

Nano Science and Nano Technology

An Indian Journal

- Full Paper

NSNTAIJ, 8(8), 2014 [328-334]

Structural and physical properties of iron nanoparticles synthesized by ionic exchange reaction

F.Blelletta, Z.Hogga*, M.Hafid Laboratory of Engineering Physics and Environment, Department of Physics, Faculty of Sciences, University Ibn Tofail, Kénitra, (MOROCCO) E-mail : hogga_Zhor@yahoo.fr

ABSTRACT

Nanometre-sized iron particles with diameters in the range 5-8.5 nm have been grown within a 30Na2O-60SiO2-10B2O3 glass matrix using a $3Na+ \leftrightarrow$ Fe³⁺ exchange reaction followed by reduction treatment in hydrogen for different temperatures. Electron diffraction pattern shows the presence of FeO and α -Fe particles. Thermal characteristics were studied by DSC while the nanoscale-related magnetic properties were investigated by VSM. The results show depression of magnetization as a function of temperature. This behaviour indicates the occurrence of spin-wave fluctuation in iron core of the studies samples. © 2014 Trade Science Inc. - INDIA

INTRODUCTION

The magnetic properties of nanoparticles are determined by many factors, the key of these including the chemical composition, the type and the degree of defectiveness of the crystal lattice, the particle size and shape, the morphology (for structurally inhomogeneous particles, the interaction of the particle with the surrounding matrix and the neighbouring particles. By changing the nanoparticle size, shape, composition and structure, one can control the magnetic characteristics of the material based on them. However, these factors cannot always be controlled during the synthesis of nanoparticles nearly equal in size and chemical composition; therefore, the properties of nano-materials of the same type can be markedly different. Therefore, magnetic behaviour of nanoparticles of both ferromagnetic and ferrimagnetic materials has attracted considerable

KEYWORDS

Iron nanoparticles; DSC; TEM; Superparamagnetism; Glass matrix.

attention in recent years^[1-4]. Such interest emanates both from new physics expected from these systems as well as their possible applications in high-density magnetic recording domain and as a consequence exhibit phenomena like superparamagnetism, quantum tunnelling of magnetization, enhanced coercivities and giant magnetoresistance^[5,6]. A number of techniques have been developed to synthesize magnetic nanoparticles. Some of these are the colloidal chemical method, high-pressure sputtering, inert gas condensation, layer deposition, mechanical attrition, and the solvated-metal-atom dispersion method^[7,12]. One of the intriguing features of these particles is the observed reduction in saturation magnetization Ms^[6,13]. An interaction between the surface spins and those in the core has been used to explain this behaviour^[14]. More recent investigations have concentrated on the properties of heterogeneous systems consisting of a ferromagnetic metallic core and an

329

antiferromagnetic oxide shell^[6,14,15]. Nanocomposite materials composed of nanometric metal or metal-oxide particles embedded in amorphous matrices, present a variety of interesting magnetic, electric, and catalytic properties that are strongly dependent on nanoparticles size and on their distribution within the matrix^[16,17].

In this work, we have used a $3Na^+ \rightleftharpoons Fe^{3+}$ exchange reaction to prepare nanosized metallic particles and studied inside a glass matrix the growth mechanism associated with the reduction temperature treatment process. This method was used to grow nanoparticles of α -Fe FeO in a sodium-boron-silica glassy medium.

EXPERIMENTS

The glassy region in the ternary sodium-borosilicate system^[18] is wide as shown in Figure 1. Mixtures of the formula $30Na2O-60SiO2-10B2O3 \pmod{6}$ were prepared of chemically pure Na2CO3, SiO2 and B₂O₃ which were calcined first to remove moisture. Na2CO3 and SiO2 were calcined at $180^{\circ}C$ for 4 hours. The appropriate quantity of the mixture was ground and melted in platinum crucible in an electric furnace, at a temperature of above $1450 \,^{\circ}C$. The molten glass was poured into a specially prepared steel mould. The obtained compound was then placed in a temperature of about $450^{\circ}C$ in order to accomplish the annealing process. Sample was maintained in this temperature for 1 hour and cooled to the ambient temperature by steps of 1 °K per minute.

