We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

5,500
Open access books available

136,000
International authors and editors

170M
Downloads

154
Countries delivered to

TOP 1%
Our authors are among the most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Chapter

Magnetic Properties of Heusler Alloys and Nanoferrites

Devinder Singh and Kuldeep Chand Verma

Abstract

In this chapter, results of our recent investigations on the structural, microstructural and magnetic properties of Cu-based Heusler alloys and MFe$_2$O$_4$ (M = Mn, Fe, Co, Ni, Cu, Zn) nanostructures will be discussed. The chapter is divided into two parts, the first part describes growth and different characterizations of Heusler alloys while in the second part magnetic properties of nano-ferrites are discussed. The Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ (x = 0, 2, 4, 8 and 10 at %) alloys have been synthesized in the form of ribbons. The alloys with x ≤ 8 show the formation of Heusler single phase of the Cu$_2$MnAl structure. Further increase of Ga content gives rise to the formation of γ-Cu$_9$Al$_4$ type phase together with Cu$_2$MnAl Heusler phase. The alloys are ferromagnetically ordered and the saturation magnetization ($M_s$) decreases slightly with increasing Ga concentration. Annealing of the ribbons significantly changes the magnetic properties of Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ alloys. The splitting in the zero field cooled (ZFC) and field cooled (FC) magnetization curves at low temperature has been observed for alloys. Another important class of material is Nanoferrites. The structural and magnetization behaviour of spinel MFe$_2$O$_4$ nanoferrites are quite different from that of bulk ferrites. X-ray diffraction study revealed spinel structure of MFe$_2$O$_4$ nanoparticles. The observed ferromagnetic behaviour of MFe$_2$O$_4$ depends on the nanostructural shape as well as ferrite inversion degree. The magnetic interactions in Ce doped CoFe$_2$O$_4$ are antiferromagnetic that was confirmed by zero field/field cooling measurements at 100 Oe. Log R (Ω) response measurement of MgFe$_2$O$_4$ thin film was taken for 10–90% relative humidity (% RH) change at 300 K.

Keywords: Heusler alloy, nanoferrites, magnetization, microstructure, sensor

1. Introduction

Heusler alloys were discovered in 1903 when Heusler reported that the addition of sp. elements (Al, In, Sb, Sn or Bi) turn Cu-Mn alloy into a ferromagnetic material even though the alloy contains none of the ferromagnetic elements [1, 2]. Heusler reported that these alloys have stoichiometric composition X$_2$YZ and exhibit an ordered $L_2$ crystal structure with space group $Fm3m$ [3, 4]. Ferrites are ferrimagnetic compounds of iron oxides Fe$_2$O$_3$ and FeO with general formula: $Fe^{3+}[Fe^{3+}_{1-y}Fe^{2+}_{y}]_{1.67}O_4$ (*indicates vacancies), which can be partly changed by other transition metal (TM) oxides [5]. The ferrites can be classified according to their crystalline structures: hexagonal (MFe$_2$O$_3$), garnet (M$_3$Fe$_5$O$_{12}$) and spinel (MFe$_2$O$_4$), where M = TM = Mn, Fe, Co, Ni, Cu, Zn. Both Heusler alloys and
Magnetic Skyrmions

nanoferrites are important magnetic materials owing to their promise to qualify for many potential applications.

1.1 Heusler alloys

Heusler alloys have attracted avid attention due to their various properties suitable for technological applications such as high-density magnetic recording or magneto-optics applications [6–8]. It has been shown that the ordered combination of two binary B2 compounds XY and YZ leads to the formation of Heusler structure. Both these compounds may have CsCl type crystal structure e.g. CoAl and CoMn yield Co$_2$MnAl [9]. Thus the possible formation of new Heusler alloys will depend upon the ability of compounds to form B2 structure. It has also been observed to leave one of the four sublattices unoccupied (C1$_b$ structure). The L2$_1$ compounds are known as full-Heusler alloys while the latter compounds are often called half- or semi-Heusler alloys (Figure 1). Most of the Heusler alloys are saturate in weak magnetic field and ordered ferromagnetically. There are various parameters which are found to be very important in determining the magnetic properties [6–9, 11–13]; these include crystal structure, composition and heat treatment. The magnetic shape memory effect as well as other properties arises due to magneto-crystalline coupling in Heusler alloys [6–9, 11]. These made Heusler alloys to possess very interesting magnetic properties. A series of interesting diverse magnetic phenomenon like itinerant and localized magnetism, antiferromagnetism, helimagnetism, Pauli paramagnetism or heavy-fermionic behaviour can be studied in the same family of Heusler alloys [3, 4, 6, 7]. At low temperatures several Heusler alloys, e.g. Ni$_2$MnGa, Co$_2$NbSn etc., undergo a martensitic transition from a highly symmetric cubic austenitic to a low symmetry martensitic phase. Unlike atomic order–disorder transitions a martensitic transition is caused by non-diffusional

![Figure 1](image_url)

Figure 1. Representation of various structures of semi- and full-Heusler alloys. The lattice is consisted to have four interpenetrating f.c.c. lattices in all cases. It should be noted that if all atoms are identical, the lattice would simply become b.c.c [10].
cooperative movement of the atoms in the crystal. Heusler alloys exhibit magnetic shape memory effect (MSM), when they are magnetic in the martensitic phase [14–16]. This occurs especially in those cases when the Y constituent is Mn, but other transition elements are also possible. When these alloys are applied in the martensitic state, an external magnetic field can induce large strains.

In recent years, Ni-Mn-X (X = In, Sn, Sb) Heusler alloys have attracted much interest because of their magnetic shape memory effect and magnetic field-induced martensitic transformation [17–19]. In recent years, the interest in Heusler compounds has been increased due to the evolving field of spin-electronics [7]. These compounds have also been studied as potential spin-injector materials [6, 8, 20]. In the alloys X_2YZ, a value close to 4μB is usually observed if the magnetic moment is carried by Mn atoms. These compounds are considered as ideal model systems to study the effects of atomic disorder and changes in the electron concentration on the magnetic properties. These compounds have localized magnetic properties though they are metals. Extensive magnetic and other measurements have been performed on quaternary Heusler alloys in order to understand the role of 3d (X) and sp. (Z) atoms on magnetic properties [21]. It has been shown that both the magnetic moment formation and the type of the magnetic order get influenced by the sp. electron concentration which is very important in establishing the magnetic properties. During the past few years, the family of ferromagnetic Heusler alloy systems has been extensively studied due to their main advantages in comparison to half-metallic systems e.g. structural similarity with the binary semiconductors and predicted perfect spin polarization at the Fermi level as well as high Curie temperature [22, 23]. The effect of alloying addition on the magnetic properties has been studied in Heusler alloys [24–30].

