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Synthesis and characterization of Co_2FeAl Heusler alloy nanoparticles

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Heusler alloy Co_2FeAl (CFA) nanoparticles have been synthesized by reducing a mixture of the precursors: $CoCl_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $AlCl_3 \cdot 6H_2O$ under H_2 atmosphere. XRD, SEM and TEM techniques have been used for the characterization of the prepared material. XRD and SAED data from TEM show the formation of mixed phases of $L2_1$, B2 and A2 type crystal structure of the alloy. The estimated particle size from XRD data and TEM micrograph has been found in the range of 10 nm to 50 nm. The saturation magnetization has been found of 115 emu/g from M-H characteristics which is close to its bulk value of saturation magnetization. Chemical composition of the elements has also been estimated from EDAX, which shows a ratio of Co:Fe:Al as 2.12:1.06:0.81.

Keywords: *Heusler alloy; nanoparticles; Co_2FeAl; M-H characteristics*

1. Introduction

Nanomaterials and nanoparticles based devices have recently attracted much attention and are of great interest for research due to their unique size and interesting chemical and physical properties as compared to bulk materials [1]. The high surface to volume ratio of nanoparticles introduces many size dependent phenomena and interesting chemical, electronic, magnetic and mechanical properties [2, 3]. Synthesis of magnetic nanoparticles is a hot topic now due to their potential application in the fields of medicine, pharmaceutics, in ferrofluids, engineering, material science, high density magnetic data storage, high frequency electronics, high performance permanent magnets and magnetic refrigerants [4, 5]. There are different routes to synthesize nanomaterials such as laser ablation [6] hydrothermal synthesis [7], sol-gel [8], ultrasonic-assisted wet chemical route [9], co-precipitation [10] and CVD processes [11].

Among various classes of magnetic nanoparticles, Heusler alloys, which show half metallicity is of interest due to their significant spin polarization of 100 % at the Fermi surface. Half metallicity was first predicted in Heusler alloys by De Groot et al. [12]. Half metallic ferromagnets are the compounds which show semiconducting behaviour for one type of spin channel at Fermi surface and metallic behaviour for other type of spin channel at Fermi surface. Half metallic compounds (which have 100 % spin polarization at Fermi surface) can be used potentially in spintronics devices [12, 13]. Among the half metallic ferromagnets, Heusler alloy, especially Co-based Heusler alloy has attracted high attention due to its interesting magnetic properties such as high Curie temperature and high saturation magnetization [14, 15].

There are several ways to synthesize Heusler alloy such as arc-melting of elements in noble gas atmosphere or mechanical alloying method [16–21]. There are few reports on synthesis of Heusler alloy by chemical route. Sapkota et al. [22] synthesized Heusler alloy Co_2FeAl nanowires and studied their structural and magnetic properties. Basit et al. [23] synthesized Co_2FeGa nanoparticles chemically and investigated their structure, morphology and magnetic properties. Recently, Du et al. [24] synthesized Co_2FeAl nanoparticles by co-precipitation route and studied their magnetic and structural properties. In this report, we have used chemical route to synthesize Heusler

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alloy Co_2FeAl (CFA) nanoparticles by reducing a methanol impregnated mixture of $CoCl_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $AlCl_3{\cdot}6H_2O$. The synthesized powder material has been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) as well as energy dispersive X-ray analysis (EDAX) to determine its chemical structure, morphology, microstructure and composition. Magnetic property has been measured by recording M-H characteristics using a VSM facility.

2. Experimental details

The Co_2FeAl nanoparticles were synthesized as follows. The first step was the decomposition and reduction of $CoCl_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $AlCl_3{\cdot}6H_2O$ precursors. For synthesis of Heusler alloy Co_2FeAl nanoparticles, a solution of precursors $CoCl_2{\cdot}6H_2O$ (2.3710 g), $Fe(NO_3)_3{\cdot}9H_2O$ (2.0130 g), and $AlCl_3{\cdot}6H_2O$ (1.2029 g) was prepared in 200 ml methanol. All chemicals, $CoCl_2{\cdot}6H_2O$ (>99%), Fe $(NO_3)_3{\cdot}9H_2O$ (>99%), and $AlCl_3{\cdot}6H_2O$ (>97%) were purchased from SDFCL, sd fine-CHEM Limited, India and were used without any further purification. The solution was sonicated for 5 min. Methanol was removed using a rotary evaporator. The obtained solid was dried at 80 °C for 2 h. The solid was then gently ground to powder and annealed at 850 °C for 5 h under H_2 atmosphere with a flow rate of 50 ml/min. The samples were naturally cooled to room temperature and collected for the analysis.

