Investigations on Magnetic, Magnetocaloric and Transport Properties of Co$_2$Ti$_{1-x}$Sn$_{1+x}$ ($x = 0.25, 0.5$) Heusler Alloys

Remya. U. D$^1$, Athul. S R$^1$, Arun. K$^1$, Swathi. S$^1$, Andrea Dzubinska$^2$, Marian Reiffers$^3$, Nagalakshmi Ramamoorthi$^{1,a}$

$^1$Intermetallics and non-linear optics laboratory, Department of Physics, National Institute of Technology, Tiruchirappalli 620 015, India
$^2$CPM-TIP, University Pavol Jozef Safarik, 041 54 Košice, Slovakia
$^3$Faculty of Humanities and Natural Sciences, Presov University, Presov, Slovakia

Corresponding author: nagaphys@yahoo.com

Abstract. Co$_2$Ti$_{1-x}$Sn$_{1+x}$ ($x = 0.25, 0.5$) Heusler alloys have been prepared by arc melting technique and studied their magnetic, magnetocaloric and electrical resistivity properties. Magnetic studies show that $x=0.25,0.5$ alloys order ferromagnetically around transition temperature $T_c = 373.4$ K, $375.8$ K, respectively. Isothermal magnetization studies reveal the soft ferromagnetic nature and existence of ferromagnetic correlations above the transition temperatures of both alloys. Investigation of magnetocaloric properties results in the isothermal entropy change of 2.23 J/kg K and 1.58 J/kg K in an applied magnetic flux density change of $\Delta B = 5$ T for $x = 0.25, 0.5$ alloys, respectively. Second order nature of the magnetic transition and easy tunability of magnetic properties with stoichiometry of Ti – Sn are favorable for magnetocaloric applications. Electrical resistivity studies reveal the metallic nature of both alloys and show negative magnetoresistance.

INTRODUCTION

Quest for the designing of ferromagnetic materials from non-ferromagnetic elements ended up with the discovery of a new system known as Heusler alloy [1]. Far-flung applications in the field of spintronics, magnetocaloric, thermoelectric applications, and high compositions depended magnetic, and transport properties make them still an active research area in physics [2-3].

Heusler alloys are ‘Structurally ordered compound with either metallic or non metallic [4] properties, having stoichiometric composition $X_2YZ$ (doubly ordered $L_2$ type structure) in which $Y$ atom carries the majority of the magnetic moment. Even though Co$_2$TiZ ($Z=$Sn, Ge, Ga, Al) are one of the prime itinerant ferromagnetic series, Co atom carries the high magnetic moment and showing diverse physical properties like ‘Half metallicity,’ ‘High and constant Seebeck coefficient’[5]. Weak itinerant ferromagnet Co$_2$TiAl shows negative magnetoresistance and tuning of transition temperature can be done by doping Si in place of Al for the thermoelectric application[6]. Study on pseudo-binary system CoTi$_{1-x}$Al$_x$[7] shows anomalous behaviors depending upon their Ti and Al concentrations. They show a field-induced metamagnetic transition from paramagnetic to ferromagnetic state and also system becomes paramagnet for $x \geq 0.6$. Co$_2$TiGa is another weak itinerant ferromagnet [8]. Pseudo-binary system CoTi$_{1-x}$Ga$_x$, shows ferromagnetism for composition in range $0.3 < x < 0.7$[9]. Variation of the local environment of Co determines the magnetic properties of both systems. Large spin polarizability of half metallic compounds Co$_2$TiSi, Co$_2$TiGe, and Co$_2$TiSn make them suitable for spintronic and spin caloric applications. Studies of the doping effect of Mn in Co$_2$TiSn helps to find out a new way to tune the Heusler alloys for thermoelectric applications [10]. These Heusler alloy with Co$_2$MnSn and Co$_2$TiSn superlattices are found to be used in spintronic without any interlayer diffusion. Magnetic moment and curie temperature are found to be increased with substitution of Fe for Ti in Co$_2$TiSn [11] and Co$_2$TiSi [12] alloys with preserving their half metallicity. Curie temperature, ferromagnetic ordering and electrical resistivity of Co$_2$TiSn changes with decreasing the Co concentration in Co$_2$-Pd$_x$TiSn [13].
Doping and variation in the composition of these compounds will make a drastic change in their half metallicity, spin polarization, resistivity, and thermoelectric properties. These studies are opening a new way to tune the Co-based alloys for different applications in the field of spintronic, thermoelectric and magnetic refrigeration.

