



Stable colloidal solutions of strontium hexaferrite hard magnetic nanoparticles†

Lev A. Trusov,^{*ab} Alexander V. Vasiliev,^{ab} Maria R. Lukatskaya,^c Dmitry D. Zaytsev,^a Martin Jansen^d and Pavel E. Kazin^b

Cite this: *Chem. Commun.*, 2014, 50, 14581

Received 21st May 2014,
Accepted 24th September 2014

DOI: 10.1039/c4cc03870c

www.rsc.org/chemcomm

Herein we demonstrate an approach to prepare a colloidal solution of strontium hexaferrite via a glass-ceramic route. The as obtained colloids are stable and resistive to aggregation or sedimentation. They reveal outstanding magnetic and magneto-optical properties because of their platelet-like anisotropic shape and high permanent magnetic moment.

Ferrofluids (or magnetic fluids) are colloidal suspensions of magnetic nanoparticles in carrier liquids.¹ They attract considerable attention because of the fact that their properties are strongly dependent on moderate magnetic fields. The majority of presently available ferrofluids are based on the spinel-type ferrites (*e.g.*, magnetite Fe₃O₄, maghemite γ-Fe₂O₃, CoFe₂O₄, *etc.*) in the superparamagnetic state, featuring particles with approximately 10 nm in diameter.² Colloids containing hard ferrite particles are of particular interest because of their distinct feature, as there is high magnetocrystalline anisotropy of the material and platelet-like anisotropic particle shape.

Hard ferrites (or M-type hexaferrites) are well-known magnetic materials that are generally used for the production of ceramic magnets. They are commonly implemented in high-density magnetic tape recording³ and microwave devices.⁴ The preparation of hexaferrite-based magnetic fluids is impaired by strong inter-particle magnetic interactions that lead to agglomeration and subsequent sedimentation.

The stabilization of particles in a colloidal solution can be accomplished using two repulsion mechanisms: steric repulsion by surfactants and electrostatic repulsion by charged particle surfaces. The attraction between magnetic particles is caused by van der Waals (short-range) and magnetic dipole-dipole

(long-range) forces. Superparamagnetic particles do not display coercivity and remanence; thus, attractive interactions between them are weak (mainly provided by van der Waals attraction) and these particles can be easily dispersed in various carrier liquids. Furthermore, soft magnetic ferrites can also be formed at moderate temperatures in an aqueous medium and directly stabilized during the synthesis, *e.g.* by coating with surfactants. Unlike such soft magnetic ferrites, the production of hard ferrite particles requires temperatures higher than 500 °C, rendering direct synthesis and stabilization in a liquid impossible. To date, several attempts to prepare hard ferrite ferrofluids have been undertaken;^{5–7} however, stable colloidal solutions of the particles with a large remanent magnetic moment and high coercivity have not yet been reported.

Herein, we describe the synthesis and peculiar properties of stable colloidal solutions of strontium hexaferrite single crystal nanoparticles with large spontaneous magnetization and coercivity. We used oxide glasses in the SrO-Fe₂O₃-(Al₂O₃)-B₂O₃ system as an initial material, which was heat treated to form strontium hexaferrite embedded in a non-magnetic borate matrix^{8–10} (see Section S1 for more experimental details, ESI†). The initial dispersed, non-aggregated state of these particles within the glass-ceramic was crucial for the formation of the stable hexaferrite colloids.

Because nanoparticles and the matrix were chemically different, the colloids could be harvested by simply dissolving the matrix in diluted acids. For this purpose, glass-ceramics containing hard magnetic hexaferrite nanoparticles were ground and treated with 3% HCl at 60 °C. The magnetic particles were subsequently precipitated applying a magnetic field and separated from the solution by decantation. Finally, water was added to disperse the precipitate, with subsequent ultrasonic treatment forming the final colloidal solution. Residual particle aggregates were magnetically separated and removed.

The colloidal solutions obtained were transparent, and their colors varied between pale yellow and red-brown (depending on the concentration).

