



Thermoelectric performance of intermetallic FeGa₃ with Co doping



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ABSTRACT

Investigation on temperature-dependent electrical resistivity (ρ), Seebeck coefficient (S), and thermal conductivity (κ) of intermetallic Fe_{1-x}Co_xGa₃ ($0.005 \leq x \leq 0.5$) compounds are carried out to probe their thermoelectric performance. From resistivity study, it is observed that increase in number of valence electrons introduced by Co doping leads to a change from semiconducting to metallic behavior, which occurs between $x = 0.05$ and 0.125 . The characteristics of the Seebeck coefficient show a substantial decrease with the Co doping, due to the modifications in the band gap and the Fermi-level density of states. Analyses of thermal conductivity of the Co doped FeGa₃ compounds reveal that thermal transport is essentially due to the lattice phonons. It is also noticed that the low-temperature peak in the lattice thermal conductivity of these compounds is reduced significantly with the increase in Co content, attributing to the enhanced scattering of phonons by point-defects. The value of the figure-of-merit, $ZT = (S^2/\rho\kappa)T$, is estimated for all compounds, and the maximum room-temperature ZT value of about 0.02 was achieved for Fe_{0.95}Co_{0.05}Ga₃, and increased further with temperature to the value of about ~ 0.05 at 400 K.

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1. Introduction

Hybridization between transition metals and group III–IV elements such as Al, Si, and Ga occasionally leads to formation of energy gaps in the band structure around the Fermi level. Intermetallic compounds composed of these elements are generally metals with a few exceptions being semiconductors, such as RuAl₂ and RuGa₂ [1–4]. However, FeGa₃ and RuGa₃ compounds have also been predicted to be semiconducting using calculation of the electronic density of states [5,6]. The thermoelectric properties of these compounds have also been studied subsequently [7–9], as the semiconducting nature is favorable for thermoelectric applications.

Intermetallic FeGa₃ crystallizes in the tetragonal FeGa₃-type structure with the space group symmetry of $P4_2/mnm$. The electronic band structure calculations revealed that FeGa₃ is a narrow gap semiconductor with a band gap of about 0.3 – 0.5 eV [5,6], and such a value of band gap is in agreement with the obtained value from the resistivity measurements [8,9]. Opening of the narrow band gap in the FeGa₃ compound is originated from the overlap of the Fe $3d$ and Ga $4p$ orbitals; hence, one might expect the same behavior in other compounds with both d and p metals. From the investigation on transport properties of the CoGa₃-type

compounds, namely CoGa₃, RuGa₃, and RuIn₃ [5,10], it was found that RuGa₃ and RuIn₃ show semiconducting behavior, whereas CoGa₃ is a metallic conductor. This indicates that not only a certain combination of elements could lead to the formation of semiconducting gap in these compounds, but the number of valence electrons plays a crucial role in their physical properties. For the compounds with 17 electrons per formula unit, such as FeGa₃, RuGa₃ and RuIn₃, band structure calculations confirm that the Fermi level locates in the band gap [5,6]. For the 18 electron compounds (CoGa₃), the Fermi level shifts towards the conduction band, dividing non-bonding and anti-bonding states.

Recently, FeGa₃ compound has attracted considerable attention as a potential candidate for thermoelectric material [8,9] and spintronic applications [11–13]. It was found that a few percent (5%) of cobalt doping in FeGa₃ drastically changes the physical properties of the compound from a non-magnetic semiconductor to a paramagnetic bad-metal [11,14]. The observed doping effect on physical properties is connected with the creation of local magnetic moments and increase of valence electron concentration in FeGa₃. From these studies, it is evident that the number of valence electrons has a significant impact on transport and magnetic properties; hence, the effect of Co substitution onto the Fe sites of FeGa₃ presents a great opportunity for further investigation. Particularly, the study of thermoelectric properties on the Co doped FeGa₃ is appealing, as materials with sharp electronic band features of a

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few tens of meV from the Fermi level would be promising candidates for developing highly efficient thermoelectric materials. In the present work, we performed the electrical resistivity, Seebeck coefficients and thermal conductivity measurements on the Co doped FeGa₃ compounds, namely Fe_{1-x}Co_xGa₃ (0.005 ≤ *x* ≤ 0.5), to investigate their thermoelectric performance. We incorporate the changes in the thermoelectric properties of FeGa₃ with the effects of the reduction in band gap, the modification in the Fermi level density of states (DOS), and the mass fluctuation induced phonon scattering by Co doping.