1.2 Nanoferrites

A series of spinel-structured ferrites, MFe_2O_4, where M = TM = Mn, Fe, Co, Ni, Cu, Zn were reported for novel data storage, recording devices, microwave technology and biomedical applications [31–35]. The spinel structure has general formula AB_2O_4 which had octahedral (B) and tetrahedral (A) sites. The spinel is normal, if M^{2+} occupies only the A sites; the spinel is inverse, if it occupies only the B sites. When Mn^{2+} occupies both A and B sites, the MFe_2O_4 has formed a mixed spinel structure while the other metal ferrites have an inverse spinel structure [3]. The magnetic spins at B sites align in parallel in direction to the applied magnetic field, whereas those present at A sites align antiparallel. Spinel ferrite has general formula: \( (A^{2+})_{8/3} [B^{3+}]_{2/3} O^2_4 \); where \( A^{2+} \) and \( B^{3+} \) are the divalent and trivalent cations occupying tetrahedral (A) and octahedral (B) sites. Figure 2 shows the inverse spinel structure of NiFe_2O_4 [36]. The inverse spinel has general formula: \( (M^{2+}_{1-x}\text{Fe}^{3+}_x)_{8/3} [M^{3+}_{1-x}\text{Fe}^{2+}_x]_{2/3} O^2_4 \); the round and square brackets denote (A) and [B] sites respectively, whereas \( x \) represents inversion degree. Also for normal spinel AB_2O_4, the A^{2+} cations occupies 1/8 of the fcc tetrahedral sites (T_d) while the B^{3+} occupy 16 of the 32 available octahedral sites (O_h). An inverse spinel structure with Ni^{2+} at octahedral sites (labelled as Ni(O_h)) and Fe^{3+} equally distributed between octahedral (Fe(O_h)) and tetrahedral sites (Fe(T_d)) of the O_2^- fcc cell have been adopted for NiFe_2O_4 (Figure 2). The complete structure crystallizes into a cubic system O_h with space group 227. The oxygen atoms occupy the 32e positions, Fe(T_d) atoms occupy the 8a ones while the Ni(O_h) and Fe(O_h) atoms are distributed on the 16d positions, using Wyckoffnotations [36]. The efficacy of the material depends on its microstructural properties that are sensitive to mode of preparation. Moreover, CoFe_2O_4 is the most versatile hard ferrite with mixed cubic spinel.
structure having Fd3m space group and exhibits high coercivity ~5400 Oe, high magneto-crystalline anisotropy and moderate saturation magnetization [37, 38].

Spintronics is concerned with highly spin-polarized materials to enhance tunnelling magnetoresistance of magnetic tunnel junctions which are active members of magnetic random access memory elements. For the optimal operation of spintronics, the highly spin-polarized materials used for increasing spin-polarization of currents injected into semiconductors [38]. There is a way to achieve high spin-polarization by employing fully spin-polarized ferromagnetic metals, such as half-metals. Another way is to exploit the band structure features of tunnel barrier materials, i.e., MgO, and filtering electronic wave functions. Spinel NiFe$_2$O$_4$, CoFe$_2$O$_4$, and MnFe$_2$O$_4$ are also used as such spin filters. Spin-dependent gap should result in spin-dependent barrier for tunnelling of electrons through the insulator, giving rise to spin filtering. In particular, a spin filtering efficiency of up to 22% is reported for NiFe$_2$O$_4$ barrier [39]. The resistive switching performance characteristics of a Pt/NiFe$_2$O$_4$/Pt structure such as low operating voltage, high device yield, long retention time (up to 10$^5$ s), and good endurance (up to 2.2 × 10$^4$ cycles) can be used to demonstrate the opportunity of spinel ferrites in non-volatile memory devices [33]. Since the resistive switching memory cell has capacitor-like metal/insulator/metal configuration, which can be switched reversibly between two different resistance states, i.e., high-resistance state (HRS) and low-resistance state (LRS).

Figure 3(a) shows the current–voltage (I-V) characteristics of the Pt/NiFe$_2$O$_4$/Pt devices during repetitive switching cycles. Unipolar resistive switching characteristics were clearly observed in both the forward- and backward-bias sweeping processes. The drastic decrease in the current has been observed on increasing the forward voltage to its critical value of 0.6–1.0 V. This indicates the switching of the Pt/NiFe$_2$O$_4$/Pt device from the LRS to the HRS. The device was switched from HRS to LRS, when soft breakdown occurred on increasing the voltage in the range of 1.8–2.2 V. NiFe$_2$O$_4$ has the inverse spinel structure which has Fe–O bonds that are stronger than Ni–O bonds leads to oxygen vacancies formation [40]. Figure 3(b) shows magnetic reduction effect in changing the valence of Fe$^{3+}$ and Ni$^{2+}$ ions [41]. The oxygen vacancies and the reduction of cations may cause the decrease in magnetization and the increase
Magnetic Properties of Heusler Alloys and Nanoferrites
DOI: http://dx.doi.org/10.5772/intechopen.95466

in the electrical conductivity. Due to the annihilation of oxygen vacancies (driven by the thermal effect) and the change in the valence of cations (due to redox effect in the reset process) has led to rupture of filaments. The process of formation and rupture of the conducting filaments in NiFe$_2$O$_4$ films has been described in Figure 3(c) and (d).

2. Structure/microstructure and magnetic properties of Heusler alloys

The Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ (x = 0, 2, 4, 8 and 10) alloys with a thickness of ~40 to 50 μm and lengths of ~1 to 2 cm has been synthesized using melt spinning technique [24]. The substitution of Ga in place of Al is of special interest as it does not significantly change the lattice constant and the valence electron ratio (e/a) of the investigated alloy system [42–49]. The effect of heat treatment on the magnetic and phase transformation behaviour of Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ ribbons will be discussed. The study is focussed on the structural/microstructural changes with substitution of Ga and their correlation with magnetic properties of Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ alloys.

2.1 Microstructural and structural features

The effect of Ga substitution on the stability of Heusler phase has been investigated. The XRD patterns of melt-spun Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ (x = 0, 2, 4, 8 and 10) alloys are shown in Figure 4(a). A single Heusler phase of the Cu$_2$MnAl structure (space group: Fm$ar{3}$m, a = 5.949 Å) was observed for the alloys with x = 0, 2, 4 and 8, while the alloy with x = 10 reveals some diffraction peaks corresponding to γ-Cu$_6$Al$_4$ type phase (Space group: P43m, a = 8.702 Å). Thus it can be said that the Heusler phase was also observed in the Ga substituted alloys and is stable up to x = 8. In addition to the formation of Heusler phase, the precipitation of additional crystalline phase of γ-Cu$_6$Al$_4$ type has been observed for the alloys with x > 8. For the alloys from x = 0 to x = 8, a slight increase in the lattice parameter was observed. This is
Magnetic Skyrmions

expected due to nearly equal atomic size of Ga and Al. Table 1 shows the variation of lattice parameter with Ga content. There is no significant increase in the lattice parameter for $x = 10$ (Table 1). The formation of extra phases for concentrations $x > 8$ may be due to the excess of Ga atoms which no longer replace the corresponding number of Al atoms in the crystal structure. Thus, the lattice constant of the Heusler phase remains almost constant. It is therefore can be concluded that the Ga atoms can substitute for Al atoms in the structure only within the content range of $0 \leq x \leq 8$. Hence, $x = 8$ is the critical Ga concentration ($x_c$), beyond which the alloys are having mixed phases.