The resulting colloids remained stable for over one year. The short-term exposure of the solutions to a magnetic field led to

^a Department of Materials Science, Moscow State University, 119991, Moscow, Russia. E-mail: trusov@inorg.chem.msu.ru

^b Department of Chemistry, Moscow State University, 119991, Moscow, Russia

^c Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA

^d Max Planck Institute for Solid State Research, D-70569, Stuttgart, Germany

† Electronic supplementary information (ESI) available: Experimental details, Fig. S1–S7. See DOI: 10.1039/c4cc03870c

visible color changes (Fig. S1, ESI[†]). The ageing of the colloids in a gradient magnetic field of a NdFeB magnet for several hours resulted in the separation of a concentrated magnetic fluid phase from the solvent without any solid precipitate (Fig. S2, ESI[†]). This property corresponds to an analogous “gas–liquid” separation of colloidal particles.¹¹ The drops of the condensed phase show a clear interface even in the absence of a magnetic field and can be separated by a syringe. The formation of the liquid-like concentrated phase can be related to a subtle balance between electrostatic repulsion and dipolar magnetic attraction. However, to completely understand this effect would require a detailed separate study. The concentrated product can be ultrasonically redispersed in water to form stable colloids.

The synthesized ferrofluid samples were marked as F680, F740, FA700 and FA750, according to the glass-ceramics used for the preparation (see ESI[†] for details). The samples F680 and F740 contained undoped hexaferrite particles, while particles in FA700 and FA750 were doped with aluminum to improve coercivity.¹⁰

The colloidal solutions were dried, and the resulting powders were studied using X-ray powder diffraction analysis and magnetic measurements. According to XRD data, the powders consist of a single magnetoplumbite (M-type hexaferrite) phase (Fig. S3, ESI[†]). The unit cell parameters of F680 and F740 correspond to pure strontium hexaferrite phase, while the lattice constants of FA700 and FA750 are slightly reduced (Table S1, ESI[†]), indicating the partial substitution of iron by aluminum.¹² The substitution degree x in $\text{SrFe}_{12-x}\text{Al}_x\text{O}_{19}$ is estimated to be 1.2 ± 0.1 by both Vegard's law and EDX analysis. A considerable broadening of the diffraction peaks is observed, reflecting the small particle size. The FWHM for the (h k 0) is distinctly lower than that for the (h k l) reflexes, which indicates an anisotropic shape of the nanoparticles, with their smallest dimension along the c -axis.

Transmission electron microscopy directly reveals the platelet-like shape of the particles typical for hexaferrite nanoparticles (Fig. 1). The hexaferrite particle size in the ferrofluid samples is presented in Table 1. The selected area diffraction patterns (Fig. S4, ESI[†]) collected from single particles have confirmed that the particles are single-crystalline with the c -axis normal to the particle basal plane.

The magnetic measurements of the dried hexaferrite particles reveal their hard-magnetic behavior (Fig. S5, ESI[†], Table 1). The hysteresis loops are similar to those of randomly oriented

Table 1 Properties of colloidal hexaferrite particles

Sample	Size ^a (TEM)		Zeta-potential (mV)	Magnetic properties		
	d (nm)	h (nm)		M_s (emu g ⁻¹)	M_r (emu g ⁻¹)	H_c (Oe)
F680	65	6	+46	58	30	2800
F740	70	7	+63	59	30	3800
FA700	60	5	+45	46	24	4500
FA750	80	7	+48	50	27	5600

^a d and h correspond to mean diameter and thickness of plate-like particles.

single-domain Stoner–Wohlfarth particles, and the M_r/M_s ratio is close to 0.5. The M_s values of the undoped samples approach 60 emu g⁻¹, which is typical for strontium hexaferrite fine powders.¹³ This additionally confirms the good crystallinity and high phase purity of the particles. Doping with aluminum leads to a decrease in the specific magnetization and also provides a significant rise in coercivity of up to 5600 Oe. The samples likely reveal the highest M_r and H_c values for hexaferrite nanoparticles being stabilized in a colloidal solution. Previously reported colloidal particles obtained hydrothermally possessed H_c and M_s values less than 2000 Oe and 22 emu g⁻¹, respectively.⁷