2. Experiments

The intermetallic solid solution Fe_{1-x}Co_xGa₃ with 0.005 ≤ *x* ≤ 0.5 was synthesized using a flux technique with excess gallium and characterized, as described elsewhere [12]. All samples were cut to a rectangular parallelepiped shape with a typical size of about 1.5 × 1.0 × 6.0 mm³ for the transport measurements. Electrical resistivity of these Co doped FeGa₃ compounds were measured in the temperature range of 10–400 K using a standard four-probe method during the warming process. For the electrical resistivity measurement, four indium pads were deposited on the samples by thermal evaporation, on which copper wire contacts were made using silver paint. It consists of four-probe arranged linearly in a straight line at nearly equal distance (~2 mm) between each other. A constant current (1 mA) was applied to the two outer probes, and the voltage across the two inner probes was measured using Keithley 2182 nanovoltmeter. Measurement of the Seebeck coefficients for these compounds was carried out using dc pulse technique in a closed-cycle refrigerator [8,15]. Seebeck voltages were detected using a pair of thin Cu wires which were electrically connected to the sample with silver paint at the same positions as the junction of differential thermocouple. The stray thermal emfs were eliminated by applying long current pulses (~100 s) to a chip resistor which served as a heater, where the pulses appeared in an off-on-off sequence. Thermal conductivity of the Co doped FeGa₃ compounds were measured in the temperature range of 10–400 K using a direct heat-pulse technique [8,15]. For the thermal conductivity measurement, one end of the sample was glued (with thermal epoxy) to a copper block that served as a heat sink, while a calibrated chip resistor (100 Ω at room-temperature) as a heat source was connected to the other end. The temperature difference was detected by using an E-type differential thermocouple with junctions thermally attached to two well-separated positions along the sample. The temperature difference was controlled to be less than 1 K to minimize the heat loss through thermal radiation, and the sample space was also maintained in a good vacuum (~10⁻⁴ torr) during measurements to avoid heat loss through convection.

3. Results and discussion

3.1. Electrical resistivity

The temperature dependence of electrical resistivity, $\rho(T)$, of the Fe_{1-x}Co_xGa₃ (0.005 ≤ *x* ≤ 0.5) compounds is displayed in Fig. 1.

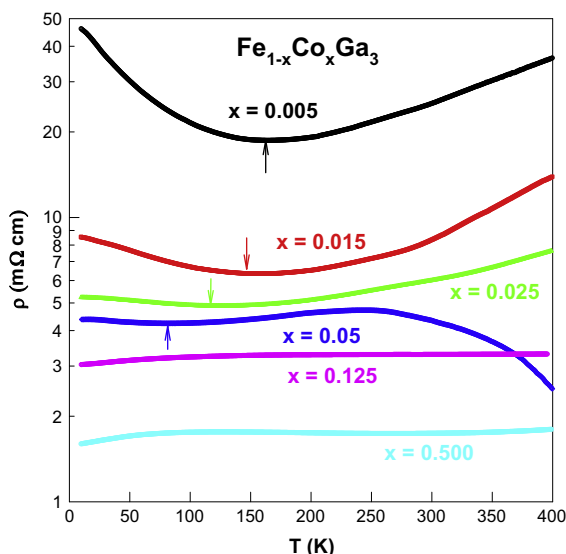


Fig. 1. Temperature-dependent electrical resistivity of the intermetallic Fe_{1-x}Co_xGa₃ samples.