The phase transformation behaviour of Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ alloys on heat treatment has been investigated. The alloys with $x = 0$ and $x = 8$ are annealed at 903 K for 30 hrs and there XRD patterns are shown in Figure 4(b). The XRD pattern for $x = 0$ shows the presence of Cu$_2$MnAl, $\beta$-Mn and $\gamma$-Cu$_9$Al$_4$ phases. The decomposition reaction of the Cu$_2$MnAl phase during the annealing process leads to the appearance of these two phases. Based on the previous studies done on the decomposition process of Cu-Mn-Al alloys, it has been shown that the Cu$_2$MnAl phase is metastable and can decompose into $\beta$-Mn and $\gamma$-Cu$_9$Al$_4$ phases at annealing temperatures from 800 to 900 K [50, 51]. This decomposition then follows the reaction (Cu$_2$MnAl $\rightarrow$ $\beta$-Mn + $\gamma$-Cu$_9$Al$_4$). However, the $x = 8$ alloy shows different decomposition behaviour. The Cu$_2$MnAl phase decomposes into only $\gamma$-Cu$_9$Al$_4$ on annealing. There are no traces of $\beta$-Mn phase here. In addition to this, Cu$_2$MnAl precipitated as a majority phase for the alloy with $x = 0$ while for the alloy with $x = 8$, $\gamma$-Cu$_9$Al$_4$ precipitated as a majority phase.

| x (at %) | As-synthesized ribbons | Annealed ribbons |
|---------|------------------------|------------------|
|         | Lattice parameter $a$ (Å) | $M_s$ (emu/g) at 5 K | $M_s$ (emu/g) at 300 K | $M_s$ (emu/g) at 5 K | $M_s$ (emu/g) at 300 K |
| 0       | 5.947                  | 95               | 85                | 53                | 45                |
| 4       | 5.960                  | 88               | 79                | —                 | —                 |
| 8       | 5.986                  | 83               | 73                | 5                 | 3                 |
| 10      | 5.981                  | 20               | 16                | —                 | —                 |

Table 1. The lattice constants, saturation magnetization ($M_s$) at 5 K and 300 K for melt-spun and annealed ribbons of Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ (x = 0, 4, 8 and 10) alloys (Reprinted from reference [24] with kind permission from Elsevier, Copyright 2012, Elsevier).
Further TEM characterization studies of melt-spun as well as annealed samples were carried out. TEM microstructure and its corresponding diffraction pattern of Cu$_{50}$Mn$_{25}$Al$_{25}$ and Cu$_{50}$Mn$_{25}$Al$_{17}$Ga$_8$ melt-spun alloys are shown in Figure 5 (on the left). The formation of nano-meter sized grains in the range of 100 to 200 nm of the alloys with $x = 0$ and $x = 8$ have been observed (c.f. Figure 5(a)-(d)). The substitution of Ga in Cu$_{60}$Mn$_{35-3x}$Ga$_x$ alloy system does not result in any significant microstructural variation. The confirmation of Cu$_2$MnAl Heusler phase has been done based on the analysis of selected area diffraction pattern (SADP) of the alloys. The TEM microstructure and diffraction pattern for the annealed ribbon of $x = 8$ are shown in Figure 5 (on the right). The SADP analysis reveals two crystalline phases; Cu$_2$MnAl and $\gamma$-Cu$_9$Al$_4$. This is consistent with the result obtained by XRD analysis which also shows the formation of Cu$_2$MnAl and $\gamma$-Cu$_9$Al$_4$ phases. The large grains belong to Cu$_2$MnAl phase while the small ones identified as $\gamma$-Cu$_9$Al$_4$ phase. As one might know, Cu$_2$MnAl phase is ferromagnetic while $\gamma$-Cu$_9$Al$_4$ phase is paramagnetic in nature [50].

### 2.2 Magnetic properties

The temperatures of 5 K and 300 K were used to measure the magnetization curves (M-H curves) of Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ ($x = 0, 4, 8$ and $10$) alloys. Based on the results presented in Figure 6(a) and (b), It can be said that the magnetization is saturated in a magnetic field of about 1500 to 2500 Oe, indicating that ribbons are fairly homogenous ferromagnets [51]. The soft ferromagnetic behaviour (at 5 K and 300 K) were observed for the Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ ($x = 0, 4, 8$ and $10$) alloys. Table 1 gives the list of the saturation magnetization ($M_s$) derived from the M-H curves for all the compositions. The $M_s$ for the composition with $x = 0$ at 5 K is ~95 emu/g and at 300 K is ~85 emu/g respectively. These are very close to the reported magnetization values for this alloy [52]. It can be seen from Table 1 that $M_s$ decreases with increasing Ga content. This decrease is very small from $x = 0$ (~ 95 emu/g) to $x = 8$ (~ 83 emu/g) at 5 K. However, for $x > 8$, the $M_s$ decreases from ~83 emu/g (for $x = 8$) to ~20 emu/g (for $x = 10$). The large decrease in the $M_s$ for $x = 10$ may be explained on the basis that the Cu$_2$MnAl Heusler phase which is responsible for the ferromagnetism is stable only up to $x = 8$. The decomposition of Heusler phase into $\gamma$-Cu$_9$Al$_4$ type crystalline phase for the alloys with $x > 8$, is responsible for the significant decrease in the $M_s$ for $x = 10$. The $M_s$ values in the range 95–83 emu/g (at 5 K) has

---

**Figure 5.**
(left) TEM microstructures and the corresponding selected area diffraction patterns of the melt-spun alloys with $x = 0$ (a and b) and $x = 8$ (c and d) showing the formation of Cu$_2$MnAl Heusler phase. (Right) TEM microstructures and the corresponding selected area diffraction patterns of the annealed alloy of $x = 8$ showing the existence of (a and b) Cu$_2$MnAl and (c and d) $\gamma$-Cu$_9$Al$_4$ phases (Reprinted from reference [24] with kind permission from Elsevier, Copyright 2012, Elsevier).
Magnetic Skyrmions

been observed for the alloys with x = 0, 4 and 8 while the $M_s$ value of 20 emu/g (at 5 K) has been observed for x = 10. Thus there is very slight variation in the $M_s$ for x = 0, 4 and 8. The slight decrease in the $M_s$ for x = 4 and x = 8 as compared to x = 0 may be due to several reasons. In the present alloy system, Ga is a non-magnetic element. The concentration of Al is only varied while the concentration of Cu and Mn remains fixed in Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ alloy system. It has been reported that Mn-Mn coupling is responsible for the magnetic properties of Cu$_{50}$Mn$_{25}$Al$_{25}$ alloy [52, 53]. As discussed earlier, the substitution of Ga may increase the Mn-Mn distance in the lattice. This is due to slight increase in the lattice constant (see Table 1). Thus, the decrease in the magnetization has been observed due to increase in the lattice constant which reduces the ferromagnetic coupling of Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ alloy system. Such type of observation has also been reported in other alloy systems [14, 26, 29, 30]. Also, it is well known that Ga$^{3+}$ is normally substituted in isovalent state vis-a-vis that of Al$^{3+}$ [54–59]. However, it is worth mentioning here that Ga$^{1+}$ may possess monovalent state. It has been confirmed Al, Ga mainly provide conduction electrons for the exchange interaction and the Mn atoms show a localized moment in this material [3]. It may be said by considering the varied concentration ratio of Al and Ga that the concentration of conduction electron plays a very important role in determining the magnetic properties. Thus, the magnetic properties may be affected by the presence of mixed valence states of Ga. The concentration of Ga and the disordered occupation of Mn atoms may also be important factors which affects the magnetic properties. Therefore, the conduction electron concentration is believed to be critical in stabilizing the Heusler structure [3]. In the present case,

Figure 6.
Magnetization curves at 5 K (a) and 300 K (b) for melt-spun ribbons of Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ (x = 0, 4, 8 and 10) alloys. Magnetization curves (c) and (d) shows a small increase in M with H for the alloy with x = 10 (Reprinted from reference [24] with kind permission from Elsevier, Copyright 2012, Elsevier).
the concentration of Mn is fixed i.e. 25 at.%. Thus, the ferromagnetism behaviour of this material may be related to the concentration of Mn, atomic sites and situation of conduction electrons provided by Cu, Al and Ga. Further, the M-H curves for the melt spun alloy with x = 10 at 5 K and 300 K respectively are shown in Figure 6(c) and (d). A close observation of the curves indicates a small increase in M with H superimposed on the flat saturated ferromagnetic M-H curve. This may be due to the formation of a paramagnetic phase (γ-Cu₉Al₄) in addition to the majority CuₓMnAl ferromagnetic phase in the alloy with x = 10.