According to zeta-potential measurements taken at pH = 5 (pH of the formed suspensions varies from 3 to 6), the particles in the colloids are positively charged (Table 1). The value of zeta-potential is higher than +45 mV, which corresponds to a good electrostatic stabilization of colloidal systems. We suppose that positive charge is provided by the adsorption of the H⁺ ions from the acidic medium. During colloid preparation, after the treatment of glass-ceramics with acid, the concentration of dissolved ions in the resulting solution is high, resulting in a high ionic strength. This leads to a screening of the surface charge and agglomeration of the particles. Therefore, the addition of DI water to the extracted wet particles results in the ionic dilution and stabilization of the colloids. However, an excessive dilution can lead to an increase in pH and deprotonation of the particle surface. Hence, at pH > 6 the colloids tend to sediment.

Dynamic light scattering measurements show that the diameter distribution profiles are represented by a single peak at 80–100 nm (Fig. S5a, ESI[†]), which correlates with the particle diameter. This indicates that formed colloidal solutions contain only non-aggregated hexaferrite particles.

The magnetic properties of the hexaferrite colloids significantly differ from the magnetic properties of conventional ferrofluids containing superparamagnetic nanoparticles. The hexaferrite hard-magnetic particles possess large permanent magnetic moments fixed along their easy-magnetization axis (crystallographic c -axis) and can freely rotate in a carrier medium when subjected to magnetic field, aligning their magnetic moments along the field direction. On the other hand, thermal motion increases the disorder of the moments. Because of the strong interaction of the particles with the magnetic field, the magnetization curves of the colloids saturate at 10% of the H value of typical superparamagnetic ferrofluids. Therefore, the colloids are very sensitive to the magnetic fields applied: 50% and 95% of saturation magnetization of the F680 sample are achieved at 5 Oe and 150 Oe,

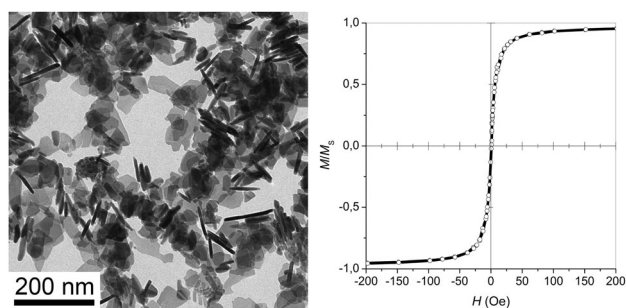


Fig. 1 TEM micrograph of F680 colloidal hexaferrite particles (left) and $M(H)$ curve of the colloid (right).

respectively (Fig. 1). The curve reveals no hysteresis because of free rotation of the particles in the solution. The comparison of specific magnetization of the colloids and respective extracted particles allow calculation of the magnetic phase content. The estimated concentration of strontium hexaferrite in colloidal solutions is about 300 mg l^{-1} . After prolonged condensation in a magnetic field, the resulting concentrated fluids contain about 25 g l^{-1} of strontium hexaferrite.

In addition to high particle coercivity and magnetization, strontium hexaferrite colloids feature an anisotropic platelet-like shape of the nanoparticles. This provides new possibilities as compared to conventional ferrofluids containing spherical particles. For example, previously we have reported self-organization of hexaferrite nanoparticles in anodic alumina channels forming layered aligned nanostructures with anisotropic magnetic properties.¹⁴ Another interesting effect is the formation of the monolayers of aligned plate-like hexaferrite nanoparticles by electrostatic adsorption.¹⁵

Another very important effect is the magnetic field dependent optical transmission of these colloids. It is related to linear dichroism resulting from unequal absorption of polarized light by colloidal solution for different orientations of an anisotropic particle.¹⁶ High absorption takes place when the electrical field vector E of the incident light coincides with the longest particle dimension and *vice versa*. Magnetic field forces the particles to align, resulting in pronounced magneto-optical effect. In non-polarized light, the high absorption is observed when the magnetic field H is oriented parallel to the light propagation direction K . The effect was previously discussed in greater detail for hexaferrite suspensions obtained using hydrothermal treatment.⁷ In Fig. 2A the dependence of transmission on the wavelength of light is shown. The effect is observed in the entire range of visible light. The optical transmission is also highly sensitive to the magnetic field applied (Fig. 2B) as the particles can easily rotate and align.