The chosen composition (30Na2O-60SiO2-10B2O3) for our studies is justified by:

i The fact this composition doesn't show any phase mixture and therefore a homogenous distribution of



Figure 1 : (SiO2-B2O3-Na2O) phase diagram

nanoparticles can take place inside the matrix.

i In Na20-B2O3-SiO2 glass system, when Na2O exceeds _{B2O3}, some threefold-coordinated B (triangular) are left in the glass, with the Na + distributed between (BO4)⁻ tetrahedral and nonbriding oxygen^[19].

According to these facts, the glass samples prepared as mentioned above were pulverized to form micrometric particles. The obtained glassy fine powder was mixed to an appropriate quantity of FeCl₃ and heated up to 300°C for 72 hours in a sealed Pyrex container. As we mentioned above the glassy composition contains Na⁺ distributed between (BO4)⁻ tetrahedral and nonbriding oxygen.

The reaction under temperature of such spices with (Fe³⁺, 3 Cl⁻) liberates Fe³⁺ ions in the sample. The obtained compound is then cleaned out using distilled water and submitted to a hydrogen reduction at temperature in the range of 550°C to 650°C during time periods taking 20 min and 1.5 hours.

The microstructures of these powders were studied by a JEM 200CX transmission electron microscope.

Full Paper

Transition temperatures (Tg) were determined using an SII Seiko instrument (SSC/5200) differential scanning calorimeter (DSC) at heating rate of 10 K/min. Magnetic measurements were carried out with the vibrating sample magnetometry (VSM :Digital Measurement System HP model 1660) in the temperature range 20 to 300 K.

RESULTS AND DISCUSSION

Structure

The presence of metallic iron particles has been checked out by electronic transmission microscopy (TEM). Figure 2a, shows the transmission electron micrograph for a specimen whose hydrogen reduction process has been made at 650°C during 20 min; while Figure 2b, the corresponding electron diffraction pattern.

These are typical of all the samples in the present studied system. The values of interplanar spacing d_{hk1} were calculated from the diameters of the rings shown in Figure 2b.

In TABLE 1 the experimental d_{hkl} values are presented and compared with standard (ASTM) data for α -Fe and FeO.

It is evident that the particles are composed of iron and that the most of the observed spices belongs to the α -Fe phase while some of them belong to the FeO phase.



Figure 2a : Transmission electron micrograph for specimen no.3 (TABLE 2)

Aano Soience and Aano Technology Au Judiau Journal



Figure 2b : Electron diffraction pattern for Figure 2a

The same results have been found out for all the studied samples.

TABLE 2, reports the mean size of the particles as function of the reduction temperature under hydrogen atmosphere as well as time treatment.

It emerges from these data that the size of the particles increases with the reduction temperature and/or with the treatment time (Figure 2c). This behaviour agrees with the growth process of metallic particles by "controlled process" inside a glassy matrix^[21].

TABLE 1 : Comparison of interplanar spacings for specimenreduced in hydrogen atmosphere at 650°C during 20 minwith standard ASTM data^[20]

Observed d _{hkl} (nm)	d _{hkl} ASTM standard (nm)		
	α-Fe	FeO	
0.216		0.2153	
0.203	0.2027		
0.143	0.1433		
0.124		0.1243	
0.117	0.1170		
0.101	0.1013		
0.091	0.0906	0.963	
0.083	0.0827		

Temperature transition

Figure 3, shows a typical DSC curve recorded in the studied samples and from which we deduced the glass temperature transition Tg and the thermal stable

> Full Paper

TABLE 2 : mean size of the particles as function of the reduction temperature under hydrogen atmosphere as well as time treatment

Sample	Reduction temperature under hydrogen atmosphere	Mean diameter (nm)	
1	550 °C during 20min	5,5	
2	600 °C during 20 min	6,5	
3	650 °C during 20min	7,1	
4	650 °C during 40min	7,7	
5	650°C during 1,5 h	8,5	



Figure 2c : Evolution of the iron particle size. Sample numbers referred to temperature and time treatment

domain of the compounds.

The recorded data are treated by Origin Pro6.1 Serial: G73S4-6489-7483215 programme. The deduced transition temperatures (Tg) are listed in the TABLE 3. It is shown that the glass matrix is stable in large thermal domain.

Magnetic properties

Magnetic measurements have been carried out us-

ing a Vibrating Sample Magnetometer (VSM). This technique is based on vibrating a sample in a magnetic field to produce an alternating electromagnetic force (emf) within a set of suitably placed pick-up or sensing coils. This induced emf is directly proportional to the magnetic moment m or magnetization M of the sample under test.

