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Thermoelectric behaviour with high lattice thermal conductivity of Nickel base Ni$_2$CuCrFeAl$_x$ ($x = 0.5, 1.0, 1.5$ and $2.5$) high entropy alloys

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Abstract

In this article, investigated Ni-based Ni$_2$CuCrFeAl$_x$ ($0.5 \leq x \leq 2.5$) alloys were prepared by powder metallurgy route. On varying $x$, the alloy changes from single FCC to single BCC with a transition duplex in FCC/BCC region. The severe scattering effect of lattice in these high-entropy alloys was observed by weak x-ray diffraction intensities. Also, owing to this lattice effect, the observed electrical and thermal conductivity are much smaller than those of pure metal components. On a contrary, because of additional scattering effect of FCC/BCC phase boundaries in the alloys, both conductivity values are even higher than those in the duplex phase region. Present work explains the properties of temperature dependent High-Entropy alloys (HEA’s) as a potential new class of thermoelectric materials. The thermoelectric properties can be controlled significantly by changing the valence electron concentration via appropriate substitutional elements. Both the electrical and thermal properties were found to decrease with a lower VEC number. These findings highlight the possibility to exploit HEA’s as a new class of futuristic high temperature TE materials.

1. Introduction

Now-a-days, the severe issue related to energy which the world is currently facing is its supply and consumption. On this counterpart, the continuous increase in greenhouse effect is also one of the primary concern on the environment [1]. Therefore, to resolve this issue, the demand for obtaining more useful energy which must be economical and environment-friendly is a great challenge for researchers. Hence, thermoelectricity is now one of the key solution for developing high-efficiency potential device.

Thermoelectricity is the phenomenon that dates back to the early 1800s for direct conversion of temperature into electricity. The concept of thermoelectricity has many potential applications along with a challenge to upsurge the performance by means of thermoelectric devices.

Thermoelectric devices are essential for futuristic potential application in waste energy recovery from a renewable energy source. Since, during the last two decades, most of the research is confined to have an interest in thermoelectric materials, which is suitable for the conversion of useful energy from the renewable energy source at low temperature. In view of search for efficient high entropy thermoelectric material with high energy conversion rate, the dimensionless thermoelectric figure of merit (ZT) has been used to evaluate the performance at a different temperature which is expressed as:

$$zT = \frac{S^2}{\kappa_{tot}\rho}T = \frac{S^2\sigma}{\kappa_{tot}T}$$

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where, $S$ is the Seebeck coefficients, $rac{1}{\rho} = \sigma = ne\mu$ is the resistivity, $T$ is the absolute temperature (in K) and $\kappa_{\text{tot}}$ is total thermal heat conductivity. In thermoelectric materials, the main drawback is its high thermal conductivity. The prime strategy for achieving high performance in thermoelectric materials is determined by maximizing the power factor and minimizing the thermal conductivity. However, these two fundamental quantities are inter-related by three physical quantities ($S$, $\sigma$, and $\kappa_{\text{tot}}$) and quantified by a figure of merit ($z$).

To optimize the thermoelectric material’s performance, dopants are introduced in the parent compound and simultaneously enhances the scattered heat-carrying phonons via phonon-glass paradigm [2]. The scattering of phonon at the atomic length scale from the rattling of atoms, vacancies, impurities, or the presence of interstitial or substitutional could meets the requirement of high electrical conductivity. For this, glassy structure or disorder structure is mainly required so as to furnish the need of low lattice thermal conductivity as much as possible. The density of disorder can be determined from phonon scattering, and the more disordered, more is the phonon scattering. Moreover, the materials become more substituted from the atoms, and it just raises the complexity in phonon scattering. Subsequently, in crystalline parent compounds, substitutional doping yields site occupational disorder that changes the lattice symmetry.

These findings highlight the possibility to exploit High Entropy Alloy’s (HEA’s) as a new class of futuristic high-temperature TE materials. Crystalline HEA’s consists of five constituent elements in equimolar ratios to maximize the configurational entropy [3–5]. Generally, crystalline materials are proven thermoelectric materials because of more number of available scattering phonon without any significant loss of electrical conductivity. The phonon spectrum and its propagation give an idea about the flow of heat with a wide range of wavelength and different length scale of a mean free path that decides the scattering of phonon. The scattering of phonon at the atomic length scale from the rattling of atoms, vacancies, impurities, or the presence of interstitial or substitutional would meet the requirement of high electrical conductivity [6]. The density of disorder can be determined from phonon scattering, the more disorder, more is the phonon scattering. Interestingly, the solid solution in HEA’s crystallizes either in FCC or BCC or even mixed. The relevant properties of HEA’s depend on the formation of a solid solution. In any condition, if any intermetallic is formed, the compound might played a crucial role. In general, the effective formation of FCC or BCC type solid solution can be controlled either by adjusting the alloy composition through substitution or by forming the secondary phase in order to achieve the scattering of phonon effectively. Interestingly, the common feature of a good thermoelectric material is to balance the valency and charge of all the elements. The expense of charge balance enables us to offer the electron separation in respective energy bands would enlarges the bandgap of materials. Zhang et al [7] observed the stability of different phases in HEA in terms of the difference in atomic size. Hence, the knowledge of electrical and thermal conductivity boils up new guidelines for non-linearly optimization in improving thermoelectric performance. The persistent efforts have been carried out to improve the figure of merit. Since the beginning of discovery, the TE materials like BiTe$_3$ and its alloy such as Bi$_x$Sb$_{2–x}$Te$_3$ (p-type), PbTe, PbSe shows the highest reported values of thermoelectric performance at intermediate temperature (600 K–800 K). Moreover, the convenient way to improve ZT merit is the reduction of lattice thermal conductivity without disturbing the electronic properties. In this point of view, most of the research works have been carried out to reduce the lattice thermal conductivity of nanostructured compound such as, PbTe that would emphasize the development of nanoscale properties. He et al [8] reported that the mere presence of nano-structure in the alloy is not sufficient for phonon scattering. Subsequently, the necessary condition for effective scattering of phonon from the nanostructure is comparable or less than the nanoparticles diameter and/or inter-particle spacing to phonons mean free path. Similarly, Tian et al [9] also observed the reduction of alloying in PbTe$_{1−x}$Se$_x$ thermoelectric properties of PbSe, PbTe and PbTe$_{1−x}$Se$_x$ compounds and estimated the importance of optical phonons to lattice thermal conductivity. Moreover, Tang et al [10] reported the low-temperature transport property in half-metallic Heusler alloy of Zr$_{0.25}$Hf$_{0.25}$Ti$_{0.5}$NiSn within 2 K–300 K. In this temperature regime, these materials exhibit very narrow bandgap and good thermoelectric properties with high values of ZT merit [8]. Nevertheless, the outstanding structural properties of HEA in multi-principal-element alloys (MPEA) could also be achieved which is discussed elsewhere [8, 11]. Each multi-principal component accounts exception to this composition rule that can be made for parent compounds that exhibit liquid-like phonon behaviour.

