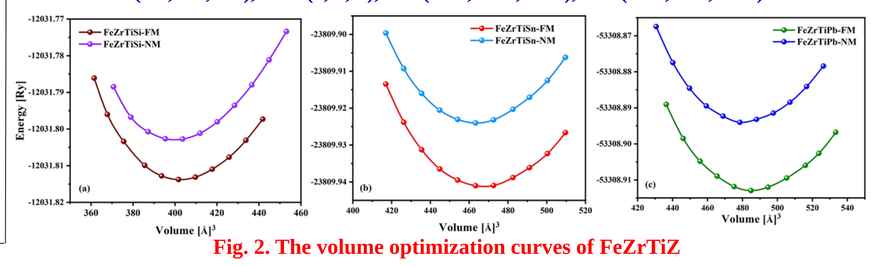


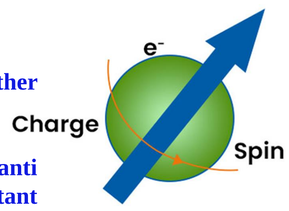
Fig. 2. The volume optimization curves of FeZrTiZ

Introduction

- Heusler alloys are not novel, they have been known for more than a century. They are named after the German chemist Friedrich Heusler , who in 1903 discovered that the full Heusler alloy Cu_2MnAl alloy exhibits a strong ferromagnetic behaviour.
- Half metalicity in Heusler alloy NiMnSb first discovered by Groot *et al*. in 1983

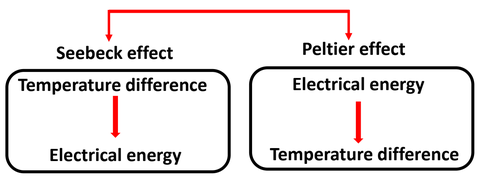
Spintronic

- Spintronics is based on the spin of electrons rather than its charge
- The electrons can rotate either clockwise or anti clockwise around its own axis with constant frequency



- The two possible spin states represented as '0' and '1' in logical operations to store the data.

Thermoelectric



$$ZT = \frac{S^2 \sigma T}{k_e + k_L}$$

Where, S-Seebeck coefficient, σ-electrical conductivity, T-temperature, κ_e- *electron based thermal conductivity* κ_L-*lattice thermal conductivity*

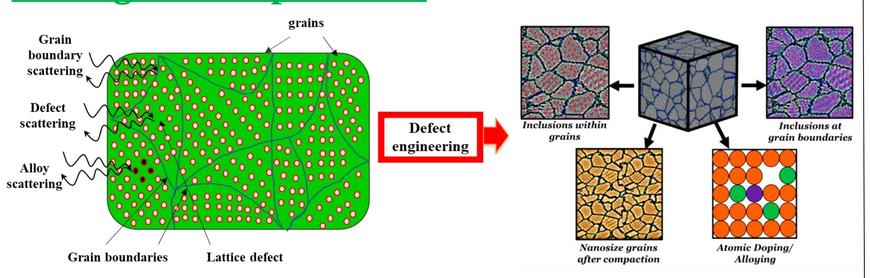
Factors affecting ZT

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} \quad \sigma = ne\mu \quad [\mu = e\tau/m^*]$$

$$\kappa_e = LT\sigma$$

$$\kappa_L = \frac{1}{3} Cvl$$

Strategies to improve ZT



Phonon engineering – to have low κ by phonon scattering

Carrier Engineering- for enhancing Power factor

2. Mechanical stability

Parameter		FeZrTiSi	FeZrTiSn	FeZrTiPb
Elastic constants (in GPa)	C_{11}	197.3	166.92	127.51
	C_{12}	132.21	108.83	113.98
	C_{44}	80.57	83.71	58.3
Youngs modulus (Y in Gpa)		208.93	181.71	153.92
Bulk modulus (B in Gpa)		153.90	128.19	118.49
Shear modulus (G in Gpa)		82.02	71.89	59.96
Pugh's ratio (B/G)		1.88	1.78	1.98
Poisson's ratio (υ)		0.27	0.26	0.28
Anisotropy factor (A)		2.48	2.88	8.62
Hardness H_V		9.61	9.40	9.18
Debye temperature θ_D (K)		491.6	397.1	323.2

- The thermodynamic stability of the materials is determined by the negative formation energy and further be confirmed by phonon dispersion curves where the material should possess all phonon modes with positive frequency in order to be dynamically stable.
- The number of atoms in the unit cell decides the number of optical modes. The 'n' number of atoms in the unit cell will exhibit 3n-n degree of optical mode of vibrations.

