Synthesis of iron selenide nanocrystals by thermal decomposition

Chun-Rong Lin (林春榮), Yu-Jhan Siao (蕭育展), and Shih-Zong Lu (盧世宗)

Institute of Nanotechnology and Department of Mechanical Engineering, Southern Taiwan University, Tainan County 710, Taiwan

We have synthesized two kinds of NiAs-type $Fe_{1-x}Se$ nanocrystals with hexagonal (H) and monoclinic (M) structures by the thermal decomposition and reaction of the ferrous chloride with selenium in a high-boiling organic solvent. The mean size of nanocrystals is about 40 nm. Magnetic moment configuration of H-phase changes from antiferromagnetism into ferrimagnetism when the temperature is raised above 130 K as shown from temperature-dependent magnetization and coercivity measurements. As for the M-phase, antiferromagnetism and ferrimagnetism coexist in the temperature between 77 and 300 K. Moreover, the saturation magnetization σ_S (300 K) and coercivity H_C(300 K) of M-phase are 4.3 emu/g and 3300 Oe, respectively. While for the H-phase the σ_S (300 K) and H_C(300 K) are 7.2 emu/g and 700 Oe, respectively. The phase transformations of $Fe_{1-x}Se$ nanocrystals were investigated using differential scanning calorimetry (DSC), transmission electron microscopy (TEM), and x-ray diffraction (XRD).

* This project is financially sponsored by National Science Council (grand no. NSC 96-2112-M-218 -001-MY3).

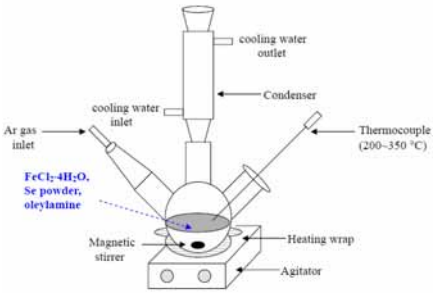
Introduction

Iron selenides Fe-Se with the NiAs-like crystal structure, which extends over a certain composition range at room temperature, at least from 51 to 59 at.% selenium. Within this range the phase exists as a hexagonal NiAs-like structure with approximate composition Fe_7Se_8, and as a monoclinic deformation of the same phase, with approximate composition Fe_3Se_4.[1,2]. Meanwhile, the magnetic behavior of Fe-Se with the NiAs-type crystal structure is strongly composition dependent [2]. In this work, we report the magnetic properties of both two NiAs-type Fe-Se compounds which were synthesized by the thermal decomposition method.

Results and discussion

Fig. 1 shows the XRD patterns for the synthesized samples recorded at room temperature. All diffraction peaks display in Fig. 1(a) and (b) can be indexed on the hexagonal and monoclinic unit cell, respectively. The composition has also been confirmed using inductively coupled plasma mass spectroscopy (ICP-MS), which indicates that the Fe:Se concentration is very close to the expected 7:8 and 3:4 ratio for H-phase and M-phase, respectively. TEM images show that the synthesized compounds have the particle sizes in the range from 100 to 200 nm. Magnetic measurements reveal that the magnetic moment configuration of H-phase changes from antiferromagnetism into ferrimagnetism when the temperature is raised above 130 K as shown from temperature-dependent magnetization σ (T) [Fig. 2(a1)], magnetization measured at 1.1 Tesla ($\sigma_{1.1\ T}$) and coercivity H_C measurements [Fig. 2(a3)]. As for the M-phase, a two-step magnetic transition was detected at temperature of 190K and 340 K [Fig. 2(b1)]. Both magnetic transitions correspond to the various Fe:Se concentration in the synthesized sample [2]. In addition, temperature-dependent H_C, remanence(σ_R), and $\sigma_{1.1\ T}$ increase to show a maximum at 270 K and dropped as the temperature decreases. This temperature indicates the antiferromagnetism and ferrimagnetism coexist in the temperature between 77 and 270 K [Fig. 2(b2) and (b3)]. Moreover, the magnetization $\sigma_{1.1\ T}$ (300 K) and coercivity H_C(300 K) of M-phase are 4.3 emu/g and 3300 Oe, respectively. While for the H-phase the $\sigma_{1.1\ T}$ (300 K) and H_C(300 K) are 7.2 emu/g and 700 Oe, respectively. Detailed magnetic behavior of both compounds was discussed in terms of iron vacancies distribution over the crystal lattice.

Experiments



Apparatus for the preparation of magnetic nanoparticles..