Thermoelectric compounds usually composed of base components and in order to distinguish from conventional doped semiconductors and semi-metals. Recent reports proved that Half Heusler (HH) alloys also shows the thermoelectric property owing to presence of 18 electrons in valence shell and the position of Fermi-level ($E_F$) lies above-occupied valence shell that would results in better semiconducting behaviour. Wu et al [12, 13] observed the thermoelectric behaviour in TiCoSb Half-Heusler which generally exhibits n-type conduction and tried to tune n-type behaviour to p-type by substitution of Ge by Sb and found the enhanced thermoelectric properties from room temperature to 880 K. Makongo et al [14] presented the thermoelectric and electronic transport behaviour of bulk nanostructured Zr$_{0.25}$Hf$_{0.75}$NiSn composites containing various mole fraction of Full-Heusler inclusions. Moreover, the formation of coherent phase from Full Heusler inclusions (FH) into the
HH matrix is due to the formation of an interface by the solid-state diffusion of Ni into the vacant sites. The electronic, thermal and mechanical properties of the nanostructured materials are markedly different from precursor used in composites. Over the past few years, it was realized that nano-structuring plays an important role in significantly enhancing the TE performance of several High entropy alloys.

Guo et al\[15\] reported the stability of the various phase of high entropy alloy based on valence electron concentration. A high entropy alloy, Ni$_2$CuCrFeAl$_x$ with different Al-content, is a promising candidate as a thermoelectric material for power generation over a span of temperature because of its high thermoelectric power factor $PF = S^2/\rho$. Based on the parabolic bandgap, for metals or degenerated semiconductor, the Seebeck coefficient can be expressed as:

$$S = \frac{8\pi^2k_B^2m^*}{3eh^2} T \left(\frac{\pi}{3n}\right)^{1/3}$$

where, $n$ is the carrier concentration and $m^*$ defined the effective mass of the carrier. The formulation for calculating effective mass ($m^*$) have been discussed elsewhere [16]. Generally, the essential step to achieve a high ZT of TE material is to reduce the thermal scattering. This scattering centre in thermoelectric comes from the two sources: (i) transporting heating ($\kappa_{el}$) from holes and electron and (ii) propagation of phonon from the lattice vibration ($\kappa_{l}$). The Wiedemann–Franz law [17] is directly used to calculate the heat transport rate and expressed by the following relationship: $\kappa = \kappa_{el} + \kappa_{l}$ and $\kappa_{el} = \frac{L\tau T}{n_q}$, where $L$ is the Lorenz factor, $2.4 \times 10^{-8} \text{J} \cdot \text{K}^{-2} \cdot \text{C}^{-2}$ for free electrons. The carrier concentration affects the Lorenz factor. The uncertainties in $\kappa_{el}$ is found from presence of low carrier concentration in materials. The additional uncertainty in $\kappa_{l}$ arises from the mixed conduction which includes the bipolar term in thermal conductivity. In most of the design, the electrical conductivity is high and thermal conductivity should be as low as possible for high ZT. For very high electrical conducting material generally metal or very low $\kappa_{l}$, the Seebeck coefficient is the only parameter to determine ZT and is expressed by:

$$ZT = \frac{S^2/L}{1 + \frac{\kappa_{el}}{\kappa_{l}}}$$

From the literature, it was found that most of the research on TE of HEA’s has not been focused yet. Therefore, the numbers of possibilities are explored to design the thermoelectric materials of HEA. These materials have a limited application because of less tuning in the charge carrier concentration of the metals. Another possibility in HEA's to reduce the thermal conductivity from phonon scattering is to develop the complexities in nanostructured compounds by substituting the extra atoms in the lattice. The complexities raise the disordered in the FCC or BCC or mixed structure would reduces the phonon scattering.

Henceforth, based upon the earlier mentioned discussion, present work describes the development of Ni$_2$CuCrFeAl$_x$ alloy from powder metallurgy technique followed by sintering via pulse current technique as a potential application of high entropy thermoelectric material. The formation of FCC, BCC and FCC + BCC mixed phase of the cast HEA’s can be optimized by tuning the valence electron concentration (VEC). Mainly, the elements with higher valence electron concentration can be used to obtain the stable phase of FCC, while its lower values tend to favour the stable BCC-type solid solution and tuning in VEC observe the change in electrical conductivity and Seebeck coefficients of these materials within the required limit. Based on VEC, a series of Ni$_2$CuCrFeAl$_x$ alloys have been designed as a result of adding Al in order to decrease the VEC which preferentially decrease the electrical conductivity simultaneously followed by an increased Seebeck coefficient. Therefore, $\kappa_{l}$ was reduced drastically by lowering the electrical contribution along with increasing the number of grain boundaries and improving thermoelectric performance.