The chemical structure was characterized by X-ray diffraction (X'Pert Pro PANalytical diffractometer) technique using CuKα ($\lambda = 1.54060$ Å) radiation source. Surface morphology of the synthesized powder of Co_2FeAl alloy was characterized by SEM (Philips-XL 20) technique. To analyze the microstructure of the synthesized alloy, TEM examination with Tecnai $20G^2$ was carried out. The composition of the alloy was determined from EDAX, attached with TEM facility. Magnetic properties were characterized by M-H characteristics using a vibrating sample magnetometer (EV7 VSM, ADE technologies) facility.

3. Results and discussion

3.1. XRD study

The XRD pattern of the synthesized powder has been shown in Fig. 1. The observed peaks have been identified with the JCPDS data. There are two peaks observed at 2θ of 45° and 65° which are identified and indexed as (220) and (400) lattice planes of Co_2FeAl alloy phase. Diffraction pattern of full-Heusler alloy, which is in chemical form of X_2YZ can be divided into odd superlattice, even superlattice diffraction and fundamental diffraction [25]. For odd superlattice diffraction, peaks are obtained at odd hkl values. Only $L2_1$ crystal structure displays odd superlattice diffraction. For even superlattice diffraction, peaks are obtained at hkl values which satisfy $h + k + l = 4n + 2$, where n is a positive integer. Both B2 and $L2_1$ structures show even superlattice. For fundamental diffraction, hkl values satisfy the relation $h + k + l = 4n$. This type of diffraction has been shown by A2, B2 and $L2_1$ types of crystal structures. So the observed peaks of the synthesized CFA nanoparticles at 2θ of 45° and 65° correspond to mixed phases of $L2_1$, B2 and A2 structure. In A2 structure all the constituents randomly occupy the lattice sites.

Crystallite size, σ, has also been estimated from the Scherrer relation [26]; $\sigma = 0.9\lambda\ (\omega \cdot \cos\theta)^{-1}$, where ω is the full width at half maximum (FWHM) of the diffraction peak, λ is the wavelength of the X-ray source (of CuK$_\alpha$; $\lambda = 1.54060$ Å, in our case) and θ is the Bragg angle. The FWHM has been found to be of 0.1968° and 0.1800° from XRD pattern. The FWHM values have been used to estimate the crystallite size which has been found to be of 46 nm and 53 nm.

3.2. Morphological study

The morphology of the as synthesized powdered sample of Co_2FeAl alloy has been observed with SEM. Fig. 2 shows the SEM micrograph of synthesized powder of Co_2FeAl alloy. The SEM micrograph shows formation of granular like morphology. The grain size, estimated from SEM micrograph has been found to range from 80 nm to 500 nm. The SEM micrograph shows an agglom-

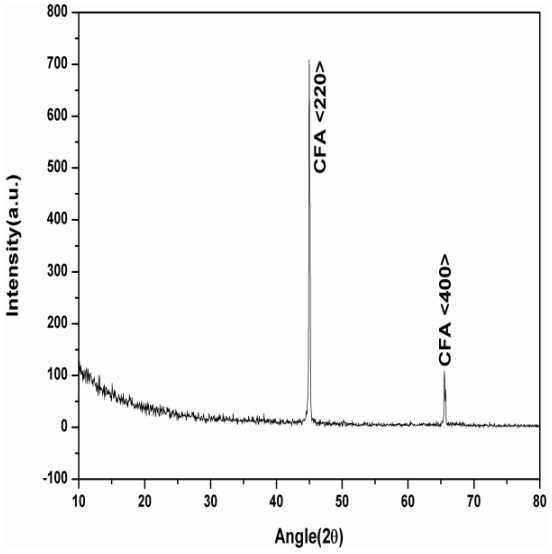

Fig. 1. X-ray diffraction pattern of the synthesized Co_2FeAl nanoparticles.

