

# Synthesis and Magnetic Properties of $\text{Co}_{1-x}\text{Ir}_x$ Alloy Nanoparticles for High-Frequency Applications

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$\text{Co}_{1-x}\text{Ir}_x$  ( $x = 10, 20, \text{ and } 30$ ) alloy nanoparticles were prepared using a high-temperature chemical reduction technique in an inert atmosphere for the first time. High-resolution electron microscopy studies show the formation of nearly monodispersed  $\text{Co}_{1-x}\text{Ir}_x$  alloy nanoparticles having the hexagonal close packed structure. The sizes of the particles were dictated by controlling the reaction parameters and the type of surfactants. Superconducting quantum interference device (SQUID) magnetometry studies showed soft magnetic behavior at 300 K and also at 5 K. The as-prepared, nearly dispersed nanoparticles were assembled and fixed on a polymer substrate. The microwave properties measured by ferromagnetic resonance at 9.61 GHz indicate a minimum line width of about 300 Oe.

**Index Terms**—Chemical synthesis and high-frequency applications, Co-Ir alloy nanoparticles, nanoparticles.

## I. INTRODUCTION

HEXAGONAL close packed (hcp)-Co-based metallic alloys are important magnetic materials for the high-density magnetic recording media [1]. The recording characteristics have been shown to be improved by the addition of 5d transition elements to the Co based thin film media. On the other hand, for high-frequency device applications, much research has been done on the magnetization dynamics in ferromagnetic materials [2]–[4]. However, to improve the high-frequency isotropic magnetic properties using ferromagnetic materials, the ferromagnetic resonance frequency,  $f_r$ , of the material should be increased by increasing the magnetic anisotropy field. Superparamagnetism has isotropic magnetic properties and no hysteresis loss in a dc field and its thermal equilibrium magnetic susceptibility, can be described as

$$\chi_{\text{dc}}^{\text{particle}} = VM_s^2/3k_B T. \quad (1)$$

Here,  $V$  is the volume of the superparamagnetic nanoparticles,  $M_s$  is the saturation magnetization,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature. In an ac field, the magnetic susceptibility  $\chi_{\text{ac}}^{\text{particle}}$  can be described as

$$\chi_{\text{ac}}^{\text{particle}} = \chi_{\text{dc}}^{\text{particle}} \left( \frac{1}{1 + (f/f_b)^2} - i \frac{f/f_b}{1 + (f/f_b)^2} \right) \quad (2)$$

$$f_b = f_0 \exp(-\Delta EV/k_B T) \quad (3)$$

where  $f$  is the frequency,  $f_b$  is the blocking frequency defined as the magnetic potential barrier height per unit volume, and  $f_0$  is the maximum relaxation frequency which is roughly the same as the ferromagnetic resonance frequency  $f_r$  [4]. According to (2) and (3), the superparamagnetic properties are maintained up to  $f_b$ . Therefore, in order to make  $f_b$  and  $\chi_{\text{dc}}^{\text{particle}}$  higher, high

$f_r$  and low  $\Delta E$  are needed. However, in the case of magnetic materials with positive uniaxial magnetocrystalline anisotropy,  $f_r$  and  $\Delta E$  are described as

$$f_r = \gamma K_u / \pi M_s$$

$$\Delta E = K_u \quad (4)$$

where  $K_u$  is magnetic anisotropy energy and  $\gamma$  is gyromagnetic constant. Thus, both high  $\Delta E$  and low  $K_u$  cannot be satisfied simultaneously. Since 5d transition elements possess large spin-orbit coupling, it is expected that these elements significantly influence the magneto crystalline anisotropy energy of the ferromagnetic 3-d alloys. For example, face centered tetragonal (fct) 3-d–5d alloys with  $L1_0$  structure, viz., FePt and CoPt, the 5d elements greatly enhance the magnetocrystalline anisotropy energy  $K_1$  through its large spin-orbit coupling and strong 3-d–5d hybridization [5]. In contrast, Kikuchi *et al.* showed that as the Ir content increases, the sign of  $K_1$  changes from positive to negative indicating that the easy axis of magnetization rotates from the  $c$  axis to the  $c$ -plane in the case of thin films [6]. We have also proposed the hexagonal close packed structured  $C$ -plane oriented soft magnetic  $\text{Co}_{1-x}\text{Ir}_x$  alloy thin films for high-frequency applications [7]. In order to realize the same phenomena in nanoparticles, we synthesized  $\text{Co}_{1-x}\text{Ir}_x$  alloy nanoparticles and studied its structural and magnetic properties.