One of the recent applications of Co-based Heusler alloys is the magnetic refrigeration [2]. Pollution-free, energy-efficient magnetic refrigeration is a vital demand of modern society. Research is progressing on the way to find the good magnetocaloric materials which are rare-earth free and show near room temperature magnetic ordering with reversible magnetocaloric effect. Economical Heusler alloys are one of the best alternatives and composition dependence of ordering temperature makes them a nice preference for room temperature refrigeration.

In Co\textsubscript{2}TiZ series, the compositions of Ti and Z have major roles in forming their physical properties and ordering temperatures. Among them, Co\textsubscript{2}TiSn alloy is of great interest as it shows half metallic property [14]. Other than properties useful for spintronic application, Co\textsubscript{2}TiSn shows ferromagnetic transition around room temperature (355 K). Thus, near room temperature ferromagnetic transition and variation of magnetic properties with doping make these material suitable for magnetocaloric applications. As it is significant to study the influence of the stoichiometry on the fundamental properties of these alloys, in our work, we have synthesized Co\textsubscript{2}TiSn based alloys with different stoichiometries and studied their influences on magnetic and transport and magnetocaloric properties.

**EXPERIMENTAL DETAILS**

Polycrystalline alloys of Co\textsubscript{2}Ti\textsubscript{1-x}Sn\textsubscript{1+x} (x = 0.25, 0.5) were prepared by arc melting of the constituent elements Co (99.9+%), Ti (99.9%), and Sn (99.999%) taken in stoichiometric ratios. Then thermal annealing of the prepared ingots have been done at 1073 K for five days. During the arc melting, the prepared ingot was flipped and remelted five times to ensure the homogeneity. Phase purity and crystal structure were determined from Rietveld refinement of powder X-ray diffraction (XRD) pattern of the prepared alloys. Vibrating Sample Magnetometer (VSM) and Physical property Measurement System (PPMS) in DYNACOOL device of Quantum Design were used to study the magnetization, heat capacity and electrical resistivity of the prepared samples in the temperature range of 2 – 400 K and in an applied magnetic flux density of 0 – 9 T. Magnetization studies have been done in both Zero – Field - Cooling (ZFC) and Field - Cooling (FC) modes.

**RESULT AND DISCUSSION**

*Structural analysis*

Rietveld Refinement of the room temperature XRD data of Co\textsubscript{2}Ti\textsubscript{1-x}Sn\textsubscript{1+x} (x = 0.25, 0.5) alloys confirm that the samples were formed in binary phase viz., Co\textsubscript{2}TiSn phase (SG = Fm-3m) and CoSn phase (SG = P6/mmm). For a small value of x = 0.25, CoSn phase fraction is meager (3.35 wt%), while on increasing x to 0.5, CoSn phase dominates (54.90 wt%) implying that, the crystal structure of Co\textsubscript{2}Ti\textsubscript{1-x}Sn\textsubscript{1+x} alloy is highly sensitive to Ti-Sn

![FIGURE 1](image1.png)

**FIGURE 1.** Rietveld refined room temperature XRD patterns of Co\textsubscript{2}Ti\textsubscript{0.75}Sn\textsubscript{1.25} alloy (a) and Co\textsubscript{2}Ti\textsubscript{0.5}Sn\textsubscript{1.5} alloy (b).
Magnetic properties and Magnetocaloric effect