The effect of heat treatment on the magnetization has also been studied. On annealing, the magnetic properties of the alloy have changed. The hysteresis loops of the annealed ribbons (for x = 0 and x = 8) at 5 K and 300 K are shown in Figure 7. The Mₛ of the annealed ribbons are found to be lower than their respective as-synthesized ribbons (Table 1). The Mₛ ~ 53 emu/g has been found for annealed ribbon of x = 0 from the magnetization curve (M-H) at 5 K, which is lower than that of the value found for the as-synthesized ribbons of x = 0 i.e. Mₛ ~ 95 emu/g. The decomposition of CuₓMnAl ferromagnetic phase into β-Mn and γ-Cu₉Al₄ paramagnetic phases may decrease the magnetization [50]. However, along with these phases, CuₓMnAl Heusler phase is still a majority phase for the alloy with x = 0. The drastic decrease in the magnetization value at 5 K from ~83 emu/g to ~5 emu/g has been observed for x = 8. This is attributed to the different decomposition behaviour of x = 0 and x = 8 alloys. The M-H curves of the annealed ribbon for x = 8 (at 5 K and 300 K) are shown in Figure 7(c) and (d) (c & d). The increase in M with increase in the applied field is

---

Figure 7.
Magnetization curves at 5 K (a) and 300 K (b) for annealed ribbons of CuₓMnAl₂₋ₓGaₓ (x = 0 and 8) alloys. Magnetization curves (c) and (d) shows an increase in M with H for the alloy with x = 8 (Reprinted from reference [24] with kind permission from Elsevier, Copyright 2012, Elsevier).
clearly evident. This may be due to the precipitation of paramagnetic phase (γ-Cu₅₅Al₄ type) as a majority phase for the alloy with x = 8.

The temperature dependence of magnetization curves (M-T curves) for the melt-spun and annealed ribbons under a field of 500 Oe has been investigated. Figure 8(a-d) shows the M-T curves of the melt-spun Cu₅₀Mn₂₅Al₂₅-xGaₓ (x = 0, 4, 8 & 10) alloys. The alloys with x = 4 and 8 have the same type of M-T curves as the parent alloy Cu₅₀Mn₂₅Al₂₅ (x = 0) shows the characteristics of a ferromagnet. With increase in Ga concentration, the saturation magnetization M(T) decreases. At low temperature in the M-T curves for x = 0, 4 and 8, it follows the expression

\[ M(T) = M(0)(1-AT^{n}) \]

with n = 3/2 [52]. The data for T < 100 K as a function of T^{3/2} is shown in Figure 8(a)-(c). The T^{3/2} dependence of the magnetization at this low T range has been shown by the solid line in the inset graph which is a linear fit to the data. The magnetization measurements of Cu₅₀Mn₂₅Al₂₅-xGaₓ (x = 0, 4, 8 & 10) alloys in the zero field cooled (ZFC) and field cooled (FC) modes are shown in Figure 8. The magnetization measurements in ZFC and FC modes can give an estimate of magnetic ordering temperature in a system with long range magnetic order or blocking/freezing temperature in the case of medium range order [60].

The splitting in the ZFC and FC magnetization curves has been observed for the alloys with x = 0, 4, 8 and 10 (Figure 8). The alloys with x = 0, 4, 8 and 10 shows the splitting at ~145 K, ~125 K, ~25 K and ~225 K respectively. The splitting temperature found to be decreases from x = 0 to x = 8 and then increases for x = 10. The reason for this may be attributed to the fact that the alloys up to x = 8 exhibit single phase while the alloy with x = 10 is biphasic in nature. Thus, the synthesis acquired anisotropy.

Figure 8. Temperature dependence of magnetization for melt-spun ribbons of Cu₅₀Mn₂₅Al₂₅-xGaₓ alloys with x = 0 (a), x = 4 (b), x = 8 (c) and x = 10 (d) in a field of 500 Oe in the ZFC and FC modes. The data for T < 100 K as a function of T^{3/2} is shown in the inset graphs of (a), (b) and (c) (Reprinted from reference [24] with kind permission from Elsevier, Copyright 2012, Elsevier).
of the Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ (x = 0–10) melt spun alloys causes the splitting in the ZFC and FC curves. The synthesis of ribbons using the melt spinning process involves the sudden cooling of molten alloy when it falls on to the rotating Cu-wheel. The sudden and fast cooling of the molten alloy arises from the very high speed (~ 4000 rpm) of the rotating wheel. It is well known that the side of the ribbon which is in direct contact with the wheel has higher cooling rate than the one which is not in contact [61]. Thus, the variation in cooling rate along the thickness of the ribbon result in some microstructural changes between contact side (CS) and non-contact side (NCS) [61]. This has led to synthesis acquired anisotropy in the ribbons.

3. Structure/microstructure and magnetic properties of nanoferrites

3.1 XRD and AFM analysis of NiFe$_2$O$_4$, CoFe$_2$O$_4$ and MnFe$_2$O$_4$ thin films

The nanoferrites of NiFe$_2$O$_4$, CoFe$_2$O$_4$ and MnFe$_2$O$_4$ thin films were prepared by a MOD method [62]. Figure 9(a) shows the XRD pattern of NiFe$_2$O$_4$, CoFe$_2$O$_4$ and MnFe$_2$O$_4$ thin films. The ferrite peaks at 2$\theta$ = 30.481, 34.991, 37.481, 42.581, 48.021, 51.231 and 55.85° respectively attributed to (220), (311), (222), (400), (331), (422) and (511) reflections of spinel structure. A small amount of $\alpha$-Fe$_2$O$_3$ phase had also been formed as an impurity phase. The lattice constants are calculated from the XRD data i.e. $a$ (Å) ~8.161, 8.312 and 8.425, respectively for NiFe$_2$O$_4$, CoFe$_2$O$_4$ and MnFe$_2$O$_4$. These calculated values of lattice constants are closer to bulk NiFe$_2$O$_4$.
Magnetic Skyrmions

(8.17 Å), CoFe$_2$O$_4$ (8.32 Å) and MnFe$_2$O$_4$ (8.43 Å) [63, 64]. Figure 9(b)-(d) shows the AFM images respectively of NiFe$_2$O$_4$, CoFe$_2$O$_4$ and MnFe$_2$O$_4$ thin films. It exhibited homogeneous micro-structures with uniform size distribution of nano-grains. The thin film surfaces are smooth and crack-free. The grains exhibit a round shape with a small grain boundary region. The average size of grains AFM is 46, 61 and 75 nm and surface roughness is 2.5, 4 and 2 nm respectively for NiFe$_2$O$_4$, CoFe$_2$O$_4$ and MnFe$_2$O$_4$. The smaller nano-grains formation may attribute better stoichiometric ratio and low processing temperature of crystallization. Also the addition of PEG encapsulates the ferrites constituents into smaller groups during the heating process [65].

3.2 Magnetism of ferrite MFe$_2$O$_4$ nanoparticles

3.2.1 Ferromagnetism of MFe$_2$O$_4$ [M = Mn, Co, Ni, Zn] with BaTiO$_3$

The magnetic nanoparticles of multiferroic MFe$_2$O$_4$/BaTiO$_3$ [M = Mn (MnFO/BTO), Co (CFO/BTO), Ni (NFO/BTO) and Zn (ZFO/BTO)] thin films were fabricated by a MOD method [66]. The addition of ferrite MFe$_2$O$_4$ in perovskite BaTiO$_3$ results in to lattice strain due to tetragonal distortion, expansion/contraction of MFO/BTO unit cell and lattice mismatch. The tetragonal BTO, spinel MFO phases and lattice strain effects are confirmed by XRD analysis. The average grain size for MnFO/BTO, CFO/BTO, NFO/BTO and ZFO/BTO is calculated from AFM images and is found to be 25, 102, 24 and 133 nm, respectively.