2. Experimental section

2.1. Preparation of the high entropy alloy

Ni-based Ni$_2$CuCrFeAl$_x$ ($x = 0.5, 1.0, 1.5, 2.5$) HEA’s were prepared by mechanical alloying via ball milling under argon atmosphere using element powders of Ni, Cu, Fe Cr and Al in the form of fine electrolytic granules (99.99%) were used as the starting raw materials. Each composition consisting of 2 moles of Ni, 1 mole of Cu, Cr and Fe respectively with varying composition of (0.5 moles to 2.5 moles). The possibility of formation of small amounts of alumina and some intermetallics, during the processing, could not be ruled out. The ball-to-power ratio was maintained as 10:1 and the milling was carried out at a rotational speed of 350 rpm under tungsten carbide balls. To avoid agglomeration of the powder particles and excessive heating, wet milling was carried out by employing isopropyl alcohol (99% purity) as process controlling agent (PCA), and the process was interrupted at regular intervals in order to ensure the presence of homogeneity. The process was repeated several
Electrical resistivity formula. A conventional Four-Probe DC technique was used to determine the value of temperature-dependent resistivity with EDAX analysis. It is also observed that the chemical composition of each alloy is very close to the molecular formula the bulk alloy and their results are tabulated in Table 1. The observed results of chemical composition were matched by field emission microscope to identify the microstructure and morphology of the synthesized high entropy alloy. The optical microscope and field emission microscope was used to identify the microstructure and morphology of the synthesized high entropy alloy. The Archimedes principle was used to determine the density of the alloy by lab-made densiometer. The volume of the alloy was determined with respect to the free volume of loaded density bottle with xylene in terms of displacement and multiplying the known density of xylene. The weight of the sample was varied from 8 to 10 g depending upon the content of Al in the alloy and was determined with an accuracy of ±0.0001 g, while the volume of the alloys was determined up to the limit of accuracy. Differential scanning calorimeter (DSC) was carried out with small pieces of the alloy (~40–50 mg) by putting into the Al2O3 crucible and heating up to 1200 K using Netzsch SAT 449F3. The experiment was performed in cooling and heating mode at a rate of 5 °C min⁻¹ from 300 to 1200 K under Argon atmosphere. The milled powder was consolidated using a hydraulic press and high chrome steel die punch and plunger apparatus lined with tungsten carbide by applying uniaxial pressure of 600 MPa for 60 s. The pulse current sintering was used to sinter the samples to avoid the excessive development of grain growth during heat treatment and to obtain the desired microstructure. The phase structures of the sintered pellets were examined by X-ray diffractometer (Bruker D2-phaser) at 30 kV and 200 mA at a scanning rate of 3° min⁻¹ from 30° to 90°. The optical microscope and field emission microscope was used to identify the microstructure and morphology of the synthesized high entropy alloy. The inductive-coupled plasma-optical emission spectroscopy was used for determining the final composition of the bulk alloy and their results are tabulated in Table 1. The observed results of chemical composition were matched with EDAX analysis. It is also observed that the chemical composition of each alloy is very close to the molecular formula. A conventional Four-Probe DC technique was used to determine the value of temperature-dependent electrical resistivity (ρ) and Seebeck coefficient under vacuum of 5 × 10⁻⁶ Pa with helium gas in the measurement chamber and scanning temperature was 300–1200 K. The resistivity (ρ) was measured by applying the current through the rod and simultaneously observing the voltage difference along the length of the rod. The Seebeck effect was monitored by heating the end of the rod, while the voltage difference was monitored between the probe and sample. The high-temperature thermal conductivity (κ_total) of compositions Ni₂CuCrFeAlₓ (x = 0.5, 1.0, 1.5, and 2.5) were measured from Hot Disk Thermal Constant Analyzer (ULVAC TC-7000). The difference in temperature was kept minimum during the experiment for minimizing the loss of heat through radiation. The thermal diffusion coefficient (D) and the specific heat (C_p) of Ni₂CuCrFeAlₓ alloys were determined from the following expression: \( \kappa = D \rho C_p \).

3. Results

### 3.1. Phase identification in High entropy alloy after sintering at various times

In order to understand the phase evolution during sintering, Figure 1 shows the XRD profiles of 20 h MMED powder samples of Ni₂CuCrFeAlₓ HEA’s with different Al-content (x = 0.5, 1.0, 1.5, and 2.5) sintered at 800 °C for 3, 6 and 9 h respectively. It can be noticed that the XRD patterns of all the compositions after 3 h sintering consist of a mixture of three different phases, which are primarily Al-based (marked as α), Cu-based (marked as β), and Ni-based solutions (marked as γ) with FCC crystal structure. However, there was no significant shifting of any peak observed corresponding either of Al, Cu, and Ni. Therefore, these results indicate that no consequence re-distribution of alloying elements due to long-range diffusion or phase transformation occurred after 3 h of sintering. Nevertheless, some amount of localized re-distribution due to short-range diffusion of alloying elements or partial alloying cannot be ruled out. Theses observations are an indication of typical sluggish diffusion of elements in a multi-component system. From Figure 1, it can also be observed that the peaks corresponding to α, β, and γ phases are almost disappeared and many new peaks appeared after 6 h of sintering.

| Compositions     | VEC | Δχ  | ΔH  | ΔS   |
|------------------|-----|-----|-----|------|
| Ni₂CuCrFeAl₀.₅  | 8.45| 0.113| 4.199| −2.4 | 12.6 |
| Ni₂CuCrFeAl₁.₀  | 8   | 0.123| 5.317| −3.8 | 12.98|
| Ni₂CuCrFeAl₁.₅  | 7.6 | 0.126| 5.721| −6.5 | 13.4 |
| Ni₂CuCrFeAl₂.₅  | 7   | 0.134| 6.52 | −10.7| 12.68|

* In Percentage,
* In kJ mol⁻¹,
* In J K⁻¹mol⁻¹.

Table 1. Calculation of valance electron counts.
It can be noticed that the XRD pattern exhibits the presence of only two phases, consisting of a major phase with FCC crystal structure along with small amount of the second phase with a BCC crystal structure. However, with higher Al content \(x = 0.5\) \((7.42 \leq \text{VEC} < 7.62)\), the additional phases along with FCC could appear, which indicates the presence of disordered (A2) and ordered (B2) type phase. Composition of the alloy in the range \(1 \leq x \leq 2.5\) \((6 \leq \text{VEC} < 7.62)\), A2 + B2 phase would be observed. Thus, it can be inferred that the present

![XRD profiles of 20 h MMed powder samples of NiCuCrFeAl HEA’s with different Al-content \((x = 0.5, 1.0, 1.5, \text{and} 2.5)\).](image)

Figure 1. XRD profiles of 20 h MMed powder samples of NiCuCrFeAl HEA’s with different Al-content \((x = 0.5, 1.0, 1.5, \text{and} 2.5)\).
HEA system with given compositional range stabilized with primarily FCC-base together with a small amount of BCC-based phase. In our case, the mixture of FCC + BCC solid solution was perceived above $x = 0.5$, because of the continuous milling and the amount of BCC phase was increased with increasing Al-content. Other important results are the presence of superlattice peak (111) with small intensity, indicating L21 type ordering. This observation is found in Ni$_2$CuCrFeAl$_x$ alloys for all composition’s after 9 h sintering. These peaks explained the ordering of the alloy in FCC structure. The process parameter of milling along with sintering at 800°C affects the ordering of alloy and increases the intensity of superlattice peak.

