A Contrastive Analysis of Gd$_5$(Si$_x$Ge$_{1-x}$) Based Alloys Useful for Magnetic Refrigeration

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Abstract

This paper presents a contrastive analysis of Gd$_5$(Si$_x$Ge$_{1-x}$) family and its alloys magnetic refrigeration perspective. A literature survey has been conducted and to the best of authors knowledge all samples (~100 samples) with their $T_C$ (Curie temperature) in the range of 260 K-340 K been reported. For contrastive analysis samples have been grouped based on their structural and experimental conditions e.g., magnetic field, sample composition etc., and missing MCE (Magnetocaloric Effect) values calculated where possible.

The first objective of this paper is to pinpoint different variables (e.g., purity of starting materials, heat treatment, synthesis methods etc.) and the extent to which they effect MCE properties in a forementioned family.

The second objective has been to note the doping effect of different materials (e.g., Fe, Cu, Ga, Sn, Co, Al, Ni, Nb) on this family mainly to mitigate hysteresis loss and the effect of this doping on the MCE properties. Hysteresis has been the biggest stumbling block for finding a working magnetic refrigerant.

The third objective is to shortlist a composition with optimum MCE properties among this family and to suggest best practices for its fabrication as nanostructure. As previously reported, fabrication as nanostructure improves MCE properties by ~40% through broadening of the MCE curve.

Introduction

For Magnetic refrigeration technology, materials with $T_c$ near room temperature with good MCE (Magneto-caloric Effect) properties and negligible hysteresis are of special interest. In addition, similar results have been obtained for hyperthermia, chemotherapy and radiotherapy [1]. Different families such as Gd$_5$(Ge$_{1-x}$Si$_x$), LaFe$_{13-x}$Si$_x$ and MnAs$_{1-x}$P$_x$ with promising MCE properties [2] have come under consideration with new materials tried out constantly. This paper substantiate the author’s belief that instead of searching for new materials, MCE enhancement can be achieved with high performing families in three steps: (1) To understand and calculate the effect of different structural and preparation variables such as impurities, homogeneity, heat treatment, annealing, synthesis and fabrication processes on MCE properties and choosing the best practices; (2) Effect of different material’s doping on MCE properties of Gd$_5$(Ge$_{1-x}$Si$_x$) and their success in hysteresis loss reduction and (3) Choosing best performing sample in this family, proposing best fabrication processes and synthesizing the shortlisted sample as nanostructure.

Particle size, shape, morphology, chemical composition, structure, and interaction of the particle with the surrounding matrix and neighboring particles all have a profound effect on the magnetic behavior of the material. Syntheses of materials as nanostructures results in broadening of the curve, resulting in at least 40% im-
Improvement of MCE properties depending upon material and MCE curve [2]. In order to predict and evaluate the MCE of a refrigerant material, refrigerant capacity can be considered as the basis for calculating the temperature behavior of the material. The Relative Cooling Power (RCP) is defined as

\[
\text{RCP} = -\Delta S_m(T, H) \times \delta T_{\text{FWHM}}
\]

Where \(\Delta S_m(T, H)\) is the refrigerant’s magnetic entropy change as a function of temperature and magnetic field and \(\delta T_{\text{FWHM}}\) is the Full Width at Half Maximum (FWHM) of the peak of magnetic entropy. This parameter measures how much heat can be transferred between the cold and hot heat exchangers in an ideal refrigeration cycle.

\(\text{Gd}_5\text{Si}_4\) displays MCE properties nearly twice as large as those of \(\text{Gd} (~10 \text{ J/kg K})\), because the lower temperature and dominant magnetic ordering is a first-order phase transition coupled to a reversible crystallographic transition from monoclinic structure to an orthorhombic one, while \(\text{Gd}\) by itself is a second order transformation [3-5]. The two most striking features of this alloy system are: (1) The first order phase transition is reversible with respect to alternating magnetic field, i.e., the MCE effect can be utilized in an active magnetic regenerator magnetic refrigerator, and (2) The ordering temperature is tunable from ~30 to ~276 K by adjusting the Si/Ge ratio making them suitable for specific application from the production of liquid He\(_2\) (Ge rich compositions), room temperature refrigeration, hyperthermia, or even the cooling of microelectronic chips (Si rich compositions) [3,6].