According to AC-susceptibility measurements of the sample F680 (Fig. S6, ESI[†]), the real part drops while the imaginary part reveals a broad peak at 1300 Hz (300 K) attributed to Brown relaxation. The peak shifts to lower frequencies with temperature decrease as a result of viscosity rise (700 Hz at 280 K). Up to 50 Hz the imaginary part of susceptibility is close to zero since the particles readily orientate in the magnetic field. At higher frequencies the imaginary part rises, indicating the phase lag and energy losses.

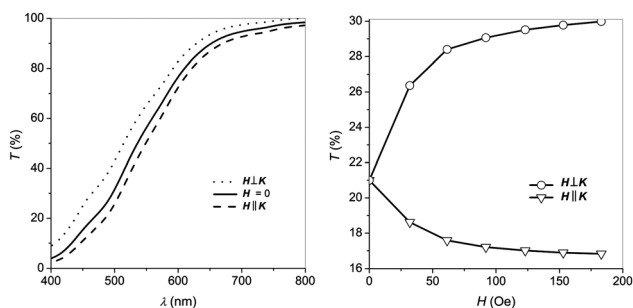


Fig. 2 Optical transmission of F680 sample vs. light wave-length at 180 Oe (left) and vs. magnetic field strength at $\lambda = 470 \text{ nm}$ (right).

The Brownian relaxation time estimated from the peak position is $\tau_B = 1/(2\pi f_{\text{peak}}) = 0.12 \text{ ms}$ (at 300 K).

In alternating magnetic field, the modulation of the optical signal occurs with a doubled frequency (Fig. S7, ESI[†]). This happens because the maximum of transmission corresponds to both positive and negative extreme field values, which is achieved twice per cycle. At low frequencies (below 50 Hz) particles follow the direction of magnetic field, and the optical response is high. On increasing the frequency the response decreases because of the rise in energy dispersion (Fig. S8, ESI[†]). This correlates well with the AC-susceptibility measurements, which provided the frequency limits for particle rotation ($\sim 1 \text{ kHz}$), *i.e.* at high frequency the particles cannot fully follow the field direction and only vibrate lowering the magneto-optical response.

In summary, synthesis of stable strontium hexaferrite colloids was developed by employing glass-ceramics as a source of non-aggregated nanoparticles. The colloidal single crystalline particles possess platelet-like shape with a mean diameter below 100 nm and a thickness of several nanometres. The particles carry a large permanent magnetic moment and exhibit the highest values of intrinsic coercivity (up to 5600 Oe) reported till now for ferrite particles in stable colloids. The colloidal particles are highly sensitive to magnetic field and almost fully align already at 150 Oe. The alignment of these anisotropic particles leads to magnetic field dependent optical transmission. The magneto-optical response with frequencies up to 1 kHz is observed in alternating magnetic fields.

In addition to light modulation by the AC magnetic field and optical detection of magnetic fields described above such colloidal solutions could have a several other potential applications. The enhanced remagnetization losses in comparison with superparamagnetic particles could be used for effective magnetic hyperthermia or technical heating.⁵ The ability for particle oscillation induced by magnetic field is perspective for magneto-mechanical treatment of cancer cells.¹⁷ High dispersibility and low particle aggregation in the colloids are the key factors for the controlled production of magnetic films, coatings and nanostructures. To demonstrate the processability of the colloids we developed anisotropic arrays of aligned hexaferrite nanorods in anodic alumina channels¹⁴ and particle monolayers on solid substrates.¹⁵ In addition the colloids are ready for common film deposition by electrophoresis or magnetic field gradient.^{18,19} Because hexaferrite nanoparticles are well suited for high-density information storage tape systems,^{3,20} our stable colloids of well-dispersed high-quality particles could lead to better performance media.

This research was funded by Russian Foundation for Basic Research, grant No. 14-03-31598.