Since the tested specimens are powder like, a powder holder is used. This holder is an injection molded plastic part that snaps into the brass trough. Sample mass of 1 mg of powder is put into the opening. A second piece compresses the powder and seals the combination. The assembly snaps into the brass trough for a secure press fit. This material covers the entire temperature range from 20 K to 400 K.

Figure 4, shows an example of the magnetization (M) vs. Magnetic field (H) hysteresis curve for specimen no. 3 at 20 K and 300 K^[27]. The values of Hc, in all the samples are higher than that for bulk iron. Such values arise due to the fact that the particle size of α -Fe is of the order of domain size^[5,6].

In the other hand the variation of the coercive field (Hc) as function of particle size and temperature treatment is reported in Figure 5.

The coercive field is increasing with size particle decreasing while it decreases when the treatment temperature increases for a particle of a given size.

In order to understand such behaviour, we analyzed the variation of the coercive field as function of temperature in the case of a non-interacting ferromagnetic particle system. For ferromagnetic particles of nanometer dimension and having no interaction between them the coercivity Hc is given by^[23]:



Figure 3 : Typical DSC curves recorded in the different studied samples

lano Solence and Aano Technology Au Indian Journal,

Full Paper (

 TABLE 3 : Tg temperatures deduced from DSC measurements

Sample	Tg temperature °C	
1	489	
2	456	
3	456	
4	478	
5	378	

 $H_c = H_{c0} \left[1 - \left(\frac{T}{T_B} \right)^{1/2} \right]$ (1)

Where Hc_0 is the coercivity at T= O K, T is the temperature of measurement and $T_{\rm B}$ the blocking tempera-

ture above which superparamagnetism sets in. TB is correlated to the effective anisotropy constant, *K* and to the ferromagnetic particle volume V:

$$T_B = \frac{KV}{25k} \tag{2}$$

(k is the Boltzmann constant)

An increase in the value of V should also increase TB. From Eq. (1) therefore it follows that the value of Hc should show an increase as the particle size becomes smaller. This is consistent with the observed results. In other side we fitted the Hc data as function of temperature (Eq. (1)) by using $_{\rm Hc0}$ and TB as fit parameters. TABLE 4, resume the calculated values.

We calculated K values for different particle size



Figure 4 : Magnetization vs. magnetic field hysteresis loop for specimen no. 3 at 20 and 300 K





Reno Solence and Reno Technology An Indian Journal

		-			
	sample N° :	Hc0 (Oe)	TB (K)	K (erg/cm ³)(x1 0 ⁷)	
	1	518	1018	4,0	
	2	548	913	2.2	
	3	369	969	1.8	
	4	324	1121	0.5	
	5	218	1084	0.4	
1					

 TABLE 4 : Calculated parameters

by substituting the particle radius and the Obtained T_{B} value in equation:

$$T_B = \frac{KV}{25k}$$

The obtained K values are much larger than that for bulk iron (K=4, 2 x 10^5 erg/cm³). Therefore the iron particles with nanometric dimension grown in the glassy matrix show a large magneto crystalline anisotropy.

The variation of saturation magnetization M as a function of temperature for specimen no. 3 is shown in Figure 6. The M values were determined by the ex-

trapolation of $H^{-1} \rightarrow 0$.

The variation of magnetisation (M) as function temperature can be described by^[3]:

$$M(T) = M(0) [1-BT^{b}]$$

(3)

333

Where B is the Bloch constant and b is the Bloch exponent. Such behaviour can be ascribed to spin-wave fluctuations^[23,24] as also reported in the case of nanosized iron particles^[3].

The studies of magnetization as function of temperature show a transition when increasing temperature. In the case of sample treated at 650 °C during 20 min (sample 3) the temperature transition is close to 150°C. This behaviour can be explained by the fact that our samples contain FeO species. Therefore, the observed transition could correspond to the Neel temperature^[25,26]. But in order to make clear this observation, intense studies of the influence of the particle size are planed. Such studies will cover particle size from nanometric to micrometric dimension.