The ferromagnetic behaviour (magnetization versus applied magnetizing field (M-H$_{dc}$)) of MFO/ BTO thin films at room temperature is shown in Figure 10(a). The values of remanent magnetization, $M_r = 0.03, 3.75, 6.76$ and 1.49 kJ m$^{-3}$ with coercivity, $H_c = 0.013 \times 10^5, 0.079 \times 10^5, 0.167 \times 10^5$ and 0.135 $\times 10^5$Am$^{-1}$ and saturation magnetization, $M_s = 1.29, 20.25, 27.64$ and 6.77 kJ T$^{-1}$ m$^{-3}$, respectively, measured for MnFO/BTO, CFO/BTO, NFO/ BTO and ZFO/ BTO. The magnetization values observed for MFO/BTO nanocomposite shown abrupt reduction than single phase MnFe$_2$O$_4$ (5.40 kJ T$^{-1}$ m$^{-3}$), ZnFe$_2$O$_4$ (230 kJ T$^{-1}$ m$^{-3}$), NiFe$_2$O$_4$ (50.60 kJ T$^{-1}$ m$^{-3}$) and CoFe$_2$O$_4$ (33.50 kJ T$^{-1}$ m$^{-3}$) [62, 67]. Due to non-magnetic

Figure 10.
(a) Room temperature M-H$_{dc}$ hysteresis of MFe$_2$O$_4$/BaTiO$_3$ thin films (h & c) M-H hysteresis of Ce doped CoFe$_2$O$_4$ nanoparticles at room temperature. Inset shows SQUID measurement for ZFC/FC experiment (Reprinted from reference [66] with kind permission from Elsevier, Copyright 2017, Elsevier).
BTO phase of nano-composite, the saturation magnetization of ferrite reduces. Since mixed pervoskite BTO acts as a non-magnetic defect, which hinders the growth of the magnetic domains of spinel MFO and their movement under an external magnetic field [68]. Thus the non-magnetic elements weaken the A-B super exchange interaction which results in the increase of distance between the magnetic moments in A and B sites in the spinel structure [69]. The weaker A-B super exchange interaction of MFO by non-magnetic BTO phase is more affected by the thermal motion, resulting in the decrease of $T_C$. Wang et al. [70] suggested that the decrease in the magnetization causes the relaxation process to increase, which might be related with oxygen vacancies redistribution. Bateer et al. [71] suggested that the decrease in particle size and the presence of a magnetic dead or anti-ferromagnetic layer on the surface results into reduction in saturation magnetization in ferrite nanoparticles.

Moreover the origin of observed ferromagnetic behavior (Figure 10) of MFO ferrites nanocomposite must be related with two different mechanisms: ferrimagnetic coupling of Fe ions at A-B sites in $(M_{1-x}Fe_x)(Fe_{2-x}M_x)O_4$ and the surface spin canting [72]. The structure of the ferrite becomes mixed spinel from its normal configuration when consider the cation inversion in which the shifting of M ions from A to B site and that of Fe ions from B to A-site changes the magnetic behavior of the nanocomposite [73]. The magnetic moments of Fe ions (at B-site) cancel out due to negative interaction among them and M ions have nothing to contribute. The Fe ions present at A-site are responsible for magnetization enhancement and contribute to net magnetic moment. Vamvakidis et al. [74] suggested that within the spinel structure, the reduction in inversion degree (~0.22) of MnFe$_2$O$_4$ (due to the partial oxidation of Mn$^{2+}$ to Mn$^{3+}$) ions results into weaker super exchange interactions between tetrahedral and octahedral sites. It contributes to weak ferrimagnetism in MnFe$_2$O$_4$. Bullita et al. [75] reported that the cation distribution of ZnFe$_2$O$_4$ at the nanoscale level is contributed by partial inverted spinel structure which results in the increase of magnetization. Peddis et al. [76] shows the typical ferrimagnetic structure of inverse CoFe$_2$O$_4$ nanoparticles with an inversion degree of 0.74. These results in the better correlation between spin canting and cationic distribution to get competitively higher value of saturation magnetization. However, Carta et al. [77] reported the degree of inversion 0.20 for MnFe$_2$O$_4$ nanoparticles, 0.68 for CoFe$_2$O$_4$ nanoparticles and 1.00 for NiFe$_2$O$_4$ nanoparticles.

3.2.2 Ferromagnetic ordering in Ce doped CoFe$_2$O$_4$ nanoparticles

It is reported that the core/shell nanoparticles of CoFe$_{2-x}$Ce$_x$O$_4$ [$x = 0.05$ (CFCeO05), 0.1 (CFCeO10)] were prepared by a chemical combustion method [37]. XRD pattern results into spinel structure with cubic space group. From TEM images, the average particles size, $D = 8$ and 10 nm, respectively, for CFCeO05 and CFCeO10 sample. Figure 10(b) and (c) shows the M-H hysteresis with $M_s = 42.54$ and 10.41 emug$^{-1}$ and $M_r = 26.68$ and 1.57, emug$^{-1}$ with $H_c = 1526$ and 140 Oe, respectively, observed for CFCeO05 and CFCeO10. These values of magnetization are larger than nanostructured pure CoFe$_2$O$_4$ but smaller than bulk value (73 emug$^{-1}$ at room temperature). This is due to higher surface energy and surface tension in the nanoparticles which changes cationic preferences of ferrite. It leads to an increase in degree of anti-site defects to cause more surface spin canted or disorder.

Recently, Georgiadou et al. [78] suggested modification in cation occupancy in nanostructured CFO due to its inverse spinel structure. The theoretical expression for the net moment of CFO is given (Ce$^{3+}$ ions occupy only the B sites for their large ionic size): $M_{\nabla} = M_B - M_A = [5 \times (1 - x) + 3.8 + x \times \mu_{\nabla}] - 5$; where $M_A$ and $M_B$ are the
wof Fe$^{3+}$ cation is fixed to 5μB (spin only) and for octahedrally coordinated Co$^{2+}$ cations is fixed to 3.8 which correspond to the $M_{sat}$ at 0 K of bulk CFO (95 emug$^{-1}$) [79]. The net magnetic moments $\mu_{Fe}$ cation is zero for the diamagnetic Ce$^{4+}$ ions and non-zero for the paramagnetic Ce$^{3+}$ ones. By replacing Fe$^{3+}$ by Ce$^{3+}$ cation, the $M_{s}$ is expected to vary as $\mu_{Ce}$ by the sequential filling of electrons in the 4$f$ shell. Unlike, a clear deviation between the theoretically predicted magnetization by above equation and the experimental one (Figure 10(b) and (c)) is observed. This is ascribed into two reasons. One is the decrease in strong negative Fe$^{3+}$-Fe$^{3+}$ interaction that resulted from the doping of Ce because the spinel ferrimagnetic CFO is largely governed by the negative Fe$^{3+}$-Fe$^{3+}$ interaction (the spin coupling of the 3d electrons). The Ce$^{3+}$-Fe$^{3+}$ interaction (4f-3d coupling) as well as the Ce$^{3+}$-Ce$^{3+}$ one (indirect 4f-5d-4f coupling) exist this is very weak [80]. The other is the rearrangement of the Co$^{2+}$ ion in the A and B sites resulted from the doping with RE Ce$^{3+}$ ions. The migration of Co$^{2+}$ ion into tetrahedral sublattice decreases the concentration of Fe$^{3+}$ ion in A site, leading to enhance $M_{s}$. Also, the value of $H_{c}$ is reduces with Ce$^{3+}$ ion concentration in CFCeO10 and shows weak ferromagnetism. This is responsible due to variation in core/ shell formation and description of CFO lattice by vibrational modes [37]. The core/shell (CeO/CFO) system result into an increase in effective magnetic anisotropy caused by surface and interface exchange coupling effects. The huge difference in the coercivity value among CFCeO samples may ascribe to surface pinning that arises due to missing coordination of oxygen atoms and the shape effect of the spinel ferrite.