Notes and references

- M. I. Shliomis, *Sov. Phys. - Usp.*, 1974, **17**, 153.
- Colloidal Magnetic Fluids*, ed. S. Odenbach, Springer, Berlin, Heidelberg, 2009.
- G. Cherubini, R. D. Cideciyan, L. Dellmann, E. Eleftheriou, W. Haerberle, J. Jelitto, V. Kartik, M. A. Lantz, S. Olcer, A. Pantazi, H. E. Rothuizen, D. Berman, W. Imano, P. O. Jubert, G. McClelland, P. V. Koeppel, K. Tsuruta, T. Harasawa, Y. Murata, A. Musha, H. Noguchi, H. Ohtsu, O. Shimizu and R. Suzuki, *IEEE Trans. Magn.*, 2011, **47**, 137.

- 4 V. G. Harris, A. Geiler, Y. Chen, S. D. Yoon, M. Wu, A. Yang, Z. Chen, P. He, P. V. Parimi, X. Zuo, C. E. Patton, M. Abe, O. Acher and C. Vittoria, *J. Magn. Magn. Mater.*, 2009, **321**, 2035.
- 5 R. Muller, R. Hergt, S. Dutz, M. Zeisberger and W. Gawalek, *J. Phys.: Condens. Matter*, 2006, **18**, S2527.
- 6 D. Primc, D. Makovec, D. Lisjak and M. Drofenik, *Nanotechnology*, 2009, **20**, 315605.
- 7 S. E. Kushnir, A. I. Gavrilov, P. E. Kazin, A. V. Grigorieva, Y. D. Tretyakov and M. Jansen, *J. Mater. Chem.*, 2012, **22**, 18893.
- 8 B. T. Shirk and W. R. Buessem, *J. Am. Ceram. Soc.*, 1970, **53**, 192.
- 9 P. E. Kazin, L. A. Trusov, D. D. Zaitsev and Y. D. Tretyakov, *Russ. J. Inorg. Chem.*, 2009, **54**, 2081.
- 10 P. E. Kazin, L. A. Trusov, D. D. Zaitsev, Y. D. Tretyakov and M. Jansen, *J. Magn. Magn. Mater.*, 2008, **320**, 1068.
- 11 E. Dubois, V. Cabuil, F. Boue and R. Perzynski, *J. Chem. Phys.*, 1999, **111**, 7147.
- 12 N. J. Shirtcliffe, S. Thompson, E. S. O'Keefe, S. Appleton and C. C. Perry, *Mater. Res. Bull.*, 2007, **42**, 281.
- 13 T. Koutzarova, S. Kolev, C. Ghelev, K. Grigorov and I. Nedkov, in *Advances in Nanoscale Magnetism*, ed. B. Aktas and F. Mikailov, Springer, Berlin Heidelberg, 2009, pp. 183–203.
- 14 M. R. Lukatskaya, L. A. Trusov, A. A. Eliseev, A. V. Lukashin, M. Jansen, P. E. Kazin and K. S. Napol'skii, *Chem. Commun.*, 2011, **47**, 2396.
- 15 S. E. Kushnir, D. S. Koshkodaev, P. E. Kazin, D. M. Zuev, D. D. Zaitsev and M. Jansen, *Adv. Eng. Mater.*, 2014, **16**, 884.
- 16 T. M. Kwon, P. L. Frattini, L. N. Sadani and M. S. Jhon, *Colloids Surf., A*, 1993, **80**, 47.
- 17 D.-H. Kim, E. A. Rozhkova, I. V. Ulasov, S. D. Bader, T. Rajh, M. S. Lesniak and V. Novosad, *Nat. Mater.*, 2010, **9**, 165.
- 18 D. Lisjak and S. Ovtar, *J. Phys. Chem. B*, 2013, **117**, 1644.
- 19 S. Kolev and T. Koutzarova, *J. Phys.: Conf. Ser.*, 2014, **514**, 012021.
- 20 O. Shimizu, T. Harasawa and H. Noguchi, *30th Symposium on Mass Storage Systems and Technologies*, Santa Clara, CA, 2014, DOI: 10.1109/MSST.2014.6855556.