Room-temperature ρ values of these Co doped FeGa₃ compounds are found to lie between 25 mΩ cm and 2 mΩ cm. For the Fe_{0.995}Co_{0.005}Ga₃, ρ decreases with increase in temperature followed by a tendency of saturation near 170 K, and then increases gradually upon further increasing temperature, due to the thermally activation of impurity donors [9]. It is evident that the dominance of a semiconducting feature in this compound is diminished at high temperatures compared to that of parent FeGa₃ [4], as indicated by the positive temperature coefficient of resistivity above 170 K. The similar $\rho(T)$ behavior is also seen for the compounds with Co content of *x* ≤ 0.05, however the saturation temperature (*T_s*) is found to be reduced gradually to 80 K (Fe_{0.95}Co_{0.05}Ga₃) from 170 K of the Fe_{0.995}Co_{0.005}Ga₃ compound. In addition, it is found that the room-temperature resistivity of the Fe_{0.95}Co_{0.05}Ga₃ (~4 mΩ cm) is comparable with the literature value of ~3 mΩ cm [16]. Whereas the compounds with Co content of *x* ≥ 0.125 show metallic nature with a resistivity value below 4 mΩ cm, and their $\rho(T)$ curves show weak temperature dependence, similar to that of metallic compound CoGa₃ [5].

The resistivity data of these compounds with *x* ≤ 0.05 follow the Arrhenius law at low temperatures below the respective saturation temperature, as shown in Fig. 2. The estimated band gap value for Fe_{0.995}Co_{0.005}Ga₃ is about 7.5 meV, which is found to be reduced significantly compared to that of parent FeGa₃ [5], and further decreases with Co doping to the value of about 0.2 meV for Fe_{0.05}Co_{0.05}Ga₃. From the electrical transport study, it is noticed that the change from semiconducting to metallic behavior in FeGa₃ is observed with Co content of *x* ≥ 0.125, as a result of the increase in valence electron concentration by the doping, which agrees with the literature data [12–14], and is similar to the observation in the isostructural RuIn_{3-x}Sn_x with *x* = 0.01 [17]. Estimated room-temperature resistivity, saturation temperature and band gap values of these Co doped FeGa₃ compounds are listed in Table 1. It is noted that the $\rho(T)$ data of FeGa₃-based compounds deviates from the Arrhenius law below 20 K (Fig. 2), and it is expected to follow the $\exp[(T_0/T)^4]$ law at low temperatures due to a characteristic of the electron conduction attributed to variable range hopping among the Anderson localized states in the system [9].

Furthermore, it is noticed that the $\rho(T)$ curve of Fe_{0.95}Co_{0.05}Ga₃ has an unusual behavior compared to that of the other Co doped FeGa₃ samples at high temperatures (Fig. 1), i.e. the measured resistivity of Fe_{0.95}Co_{0.05}Ga₃ decreases rather sharply with increasing temperature from 250 to 400 K, similar to that of the earlier report on the single crystalline FeGa₃ [9]. The origin for the observed behavior might be a result of a complex interplay of contributions to the total electrical conductivity caused by semiconducting-like behavior of valence electrons thermally activated across the energy gap and metallic-like behavior of the conduction electrons appeared either due to the in-gap states (undoped FeGa₃, see Ref. [14]) or shifting of the Fermi-level towards the conduction band at low Co doping. However, further study on the $\rho(T)$ data of these Co doped FeGa₃ samples above 400 K is needed to draw any final conclusion. Moreover, it is worth mentioning here that we have carried out the resistivity measurements on three different pieces of the Fe_{0.95}Co_{0.05}Ga₃ sample which were prepared under the same condition, and all of them show similar $\rho(T)$ behavior except a small variation in magnitude. The estimated value of *E_g* for Fe_{0.95}Co_{0.05}Ga₃ by fitting the $\rho(T)$ data in the temperature range of 300–400 K is about 0.25 eV, which is about half of that of the pure FeGa₃ (~0.5 eV) [9].

