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Iron Sulfide Nanoparticles: Preparation, Structure, Magnetic Properties

Ruslan D. Ivantsov*
Irina S. Edelman†
Andrey A. Dubrovsky‡
Kirensky Institute of Physics, Federal Research Center KSC SB RAS
Akademgorodok, 50/38, Krasnoyarsk, 660036
Russia
Sergey M. Zharkov§
Dmitry P. Velikanov¶
Kirensky Institute of Physics, Federal Research Center KSC SB RAS
Akademgorodok, 50/38, Krasnoyarsk, 660036
Siberian Federal University
Svobodny, 79, Krasnoyarsk, 660041
Russia
Chun-Rong Lin‖
Yaw-Teng Tseng
Department of Applied Physics, National Pingtung University
Pingtung City, Pingtung County, 90003
Taiwan
Kun-Yauh Shih
Department of Applied Chemistry, National Pingtung University
Pingtung City, Pingtung County, 90003
Taiwan

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The series of iron sulfide nanoparticles (NPs) were synthesized with the polyol mediated process which exploits high-boiling polyalcohol solvents at different boiling temperatures (T_B) what determined the NPs phase state from Fe_3S_4 to FeS. The XRD and HRTEM revealed the content of the Fe_3S_4 cubic phase to reduce linearly with the T_B increase, and at T_B=320°C the FeS phase became predominant. Non monotonous coercivity dependence on the NPs phase state is revealed and interpreted.

Keywords: Fe sulfides, Fe_xS_y, nanoparticles, magnetic properties.
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Iron sulphide nanoparticles (NPs) attract great attention owing, in particular, to wide range of their applications (e.g., [1–4]). Iron sulfide compounds Fe_xS_y demonstrate a wide range of

* ird@iph.krasn.ru
† ise@iph.krasn.ru
‡ andre-do@yandex.ru
§ zharkov@iph.krasn.ru
¶ adpona1@gmail.com
‖ crlin@mail.nptu.edu.tw

magnetic properties in dependence on the x:y ratio. The most frequently studied among them are FeS, Fe_7S_8, Fe_3S_4, and FeS_2, called troilite, pyrrhotite, greigite and pyrite, respectively. Many authors have shown that the phase state and properties of iron sulfide NPs are exceptionally sensitive to the technological conditions what can be used to control these properties. The present paper is devoted to the role of the boiling temperature (T_B) on the phase composition and properties of Fe_xS_y (NPs) fabricated with polyol mediated process.

All reagents are of analytic purity and were used without further purification. In a typical synthesis, a mixture of iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), sulfur powder (S), and octadecylamine (ODA) were added into a three-neck round-bottom flask equipped with a magnetic stirrer and an inlet of argon gas. The mixture was dewatered at 120 °C for 30 min, and then heated to 200 °C with a rate of 10 K/min, maintained at this temperature for 30 min, and, finely, heated to refluxing temperatures (T_B between 240 and 320 °C for 1 hr. The resulting black NPs powder was collected by a magnet and rinsed with 70 °C solvent of ethanol/hexane several times to remove ODA, and dried in a vacuum at 80 °C for 1 hr. Notations NPs 240, NPs 250, and so, will be used further in accordance with T_B.

XRD patterns of NPs powdered samples are shown in Fig. 1. Almost all peaks of NPs 240 (Fig. 1 a)) and 250 were indexed by cubic cell (Fd-3m) with parameters close to Fe_3S_4, greigite [PDF4+ No 04-008-7806], while all peaks of NPs 320 were indexed by hexagonal cell (P63/mmc) with parameters which can be referred both to Fe_7S_8, pyrrhotite [PDF4+ No04-011-1582], or to FeS, troilite. Coexistence of several phases was indicated for all other samples (Fig. 1 b)). Note that, in principle, Fe_7S_8 can exist both in hexagonal and monoclinic phases. At that, first of them is antiferromagnetic while the second one is ferromagnetic. HRTEM image of the NPs 240 has shown that most of the nanoparticles are irregular near-rectangular or hexagon plates with lateral dimensions of about 50 nm. The SAED data describing the nanoparticles local structure were identical to the XRD data. Both SAED and XRD give no unambiguous answer about the higher temperature phase: whether it was Fe_7S_8 or FeS.

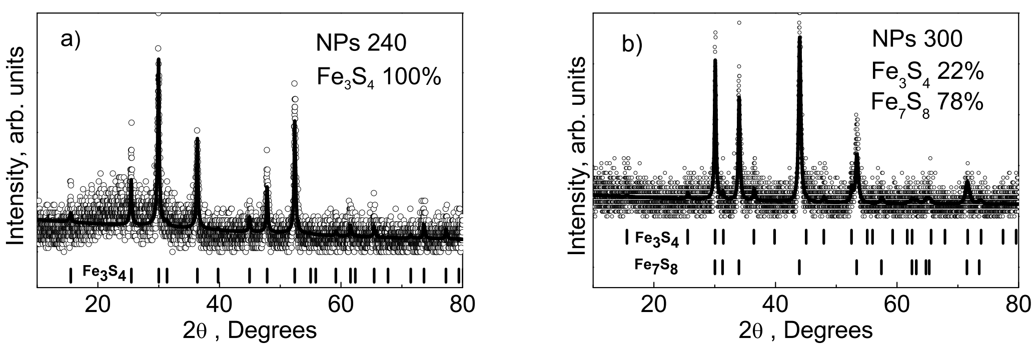

Fig. 1. The difference Rietveld plots of the samples NPs 240 (a) and NPs 300 (b)