The origin of observed room temperature ferromagnetism of CFCeO samples is evaluated by the temperature dependent magnetization $|M(T)|$ with field cooling (FC) and zero field cooling (ZFC) measurement (Figure 10(b') and (c') inset). The applied magnetic field is 100 Oe. These M-T measurements show that ZFC-FC curves of the CFCeO05 sample did not coincide with each other or slightly coincide around 300 K. It indicates that the nanoparticles are still magnetically blocked at around room temperature. However, CFCeO10 nanoparticles show blocking temperature of antiferromagnetism, spin glass etc. at about 91 K. This type of the magnetic response is due to different nano-core/ shell formation in CFCeO samples. The core/shell nanoparticles provides spin-phonon coupling in which a core of aligned spins is surrounded by a magnetically disordered shell [81].

### 3.2.3 Humidity response from MgFe$_2$O$_4$ thin films

Figure 11 shows the humidity response of MgFe$_2$O$_4$ thin films (measured in the range 10–90% RH at 25°C). The base resistance of thin film annealed at 400°C increased from 59 GΩ to 30 TΩ annealed at 800°C. There are many factors on which the resistance of ferrites depends such as porosity, vacancies and electron hopping between Fe$^{2+}$ and Fe$^{3+}$. In the present study it may be due to higher annealing temperature that increases the average pore size distribution which further creates more obstruction for the charge carrier’s movement. It can be seen from Figure 11 that with higher annealing temperature, the response of Log R (Ohm) approaches towards linearity with rising humidity 10–90% RH (relative humidity). Log R variation of the film annealed at 400°C was almost constant (up to 50% RH), after that the linear decrease was observed at high humidity value. This may be due to the presence of less pores available for adsorption and thus a very few water molecules are only able to chemisorbed in such pores. The slope of log R (with increasing humidity) increases for the film annealed at 600°C and it became almost linear for the film annealed at 800°C for the entire range of humidity which may be due to the increase of intra and inter pores.
4. Conclusion

In this chapter the recent progress in the development of Heusler alloys and nanoferrites are discussed. Formation of Heusler single phase of the $Cu_2MnAl$ structure has been found only for the $Cu_{50}Mn_{25}Al_{25-x}Ga_x$ alloys with $x \leq 8$. The size of the grains for the Heusler phase alloy is in the range 100–200 nm. Long term annealing of the alloys leads to the formation of $\beta$-$Mn$ and $\gamma$-$Cu_9Al_4$ type phases. The saturation magnetization ($M_s$) decreases with increasing Ga concentration. The decomposition of the $Cu_2MnAl$ Heusler phase into $\beta$-$Mn$ and $\gamma$-$Cu_9Al_4$ phases during annealing leads to the decrease in the magnitude of $M_s$.

The XRD pattern confirms the cubic phase of spinel ferrites in nanoferrites. The average grain’s size for these ferrites is found to be less than 100 nm. Thus it can be said that the nanostructural formation of ferrite grains depends on the selection of chemical route and annealing temperature and the magnetic properties of nanoferrites are different from the bulk ferrites. The core/shell nanocomposites formation of Ce substituted $CoFe_2O_4$ hinders the superparamagnetism formed due to small magnetic nanoparticles results into long-range antiferromagnetic interactions. $MgFe_2O_4$ thin film annealed at 800°C has a linear log R (Ohm) response towards the entire humidity range 10–90% RH.

Acknowledgements

One of the authors (Devinder Singh) gratefully acknowledges the financial support by Department of Science and Technology (DST), New Delhi, India in the form of INSPIRE Faculty Award [IFA12-PH-39] and K.C. Verma is grateful to SERB Department of Science and Technology (DST), Govt. of India for the financial support under Fast-track Scheme for Young Scientist [SR/FTP/PS-180/2013].
Magnetic Skyrmions

Author details

Devinder Singh* and Kuldeep Chand Verma

1 Amity School of Applied Sciences, Amity University, Lucknow Campus, Lucknow, UP, India

2 CSIR-Central Scientific Instrument Organisation, Chandigarh, India

*Address all correspondence to: dsingh2@lko.amity.edu

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
References

[1] Heusler F, Starck W, Haupt E, Verh d. DPG 1903;5:220.

[2] Heusler F, Verh d. DPG 1903;5:219.

[3] Tobola J, Pierre J, Kaprzyk S, Skolozdra RV, Kouacou M. A. Electronic structure and magnetism in Co–Ni Heusler alloys. J Magn Mag Materials. 1996;159:192.

[4] Pierre J, Skolozdra RV, Tobola J, Kaprzyk S, Hordequin C, Kouacou MA, Karla I, Currat R, Leliévre-Berna E. Properties on request in semi-Heusler phases. J Alloys Compd. 1997;262-263:101.

[5] Santina Mohallem ND, Silva JB, Nascimento GLT, Guimaraes VL. Study of multifunctional nanocomposites formed by cobalt ferrite dispersed in a silica matrix prepared by sol-gel process. InTech, pp. 457 (Chapter 18).

[6] Cong DY, Roth S, Liu J, Luo Q, Potschke M, Hurrich C, Schultz L. Superparamagnetic and superspin glass behaviors in the martensitic state of Ni_{43.5}Co_{6.5}Mn_{39}Sn_{11} magnetic shape memory alloy. Appl Phys Lett. 2010;96:112504.

[7] Knobel M, Nunes WC, Socolovsky LM, Biasi ED, Vargas JM, Denardin JC. Superparamagnetism and other magnetic features in granular materials: A review on ideal and real systems. J Nanosci Nanotechnol. 2008;8:2836.

[8] Marukame T, Ishikawa T, Matsuda K, Uemura T, Yamamoto M. High tunnel magnetoresistance in fully epitaxial magnetic tunnel junctions with a full-Heusler alloy Co_xCr_yFe_2Al thin film. Appl Phys Lett. 2006;88:262503.

[9] Yilgin R, Oogane M, Yakata S, Ando Y, Miyazaki T. Intrinsic Gilbert Damping Constant in Co_{2}MnAl Heusler Alloy Films. IEEE Transactions on Magnetics 2005;41:2799.

[10] Galanakis I. Theory of Heusler and Full-Heusler alloys. C. Felser and A. Hirohata (eds.), Heusler Alloys. Springer Series in Materials Science 222, DOI 10.1007/978-3-319-21449-8_1.

[11] Ouardi S, Shekhar C, Fecher GH, Kozina X, Stryganyuk G, Felser C, Ueda S, Kobayashi K. Electronic structure of Pt based topological Heusler alloys with C1b structure and “zero band gap”. Appl Phys Lett 2011;98:211901.

[12] Singh D, Singh D, Srivastava ON, Tiwari RS. Microstructural effect on the low temperature transport properties of Ce-Al (Ga) metallic glasses. Scripta Materialia 2016;118:24.

[13] Singh D, Singh D, Tiwari RS. Effect of Ga substitution on low temperature transport and magnetic response of Ce_{75}Al_{25} metallic glass. AIP Advances 2018;8:095222.