3.2. Seebeck coefficients

The temperature-dependent Seebeck coefficient, *S*(*T*), of the Fe_{1-x}Co_xGa₃ compounds is shown in Fig. 3. The Seebeck coefficients of these compounds are found to be negative in the

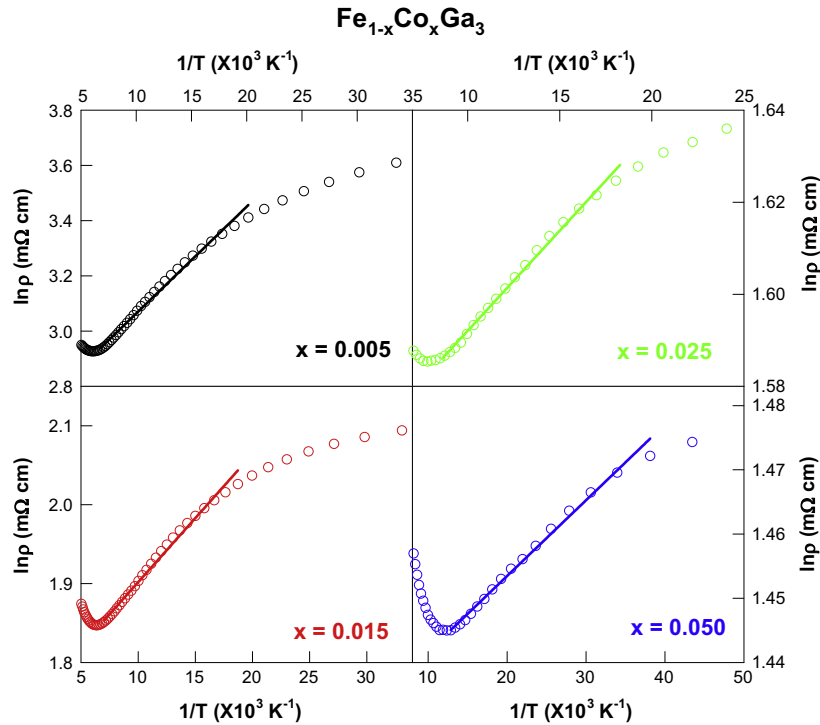


Fig. 2. The plots of $\ln \rho$ versus $1/T$ for the $\text{Fe}_{1-x}\text{Co}_x\text{Ga}_3$ compounds with $x \leq 0.05$. The solid lines represent linear fit to the corresponding data of samples.

Table 1

Room-temperature resistivity, saturation temperature and band gap values of the Co doped FeGa_3 compounds.

Co concentration	ρ_{RT} (mΩ cm)	T_s (K)	E_g (meV)
0.005	25.1	170	7.5
0.015	8.3	160	3.2
0.025	6.0	130	0.8
0.050	4.3	80	0.2
0.125	3.3	–	–
0.500	1.7	–	–

entire temperature range under investigation, suggesting that the electron-type carriers dominate the thermoelectric transport, which is consistent with the reported Hall measurement study [9]. The value of the room-temperature S varies from $-212 \mu\text{V/K}$ to $-49 \mu\text{V/K}$, showing a strong variation with the Co concentration. The observed large negative $S(T)$ of $\text{Fe}_{0.995}\text{Co}_{0.005}\text{Ga}_3$ could be originated from the enhanced effective mass for electrons due to a sharp peak of the density of states just above the band gap [15]. However, the large negative S value of $\text{Fe}_{0.995}\text{Co}_{0.005}\text{Ga}_3$ ($-212 \mu\text{V/K}$) is found to be much less than that of the pure FeGa_3 ($-350 \mu\text{V/K}$) [9], and reduced considerably with further Co doping. The observed $S(T)$ behavior of these compounds is consists of two contributions, i.e. the diffusion thermoelectric power and phonon-drag effect [18]. Upon cooling, $S(T)$ shows a shallow maximum below 50 K due to the phonon-drag effect, and S varies linearly with temperature above 200 K, as expected for the diffusion thermoelectric power of metals.