Pecharsky, et al. synthesized and measured 12 samples of \(\text{Gd}_5\text{Si}_x\text{Ge}_{1-x}\) for \(0 \leq x \leq 1\). The phase diagram can be divided into different types of magnetic and structural behavior in fields up to 10 T as shown in Figure 1 [3]. This has been corroborated in the literature review as seen in Table 1. Samples prepared and studied under different conditions, approximately align with the reference \(T_C\) line in Figure 1. The ordering temperature is tunable from ~30 to ~276 K by adjusting the Si/Ge ratio making them suitable for specific application from the production of liquid He\(_2\) (Ge rich compositions), room temperature refrigeration, hyperthermia, or even the cooling of microelectronic chips (Si rich compositions) [3,6].

As can be seen from Figure 1 on the Ge-rich region (approximately \(0 \leq x \leq 0.31\)) of the phase diagram, the

![Figure 1](image-url)

**Figure 1:** The phase diagram of the \(\text{Gd}_5\text{Si}_x\text{Ge}_{1-x}\) pseudo binary system, where the solid lines show magnetic phase boundaries and the dotted-dashed line is reference curie temperature as reported in literature [3].

**Table 1:** To the best of authors knowledge, all compositions of \(\text{Gd}_5\text{Si}_x\text{Ge}_{1-x}\) (where \(0 \leq x \leq 1\)) are reported in literature with Curie Temperature in the range of 260 K-340 K. The difference in MCE properties in samples with same composition is due to either sample preparation or experimental conditions.

| Sample | \(T_C (K)\) | \(\Delta S_m (J/Kg K)\) | \(\Delta T_{ad} (K)\) | \(\Delta H (KOE)\) | RCP (J/Kg) | Ref |
|--------|--------------|-----------------|----------------|----------------|------------|-----|
| \(\text{Gd}_5\text{Si}_4\) | 333 | 5.9 | 50 | -131 | [9] |
| \(\text{Gd}_{0.55}\text{Si}_0.45\text{Ge}_0.5\) | 260 | 14.3 | 50 | 400 | [10] |
| \(\text{Gd}_{0.53}\text{Si}_0.47\text{Ge}_0.53\) | 298 | 7 | 50 | [10] |
| \(\text{Gd}_{0.5}\text{Si}_0.5\text{Ge}_0.5\) | 304 | 50 | [10] |
| \(\text{Gd}_{0.15}\text{Si}_0.85\text{Ge}_0.15\) | 262 | 14.5 | 2.3 | 20 | [11] |
| \(\text{Gd}_{0.2}\text{Si}_0.8\text{Ge}_1.1\) | 270 | 1.65 | 20 | [12] |
| \(\text{Gd}_{0.38}\text{Si}_0.62\text{Ge}_1.4\) | 312 | 3.4 | 20 | [12] |
| \(\text{Gd}_{0.25}\text{Si}_0.75\text{Ge}_1.4\) | 322 | 3.8 | 20 | [12] |
| \(\text{Gd}_{0.15}\text{Si}_0.85\text{Ge}_1.4\) | 332 | 4.3 | 20 | [12] |
| \(\text{Gd}_{0.15}\text{Si}_0.85\text{Ge}_2.06\) | 296 | 0.01 | [7] |
| \(\text{Gd}_{0.2}\text{Si}_0.8\text{Ge}_1.2\) | 307 | 0.01 | [13] |
| \(\text{Gd}_{0.2}\text{Si}_0.8\text{Ge}_1.91\) | 280 | 0.01 | [8] |
| \(\text{Gd}_{0.375}\text{Si}_0.625\text{Ge}_1.4\) | 277 | [14] |
| \(\text{Gd}_{0.15}\text{Si}_0.85\text{Ge}_2.06\) | 260 | 14.1 | 20 | 184 | [15] |
stable structure is the Gd$_5$Ge$_4$-type (or O(II)) which presents two magnetic transitions on cooling: Paramagnetic (PM) to antiferromagnetic order and, at low temperatures, an antiferromagnetic to Ferromagnetic (FM) transition, accompanied by a structural phase change (except for the Gd$_5$Ge$_4$) from O(II) to a O(I) structure which is reversible [3,7,9,10,12,15].