Magnetization as a function of temperature $M(T)$ in ZFC and FC modes in an applied magnetic flux density of $B = 0.01$ T from 2 K to 400 K is shown in Fig. 2 (a) and (b) corresponding to $\text{Co}_2\text{Ti}_{0.75}\text{Sn}_{1.25}$ and $\text{Co}_2\text{Ti}_{0.5}\text{Sn}_{1.5}$, respectively. As temperature decreases from 400 K, both alloys exhibit a paramagnetic to ferromagnetic transition associated with a sudden increase in magnetization around $T_c = 373.4$ K and 375.8 K for $x=0.25$ and 0.5, respectively. Transition temperatures have been determined from minima in their first order derivatives of ZFC magnetizations in an applied flux density of $B = 0.01$ T. Variations of peaks in first order ZFC magnetization derivative curves are shown in the inset of Fig. 2 (a) and (b) for alloys in composition $x = 0.25$ and 0.5 for applied magnetic flux densities of $B = 0.01$T, 1T, 3T, and 5T. As applied field increases, the transition temperatures of both alloys show a high temperature shift which denotes the ferromagnetic nature of the transitions [15]. Further, low temperature regions of both the alloys are characterized by magnetic irreversibility due to domain wall pinning effect [16]. It should be noted that the magnitude of the irreversibility is highly sensitive to the stoichiometry of the alloys as demonstrated in the main panel of Fig. 2 (a) and (b).

Isothermal magnetization studies display that a complete saturation is attained even in a very small applied magnetic flux density, $B$ less than 1 T that in turn endorses their pure ferromagnetic nature (not shown in figures). Isothermal magnetization curves near to their transition temperatures are shown in Fig. 3 (a) and (b), respectively for $x = 0.25$ and $x =0.5$ composition of $\text{Co}_2\text{Ti}_{1-x}\text{Sn}_{1+x}$ alloys. They display the soft ferromagnetic nature. Both alloys show curvature in their isothermal magnetizations above their transition temperatures, which indicate the existence of ferromagnetic correlations above their transition temperatures [17]. Further increase in temperature results in a linear isothermal magnetization curve, which indicates the paramagnetic nature of high temperatures magnetic states of both alloys.
Determination of the order of the magnetic transitions is important in the application of magnetic materials as a magnetic refrigerant. First order magnetic transitions result in high entropy change with hysteresis loss. But magnetic materials with second order phase transition are free of hysteresis loss and more favorable for magnetic refrigeration. One of the widely used methods to determine the order of the magnetic transitions is Banerjee criteria in Arrott plot. According to Banerjee criteria, negative and positive slope in Arrott plot represent the first and second order nature of magnetic transitions, respectively [18]. The Arrott plots \( M^2 \) vs \( B/M \) show positive slope around ordering temperature in either cases, thereby, revealing that the ferromagnetic transition is of second order in nature (See inset of Fig. 4 (a) and (b)).

The magnetic refrigeration efficiency of a material is evaluated from the isothermal magnetic entropy change \( -\Delta S_M \) and relative cooling power (RCP). Isothermal magnetic entropy change \( -\Delta S_M \) calculated from isothermal magnetization data using Maxwell relation [19] is given below.

\[
-\Delta S_M (T, B) = \int_0^B \left( \frac{\partial M}{\partial T} \right) dB \tag{1}
\]

It is common to estimate RCP by taking the product of maximum entropy change and working temperature span of the alloys and thus to evaluate the amount of heat transferred from the system to surrounding. \( -\Delta S_M \) as a function of temperature in \( AB = 2 \) T, 5 T, 7 T is shown in the inset of Fig. 4 (a) and Fig. 4 (b) for \( x = 0.25 \) and 0.5.
respectively. For both the alloys $\Delta S_M(T)$ graphs show a symmetric peaks around their respective ordering temperatures which are often noticed in second order ferromagnetic materials [20]. The magnitudes of $\Delta S_M$ (RCP) of Co$_2$Ti$_{0.75}$Sn$_{1.25}$ and Co$_2$Ti$_{0.5}$Sn$_{1.5}$ alloys are 2.23 J/kg K (71 J/kg) and 1.58 J/kg K (45.2 J/kg) in $\Delta B = 5$ T which is comparable with previously reported alloys namely, Ni$_{50}$Mn$_{36}$Sn$_{11}$Si$_3$[21], and Mn$_{50}$Ni$_{38}$Co$_2$Sn$_{10}$ [22] alloys.