3.2. Phase identification in High entropy alloy with different composition

The XRD results can further be analyzed to understand and explore the effect of composition, with increasing Al content on the phase evolution during sintering of the present HEA. Figures 2(a) and (b) shows the combined XRD pattern of all the composition sintered at 800°C for 3 and 9 h respectively. From figure 2(a) it can be observed that all the compositions consist of three-phase with FCC crystal structure, marked as $\alpha$, $\beta$, and $\gamma$. However, it is interesting to note that the intensity of the peaks corresponding to $\alpha$-phase (Al-based solid solution) appears to be slightly decreasing with increasing the Al-content. Also, there is no apparent shifting in the peaks was observed. These observations suggest that increasing of Al does not have any significant effect on the phase evolution in the early stages of sintering. Figure 2(b) shows that, the HEA’s with different composition consist of primarily FCC phase (marked as $\beta$) together with a small amount of BCC phase (marked as $\delta$) after 9 h of sintering and no implication in the relative intensities of peaks corresponding to FCC and BCC phase with
increasing Al content was noticed. The ordering of the BCC phase in FCC mixture was seen in XRD pattern with their formation, as the ordered BCC phase in all composition of Ni$_2$CuCrFeAl$_x$ alloys were observed above and equal at $x = 0.5$ as superlattice peak in XRD pattern. Moreover, the line profile of (111) BCC superlattice peak are all symmetrical. Figure 1 shows, the XRD profile of 20 h MMed powder samples of Ni$_2$CuCrFeAl$_x$ HEA’s with different Al-content along with a small increase of FWHM (full-width half maxima) indicating the superimposition of a different set of BCC plane. Based on the calculation of VEC values, it is predicted that all the composition of the present HEA system would consist of a combination of BCC and FCC phases, except Ni$_2$CuCrFeAl$_{0.5}$ alloy, which has a calculated VEC value of 8.45 and it is expected to have only FCC phase. Mainly, significant shifting of the peak can be only observed in Ni$_2$CuCrFeAl$_{2.5}$ composition. Such a shift of peak towards the lower angle can be associated with an increment in the lattice parameter of the phase with increasing Al-content.

As shown in figures 1 and 2, all the compositions consist of BCC + FCC phase along with superlattice peak. It is also evident from the observed results that sintering of the Ni$_2$CuCrFeAl$_{0.5}$ alloy at different time, affects the intensity of the diffracted peak and it decreases with an increasing Al-content because of induced aberrance of the lattice. Subsequently, the BCC phase consists of A2 + B2 structure, while the ordering of L2$_1$ structure results in FCC [18]. The volume fraction of BCC in the homogenized state after prolonged hour of sintering at 800 °C, is more than that sample sintered at 800 °C for 3 h. The prolonged milling and sintering at 800 °C triggered to decrease the peak intensity of FCC phase and a mixed phase of BCC + FCC was noticed owing to the maximum distortion of lattice structure caused by the deformation from the mechanical milling. This indicates the increase of relative peak intensity of (200) with sintering in contrast to other relative peaks in the XRD pattern. Besides, it is also noticeable that the cooling of the sample inside the furnace increases the degree of (200) texture which are aligned in parallel with the flow of heat. The increase of BCC phase with higher Al content, results from the fact that it easily develops π-π bonding by the formation of intermetallics as intermediate state. Diffusion scattering enhanced with increasing the milling of the sample for long hours of sintering which results in smaller particles that would easily diffused through thermal agitation.

### 3.3. Thermal analysis

The background of typical metallic materials during heating and cooling was observed from the DSC measurement of sintered alloy with composition $x = 0.5$ and $x = 2.5$ (as shown in figure 3). The change in the background actually indicates the irreversible change of material behaviour with heat flow that would result in semi-metallic nature of the material at a higher temperature. The endothermic peak in heating indicates the phase transformation of austenite into martensite and ferromagnetic to paramagnetic. The sigmoid like deviation in $x = 2.5$ directs the existence of mixed-phase along with L2$_1$ structure, whereas the existence of L2$_1$ phase in $x = 0.5$ is totally disappeared. Interestingly, at high Al-content i.e., $x > 1$, the significant features are observed for the existence of L2$_1$ phase along with mixed-phase (FCC + BCC). From $x = 0.5$ to $x = 2.5$, the
overall feature in DSC results are same and extra peaks appeared at the higher temperature which indicates the formation and dissolution precipitates of ordered phase with L2₃ structure.

Finally, from $x = 0.5$ to $x = 2.5$ (B₂ + A₂ phase), smooth curves are observed with a slight change in heat flowing to different phase transition up to 1100 K, indicating the presence of intermetallics as secondary phase, while at the higher temperature, there is less stability.

3.4. Thermoelectric behaviour of high entropy alloys

3.4.1. Electrical conductivity

The temperature dependence electrical conductivity of Ni₂CuCrFeAlₓ HEA with $x = 0$ to 2.5 are shown in figure 4. The electrical conductivity ($\sigma$) of Ni₂CuCrFeAlₓ with $x = 0$ is found to increase from log(4.9047) to (log 5.2300) initially in the temperature range of 423 K–733 K, and then it starts to decrease with the increase in temperature, exhibiting semiconductor to metallic transition near 793 K. The electrical conductivity drastically decreases with an increase in temperature from 793 K to 1123 K, showing the strong evidence of metallic nature of Ni₂CuCrFe at a higher temperature. The electrical conductivity increases many folds with an increase in Al content. Similarly, at $x = 0.5$, the electrical conductivity increases from log (5.1136) to log (5.4823) and then slowly decrease to log (5.3987) Sm⁻¹ at 1123 K which suggest the phase transition from semiconductor to semimetal near to 933 K. Moreover, with further increase in Al-content, nature of alloy remains the same but conductivity increase many folds which implies the retention of intrinsic behaviour of Ni₂CuCrFeAlₓ alloy over the range of investigated temperature. The electrical conductivity at room temperature gradually increases from log (5.1587) Sm⁻¹ for $x = 0.0$ to log (5.4020) for $x = 2.5$. The types of carrier concentration and mobility as a function of Al-content in Ni₂CuCrFeAlₓ alloy is measured from the Hall Effect measurement so as to know the type of semiconducting behaviour. The electrical conductivity with lower Al-content increases slowly and decreases gradually with temperature, while with higher Al-content, it increases exponentially with temperature because of the presence of high carrier density of state and attains the maximum value at log (6.1680) at 1123 K for $x = 2.5$. From $x = 0$ to $x = 2.5$ at 1123 K, the electrical conductivity increase drastically approximately more than five times.