In the intermediate region (0.31 ≤ x ≤ 0.503), the stable phase at room temperature is the Gd$_5$Si$_2$Ge$_2$-type (or Monoclinic-M). This is the region with the highest slope of $T_C$ vs. X, as seen from the dramatic influence of Si(Ge) substitution on the magnetism of these compounds [3,7,9,10,15]. At (x = 0.5) structural transformation leading to first-order magnetostructural phase transition and MCE has been established, using band structure approach due to decrease in exchange coupling [16].

Finally, the Si-rich region has an Orthorhombic O(I) (Gd$_5$Si$_4$-type) structure with its magnetic state changing from PM to FM at high Curie temperatures [3,7,9,10,15].

**Table 2:** To the best of authors knowledge, all experimental studies conducted on Gd$_5$(Si,Ge)$_x$ as reported in literature is presented. Variation in MCE properties ($T_C$, $\Delta S_m$, $\Delta T_{ad}$ and RCP) is because of fabrication (Ball Milling, annealing, purity of starting materials etc), synthesis processes (size, shape etc) and experimental conditions.

(‘Approximation from the figures in the cited papers, “Calculat-ed from the Figures in the cited papers.”)

| Sample                  | $T_C$ (K) | $\Delta |S_m|$ (J/Kg K) | $\Delta T_{ad}$ (K) | $\Delta H$ (KOe) | RCP (J/Kg) | Ref     |
|-------------------------|-----------|-------------|-------------------|-------------------|-------------|---------|
| Gd$_5$Si$_2$Ge$_2$      | 272       | 36          | 17                | 50                | 500         | [17]    |
| Gd$_5$Si$_2$Ge$_2$      | 275       | 28          | 50                | 500               | 625         | [18]    |
| Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ | 275   | 18          | 50                | 500               | 540         | [3]     |
| Gd$_5$Si$_2$Ge$_2$      | 275       | 19.5        | 50                | 500               | 370         | [19]    |
| Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ | 276   | 19          | 15                | 50                | 228         | [5]     |
| Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ | 280   | 18.5        | 50                | 445               |             | [6]     |
| Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ | 299   | 7.5         | 50                |                   |             | [6]     |
| Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ | 279   | 14.5        | 12.6              | 224               |             | [21]    |
| Gd$_5$Si$_2$Ge$_2$      | 300       | 8.38        | 50                |                   |             | [9]     |
| (Gd$_5$Si$_2$Ge$_2$)$_2y$ | 284   | 2.9         | 15                |                   |             | [22]    |
| (Gd$_5$Si$_2$Ge$_2$)$_{1-y}$ | 286  | 1.6         | 15                |                   |             | [22]    |
| (Gd$_5$Si$_2$Ge$_2$)$_{1-y}$ | 288  | 1.8         | 15                |                   |             | [22]    |
| (Gd$_5$Si$_2$Ge$_2$)$_{1-y}$ | 293  | 2           | 15                |                   |             | [22]    |
| (Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ | 277   | 3.9         | 15                |                   |             | [23]    |
| (Gd)$_x$                | 299       | 3.3         | 15                |                   |             | [23]    |
| (Gd$_{1.5}$Si$_{1.5}$Ge$_{2.5}$)$_x$ | 246 | 2.2         | 15                |                   |             | [23]    |

| Sample                  | $T_C$ (K) | $\Delta |S_m|$ (J/Kg K) | $\Delta T_{ad}$ (K) | $\Delta H$ (KOe) | RCP (J/Kg) | Ref     |
|-------------------------|-----------|-------------|-------------------|-------------------|-------------|---------|
| Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ | 277   | 3.9         | 15                |                   |             | [23]    |
| (Gd)$_x$                | 299       | 3.3         | 15                |                   |             | [23]    |
| (Gd$_{1.5}$Si$_{1.5}$Ge$_{2.5}$)$_x$ | 246 | 2.2         | 15                |                   |             | [23]    |

**Figure 2:** The nearly approximate graphical representation of magnetic entropy change of highest reported MCE properties of Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ as reported in literature [3,6,14-16] and numerically stated in (Table 2). The magnetic field is $\Delta H = 20$KOe.
ployed, the shape of the magnetic entropy curve is same but the location and height of the peak varies depending upon the synthesis process as can be seen in Figure 2.