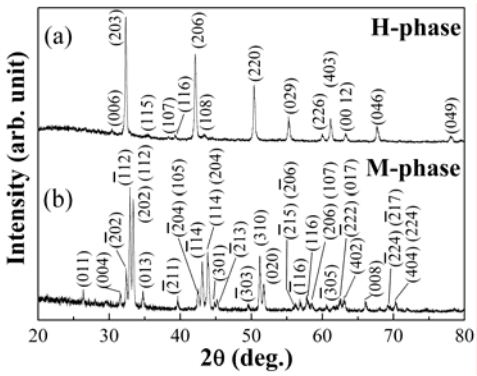


Fig. 1 X-ray diffraction patterns of Fe-Se nanocrystals with (a) hexagonal and (b) monoclinic structures.

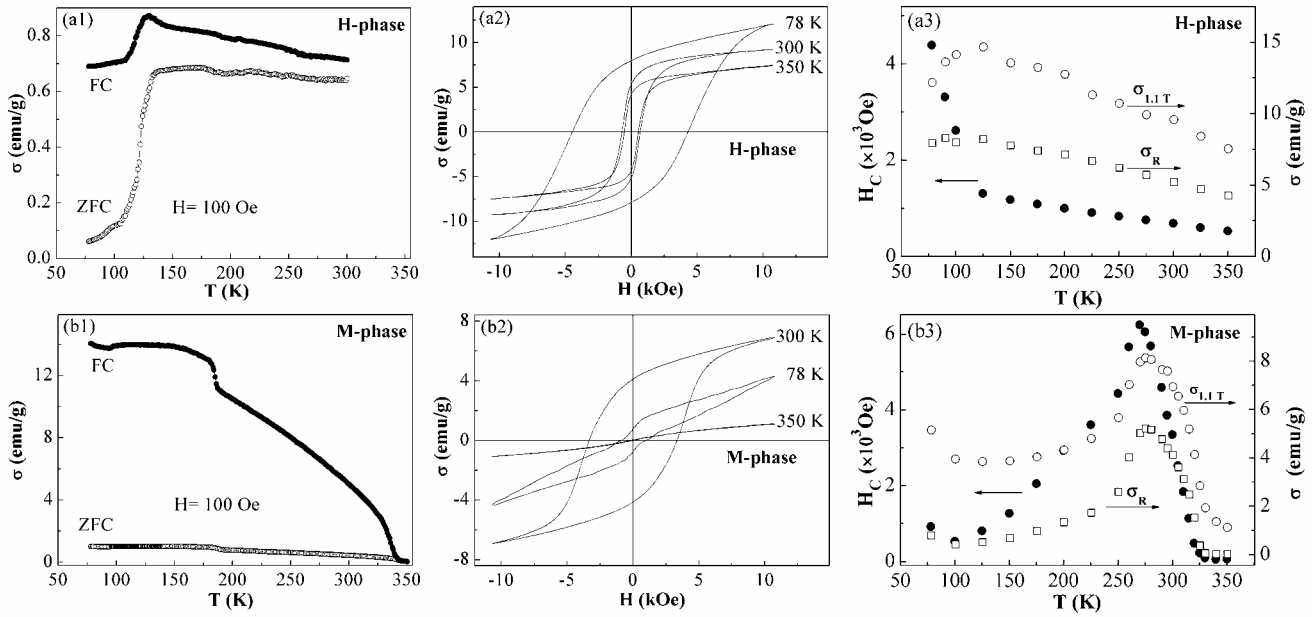


Fig. 2 Magnetic measurements for Fe-Se nanocrystals with (a) hexagonal and (b) monoclinic structures:
(a1) and (b1): Magnetization versus temperature for field-cooled (FC) and zero-field cooled (ZFC) measurements at applied field of H = 100 Oe.
(a2) and (b2): Selected hysteresis loops measured at different temperatures.
(a3) and (b3): Coercivity (H_C), remanence(σ_R), and magnetization measured at 1.1 Tesla ($\sigma_{1.1\ T}$) versus temperature.

References

[1] P. Terzieff and K. L. Komarek, Mh. Chem. 109, 651 (1978).
[2] P. Terzieff and K. L. Komarek, Mh. Chem. 109, 1037 (1978).

CONTACT :
Chun-Rong Lin
Institute of Nanotechnology and Department of Mechanical Engineering, Southern Taiwan University
E-mail : crlin@mail.stut.edu.tw; crlinspin@gmail.com
Tel : +886-6-2533131 ext. 3547
Fax : +886-6-2425092