3.4.2. Performance of seebeck coefficient with temperature

The average Seebeck coefficient values for the mixed structure of HEA’s suggest the dominant behaviour of the materials as a function of temperature. It is well known, that the measurement of Seebeck coefficient provides the probe for energy relative to the Fermi surface and also indicates the location of the Fermi level in the band structure. The Seebeck coefficient of HEA’s was measured under low pressure in presence of helium gas and the voltage difference monitored by using a pair of Cu-wire connected with sample (polished and coated with Silver paint) at the point of junction in the thermocouple. Figure 4 shows the temperature-dependent Seebeck coefficient of HEA’s. According to the molecular formula, the measured value of the Seebeck coefficient shows the positive value from 4 K to 300 K. Such finding declares that the dominant change carriers are hole type in the temperature range from 4 K to 300 K. This predict the good agreement with the calculation of valence electron concentration (VEC) in alloy which shows the great impact on the crystallinity of a solid solution phase in the
presence of similar-sized atoms and their results are also matched with band structure calculation for predicting large–hole packed near the Fermi level, density of states from density functional theory using muffin-tin orbital technique in combination with the coherent potential approximation \[19\]. Subsequently, in contrast to this, introducing Al in Ni_{2}CuCrFeAl\(_x\) alloy reverses the sign of Seebeck coefficient, which indicates the increase of electron carrier by expanding the most possible electronic configuration from the increase of the valence electron by the dopant than that from the host. The appearance of energy bandgap is due to the presence of the total number of 18 valence electron, which corresponds to the semiconducting nature of HEA’s. This small gap is still found in the density of state within pseudogap and upward shift of the Fermi-surface by a small change in carrier concentration. The upward shift of Fermi-surface reduces the hole packet and increase the density of the electron charge carrier, leading to n-type carrier dominating transport properties by the addition of Al-in Ni_{2}CuCrFeAl\(_x\) alloy, as shown in figure 5, in the temperature range from 4 K–300 K, as clearly observed from the change of sign with an increase of Seebeck coefficient as a function of temperature. The observed change in sign of the Seebeck coefficient can be explained by considering the two type of charge carrier in electrical conduction. From the above results, the Seebeck coefficient can be expressed as:

\[
S = \left( \frac{\sigma_n S_p + \sigma_p S_n}{\sigma_p + \sigma_n} \right)
\]

where, \(\sigma_{np}\) and \(\sigma_{pn}\) are the Seebeck coefficient and electrical conductivity of n and p-type charge carrier respectively. The \(S_n\) and \(S_p\) both have opposite signs and their tuning is possible by either addition of Al or study the temperature-dependent behaviour. For Ni_{2}CuCrFeAl\(_x\) alloy, with \(x = 0.5\) to 2.5, the alloy develops the broad minima at a higher temperature and their corresponding temperature which cross-over the minima temperature decreases with an increase in Al-content. The upturn of S-curve is assumed from thermally excited quasi-particles across the Fermi surface. Below critical temperature (\(T_C\)), the electrical conductivity is mainly due to hole charge carrier, but beyond this, it shows mixed conductivity from hole and electron. Interestingly, it would be worth noting that alloy from 4 K–300 K shows p-type semiconducting nature, while at a higher temperature it leads to positive S-curve and the materials becomes n-type semiconductor. Moreover, the holes are more thermally energetic and easily cross the pseudo-gap from the upward shifting of \(E_P\). In figure 5, clearly it was noticed that the plateau region from the phonon drag effect was observed between 40 K–50 K in HEA’s. This is the characteristic peak of metal and generally found at low temperature. From the result, it is analyzed that the materials become metallic in nature at low temperature and at high temperature it is semi-metallic or semiconductor owing to the appearance of more phonon scattering. On the other hand, the broad high minima in S-curve is observed in \(x > 0\) at the minimum temperature. This result indicates that the Fermi surface is moved out from the pseudo gap with increasing Al-content in HEA’s resulting metallic behaviour at the low temperature. Ni_{2}CuCrFeAl\(_x\) alloy with \(x = 2.5\) is more metallic in nature than \(x = 0\). As matter of fact, beyond the plateau region, the S-curve exhibit lunar relationship as a function of temperature which is a signature of the typical metallic material, but beyond minimum temperature, it shows exponential growth predicting the semiconducting nature at high temperature.

Figure 5. Low-temperature dependent Seebeck coefficient of Ni_{2}CuCrFeAl\(_x\) as a function of Al-content.
Figure 6 represents the variation of the Seebeck coefficient of Al-substituted Ni$_2$CuCrFeAl$_x$ alloy with varying temperature. Subsequently, owing to the metallic nature, the sign of Seebeck coefficient for Ni$_2$CuCrFeAl$_x$ with $x = 0$ is negative, but it immediately changes from negative to positive if the values change from 0 to 0.5. With further increase in temperature for $x = 0.5$ in Ni$_2$CuCrFeAl$_x$ alloy, the Seebeck coefficient firstly attained the maximum value of 256.66 $\mu$V/K at 660 K and then decreases up to 35.06 $\mu$V/K at 850 K. It is also observed that the Seebeck coefficient increases linearly with an increase in Al-content at all measured temperature. The Seebeck coefficient of the high entropy can be expressed by the following expression:

$$ S = \frac{\pi}{3} \frac{k_B}{q} T \left\{ \frac{d}{dE} \ln (\sigma(E)) \right\}_{E=E_F} = \frac{\pi}{3} \frac{k_B}{q} T \left\{ \frac{1}{n} \frac{dn(E)}{dE} + \frac{1}{\mu} \frac{d\mu(E)}{dE} \right\}_{E=E_F} $$

where, $q$ define the charge carrier depending upon the nature of the alloy, $E_F$ the Fermi energy level, $n(E)$ and $\mu(E)$ indicates the density and mobility at energy $E$ respectively. The above formulation indicates the sharp change in carrier density of states (DOS) near $E_F$ [higher $dn(E)/dE$] and selective scattering of low energy charge carrier [enhancing $d\mu(E)/dE$], both are very effective to observe high the Seebeck coefficient ($S$-values) at each temperature. Moreover, the DOS has been taken care of in accordance of [16].