Purity of the starting rare earth materials play a large role in MCE properties where the difference is approximately 2.5 times between usage of commercial and high purity Gd while preparing Gd,(Si,Ge) [6,15,17,20] as displayed in Table 2. The above average results achieved by sample are because of the sample’s synthetization from high-purity Gd. The Δ|S M| is increased by ~80% (from ~20 to 36 J/kg K) and ΔT ad is increased by ~55% (from ~11 to 17 K) as compared to the arc-melted material at magnetic field of 5T [17]. This point was validated by an approximate improvement of 105% was achieved in Δ|S M| was observed in the same composition of Gd,(Si,Ge) [6] bringing its T c to 280 K which is more in line the with T c reported by other authors as shown in Table 2. In the second case a layered structure composed of 1:2:1, 1:1:1 and 1:2:3. [23] Though re-

Table 2: To the best of authors knowledge, all Gd,(Si,Ge) based alloys as reported in literature with Curie Temperature in the range of 260 K-340 K. (Approximation from the figures in the cited papers, “Calculated from the figures in the cited papers).

| Sample                  | T c (K) | Δ|S M| (J/Kg K) | ΔT ad (K) | ΔH (KOe) | RCP (J/Kg) | Ref |
|-------------------------|--------|-------------|-----------|-----------|-----------|------------|-----|
| Gd,GaSi 0.4Ge 0.1Cu 0.1 | 305    | 7.5         | 50        | ~750      | [19]      |
| Gd,MgGe 0.6Si 0.4      | 292    | 7           | 50        |           |           |            |     |
| Gd,MgGe 0.6Si 0.4      | 296.8  | 6.93        | 7.1       | 50        | ~620      | [25]       |
| Gd,GaSi0.4Ge0.1Ni 0.03 | 300    | 4.4         | 20        | 122       |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Ni 0.03 | 301    | 5           | 20        | 90        |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Ni 0.03 | 263    | 10          | 15        | ~50       |           |            |     |
| Gd,GaSi0.4Ge0.1Ni 0.03 | 268    | 14          | 20        | ~154      |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Ni 0.03 | 274    | 9.8         | 20        | ~206      |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Ni 0.03 | 276    | 4           | 20        | ~80       |           |            |     |
| Gd,GaSi0.4Ge0.1Fe 0.06 | 304    | 4           |           | 20        |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 306    | 3           |           | 20        |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 311    | 1           |           | 20        |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 260    | 14.1        | 20        | ~184      |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 273    | 22          | 20        | ~132      |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 277    | 28.9        | 20        | ~87       |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 268    | 25          | 20        | ~188      |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 260    | 23          | 20        | ~69       |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 264    | 10.7        | 20        | 148       |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 264    | 15.1        | 52        | 488       |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 290    | 7.6         | 20        | 115       |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 293    | 9.6         | 20        | 108       |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 282    | 6.6         | 20        | 73        |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 277    | 5           | 20        | 83        |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 302    | 1.05        | 5.2       | 94        |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 305    | 1.45        | 5.2       | ~51       |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 300    | 0.7         | 5.2       | ~25       |           |            |     |
| Gd,MgGe0.6Si0.4Ge0.1Fe 0.06 | 270    | 8.8         | 55        |           |           |            |     |

Another approach for MCE enhancement is layered structure samples which though exhibiting larger temperature span covering a large working temperature range didn’t enhanced the MCE properties [22,23]. The first example is synthesized from a binary composite Gd-xGd 5 Si 2 Ge -x (where x = 0.3, 0.5, 0.7) by SPS technique [22]. The direct measurements of the MCE showed that though ΔT ad peak shifted from 286 to 293 K and the peak values of ΔT ad slowly increased from 1.6 to 2.0 K when x was increased from 0.3 to 0.7 but it still was less than 2.9 K for (Gd,Si,Ge) studied in the same paper [22] as can be seen in Table 2. In the second case a layered structure (Gd,Si,Ge) (Gd) 0.5Gd 5 Si 2 Ge -0.5 was prepared and studied in ratio of 1:2:1, 1:1:1 and 1:2:3. [23] Though resulting in enlargement of the temperature span, it had no effect on MCE enhancement.