It is well known that the Seebeck coefficient measurement could yield information about the Fermi level band structure. Since the S data vary quite linearly with temperature above 200 K for these Co doped FeGa_3 compounds, the electron diffusion contribution to the Seebeck coefficient can be extracted by the simple linear temperature dependence through the Mott's formula

$$S = \frac{\pi^2 k_B^2}{2eE_F} T = bT, \quad (1)$$

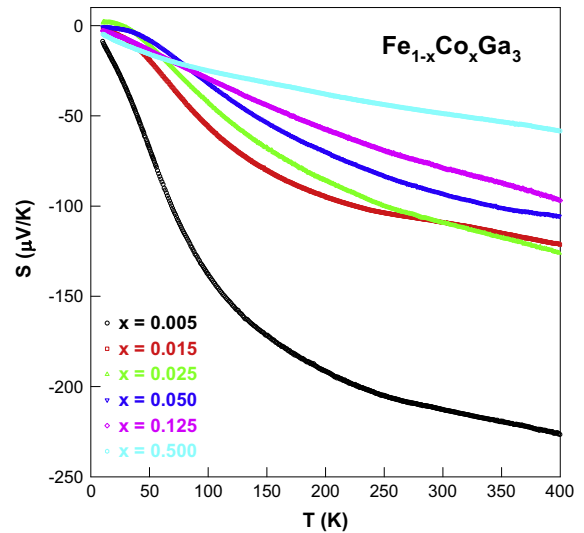


Fig. 3. Temperature dependence of Seebeck coefficients of the $\text{Fe}_{1-x}\text{Co}_x\text{Ga}_3$ compounds.

assuming a one-band model with an energy-independent relaxation time. Here, E_F and k_B are the Fermi energy and the Boltzmann constant, respectively. From the fitting of Seebeck coefficient at high temperatures, the estimated value of slope (b) of these compounds varies from $0.10 \mu\text{V/K}^2$ to $0.18 \mu\text{V/K}^2$. The magnitude of b is found to be increased with Co content up to $x \leq 0.125$, and then decreased slightly for the Co content of $x = 0.5$. Since the parameter b is inversely proportional to the Fermi energy E_F , the increase in b value with Co content suggests a slight shift in the position of E_F , which is consistent the resistivity data as well as the ab initio band structure calculations of the Co doped FeGa_3 compounds [12]. The shift in the position of E_F has an effect of enhancing the metallicity of the $\text{Fe}_{1-x}\text{Co}_x\text{Ga}_3$ system, which in turn leads to the observed reduction in its Seebeck coefficient.

3.3. Thermal conductivity

The measured thermal conductivity data, $\kappa(T)$, of the $\text{Fe}_{1-x}\text{Co}_x\text{Ga}_3$ compounds are illustrated in Fig. 4. The room-temperature thermal conductivity value of these compounds lies between 2.6 W/m K and 4 W/m K, moderately affected by the Fe/Co ratio. Upon the cooling process, it is observed that a gradual increase in κ is followed by a well-defined maximum near 40 K, and then a steep fall below 40 K. This feature is a typical behavior of solids due to a generalized Umklapp process. It is noticed that room-temperature value of κ for the slightly doped $\text{Fe}_{0.995}\text{Co}_{0.005}\text{Ga}_3$ compound (~ 4 W/m K) is quite low compared to that of the pure FeGa_3 (~ 7 W/m K) [8]. Furthermore, the magnitude and characteristics of thermal conductivity differ considerably with Co concentration at low temperatures. The height of the low-temperature peak in the $\kappa(T)$ of these compounds is found to decrease gradually with increase in Co content, suggesting a strong enhancement in the phonon scattering by the Co doping.

For metals and semimetals, the Wiedemann–Franz law is generally applicable, i.e., the thermal conductivity and electrical resistivity are commonly related over certain temperature ranges through the relationship, $\kappa_e(T)\rho(T) = L_0T$. Here, $\kappa_e(T)$ is the charge carriers contribution to the thermal conductivity, $\rho(T)$ is the electrical resistivity, and $L_0 (=2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2})$ is the Lorenz number. The calculated $\kappa_e(T)$ characteristics of these compounds using the above relation are also displayed in Fig. 4. This estimation gives a very small contribution of κ_e , suggesting that the thermal transport is essentially due to the lattice phonons, similar to the earlier reports [8,9]. Hence, the lattice thermal conductivity (κ_L) can be determined by subtracting κ_e from the measured κ , which is nearly the same in magnitude as the total thermal conductivity. This is expected because the electronic contribution to the heat transport is found to be negligible compared to that of its phonon counterpart.