The alloy Ni$_2$CuCrFeAl$_x$ with $x = 0$ shows negative coefficient at room temperature and phase transformation from semiconductor to metallic. Such a negative Seebeck coefficient of Ni$_2$CuCrFeAl$_x$ at $x = 0$ can be attributed from the compensation of $S$-values resulting from the increment in the slope of carrier density of states and with increase in the number of charge carriers due to localized Fermi level from the d-band of Cu or Cr depending upon the randomness of the microstate in high entropy alloys. For heavily doped Ni$_2$CuCrFeAl$_x$ alloy, the Seebeck coefficient can be expressed in simplified form by Mott equation as:
is being more populated in conduction band by thermally excited holes with increasing temperature. Although envisaged from the results, the explanation for enhancement of thermopower for the alloy with more Al-content power increases linearly with increasing Al-concentration, and a maximum value of 2.0174

\(\mu = 0.4576\)

\(\mu = 1.5\)

\(\mu = 2.5\)

\(\mu = 0.0\)

\(\mu = 0.5\)

\(\mu = 1.0\)

\(\mu = 1.5\)

\(\mu = 2.5\)

\(S = \frac{8\pi^2k_B^2T}{3qh^2}m^*\left(\frac{\pi}{3n}\right)^{2/3}\)

\(h\) is plank constant and \(m^*\) is the carrier effective mass by assuming a sharp density of state from the presence of free electron and also due to energy independent scattering. It is also observed from figure 6(a) that the higher doping concentration of Al in Ni2CuCrFeAl x alloy is carefully maintained for high Seebeck coefficient without affecting the electrical conductivity, which confined through the presence of a type of charge carriers. The presence of different charge carriers from percentage replacement or introducing another element in the lattice would also be responsible for optimizing the doping level of n or p-type of high entropy alloy.

\(\sigma\) is the electrical conductivity, which consequently changes the sign of the Seebeck coefficient, Table 3 also reports the data of charge carrier density, Seebeck coefficient and electrical conductivity Ni2CuCrFeAl x alloy at room temperature as well as high temperature.

\(S_{20K}\) at 300 K which rapidly increases with increase in temperature and attains the maximum value of about 3.6575 \(\mu W/\text{K}^2\text{cm}\) at 850 K. The thermopower of Ni2CuCrFeAl x in \(x = 2.5\) is four-to-five times suggesting that p-type carriers found in Ni2CuCrFeAl x alloy by more number of holes and which increases with increase of Al content. It is also evident from the results that, as the temperature increase, p-type carriers in Ni2CuCrFeAl x alloy become the major charge carrier for electrical transport properties. As it was clearly envisaged from the results, the explanation for enhancement of thermopower for the alloy with more Al-content is being more populated in conduction band by thermally excited holes with increasing temperature. Although Al being substituted along with the existing alloy with composition \(x = 0\) maintaining p-type semiconducting behaviour. The temperature dependence of thermopower of Ni2CuCrFeAl x in HEA with \(x = 0\) shows a slow increment in the slope of carrier density of state, while the alloy with another composition shows a rapid increase in the slope of carrier density and selective scattering of low energy charge carrier indicating that Al-substitution in Ni2CuCrFeAl x alloy modifies the electrical transport properties. However, at room temperature, the thermopower increases linearly with increasing Al-concentration, and a maximum value of 2.0174 \(\mu W/\text{K}^2\text{cm}\) for \(x = 2.5\) is observed but at 850 K, the thermoelectric power is 7.274 \(\mu W/\text{K}^2\text{cm}\). The power factor is still negligible at very low temperature (say below 300 K) for all samples, and composition with high Al-content shows a sharp increase with increasing temperature.

The values of charge carrier density, Seebeck coefficient and electrical conductivity Ni2CuCrFeAl x alloy with \(x = 0\) to \(x = 2.5\) at room temperature are tabulated in table 3. Since Al contains one fewer valence electrons, therefore it acts as a source of electron donor and thus compensates the charge carrier in Ni2CuCrFeAl x alloy. The change of hole to electron carrier concentration is responsible for increasing the electrical conductivity and consequently changes the sign of the Seebeck coefficient. Table 3 also reports the data of charge carrier density,
Seebeck coefficient and electrical conductivity Ni\textsubscript{2}CuCrFeAl\textsubscript{x} alloy at the high temperature. It can also be seen from table 3, that all the data increase with increasing the temperature, suggesting that conduction is being more and more populated from hole owing to the presence of Al in Ni\textsubscript{2}CuCrFeAl\textsubscript{x} alloy.

### 3.4.4. Thermal conductivity

Low thermal conductivity of the alloy indicates the most prominent feature of a thermoelectric application. However, the thermal conductivity of HEA is relatively high from the known exiting material such as Half-Heusler alloy and Bi\textsubscript{0.4}Sb\textsubscript{1.6}Te\textsubscript{3} \cite{7}. The lattice vibration and electronic scattering give the high thermal conductivity of HEA. From the doping of Al in Ni\textsubscript{2}CuCrFeAl\textsubscript{x} alloy, predominant contribution arises from the lattice thermal conductivity. Figure 7(a) shows the temperature dependence thermal conductivity ($\kappa$) of Ni\textsubscript{2}CuCrFeAl\textsubscript{x} alloy. The thermal conductivity of the Ni\textsubscript{2}CuCrFeAl\textsubscript{x} alloy with $x = 0$ to 2.5 decreases with increasing $x$ with measured temperature range and hence the change of electrical conductivity of the alloy can be explained on the basis of simple VEC concept. The remarkable feature found in the variation of $\kappa$ is high values at low temperature which gradually decrease with increasing Al in alloy indicating the strong enhancement of phonon scattering. The Wiedemann–Franz law (with Lorentz number $L = 2.45 \times 10^{-8}$V$^2$K$^{-2}$) was used to predict the thermal conductivity of the Ni\textsubscript{2}CuCrFeAl\textsubscript{x} alloy. The lattice thermal conductivity can be effectively obtained by subtracting the electronic thermal conductivity ($\kappa_e$) to the total thermal conductivity ($\kappa$). Figure 7(b) shows the variation of lattice thermal conductivity ($\kappa_L$) with Al-content as a function of temperature. It is clearly observed from the analysis of the results that the origin for the reduction of $\kappa_L$ as a function of temperature can be explained using Debye approximation. Such analysis was successfully applied to the p-type skutterudites and other materials also at a low temperature and their fitted parameter would provide a better explanation for the scattering of phonons in these alloys. By using Debye approximation, $\kappa_L$ as a function of temperature can be expressed as:
4. Discussion and conclusion