Enhancement of MCE properties using hydrostatic and barocalaric effects have been attempted. The effects of hydrostatic pressures of up to 9.2 k bar on magnetic and MCE properties of Gd,Si,Ge 2 [18], were undertaken with minimal effect [18]. When pressure of up to ~7.2 GPa was applied on Gd-xGd 5 Si 2 Ge -x in Table 1. A linear increase in T c up to ~277 K was observed because of the unit cell volume reduction by Si doping and is associated with the volume-driven Monoclinic (M) to Orthorhombic (O) structural transition [14]. The range of pressures required to achieve a large entropy change at least for Gd 3 (Si 2 Ge 2 ) is moderate [24].

**Gd(Si, Ge) Alloys**

The MCE results from changes in the magnetic order of materials, with the most optimum MCE near the

Table 3: The above average results achieved by sample are because of the sample’s synthetization from high-purity Gd.
magnetic phase transitions especially First-Order Transitions (FOT). Though hysteresis losses are higher than Second-Order Transition (SOT). Prime example of this is Gd\(_5\)(Si\(_{2}\)Ge\(_2\)) family one of only few to exhibit large MCE, with Gd\(_5\)(Si\(_{2}\)Ge\(_2\)) achieving optimum MCE properties undermined by its thermal hysteresis, 15 J/Kg at zero field [25], 55 J/Kg at 2 T [15], and width of the thermal hysteresis of ~2 K [5], depending upon material’s purity, fabrication, equipment and methods to observe it. A lot of effort have gone in hysteresis loss reduction through doping of Fe, Cu, Co, Ga, Mn, Ni, Nb or Al for Si/Ge in Gd\(_5\)(Si\(_{1-x}\)Ge\(_x\)) compound between 270 K and 300 K as can be seen in Table 3. Two side effects have been observed: (1) Broadening of MCE peak on account of suppression of the reversible field-induced first-order monoclinic-to-orthorhombic phase transition, and (2) Shifting of MCE peak position between 270 K and 300 K temperature range [15,19,25-27].

Though most investigation were made for Ge substitution, a significant reduction in Δ|\(S_M\)| because of the suppression of the structural transformation has been observed so it is suggested that Si and Ge should be substituted simultaneously for Fe and Sn doping as can be seen in Table 3 [15,28-31]. A small substitution with iron (substituting for 5% of the germanium, otherwise it will have deleterious effect on MCE properties and minimal effect on reducing hysteresis losses [28,30]) reduced the losses by 90% thus resulting in 20%-50% higher RCP value, though it overall reduced the Δ|\(S_M\)| to only one-third of its original value [27,29,30]. The T\(_C\) of the matrix phase was found to increase when Fe was substituted for Ge but it rather decreased rapidly when it was substituted for Si as can be seen in Table 3 [30]. However, in the case of doping the same amount of either Ni or Bi had a negligible effect on the magnetocaloric properties [26,27]. Experimental results have shown that a small amount of Sn doping enhances its MCE properties as well as increase its T\(_C\) [15] but either leads to increase in hysteresis loss or has negligible effect on its reduction [15,27,31]. Moreover, Nb and Al doping on Gd\(_5\)(Si\(_{1-x}\)Ge\(_x\)) failed to produce desired results [32,33].

In order to assess the various samples of Gd\(_5\)(Si\(_{2}\)Ge\(_2\)) based alloys we combined in Figure 3. The various results of the magnetic entropy change versus temperature were plotted, as we did for Figure 2 [15,29,31]. Out the five samples with Sn doping presented in Table 3. Gd\(_5\)Si\(_{1.935}\)Ge\(_{2.035}\)Sn\(_{0.03}\) is the best candidate for synthesizing as nanostructure because of its MCE curve’s peak and narrowness as shown in Figure 3. Though Fe was instrumental in reducing hysteresis, the resulting MCE curve doesn’t have enough peaks to be broadened when synthesized as nanostructure. The Dy substitution in Gd\(_5\)Si\(_{2}\)Ge\(_2\) leads to a lowering of T\(_C\), an increase in coercivity, and loss of the FOT in the parent compound [34].