In order to analyze the influence of Co doping on the phonon scattering processes in these FeGa_3 -based compounds, we estimated the temperature-dependent lattice thermal conductivity using the Debye approximation [19]. This analysis has already been successfully applied to the transition-metal silicides [19–21]. The lattice thermal conductivity (κ_L) in the Debye approximation can be written as

$$\kappa_L = \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \frac{\xi^4 e^\xi}{\tau_p^{-1}(e^\xi - 1)^2} d\xi, \quad (2)$$

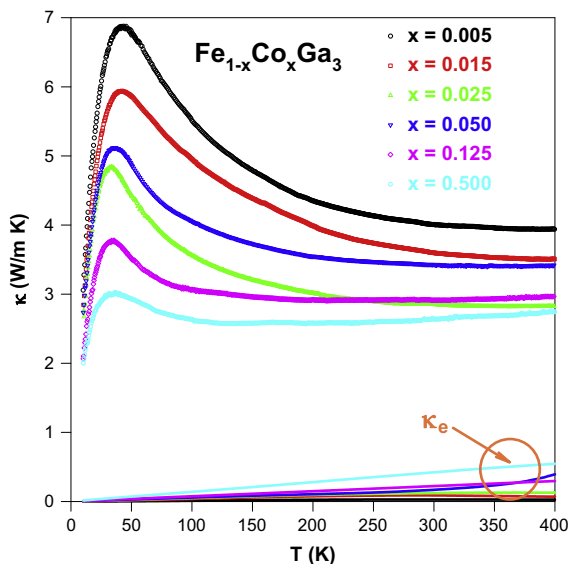


Fig. 4. Measured thermal conductivity data, $\kappa(T)$ of the $\text{Fe}_{1-x}\text{Co}_x\text{Ga}_3$ compounds. The solid lines represent the calculated κ_e of the Co doped compounds.

where $\xi = \hbar\omega/k_B T$, and ω , θ_D and τ_p^{-1} are the phonon frequency, Debye temperature and phonon scattering relaxation time, respectively. Here, τ_p^{-1} can be expressed as the combination of three scattering mechanisms, which is given by

$$\tau_p^{-1} = \frac{v}{L} + A\omega^4 + B\omega^2 T \exp\left(\frac{-\theta_D}{3T}\right), \quad (3)$$

where v is the average phonon velocity, L is the grain size, and the coefficients A and B are the fitting parameters. The terms in Eq. (3) are the scattering rates for the grain-boundary, point-defect, and phonon–phonon Umklapp scattering, respectively. It is apparent that the experimental data of these FeGa_3 -based samples can be fitted reasonably well in the low-temperature region below 160 K, as shown in Fig. 5a. The value of the Debye temperature (θ_D) used here is about 242 K for the calculation of κ_L of the compounds, which is close to that the value ($\theta_D = 258$ K) of isostructural RuIn_3 [22]. However, the deviation between the measured and calculated data at high temperatures can be associated with number of parameters such as radiation losses during the experiments, temperature-dependent Lorenz number and Debye temperature. These factors have minor impact at low temperatures, but have substantial effect on the heat transport at high temperatures for these compounds. Nevertheless, the radiation loss has been minimized to a large extent by the controlling of temperature difference at about ~ 0.5 K during measurements above 100 K.