[14] Singh RK, Raja MM, Mathur RP, Shamsuddin M. Effect of Fe substitution on the phase stability and magnetic properties of Mn-rich Ni-Mn-Ga ferromagnetic shape memory alloys. J Magn Mag Materials 2011;323:574.

[15] Kaul SN, Annie D’Santhoshini B, Abhyankar AC, Barquin LF, Henry P. Thermoelectric martensitic transformation in ferromagnetic Ni–Fe–Al alloys: Effect of site disorder. Appl Phys Lett 2006;89:093119.

[16] Li Y, Jiang CB, Liang T, Ma YQ, Xu HB. Martensitic transformation and magnetization of Ni–Fe–Ga ferromagnetic shape memory alloys. Scripta Materialia 2003;48:1255.

[17] Liu J, Woodcock TG, Schoerbaum N, Gutfleisch O. Influence of annealing
Magnetic Skyrmions

on magnetic field-induced structural transformation and magnetocaloric effect in Ni–Mn–In–Co ribbons. Acta Materialia 2009;57:4911.

[18] Karaca HE, Karaman I, Basaran B, Ren Y, Chumlyakov YI, Maier HJ. Magnetic Field-Induced Phase Transformation in NiMnCoIn Magnetic Shape-Memory Alloys: A New Actuation Mechanism with Large Work Output. Adv Funct Mater 2009;19:983.

[19] Kainuma R, Ito W, Umetsu RY, Oikawa K, Ishida K. Magnetic field-induced reverse transformation in B2-type NiCoMnAl shape memory alloys. Appl Phys Lett 2008;93:091906.

[20] Biswas C, Rawat R, Barman SR. Large negative magnetoresistance in a ferromagnetic shape memory alloy: Ni$_{2+x}$Mn$_{1-x}$Ga. Appl Phys Lett 2005;86:202508.

[21] Webster PJ, Ziebeck KRA. Alloys and Compounds of d-Elements with Main Group Elements - Part 2. H. P. J. Wijn, Landolt-Bornstein, New Series, Group III, 19/c (Springer, Berlin), (1988).

[22] Groot RAD, Muller FM, Engen PGV, Buschow KJH. New Class of Materials: Half Metallic Ferromagnets. Phys Rev Lett 1983;50:2024.

[23] Fujii S, Sugimura S, Ishida S, Asano S. Hyperfine fields and electronic structures of the Heusler alloys Co$_2$MnX (X=Al, Ga, Si, Ge, Sn). J Phys Condens Matter 1990;2:8583.

[24] Singh D, Tiwari RS, Srivastava ON. Structural and magnetic properties of Cu$_{50}$Mn$_{25}$Al$_{25-x}$Ga$_x$ Heusler alloys. J Magn Mag Materials 2013;328:72.

[25] Nayak AK, Suresh KG, Nigam AK. Magnetic, electrical, and magnetothermal properties in Ni-Co-Mn-Sb Heusler alloys. J Appl Phys 2010;107:09A927.

[26] Luo H, Mang F, Jiang Q, Liu H, Liu E, Wu G, Wang Y. Effect of boron on the martensitic transformation and magnetic properties of Ni$_{13}$Mn$_{20.3}$Sb$_{13.5}$B$_x$ alloys. Scripta Materialia 2010;63:569.

[27] Chattopadhyaay MK, Manekar MA, Sharma VK, Arora P, Tiwari P, Tiwari MK, Roy SB. Contrasting behavior of Ni$_{50}$Mn$_{35}$In$_{15}$ and Ni$_{50}$Mn$_{44.3}$In$_{15.5}$ alloys. J Appl Phys 2010;108:073909.

[28] Pathak AK, Khan M, Gautam BR, Stadler S, Dubenko I, Ali N. Exchange bias in bulk Ni-Mn-In based Heusler alloys. J Magn Mag Materials 2009;321:963.

[29] Gautam BR, Dubenko I, Pathak AK, Stadler S, Ali N. The structural and magnetic properties of Ni$_2$Mn$_{1-x}$B$_x$Ga Heusler alloys. J Magn Mag Materials 2009;321:29.

[30] Li S, Liu M, Yuan Z, Lu LY, Zhang Z, Lin Y, Du Y. Effect of Nb addition on the magnetic properties and magnetocaloric effect of CoMnSb alloy. J Alloys & Compds 2007;427:15.

[31] Singh S, Verma KC, Kotnala RK, Ralhan NK. Structure and magnetic properties of NiFe$_2$O$_4$nanoferrite prepared by chemical combustion route. AIP Conf Proc 2011;1393:215.

[32] McCurrie RA. Ferromagnetic Materials: Structure and Properties. Academic Press, New York, 1994.

[33] Hu W, Qin N, Wu G, Lin Y, Li S, Bao D. Opportunity of Spinel Ferrite Materials in Nonvolatile Memory Device Applications Based on Their Resistive Switching Performances. J Am Chem Soc 2012;134,14658.

[34] Zhu W, Wang L, Zhao R, Ren J, Lu G, Wang Y. Electromagnetic and microwave-absorbing properties of magnetic nickel ferrite nanocrystals. Nanoscale 2011;3:2862.
[35] Colombo M et al. Biological applications of magnetic nanoparticles. Chem Soc Rev 2012; 41:4306.

[36] Perron H et al. Structural investigation and electronic properties of the nickel ferrite NiFe$_2$O$_4$: a periodic density functional theory approach. J Phys: Condens Matter 2007; 19:346219.

[37] Verma KC, Kotnala R.K. Core/shell nanostructures due to Ce into CoFe$_2$O$_4$ induce lattice and vibrational defects for magnetic and dielectric enhancement. Adv Mater Lett 2016; 7(8):622.

[38] Szotek Z, Temmerman WM, Kodderitzsch D, Petit L, Winter H. Electronic structures of normal and inverse spinel ferrites from first principles. Phys Rev B 2006; 74:174431.

[39] Luders U et al. Hybrid perovskite-spinel magnetic tunnel junctions based on conductive ferrimagnetic NiFe$_2$O$_4$. Appl Phys Lett 2006; 88:082505.

[40] Singh S, Singh M, Ralhan NK, Kotnala RK, Verma KC. Improvement in ferromagnetism of NiFe$_2$O$_4$ nanoparticles with Zn doping. Adv Mat Lett 2012; 3(6):504.

[41] Singh S, Ralhan NK, Kotnala RK, Verma KC. Nanosize dependent electrical and magnetic properties of NiFe$_2$O$_4$ ferrite. Ind J Pure Appl Phys 2012; 50:739.

[42] Singh D, Yadav TP, Tiwari RS, Srivastava ON. Phase formation in rapidly quenched Cu–based alloys. J Mater Sci. 2009; 44:3883.

[43] Singh D, Yadav TP, Mandal RK, Tiwari RS, Srivastava ON. Effect of Ga substitution on the crystallization behaviour and glass forming ability of Zr-Al-Cu-Ni alloy. Mater Sci Eng A. 2010; 527:469.

[44] Singh D, Mandal RK, Tiwari RS, Srivastava ON. Effect of cooling rate on the crystallization and mechanical behaviour of Zr-Ga-Cu-Ni metallic glass composition. J Alloys & Compds. 2015; 648:456.

[45] Singh D, Mandal RK, Tiwari RS, Srivastava ON. Nanoindentation characteristics of Zr$_{0.95}$Al$_{0.5}$-xGa$_x$Cu$_{12}$Ni$_{11}$ glasses and their Nanocomposites. J Alloys & Compds 2011; 509:8657.

