Low field magneto caloric effect in (Gd$_{1-x}$ Pr$_x$)$_5$Si$_{3.2}$Sn$_{0.8}$ alloys

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Abstract. The structural, thermal and magnetic properties of the arc melted (Gd$_{1-x}$ Pr$_x$)$_5$Si$_{3.2}$Sn$_{0.8}$ alloys with \(x = 0, 0.05, 0.1\) and 0.15 were studied. A maximum magnetic entropy change of 1.2034 J/kgK occurs for the \(x = 0.1\) alloy at 299 K for a low magnetic field change of 1.58 T. The Arrott plot technique confirms a second order ferromagnetic to paramagnetic phase transition in all these Si rich orthorhombic samples. Tuneable \(T_c\) around room temperature, moderate values of \(\Delta S_m\) in low magnetic fields and absence of magnetic hysteresis make these alloys useful with regard to room temperature magnetic refrigeration.

1. Introduction
The rising concern for the environment has created much interest in using the energy efficient and eco-friendly magnetic refrigeration based on the magneto caloric effect (MCE) as an alternative to the conventional vapour cycle refrigeration and there is an extensive search for magnetic materials with better MCE values following the discovery of giant MCE in Gd$_5$Si$_2$Ge$_2$ alloy [1]. The thermal hysteresis and the magnetic hysteresis associated with the first order transition in Gd$_5$Si$_2$Ge$_2$ alloy, the high cost of Gd and Ge and the need for a high magnetic field to produce GMCE make the commercialization of this technique difficult. For practical applications, we need magneto caloric materials of little hysteresis, exhibiting high magnetic entropy change around room temperature. Minor alloying additions on the magnetic Gd part and non-magnetic Si/Ge lattice can reduce the hysteresis loss, adjust the Curie temperature (\(T_c\)) and enhance the magnetic entropy change in low applied magnetic field. Much research has been conducted on the structural and magnetic properties of the Gd$_x$(Si$_x$Sn$_{1-x}$)$_4$ alloy system, which exhibits a phase similarity with the Gd$_x$Si$_x$Ge$_{4-x}$ system [2, 3]. Usually, heavy rare earth metals having high magnetic moment are preferred for MCE. In contrast, this paper presents the preparation and characterization of (Gd$_{1-x}$ Pr$_x$)$_5$Si$_{3.2}$Sn$_{0.8}$ alloys, with \(x = 0, 0.05, 0.1\) and 0.15, in which a portion of the heavy Gd is replaced by the lighter Pr.

2. Experimental
Alloy buttons of \(\sim 5\) g with the nominal composition (Gd$_{1-x}$ Pr$_x$)$_5$Si$_{3.2}$Sn$_{0.8}$, where \(x = 0, 0.05, 0.1\) and 0.15, were prepared by repeatedly arc melting appropriate quantities of very high pure constituent elements in a water-cooled copper hearth under Argon atmosphere. The alloys were studied in the as
cast condition without any heat treatment. The XRD spectrum was recorded on a Philips XPERT-PRO diffractometer with Cu Ka radiation and calorimetric measurements were performed using Thermal Analysis Differential Scanning Calorimeter (Mettler Toledo DSC 822e). The $M(T)$ and $M(H)$ studies were carried out using a vibrating sample magnetometer (Lakeshore, Model No: 7407). The isothermal magnetic entropy change $\Delta S_m(T, H)$ was calculated from the isothermal magnetization measured at discrete temperatures, using the numerical formula:

$$\Delta S_m = \sum_i \frac{1}{T_{i+1} - T_i} (M_i - M_{i+1}) \Delta H_i$$  \hspace{1cm} (1)

where, $M_i$ and $M_{i+1}$ are the magnetization values measured in a field $H$ at temperatures $T_i$ and $T_{i+1}$ respectively and $\Delta H_i$ is the magnetic field step within each isotherm [4].

3. Results and discussion

3.1. Structural analysis

The powder XRD patterns of the quaternary alloys, $(\text{Gd}_{1-x}\text{Pr}_x)_5\text{Si}_{3.2}\text{Sn}_{0.8}$ ($x = 0, 0.05, 0.1, 0.15$), are shown in figure 1. The diffraction peaks were identified using the JCPDS database and the most intense peaks at $\sim 31.9^\circ$, $32.1^\circ$ and $33^\circ$ in all the samples confirmed an orthorhombic Gd$_5$Si$_3$-type phase for all the alloys (PDF 87-2319) [5]. However, the peaks at $\sim 29.9^\circ$, present in all the samples, are more intense than that is expected for the Gd$_5$Si$_3$ orthorhombic system. This peak is indicative of the presence of an orthorhombic GdSi-type minor phase (PDF 80 - 0705) [6]. The crystal structure remained invariant with Pr addition except for the slight shift of the peaks to lower angles, indicating a lattice expansion arising from the differences in the atomic radius of Gd (2.54 Å) and Pr (2.64 Å).