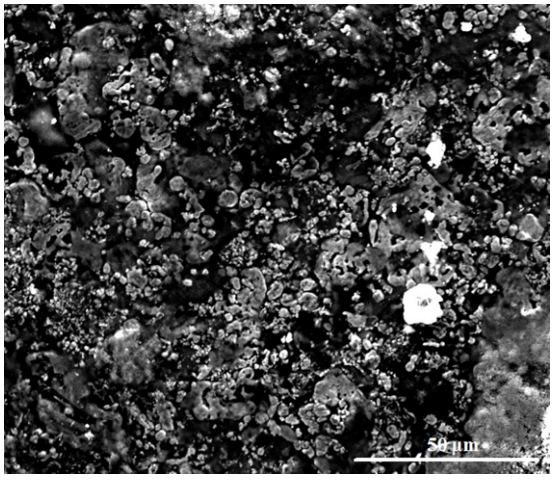

Fig. 2. Scanning electron microscopy (SEM) micrograph of the synthesized Co_2FeAl nanoparticles.

eration of smaller grains to transform into bigger grains. For a better resolution of morphological details, TEM has been used.

Fig. 3(a) shows the TEM micrograph of the synthesized powder of Co_2FeAl alloy. The insets in Fig. 3(a) show the selected area electron diffraction (SAED) of the Co_2FeAl alloy powder and the high resolution image of the marked portion on the TEM micrograph. A typical SAED pattern shown in the inset of Fig. 3(a) clearly reveals the polycrystalline nature of the alloy. The SAED pattern (Fig. 3(a)) has been indexed as (222), (330) and (531) crystal planes which also confirms the formation of Co_2FeAl alloy. Particle size has also been estimated from the TEM micrograph which clearly shows the formation of nanoparticles with the size varying from 10 nm to 50 nm. The particle sizes are in good agreement with crystallite size estimated from XRD data. Fig. 3(b) shows the particle size distribution histogram for the synthesized Co_2FeAl nanoparticles which has been estimated from the TEM image (Fig. 3(a)).

The composition of the synthesized powder of Co_2FeAl Heusler alloy was estimated from EDAX, attached with TEM facility. Fig. 4 shows the EDAX spectrum of the observed nanoparticles which clearly shows the presence of Co, Fe and Al elements. The observed Cu peak in the EDAX spectrum is due to copper grid that was used for mounting the sample in the TEM machine. The ratio of Co:Fe:Al comes out to be as 2.12:1.06:0.81 which is nearly 2:1:1.

3.3. Magnetization (M-H) study

The magnetic property of as synthesized nanoparticles of CFA alloy was investigated with a vibrating sample magnetometer (VSM). Fig. 5 shows the M-H characteristics of CFA powder. M-H characteristics of CFA alloy show ferromagnetic nature with a small value of remanence and coercivity. The coercivity, estimated from M-H loop is found to be of 65 Oe. The coercivity (H_c) has been estimated as $H_c = (H_c^+ - H_c^-)/2$, where H_c^+ and H_c^- are $+$ve and $-$ve coercive fields. The value of remanence (M_r) has been estimated at the zero field intercept at the magnetization axis and found to be of 7.56 emu/g (inset of Fig. 5). The room temperature saturation magnetization of synthesized CFA alloy is of 115 emu/g. This value of saturation magnetization is close to the value given by Slater-Pauling rule [14, 15, 27].

According to Slater-Pauling rule, magnetic moment per unit cell is given by $M = N_v - 24$, where N_v is the number of valence electrons in one unit cell. The value of M_s obtained for CFA nanoparticles different from the bulk value seems to be due to mixed phases of $L2_1$, B2 and A2 type structure.