Lattice thermal conductivity in Ni$_2$CuCrFeAl structural disordered at the high temperature. Therefore, the strain with high Al content composition with low Al-content is varied linearly in the temperature range from 150 K to 850 K, while alloy fluid field difference. For Ni$_2$CuCrFeAl alloy with x = 0 to x = 2.5, the electronic thermal conductivity ($\kappa_e$) is observed to be in the range of 0.018–0.23 W m$^{-1}$ K$^{-1}$ at 300 K, while total conductivity with x = 0 to x = 2.5 change from 20.83 to 13.03 W m$^{-1}$ K$^{-1}$. Since the electronic contribution is very little, therefore, the total conductivity is observed only from the contribution of the lattice. As expected from the results, $\kappa_e$ decreases dramatically with increasing x. This loss can be attributed to increasing the entropy of the alloy from the substitution of Al which suppress the phonon scattering at point defect and grain boundaries which arise by the presence of a small mass difference between iso-electronic element and strain fluctuation scattering of the phonon in HEA’s can be attributed to the substitution of more Al in the lattice without disturbance, which create point defect in scattering of the phonon due to increased mass fluctuations and develop strain field fluctuations (from the large density of dislocation and change of resorting force from change in interatomic distance) between the host and the parent lattice.

For Ni$_2$CuCrFeAl$_x$ alloy with x = 0 to x = 2.5, the electronic thermal conductivity ($\kappa_e$) is observed to be in the range of 0.018–0.23 W m$^{-1}$ K$^{-1}$ at 300 K, while total conductivity with x = 0 to x = 2.5 change from 20.83 to 13.03 W m$^{-1}$ K$^{-1}$. Since the electronic contribution is very little, therefore, the total conductivity is observed only from the contribution of the lattice. As expected from the results, $\kappa_e$ decreases dramatically with increasing x. This loss can be attributed to increasing the entropy of the alloy from the substitution of Al which suppress the phonon scattering at point defect and grain boundaries which arise by the presence of a small mass difference between iso-electronic element and strain field difference (observed from the sizes of element in 3d series) between host and doping elements. 

From the investigation of the measured data of electrical and thermoelectric properties at room temperature, the figure of merit (ZT) is calculated and their variation is shown in figure 8. From figure 8, it was observed that ZT increases monotonously with increasing temperature. The dependence of figure of merit (ZT) of Ni$_2$CuCrFeAl$_x$ alloy on temperature is strongly affected by Al-concentration. The ZT of composition with low Al-content is varied linearly in the temperature range from 150 K to 850 K, while alloy for composition x = 2.5 shows the exponential rise of ZT with T reaching maximum value of 0.2731 at 850 K for composition x = 2.5 which is 1.3 times more than that x = 0. The results suggest that the significant improvement in electrical conductivity carrier are still research for promising a new thermoelectric material which can be modified either by introducing p-type compound or n-type.

4. Discussion and conclusion

The alloying elements are all FCC or BCC type. As a matter of interesting fact, Ni$_2$CuCrFeAl$_x$ shows FCC structure at composition x = 0.5 while the same alloy at a composition x = 2.5 with 20 h milling and 9 h of sintering represents a mixed behaviour of structure as confirmed from XRD analysis, i.e., as x increases, structure changes from FCC to FCC + BCC. For thermoelectric power generation, high performance at elevated temperature is the prime requirement. The theoretical crystal parameter, can be calculated from rule-of-mixture and expressed by: $a_{\text{mix}} = \sum c_i a_i$ where, $c_i$ and $a_i$ is the atomic fraction and lattice parameters of the alloy.
the ith elements. Recently, Huang et al [20] reported that with increasing the Al-content in FeCrCoAl alloys, the paramagnetic behaviour suddenly changes into ferromagnetic at the room temperature. The valence electron concentration (VEC) and itinerant electron e/a ratio are used for the prediction of different phases i.e., $\text{VEC} = \sum_{i=1}^{8} N_i(\text{VEC})$ and $e/a = \sum_{i=1}^{8} x_i e/a$ In fact, low VEC and high e/a ratio favours the formation of BCC solid solution and FCC phase appears at high VEC and low e/a ratio. The HEA’s are considered to be single-phase alloys and their intermetallics are crystallized into B2 or L2$_1$ structure. Guo et al [15] also reported the microstructure of as-cast Al$_2$CuCrFeNi$_2$ alloy which consists of the eutectic colony like BCC and B2 phase. 

The HEA’s is semiconducting in nature and crystallizes in a mixed phase with half–Heusler like structure consists of four interpenetrating sub lattice, and one of the sublattices as a vacancy. In an open cage structure, any kind of disordered raised from mechanical milling on the vacancy sub-lattice mobility have considerable impact on the band gap and consequently modified the transport behavior. Each of the filled sub-lattice can be easily tuned the TE behavior of HEA’s. Doping of Al in Ni$_2$CuCrFeAl$_x$ alloy behaves perfectly as semiconductor with resulting net power gain as $(S^2T/\rho)$. The doping offers the charge carriers to play a fundamental role to improve the power factor and hence it maximizes the TE efficiency.

The increase in temperature-dependent conductivity is modified with the addition of the Al-content in Ni$_2$CuCrFeAl$_x$ alloy and hence the alloy with $x = 2.5$ provides more charge carrier as compared to $x = 0.5$. Therefore, alloy with $x = 2.5$ is a semiconductor and $x = 0.5$ has some covalent character along with metallic bonding. This semiconducting behaviour changes with change in temperature i.e., at low temperature, it is p-type while at the higher it behaves as n-type semiconductor, as observed intemperature-dependent Seebeck plots. At the higher temperature, the maximum hole is recombined with an electron and the only electron have sufficient thermal energy to cross the band gap and raised the Seebeck coefficient. For higher doping level, it provides more thermally excited charge carrier and thus higher temperature is needed for decreases the S-curve [21].