**Transport properties**

![Image](a) Electrical resistivity ratio ($\rho/\rho_0$) as a function of temperature ($T$) for Co$_2$Ti$_{0.75}$Sn$_{1.25}$ and Co$_2$Ti$_{0.5}$Sn$_{1.5}$ alloys in absence of applied magnetic flux density. (b) Electrical resistivity ratio ($\rho/\rho_0$) as a function of temperature ($T$) for Co$_2$Ti$_{0.5}$Sn$_{1.5}$ alloy in an applied magnetic flux densities $B = 0$T and 9T. Inset display the calculated MR% for 9T field change. Where $\rho$, $\rho_0$ denotes the electrical resistivity at different temperatures and at 2 K.

Electrical resistivity studies ($\rho(T)$) in a temperature range of 2- 400 K for different applied magnetic flux densities indicate that both the alloys are metallic in nature up to magnetic ordering temperature. The plot of the variation of $\rho/\rho_0$ as a function of temperature at $B = 0$ T for both alloys is shown in Fig. 5 (a). Here $\rho_0$ denotes the electrical resistivity at 2 K. Both alloys show a slight hump around their transition temperatures. The residual resistivity ratios for $x = 0.25$, 0.5 are calculated to be 13, 15, respectively. These values are quite good for the case of the polycrystalline materials [23]. Co$_2$Ti$_{0.5}$Sn$_{1.5}$ shows a negative magnetoresistance of -3.2% around its ordering temperature in $B = 9$ T (See Fig. 5 (b) inset ). Negative magnetoresistances around their transition temperatures also confirm the ferromagnetic characteristics below $T_C$. Even for a slight change in stoichiometry, our work signifies the influence of Ti-Sn concentration on physical properties of Co$_2$TiSn alloy. To summarize, soft ferromagnetic nature along with easy tunability of Co$_2$Ti$_{1-x}$Sn$_{1+x}$ alloy enable these alloys to deploy it for practical applications.

**CONCLUSION**

Cobalt based Heusler alloys Co$_2$Ti$_{1-x}$Sn$_{1+x}$ for $x = 0.25$, 0.5 have been prepared by arc melting technique and formed in Co$_2$TiSn and CoSn phases. Magnetic, magnetocaloric and electrical resistivity studies have been done. Both prepared Heusler alloys with Ti – Sn stoichiometry $x = 0.25$, 0.5 are ordered ferromagnetically around $T_C = 373.4$ K and 375.8 K, respectively. Isothermal magnetization measurement and Arrott plot denote the soft ferromagnetic second order nature of magnetic transitions in both alloys. Magnetocaloric properties of Co$_2$Ti$_{0.75}$Sn$_{1.25}$, and Co$_2$Ti$_{0.5}$Sn$_{1.5}$ alloys are characterized with $\Delta S_M$ (RCP) equal to 2.23 J/kg K (71 J/kg) and 1.58 J/kg K (45.2 J/kg) in $\Delta B = 5$ T. Electrical resistivity studies explored the metallic nature of both alloys. Magnetic, magnetocaloric, and magnetotransport properties of Co$_2$Ti$_{1-x}$Sn$_{1+x}$ alloy for $x = 0.25$, 0.5 alloys emphasize the high stoichiometric dependence of physical properties of these alloys.
ACKNOWLEDGMENTS

The author Remya thanks MHRD, India for awarding GATE fellowship and the author Athul S R, thanks CSIR, Govt. India for awarding JRF through CSIR fellowship (No. 09/895(0013)/2019-EMR-I). The authors are grateful to Mr. Nilesh Kulkarni and Mrs. Bhagyashree Chalke, Department of Condensed Matter Physics, Tata Institute of Fundamental Research, Mumbai, India in structure and compositional measurements. This research work is a part of the Project implementation: University Science Park TECHNICOM for Innovation Applications Supported by Knowledge Technology, ITMS: 26220220182, supported by the Research & Development Operational Programme funded by the ERDF; project No. 001PU-2-1/2018 and also by VEGA 1/0705/20, 1/0611/18, 1/0956/17 and APVV-16-0079.

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