From the κ_L fitting, we estimated a few parameters that characterize the strength of the phonon–grain boundary, phonon–point-defect and phonon–phonon scattering processes, which are listed in Table 2. It is seen that there is no systematic variation in the values of v/L and B with respect to the Co concentration. On the other

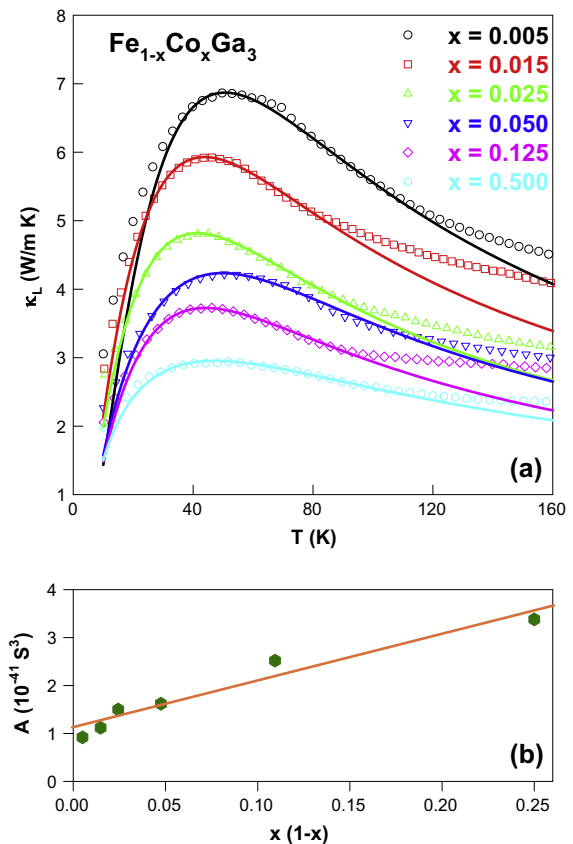


Fig. 5. (a) Temperature-dependent lattice thermal conductivity of the $\text{Fe}_{1-x}\text{Co}_x\text{Ga}_3$ compounds. The dashed lines represent the non-linear fits based on Eqs. (2) and (3), and (b) the pre-factor A as function of $x(1-x)$ for the Co doped FeGa_3 compounds.

Table 2

The estimated parameters from lattice thermal conductivity (κ_L) fitting of the $\text{Fe}_{1-x}\text{Co}_x\text{Ga}_3$ compounds using Eqs. (2) and (3).

Co concentration	v/L (10^9 s^{-1})	A (10^{-41} s^3)	B (10^{-18} s/K)
0.005	1.67	0.92	7.8
0.015	1.60	1.12	11.0
0.025	1.58	1.50	15.0
0.050	2.30	1.62	11.6
0.125	1.20	2.52	12.0
0.500	1.40	3.38	9.2

hand, the pre-factor A is found to increase gradually with increase in Co content, which confirms the importance of point-defect-phonon scattering for the lattice thermal transport in the Co doped FeGa_3 compounds. Generally, the grain boundary scattering is a dominant mechanism at low-temperature; however, the point-defect scattering has a strong influence on the appearance of the shape and position of the phonon peak in lattice thermal conductivity. Hence, it can be concluded that the change in lattice thermal conductivity at low temperatures in these compounds is possibly due to the modifications in the phonon-point-defect scattering. According to the model proposed by Klemens [23], the pre-factor A is proportional to $x(1-x)$, where x is the relative concentration of point-defects. As shown in Fig. 5b, the parameter A scales quite linearly with $x(1-x)$, suggesting that the effect of Co doping onto the Fe sites of FeGa_3 is strongly related to the appearance of point-defects by the Co doping. We argue that the point-defect scattering is most likely originated from the mass fluctuations between Co and Fe, since their atomic size and mass differences are quite large (>5%). In addition, other lattice imperfections such as vacancies and other defects may also be introduced via the doping, which could also induce point defects in the present Co doped compounds. Apart from the significant reduction in the low-temperature κ_L , the lattice thermal conductivity also shows a considerable reduction above 200 K in these compounds with the room-temperature κ_L value of $\sim 2\text{--}4 \text{ W/m K}$. Efforts can be made to further lower κ_L in addition to the mass fluctuation scattering in the FeGa_3 compound.