Fig. 2 a) shows the magnetization curves of several samples with hysteresis loops indicating the typical ferromagnetic behavior. The magnetization curve characteristics of NPs 240 are in good agreement with that reported for Fe_3S_4. Identity of hysteresis loops shape of NPs 240–280 and the gradual magnetization decrease from NPs 240 to NPs 280 allow statement that they consist of the ferromagnetic Fe_3S_4 phase and the phase having no resulting magnetic

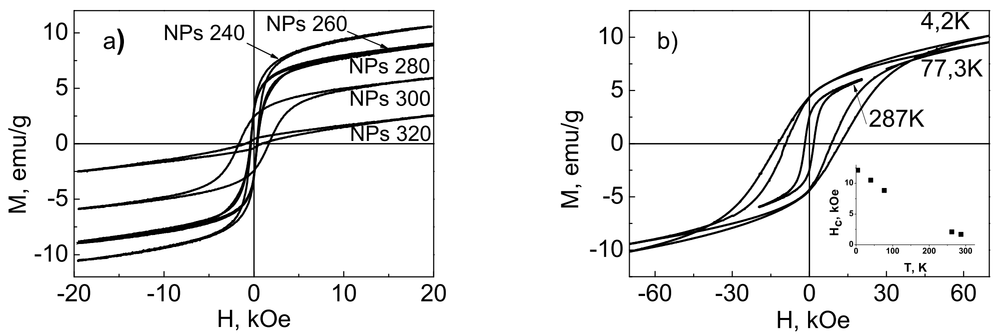

Fig. 2. a) Room temperature hysteresis loops of nanoparticles, NPs numbers are shown in the graph. b) Hysteresis loops of NPs 300 at different measurement temperatures. Inset: The sample NPs 300 H_c temperature dependence

moment, that is, FeS or/and hexagonal Fe_xS_y. For NPs 300, the hysteresis loop shape changes dramatically: room temperature coercivity, H_c, becomes approximately one order of value larger comparing to other samples and it increases strongly with the temperature decrease (Fig. 2 b)) while for other samples H_c is almost independent of temperature (Fig. 3). The NPs 300 H_c temperature behavior (inset in Fig. 2 b)) recollects the H_c increase observed for the monoclinic Fe_7S_8 NPs observed in Ref. [5]. At the same time, XRD detects the hexagonal phase prevalence in NPs 300. So, one can conclude that ferromagnetic state can be realized in the hexagonal Fe_7S_8 NPs, possibly, because of small lattice distortions or strains. The assumption can be supported by the fact that after the additional heating of this sample at 200 °C during 1 hr, peculiarities of the hysteresis loop disappears and it becomes similar to loop of NPs 240–280. For NPs boiled at higher temperatures, hysteresis loop changes again. Magnetization curve looks like the superposition of the wide hysteresis loop with very low M_s and paramagnetic contribution.

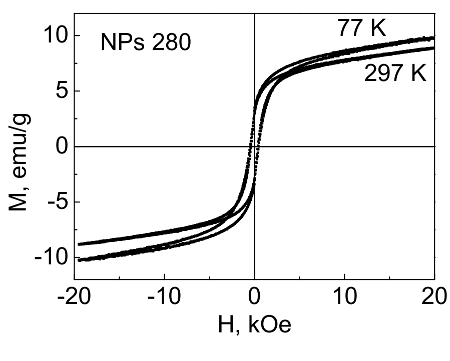

Fig. 3. Hysteresis loops of NPs 280 at temperatures 297 and 77 K

Combining the results of magnetic measurements with the structural data, the next phase compositions of NPs ensembles under study could be proposed. NPs 240 contains the Fe_3S_4 phase only. NPs 250, 260, 280 contain Fe_3S_4 phase in the diminishing concentrations and FeS in the growing concentrations. NPs 300, 310 contain Fe_7S_8 phase, at that high coercivity ferromagnetic state is possible in the hexagonal Fe_7S_8. NPs 320 contain some nonmagnetic phase and Fe_3O_4 phase in superparamagnetic state at higher temperatures and in the frozen ferrimagnetic state at lower temperatures. Phase composition and magnetic properties of iron sulphide NPs synthesized with polyol mediated process can be governed by the boiling temperature.

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Наночастицы сульфида железа: синтез, структура, магнитные свойства

Руслан Д. Иванцов, Ирина С. Эдельман, Андрей А. Дубровский
Институт физики им. Л. В. Киренского, КНЦ СО РАН
Академгородок, 50/38, Красноярск, 660036
Россия
Сергей М. Жарков, Дмитрий П. Великанов
Сибирский федеральный университет
Свободный, 79, Красноярск, 660041
Россия
Чун-Рон Лин, Йау-Тенг Чжень, Кун-Йау Ши,
Департамент прикладной физики, Национальный университет Пинтунга
Пинтунг, район Пинтунга, 90003
Тайвань

Серия наночастиц (NPs) сульфидов железа синтезирована с помощью полиольного метода, в котором используются высокотемпературные растворы полиспиртов при различных температурах (T_B), что определяет фазовый состав NPs от Fe_3S_4 до FeS. XRD и HRTEM показали, что содержание кубической фазы Fe_3S_4 в NPs линейно уменьшается при увеличении T_B и при T_B=320° C гексагональная фаза FeS становится преобладающей. Обнаружена и объяснена немонотонная зависимость коэрцитивной силы NPs от их фазового состава.

Ключевые слова: сульфиды железа, Fe_xS_y, наночастицы, магнитные свойства.