[46] Singh D, Yadav TP, Mandal RK, Tiwari RS, Srivastava ON. Indentation characteristics of metallic glass and nanoquasicrystal–glass composite in Zr–Al(Ga)–Cu–Ni alloys. Intermetallics 2010; 18:2445.

[47] Singh D, Singh M, Yadav TP, Mandal RK, Tiwari RS, Srivastava ON. Nanoindentation studies of metallic glasses and nanoquasicrystal-glass composites in Zr-Al(Ga)-Cu-Ni alloys. International Journal of Nanoscience 2011; 10:929.

[48] Singh D, Yadav TP, Mandal RK, Tiwari RS, Srivastava ON. Effect of Ti addition on the quasicrystalline phase formation and indentation characteristics of Zr$_{0.95}$Al$_{0.5}$Cu$_{12}$Ni$_{11}$ alloy. Philosophical Magazine 2011; 91:2837.

[49] Singh D, Singh D, Yadav TP, Mandal RK, Tiwari RS, Srivastava ON. Synthesis and indentation behavior of amorphous and nanocrystalline phases in rapidly quenched Cu–Ga–Mg–Ti and Cu–Al–Mg–Ti alloys. Metallography, Microstructure, and Analysis 2013; 2:321.

[50] Bang D, Dan NH, Hung LT. Effect of microstructure on magnetism and transport properties of Cu-Mn-Al granular ribbons. J Phys D: Appl Phys 2008; 41:155006.

[51] Sakka Y, Nakamura M. Mechanical and magnetic properties of the rapidly quenched Cu$_{0.66}$MnAl. J Mater Sci 1990; 25:2549.

[52] Zhang M, Liu G, Cui Y, Hu H, Liu Z, Chen J, Wu G, Sui Y, Qian Z,
Zhang X. Magnetism and transport properties of melt-spun ribbon Cu₂MnAl Heusler alloy. J Magn Mag Materials 2004;278:328.

[53] Robinson J, McCormick P, Street R. Structure and properties of Cu₄MnAl synthesized by mechanical alloying. J Phys: Condens Matter 1995;7:4259.

[54] Heinzig M, Jenks CJ, Hove MV, Fisher I, Canfield P, Thiel PA. Surface preparation and characterization of the icosahedral Al–Ga–Pd–Mn quasicrystal. J Alloys & Compds 2002;338:248.

[55] Singh D, Singh D, Mandal RK, Srivastava ON, Tiwari RS. Glass forming ability, thermal stability and indentation characteristics of Ce₇₅Al₂₅₋ₓGaₓ metallic glasses. J Alloys & Compds 2014;590:15.

[56] Mandal RK, Tiwari RS, Singh D, Singh D. Influence of Ga substitution on the mechanical behavior of ZrₓGaxPd₃₋ₓNi₃ compositions. MRS Proceeding. 2015;1757. doi:10.1557/opl.2015.45.

[57] Yadav TP, Singh D, Shahi RR, Shaz MA, Tiwari RS, Srivastava ON. Formation of quasicrystalline phase in AlₓGa₄PdₓMn₃ alloys. Phil Mag. 2011;91:2474.

[58] Singh D, Singh D, Mandal RK, Srivastava ON, Tiwari RS. Effect of annealing on the devitrification behavior and mechanical properties of rapidly quenched Ce-based glassy alloys. J. Non-Cryst. Solids 2016;445:53.

[59] Singh D, Singh D, Mandal RK, Srivastava ON, Tiwari RS. Effect of quenching rate on the microstructure and mechanical behavior of Ce₇₅Al₂₅Gaₓ glassy alloy. Materials Characterization 2017;134:18.

[60] Konopolyuk SM, Kokorin VV, Kolomiets OV, Perekos AE, Nadutov VM. Magnetoresistance of Cu-Mn-Al melt-spun ribbons containing the system of interacting ferromagnetic inclusions. J Magn Mag Materials 2011;323:763.

[61] Lalla NP, Tiwari RS, Srivastava ON. Transmission electron microscopic investigations of rapidly solidified Al-Mn-Ni quasicrystalline alloys. Phil Mag B 1991;63:629.

[62] Verma KC, Singh VP, Ram M, Shah J, Kotnala RK. Structural, microstructural and magnetic properties of NiFe₂O₄, CoFe₂O₄ and MnFe₂O₄ nano ferrite thin films. J Magn Magn Mater 2011;323:3271.

[63] Singh D, Singh M, Balan N K, Kotnala RK, Verma KC. Ferromagnetic and Dielectric Properties of Niₓ₋ₓZnₓFe₂O₄ Nanoparticles Prepared via Chemical Combustion Route. Adv Sci Engg Med 2014; 6(6):688.

[64] Verma KC, Singh S, Tripathi SK, Kotnala RK. Multiferroic Ni₀.₆Zn₀.₄Fe₂O₄-BaTiO₃ nanostructures: Magnetoelastic coupling, dielectric, and fluorescence. J Appl Phys 2014;116:124103.

[65] Verma KC, Sharma AK, Bhatt SS, Kotnala RK, Negi NS. Synthesis and characterization of nanostructured (Pbₓ₋ₓSrₓ)TiO₃ thin films by a modified chemical route. Phil Mag 2009;89(27):2321.

[66] Verma KC, Singh D, Kumar S, Kotnala RK. Multiferroic effects in MFexO3/BaTiO3 (M = Mn, Co, Ni, Zn) Nanocomposites. J Alloys Compds 2017;709:344.

[67] Sultan M, Singh R. FMR Studies on Nanocrystalline Zinc Ferrite Thin Films. J Phys: Conf Series 2010;200:072090.

[68] Verma KC, Kotnala RK. Nanostructural and lattice contributions to multiferroism in NiFe₂O₄/BaTiO₃. Mater Chem Phys 2016;174:120.

[69] Zhou JP, Lv L, Liu Q, Zhang YX, Liu P. Hydrothermal synthesis and...
properties of NiFe₂O₄@BaTiO₃ composites with well-matched interface. Sci Technol Adv Mater 2012;13:045001.

[70] Wang P, Jin C, Zheng D, Li D, Gong J, Li P, Bai H, Strain and Ferroelectric- Field Effects Co-mediated Magnetism in (011)-CoFe₂O₄/ Pb(Mg₁/₃Nb₂/₃)₀.₇Ti₀.₃O₃ Multiferroic Heterostructures. ACS Appl Mater Interf 2016;8:24198.

[71] Bateer B et al. Synthesis, size and magnetic properties of controllable MnFe₂O₄ nanoparticles with versatile surface functionalities. Dalt Trans 2014;43:9885.

[72] Singh JP et al. Observation of bulk like magnetic ordering below the blocking temperature in nanosized zinc ferrite. J Magn & Mag Mater 2012;324:2553.

[73] Goya GF, Rechenberg HR. Magnetic properties of ZnFe₂O₄ synthesized by ball milling. J Magn & Mag Mater 1999;203:141.

[74] Vamvakidis K et al. Reducing the inversion degree of MnFe₂O₄ nanoparticles through synthesis to enhance magnetization: evaluation of their ¹H NMR relaxation and heating efficiency. Dalton Trans 2014;43:12754.

[75] Bullita S et al. ZnFe₂O₄ nanoparticles dispersed in a highly porous silica aerogel matrix: a magnetic study. Phys Chem Chem Phys 2014;16:4843.

[76] Peddis D et al. Cationic distribution and spin canting in CoFe₂O₄ nanoparticles. J Phys Condens Matter 2011;23:426004.

[77] Carta D et al. A Structural and Magnetic Investigation of the Inversion Degree in Ferrite Nanocrystals MFe₂O₄ (M = Mn, Co, Ni). J Phys Chem C 2009;113:8606.