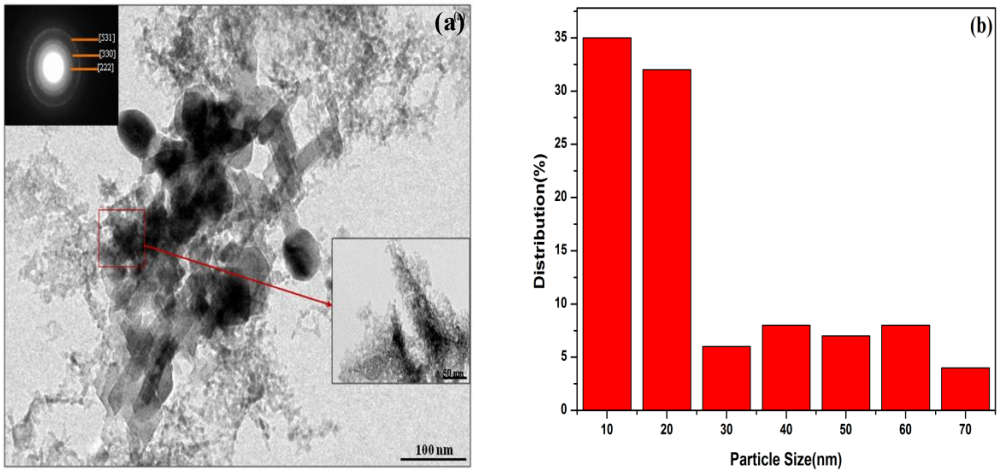

Fig. 3. (a) Transmission electron microscopy (TEM) micrograph of the synthesized Co_2FeAl nanoparticles; the insets show the selected area electron diffraction pattern and high resolution image of marked portion and (b) Particle size distribution histogram from TEM image (Fig. 3(a)).

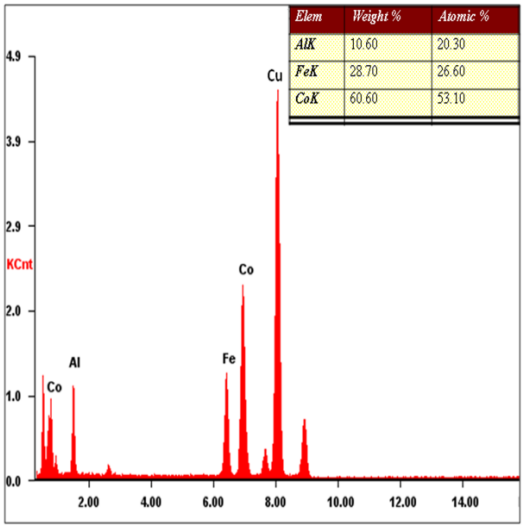

Fig. 4. Energy dispersive X-ray analyzed (EDAX) spectrum of the synthesized Co_2FeAl nanoparticles.

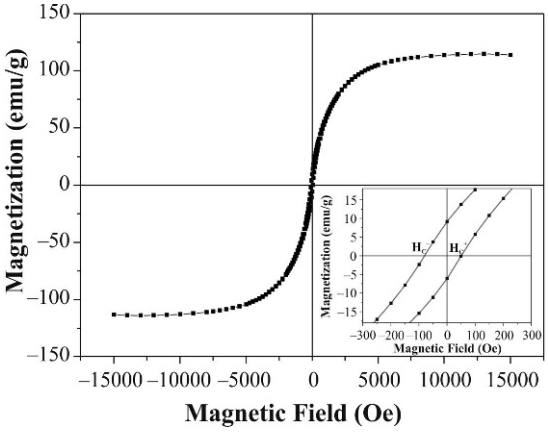

Fig. 5. Magnetization (M-H) characteristics of the synthesized Co_2FeAl nanoparticles.

4. Conclusions

In this report, the synthesis and characterization of Heusler alloy Co_2FeAl nanoparticles have been demonstrated. XRD and SAED results confirm the formation of CFA alloy phases ($L2_1$, B2 and A2). TEM analysis shows the formation of nanoparticles size ranging from 10 nm to 50 nm which is in good agreement with crystallite size estimated from XRD. The magnetization behaviour of CFA nanoparticles shows ferromagnetic behaviour at room temperature with a saturation magnetization of 115 emu/g, which is close to bulk value of CFA alloy as reported by Slater-Pauling curve.

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