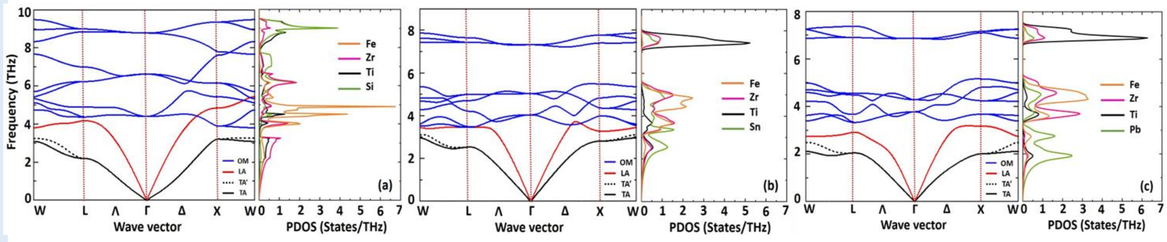


Fig. 3. The phonon dispersion frequency band and its corresponding PDOS of FeZrTiZ

4. Electronic property

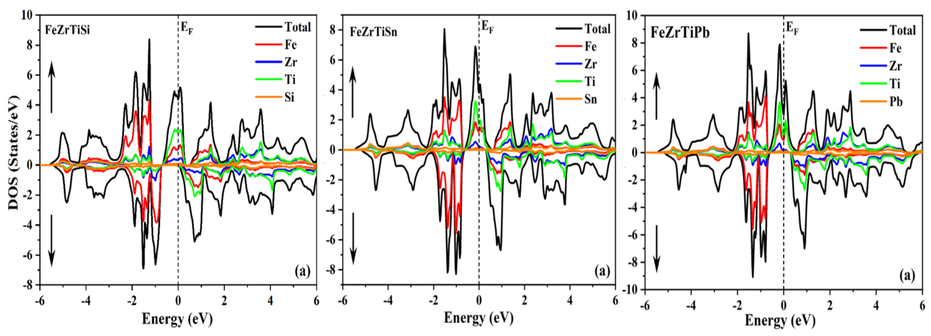


Fig. 4. TDOS and PDOS of FeZrTiZ

Alloys	E_{VBM} (eV)	E_{CBM} (eV)	E_g (eV)	E_{HMG} (eV)	Nature	Magnetic moment (μB)
FeZrTiSi	-0.79	0.36	1.15	0.79	Indirect	2.0
FeZrTiSn	-0.62	0.48	1.10	0.62	Indirect	2.0
FeZrTiPb	-0.60	0.40	1.00	0.60	Indirect	2.0

Table 3. The calculated band gap and magnetic moment of FeZrTiZ

5. Thermoelectric property

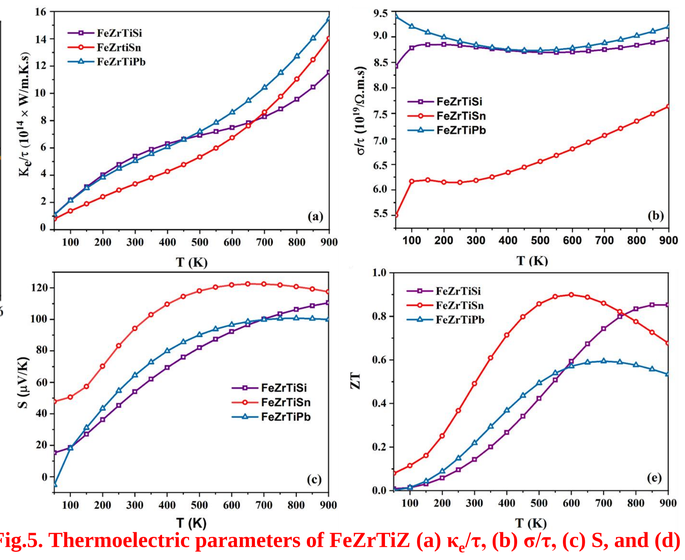


Fig.5. Thermoelectric parameters of FeZrTiZ (a) κ_e/τ, (b) σ/τ, (c) S, and (d) ZT

Conclusion

- From the structural phase stability study we found that these compounds exhibit ferromagnetic behavior in their ground state and the calculated equilibrium volume and lattice parameters are listed. From the total energy calculations, we have found that all these three compounds are having negative formation energy and hence they can synthesize experimentally as stable compounds.
- The calculated elastic constants convey the mechanical stability of these alloys and they exhibit strong mechanical anisotropy with ductile behavior. The phonon dispersion curves obtained using finite difference method with the quasi harmonic approximation show all phonon frequencies possessing positive values suggesting they are dynamically stable.
- From the analysis of calculated electronic structure, we found that these materials are having half metallic behavior with band gap value of 1.15eV, 1.1eV, 1.0eV for FeZrTiSi, FeZrTiSn and FeZrTiPb, respectively in their minority spin channel. The observation of HM behavior suggest that these materials can be used in spintronic applications.
- The maximum obtained PF values are 10.93 × 10^{11} W/m.K^2.s at 900K in FeZrCrSi, 10.10 × 10^{11} W/m.K^2.s at 600K in FeZrTiSn and 9.04 × 10^{11} W/m.K^2.s at 750K. From the calculated transport properties, we conclude that these materials possess reasonably high figure of merit at high temperature and hence they can be use in high temperature waste heat recovery process.

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