3.2. Thermal studies (Differential scanning calorimetry - DSC)

The heat flow from the samples were measured as a function of temperature from 225 to 375 K, under zero magnetic field and the results are shown in figure 2. Absence of large peaks in the thermal curves arising from the structural transition near the Curie temperature ($T_C$) revealed the existence of only a second order magnetic transition ($\sim 300$ K) in the samples.
3.3. Magnetic studies

The $M$-$T$ curves for the samples for a temperature range of 400 K to 200 K in a field of 1.6 T, are shown in figure 3. The minimum of the $\frac{\partial M}{\partial T}$ versus $T$ curve gives the Curie temperature ($T_c$). The substitution of Pr with Gd has led to a decrease in $T_c$ up to $x = 0.1$ and from there $T_c$ increases with Pr content which is attributed to the change in exchange energy between these magnetic atoms with doping.

In order to calculate the maximum value of the isothermal magnetic entropy change ($\Delta S_m$), the field dependant isothermal magnetization ($M$-$H$) up to 1.58 T was measured 4 K above and below the ordering temperature (figure 4).

![Figure 3.](image1.png)  
**Figure 3.** $M$-$T$ curves for the alloys. The inset figure show the variation of $T_c$ with $x$.

![Figure 4.](image2.png)  
**Figure 4.** The $M$-$H$ curves for the alloys in a magnetic field of 1.58 T.

The $M$-$H$ isotherms taken around $T_c$ are completely reversible and show a typical ferromagnetic nature below $T_c$. The magnetization varies nearly linearly with the magnetic field for low fields at $T > T_c$, showing a paramagnetic behaviour. The saturation magnetization was not reached in low magnetic fields due to the magneto crystalline anisotropy of the sample. The $\Delta S_m$ values of the (Gd$_{1-x}$Pr$_x$)$_5$Si$_{3.2}$Sn$_{0.8}$ alloys, at their ordering temperatures are 0.6779, 0.9322, 1.2034 and 0.2138 J/kgK respectively for $x = 0,0.05,0.1,0.15$ in a low magnetic field of 1.58 T. These values are comparable with that of the Gd$_5$Si$_3$Sn$_{4.8}$ second order transition system (1.69 J/kgK at 301.5 K for Gd$_5$Si$_{2.8}$Sn$_{1.2}$ and 2.26 J/kgK at 290.5 K for Gd$_5$Si$_{2.6}$Sn$_{1.4}$ for $\Delta H = 1.8$ T) [3]. It is evident that Pr doping up to $x = 0.1$ would lead to an increase in the maximum magnetization and in the magnitude of the maximum entropy change for these alloys. The lower values of the magneto caloric effect are due to the absence of structural transitions in the samples as inferred from the calorimetric measurements. Although the first order transition (FOT) systems have higher MCE values, the hysteresis and the narrow temperature span of those systems will adversely affect the refrigerant capacity and relative cooling power. Therefore, second order transition (SOT) systems exhibiting MCE over a wide temperature range with little hysteresis are of commercial importance. Figure 5 shows the Arrott plot ($M^2$-$H/M$) of the samples which could be used for confirming the order of magnetic phase transition using the Banerjee criterion [7]. When the slope of the $M^2$ versus $H/M$ curve is negative, the system undergoes a first order magnetic phase transition and a positive slope corresponds to a second order magnetic phase transition. All the curves presented in figure 5 show a positive slope and therefore (Gd$_{1-x}$Pr$_x$)$_5$Si$_{3.2}$Sn$_{0.8}$ alloys have a second order magnetic phase transition at $T_c$ which is consistent with the result obtained from
M-T, M-H and calorimetric measurements. Thus, the alloys are soft ferromagnetic materials with no magnetic hysteresis, which is highly beneficial for magnetic refrigeration.

4. Conclusions
The effect of substituting Pr for Gd, on the crystal structure, magneto caloric effect and order of magnetic phase transition of Gd$_5$Si$_3.2$Sn$_{0.8}$ alloy has been investigated. A Gd$_5$Si$_4$-type orthorhombic structure has been identified in all the samples and the crystal structure remains invariant with the amount of Pr content. All the samples are soft ferromagnetic materials with nearly zero coercivity and show a second order ferromagnetic to paramagnetic phase transition, confirmed by the Arrott plots. The Curie temperatures of the (Gd$_{1-x}$Pr$_x$)$_5$Si$_{3.2}$Sn$_{0.8}$ alloys are 320 K, 299 K, 299 K, 309.5 K respectively for $x = 0, 0.05, 0.1, 0.15$ and the corresponding maximum magnetic entropy changes are 0.6779, 0.9322, 1.2034 and 0.2138 J/kgK in a magnetic field of 1.58 T. The moderate values of $\Delta S_m$ in a low magnetic field near room temperature, absence of magnetic hysteresis and adjustable $T_c$ are the major features of these alloys.

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