## II. EXPERIMENTAL PROCEDURE

The experiments were carried out using standard airless procedures. In a typical synthesis: 1) 25 ml octyle ether, 2 mmol of 1,2 hexadecanediol, anhydrous  $\text{CoCl}_2$  and  $\text{Ir}(\text{acac})_3$  in the respective ratios were added together and temperature was increased to 100°C and kept for 10 min. 2) 0.5 mmol of oleic acid (OA) and 0.5 mmol of oleylamine (OY) or triphenylphosphine (TOP) were added and the temperature was increased to 200°C and kept for 15 min. 3) A solution of super hydride ( $\text{LiBEt}_3\text{H}$  of 1 M THF solution, 2 ml) was added dropwise, and the reaction temperature was increased to 260 °C. The reaction was held at

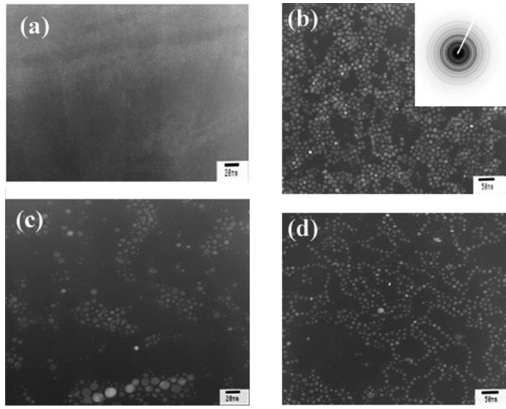


Fig. 1. TEM micrographs of the as-synthesized  $\text{Co}_{1-x}\text{Ir}_x$  alloy nanoparticles. (a) and (b) show the size-controlled synthesis of  $\text{Co}_{90}\text{Ir}_{10}$  alloy nanoparticles using different surfactants, (c)  $\text{Co}_{80}\text{Ir}_{20}$ , and (d)  $\text{Co}_{70}\text{Ir}_{30}$  alloy nanoparticles. Inset of (b) shows the electron diffraction pattern for the same sample.

260 °C for 30 min. The black solution was cooled to room temperature and washed with ethanol several times and redispersed in hexane without any size-selective precipitation.

The structure, size, and morphology of the Co-Ir alloy nanoparticles were investigated using transmission electron microscopy (TEM, JEOL-200 CX operating at 200 kV) equipped with an energy dispersive X-ray spectroscopy (EDXS) option. The samples for TEM analysis were prepared by depositing one drop of hexane dispersion of Co-Ir particles on carbon coated copper grids followed by natural evaporation. Magnetization measurements were carried out with an Quantum Design model 5000 MPMS magnetometer over the temperature range from 5–300 K and in an applied magnetic fields up to 5 T. X-band frequency ferromagnetic resonance (FMR) was performed with in plane and out-of-plane FMR conditions by using  $\text{TE}_{102}$  rectangular cavity at room temperature.

### III. RESULTS AND DISCUSSION

Fig. 1 shows the TEM images of  $\text{Co}_{1-x}\text{Ir}_x$  ( $x = 10, 20,$  and  $30$ ) alloy nanoparticles. The average shape of the particles is spherical in nature and in the range of 3–6 nm. The electron diffraction pattern [Fig. 1(b) inset] clearly showed the formation of hcp structure. The sizes of the particles are dictated by control of the surfactants. For example, in the case of  $\text{Co}_{90}\text{Ir}_{10}$  alloy nanoparticles, when the surfactants oleic acid and oleamine were used at a ratio of 1 : 1, the effective particle size was as small as  $\sim 3$  nm [Fig. 2(a)]. However, when the surfactants of oleamine and triphenylphosphine were used as 1 : 1 ratio, the particle size was  $\sim 6$  nm as shown in Fig. 1(b)–(d). Fig. 2 shows magnetization curves for the average particle size of 6-nm  $\text{Co}_{90}\text{Ir}_{10}$  alloy nanoparticles measured at 300 and at 5 K using the MPMS 5-SQUID magnetometer. The hysteresis loop showed soft ferromagnetic behavior. The coercivity values were only about 100 Oe at 300 K and as well as 5 K. The zero field cooled (ZFC) and field cooled (FC) measurements for the  $\text{Co}_{90}\text{Ir}_{10}$  nanoparticles in Fig. 3 depicted that the blocking temperature ( $T_b$ ) fall above the room temperature. The ferromagnetic behavior was also observed for the  $\sim 6$ -nm  $\text{Co}_{80}\text{Ir}_{20}$  and  $\text{Co}_{70}\text{Ir}_{30}$  alloy nanoparticles [Fig. 1(c) and (d)] except for the

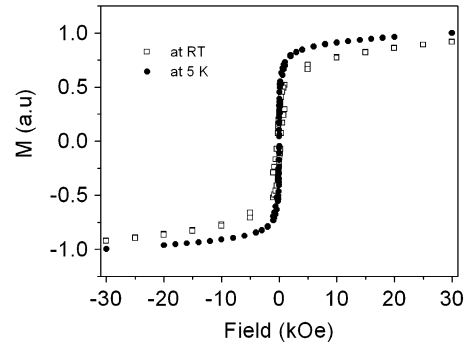


Fig. 2. DC magnetization curves of 6-nm  $\text{Co}_{90}\text{Ir}_{10}$  nanoparticles measured at 5 and 300 K.