3.4. Figure-of-merit

Fig. 6 illustrates the figure-of-merit, ZT , as a function of temperature for the Co doped FeGa_3 compounds. It is observed that a

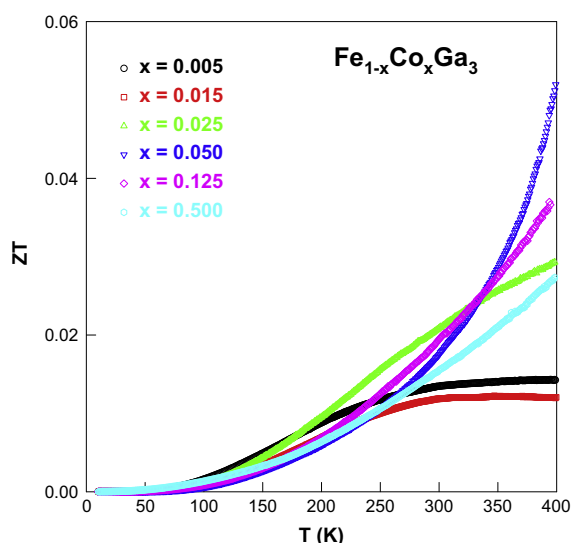


Fig. 6. Temperature-dependent figure-of-merit, ZT value of the intermetallic $\text{Fe}_{1-x}\text{Co}_x\text{Ga}_3$.

significant enhancement in the thermoelectric power factor (PF) and ZT ($=S^2/\rho\kappa$) value of the Co doped compounds with the maximum room-temperature PF and ZT values of about $2.6 \times 10^{-4} \text{ W m}^{-1} \text{ K}^2$ and 0.02 for $\text{Fe}_{0.95}\text{Co}_{0.05}\text{Ga}_3$ compound, respectively. The ZT value is further increased with temperature, and reaches the value of about ~ 0.05 at 400 K for the compound with $x = 0.05$, relatively high compared to that of the parent FeGa_3 ($ZT \sim 10^{-4}\text{--}10^{-3}$) [9,16], and $\text{Fe}_{0.99}\text{Co}_{0.01}\text{Ga}_{2.991}\text{Ge}_{0.009}$ ($ZT \sim 10^{-2}$) [16]. However, the highest ZT value of the $\text{Fe}_{0.95}\text{Co}_{0.05}\text{Ga}_3$ compound is still much smaller compared to that of the optimized thermoelectric material, Bi_2Te_3 ($ZT \sim 0.8$) [24]. Nevertheless, it is demonstrated that the figure-of-merit and thermoelectric power factor of the intermetallic FeGa_3 compound can be effectively enhanced by the Co doping.

4. Conclusion

Temperature-dependent electrical resistivity, Seebeck coefficients and thermal conductivity of the $\text{Fe}_{1-x}\text{Co}_x\text{Ga}_3$ ($0.005 \leq x \leq 0.5$) compounds were measured to study their thermoelectric performance. It is found that the room-temperature resistivity of the Co doped FeGa_3 compounds decreased systematically with increase in Co content. The metallic behavior was observed for the compounds with Co content of $x \geq 0.125$, as a consequence of the increase in the concentration of valence electrons by the doping. The Seebeck coefficient characteristic of these compounds has contribution from both the diffusion thermoelectric power and phonon-drag effect. A substantial reduction in Seebeck coefficient with Co doping was observed, most likely due to the modification in the band gap and the density of states at the Fermi level. The measured thermal conductivity is found to be suppressed significantly via the doping of Co in FeGa_3 . In addition, it is found that the substantial reduction in low-temperature lattice thermal conductivity of the Co doped FeGa_3 compounds is due to the phonon-point-defect scattering, presumably arising from the mass fluctuations between Fe and Co. Finally, the maximum ZT value of ~ 0.05 was achieved for $\text{Fe}_{0.95}\text{Co}_{0.05}\text{Ga}_3$ at 400 K, which ten times higher than that of the parent FeGa_3 . From this study, it is demonstrated that the doping of Co onto the Fe sites of FeGa_3 compound presents a good opportunity for improving its thermoelectric performance through the enhancement of thermoelectric power factor and the reduction in lattice thermal conductivity.

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