The temperature range presented in HEA’s of Ni$_2$CuCrFeAl$_x$ alloy during the investigation is a close proximity to an important gap between half-Heusler compound and most of n-type materials as well Si-Ge type materials which works better at 1123 K to 373 K. To compare with Half-Heusler, the HEA’s possess complex microstructure and the design of the following parameter such as (a) VEC (b) the difference in sizes of the respective elements (c) formation of the enthalpy of the element. Combining all these parameters, we will use to design high-performance thermoelectric materials for future high-temperature application. From the observation of the results of conductivity, there is no large difference between the conductivity of BCC or FCC or mixed phase regarding the Seebeck coefficient at a different temperature as consequence for the existence of narrowband with heavy carrier mass raised from the substitution of Al-content in Ni$_2$CuCrFeAl$_x$ alloy [22]. On the other hand, the lattice gets expanded after the substitution of more in Ni$_2$CuCrFeAl$_x$ alloy because of the similar size of Ni, Cr, Cu, and Fe. The Al occupies the octahedral holes of Ni$_2$CuCrFeAl$_x$ lattice and developed maximum strain from the disordered on both the Al and Ni$_2$CuCrFeAl$_x$ by the multiplication of large number of dislocation. All kinds of disturbances increases from the mass fluctuation and mean free path of phonon scattering are reduced. Such a strong influence of disordered of the lattice from mechanical alloying at higher speed modified the transport properties and also improved the thermoelectric properties. For potential
application at the high temperature, it is worth considerable for the stability of the materials. It has been observed from the results that the structural disordered leads to having a more stable configuration with lower DOS the Fermi energy level and a broad bandgap of Ni$_2$CuCrFeAl$_x$ alloy will change the charge carrier from p-type to n-type and hence changes the electrical conductivity. Thus with increased electron concentration, the sequence of the stable phase is observed as FCC-BCC-FCC as FCC with low Al-content as confirmed from XRD-analysis. The resulting band structure is lying bottom of the p-band which indicates the first derivative of the energy function, i.e., the Fermi energy difference $\Delta E_F$. The negative slope indicates the BCC DOS that lies above the FCC DOS and vise versa. Therefore, the Fermi energy difference causes rapid change to zero at some higher electron number, showing an extreme in Fermi energy difference. Basically average number of itinerant electron per atom, $e/a$, and total number of electrons available in d-orbital accommodated in the valence band decides the stability of the materials at high temperature. During the experimental investigation, Al-content from $x = 0.5$ to $x = 2.5$ changes the FCC structure to FCC + BCC structure and order of the alloy from A2 + B2 to L2$_1$ could increase the carrier concentration resulting in higher conductivity and Seebeck coefficient. In multi-component system, the disordered phase arises from the substitution of the extra atom into the lattice and method of the preparation of the alloy. The mechanical milling along with the substitution of Al-atom in Ni$_2$CuCrFeAl$_x$ alloy develops more and more disorderness in the system. In HEA’s, the size of the Al is much closer to Ni and Cr than that of Fe and Cu atom. The similar sizes observed between Al and Ni/Cr may lead to developing a higher degree of mutual substitution and hence creates the disorderness on both the Ni and Cr substances. The mass fluctuation scattering increases by increasing the extra atom in the lattice and reduce the mean free path for phonon scattering. Such disorders in the alloy havea strong impact on the transport behaviour that would increase the thermal conductivity and lowers the thermoelectric performance at a higher temperature.

From the results, we can conclude that the phonon contribution in Ni$_2$CuCrFeAl$_x$ HEA is relatively high among the known and exiting materials. Their variation can be classified in two regions: (I) low-temperature region, where the total conductivity increases with increase in temperature from the scattering of grain boundary by the complex microstructure and (II) large increase of thermal conductivity with temperature and attain the highest value at $T_{max}$ from the phonon-phonon umklapp scattering. Moreover, beyond that, the thermal conductivity decreases with an increase in temperature due to the mobility of the grain boundary.

Tang et al [23] reported the increase of the thermal conductivity of the half-Heusler alloy at low temperature due to lattice phonon. The atomic disordered play a crucial role to decrease the conductivity and their low values are observed very close to clathrates and skutterudites at the high temperature. In the present scenario, HEA’s have still considerable position for the improvement of high-temperature thermoelectric properties. The future development of HEA’s in regards to TE properties might lead to show high performance in terms of good electrical contact than with other materials also, such as SiGe, MgSi so as to become more compatible for designing the TE generator. The high entropy alloys open a new possibility to use as TE materials for ultra-high-temperature application such as space or air. An additional improvement is also possible to reduce lattice thermal conduction by precipitating the suitable intermetallic phase or using the powder metallurgy route for introducing the additional complexity in the microstructure. Furthermore, it has also seen observed that the correlation between Seebeck effect and electrical conductivity can be explained on the basis of geometrical factor and atomic radii of the alloying element which greatly influences the solid solubility of different phases. Nevertheless, not so much work has been done for the improvement of ZT of HEA’s. Recently, Shafeie had reported the thermoelectric performance (TE) of Al$_x$CoCrFeNi alloy at high temperature. They found values of ZT around 0 to 0.015 in varying $x = 0$ to $x = 2.5$, but the materials not enough efficient for the device fabrication. From the observation of the aforesaid results, HEA’s open the new possibility towards TE materials by changing the composition of the alloy. To compare with Heusler alloy, their microstructure and compositional feature are designed on the basis of (a) VEC (b) $e/a$ ratio (c) $\Delta H_f$ between the different elements. Combining all these features, including thermal stability of the alloy at higher temperature, the design of high efficient thermoelectric alloy will judge the suitable application in future. Consequently, band structure of FCC and BCC would also explain the variation of Seebeck effect in different structure and draw the attention in establishing good correlation between Seebeck effect and electrical conductivity. This correlation actually motivates us to investigate numerous application of broad range spectrum in HEA’s based on appropriate value of VEC and $e/a$ ratio as a starting place to design the devices for thermoelectric application.

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