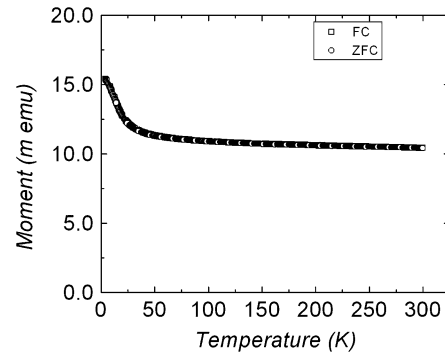


Fig. 3. ZFC and FC curves of the  $\text{Co}_{90}\text{Ir}_{10}$  alloy nanoparticles.

$\sim 3$ -nm  $\text{Co}_{90}\text{Ir}_{10}$  alloy nanoparticles which showed superparamagnetic behavior. From the above results we believe that the superparamagnetic limit for these nanoparticles will be below 6 nm. Since 5d transition elements like Ir possess very large spin-orbit coupling, it is expected that these elements will significantly influence the magneto crystalline anisotropy energy (MAE) of the ferromagnetic 3-d metals like Co. Hence, by controlling the Ir content it is possible to produce soft magnetic  $\text{Co}_{1-x}\text{Ir}_x$  alloys with different compositions.

In the case of  $K_u$  measurement, one can easily orient the  $c$  axis of the nanoparticles with positive  $K_u$  by packing the particles to polymer in a strong external magnetic field. Unfortunately, the  $K_u$  value of these  $\text{Co}_{1-x}\text{Ir}_x$  alloy nanoparticles with negative  $K_u$  cannot be evaluated using the saturation torque method, since it is difficult to orient the  $c$  axis of all particles with negative  $K_u$  in one direction by using magnetic field, because the  $c$  axis of the particle with negative  $K_u$  is not an easy axis. Also, by using rotational torque loss method, one can evaluate the maximum switching field as  $H_k$  of random oriented nanoparticles with positive  $K_u$ . However, in the case of negative  $K_u$ , the maximum switching field depend on not  $K_u$  but  $K_4$  as  $c$ -plane anisotropy. Hence, using the rotational torque loss method, even if we can evaluate  $K_4$  value,  $K_u$  cannot be evaluated. Since our  $\text{Co}_{1-x}\text{Ir}_x$  alloy nanoparticles possess hcp structure with soft magnetic properties as in the case of thin films [7], the existence of negative  $K_u$  will also be possible. For the high-frequency applications (construction of microinductors and nanoinductors with high permeability) the soft magnetic materials must have narrow line width in addition to the other parameters. Hence as-produced nanoparticles were

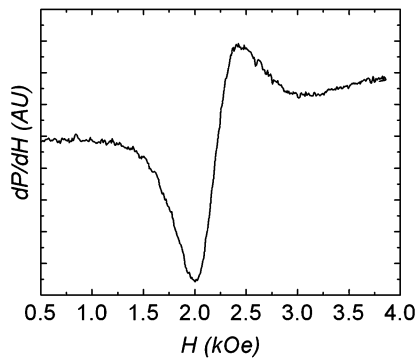


Fig. 4. Room temperature in-plane ferromagnetic resonance spectra of the 6-nm  $\text{Co}_{90}\text{Ir}_{10}$  alloy nanoparticles.

measured for microwave properties (ferromagnetic resonance) at X-band frequency (9.61 GHz). The as-prepared, nearly dispersed  $\text{Co}_{90}\text{Ir}_{10}$  alloy nanoparticles were assembled and fixed on a thin polymer substrate using an epoxy. The microwave properties measured by ferromagnetic resonance (FMR) at 9.61 GHz indicate a minimum line width of about 300 Oe as shown in Fig. 4.

In conclusion, the size- and composition-controlled  $\text{Co}_{1-x}\text{Ir}_x$  alloy nanoparticles have been synthesized using the chemical reduction technique. The as-synthesized particles show the soft magnetic behavior and the ferromagnetic resonance measurements at 9.61 GHz show the average line width of about 300 Oe.

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