Figure 6: Variation of magnetization as function of temperature (sample 3)

CONCLUSION

Iron metallic nanoparticles with α -Fe and FeO phases have been grown within a 30Na2O-60SiO2-10B2O3 (mol %) glass matrix using an ionic (3Na⁺ \leftrightarrow Fe³⁺) exchange reaction. The depression of magnetization as a function of temperature indicates the oc-

currence of spin-wave fluctuation in iron core. This is ascribed to an exchange interaction between the ferromagnetic core of the nanoparticles and the oxide surface with disordered spins. The strong temperature dependence of coercivity is believed to arise due to the fact that the frozen surface constitutes a strong hindrance to the reversal of magnetic moment of the ferromagnetic phase. Also, owing to the small size of the iron

Full Paper

core some particles may be superparamagnetic at room temperature which would result in a further decrease of Hc.

REFERENCES

- [1] R.H.Kodama, A.E.Berkowitz, E.J.McNiff., S.Foner; Phys.Rev.Lett., **77**, 394 (**1996**).
- [2] B.Martinez, X.Obradors, Ll.Balcells, A.Rouanet, C.Monty; Phys.Rev.Lett., 80, 181 (1998).
- [3] D.Zhang, K.J.Klabunde, C.M.Sorensen, G.C.Hadijipanayis; Phys.Rev.B, 58, 14167 (1998).
- [4] R.H.Kodama, A.S.Edelstein; J.Appl.Phys., 85, 4316 (1999).
- [5] Juh Tzeng Lue; Physical Properties of Nanomaterials, Encyclopaedia of Nanoscience and Nanotechnology, H.S.Nalwa, (Ed); 10, 1–46 (2007).
- [6] S.P.Gubin, Yu A.Koksharov, G.B.Khomutov, G.Yu.Yurkov; Magnetic nanoparticles: Preparation, structure and properties, Russian Chemical Reviews, 74(6), 489-520 (2005)
- [7] E.M.Chudnovsky, L.Gunther; Phys.Rev.Lett., 60, 661 (1988).
- [8] E.F.Kneller, F.E.Luborsky; J.Appl.Phys., 34, 656 (1963).
- [9] A.E.Berkowitz, J.R.Mitchell, M.J.Carey, A.P.Young, S.Zhang, F.E.Spada, F.T.Parker, A.Hutten, G.Thomas; Phys.Rev.Lett., 68, 3745 (1992).
- [10] J.P.Chen et al.; Phys.Rev.B, 51, 11527 (1995).
- [11] J.A.Becker et al.; J.Chem.Phys., 103, 2520 (1995).
- [12] A.S.Edelstein et al.; Studies of Magnetic Properties of Fine Particles, Elsevier Science, New York, 47 (1992).
- [13] S.Banerjee, S.Roy, J.W.Chen, D.Chakravorty; Journal of Magnetism and Magnetic Materials, 219, 45-52 (2000).

- [14] T.Kinoshita, S.Seino, K.Okitsu, T.Nakayama, T.Nakagawa, T.A.Yamamoto; Journal of Alloys and Compounds, 359(1-2), 46-50 (2003).
- [15] A.M.Tishin, Yu I.Spichkin; The Magnetocaloric Effect and its Applications, Bristol, Philadelphia: Institute of Physics Publ., (2003).
- [16] H.Singh Nalwa; Handbook of Nanostructured Materials and Nanotechnology, Academic Press, San Diego, Calif, USA, (2000).
- [17] K.J.Klabunde; Nanoscale Materials in Chemistry, Wiley Interscience, New York, NY, USA, (2001).
- [18] J.Zarzycki; Le verre et l'état vitreux, Dunod ISBN-13, 978-2225690365 (1997)
- [19] T.Furukawa, W.B.White; Raman spectroscopic investigation of sodium borosilicate glass structure. Journal of Materials Science, 16, 2689-2700 (1981).
- [20] Power Diffraction File, American Society for Testing and Materials, (1972)
- [21] C.Souche, B.Jouffrey, G.Hug, M.Nelhiebel; Orientation sensitive EELS-analysis of boron nitride nanometric hollow spheres. Micron., 29, 419-424 (1998).
- [22] R.Kubo, T.Nagamiya; Solid State Physics, McGraw-Hill, New York, (1968).
- [23] E.H.Frei, S.Shtrikman, D.Treves; Phys.Rev., 106, 446 (1957).
- [24] A.J.Dekker; Electrical Engineering Materials NJ, 120 (1959).
- [25] Neil W.Ashcroft, N.david Mermin; «Solid State Physics » Cornell University, (1976).
- [26] F.Blelita; PhD Thesis Ibn Tofail University to be published, (2010).