Only Ga was found not to suppress Δ|\(S_M\)| and then only for small substitutions [29]. The potential of Gd\(_5\)Si\(_{2}\)Ge\(_{1.9}\)Ga\(_{0.1}\) is evident by complete disappearance of thermal hysteresis, where though a loss in Δ|\(S_M\)| is noted but Ga doping is also instrumental in broadening of its MCE curve resulting in second highest RCP in this family as

![Figure 3: The nearly approximate graphical representation of magnetic entropy change of highest reported MCE properties of Gd\(_5\)(Si\(_{2}\)Ge\(_2\)) alloys as reported in literature and numerically stated in Table 3. The magnetic field is ΔH = 20KOe.](image)
seen in Table 3 [25]. As can be seen from Table 3 most of materials used for doping except Sn have deleterious effects on the MCE properties and other than Fe or Ga have not been successful in reducing hysteresis.

**Conclusion**

This paper is an effort to support the author’s opinion that instead of searching for new materials, already well established families with high MCE properties should be further analyzed and studied. For this purpose, comparative analysis of Gd₅(Si₁₋ₓGeₓ)₄ family and its alloys was undertaken whose MCE properties are already established as among the best in literature. The authors aimed to achieve this enhancement through; (1) Analyzing effects of variables such as synthesis, fabrication processes, starting materials purity, heat treatment etc on MCE properties and proposing best practices for optimal MCE properties achievement, (2) Effects of different material doping on MCE properties and hysteresis loss of Gd₅(Si₁₋ₓGeₓ)₄ family, (3) Choosing the best performing composition from this family and suggesting the best fabrication processes to synthesize it as nanostructures.

First of all a contrastive analysis was done on the effects of variables such as synthesis, fabrication processes, starting materials purity, heat treatment etc on MCE properties. It was observed that though Gd₅(Si₄Ge₄) sample was reported by 10 different authors as can be seen in Table 1 with wide ranging results, the main difference has been purity of starting rare earth materials [17], in homogeneity and impurity phases. Samples with high-temperature annealing and higher cooling rate from arc melting [35] shows clear enhancement of MCE properties over arc-melted samples without post-annealing [17]. Purity of starting materials plays an oversized role, enhancing MCE properties by an average of ~40% as can be seen in Table 1 for Gd₅(Si₄Ge₄) with Δ|Sₘ| of 36 K and RCP of about ~600 J/Kg [17].

Secondly, doping of different materials on Gd₅(Si₁₋ₓGeₓ)₄ family was observed from hysteresis reduction and MCE properties enhancement perspective. Although as reported in literature, Gd₅(Si₁₋ₓGeₓ)₄ family has been doped with many different materials the resulting compositions push its Tₗ outside 260-340 K window thus rendering it unsuitable for magnetic refrigeration except Fe, Cu, Ga, Sn, Co, Al, Ni, Nb as can be seen in Table 3. Out of these only Fe and Ga were able to reduce hysteresis losses but at the cost of MCE properties. On the other hand, Sn doping though almost having negligible effect on hysteresis loss nearly doubled Δ|Sₘ| of Gd₅Si₁₋ₓGeₓ from 14.1 to 28.9 J/Kg K in case of Gd₅Si₁₋ₓGeₓ [15].

Lastly, as already established in literature, synthesis as nanostructures can enhance MCE properties by at least 40% depending upon material and synthesis process. [2] Examples are enhancement of MCE properties by movement, broadening and sharpening of magnetic entropy peak (Tₗ) of Gd, Pr, Fe₁₋ₓ, and Ne₅Feₓ when synthesized as nanostructures [2]. It is thus proposed that among this family, Gd₅(Si₄Ge₄) reported in [14] should be synthesized as nanostructure in different sizes to observe the positive effects on its MCE properties through broadening of its magnetic entropy curve. In the second step, the above-mentioned sample should be doped with Sn which is reported to double the magnetic entropy [15] and synthesized as nanostructure. An enhancement of at least 40-70% in MCE properties and nullification of hysteresis loss is expected depending upon the size.

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