Structural and Magnetic Properties of Mechanochemically Prepared Li Ferrite Nanoparticles

M. Haddadi, M. Mozaffari*, and J. Amighian

Department of Physics, Faculty of Science, University of Isfahan, Isfahan 81746-73441, Iran

In this work, lithium ferrite ($Li_{0.5}Fe_{2.5}O_4$) nanoparticles were prepared via mechanochemical processing and subsequent heat treatment at a relatively low (600 °C) calcining temperature. The raw materials used were high purity Fe_2O_3 and Li_2CO_3 that were milled for between 2 and 20 h. The milled powders were then calcined at temperatures of 500 and 600 °C for 5 h in air. XRD results show that optimum conditions to obtain single phase lithium ferrite nanoparticles with a mean crystallite size of about 23 nm, using Scherrer's formula, are 10 h milling and calcination at 600 °C. Saturation magnetization and coercivity of the single phase Li ferrite nanoparticles are 44.6 emu/g and 100 Oe respectively, which are both smaller than those of the bulk Li ferrite. The Curie temperature of the single sample was determined by a Faraday balance, which is 578 °C and smaller than that of bulk Li ferrite.

Keywords : lithium ferrite, mechanochemical processing, magnetic properties

1. Introduction

Lithium ferrite is one of the most important ferrimagnetic materials for application in microwave frequencies and has long been studied as a substitution for yttrium iron garnet (YIG) with the same bandwidth but with a higher Curie temperature, a higher saturation magnetization and a lower price [1, 2].

Lithium ferrite is prepared by different methods [3-8], with the most common being the conventional ceramic method. In this method, iron oxide and lithium carbonate are mixed in a proper portion and react by solid state reaction at a relatively high temperature of at least 1200 °C. Solid state reaction has some disadvantages, such as coarse particles, lithium-loss and some impurity phases, such as α-Fe_2O_3 and Fe_3O_4, because of high temperature calcination [9, 10]. Among other methods, wet chemical methods, such as coprecipitation, sol-gel and hydrothermal, are used to prepare lithium ferrite nanoparticles. These are suitable methods because they allow particle size to be controlled. However, they have some disadvantages, such as chemical waste and environmental pollution, and are not suitable for mass production [3, 4].

Mechanical milling (or alloying) is a simple and an inexpensive method for the preparation and mass production of the nanoparticles (or alloys), and was used for the first time in the 1960s [11, 12]. In mechanical milling (or alloying), high-energy ball mills are utilized for the preparation of the compounds (or alloys) from metal powders [12]. It was found that after a heat treatment, the characteristics of the alloys prepared by mechanical alloying are superior to those prepared by the conventional method. In mechanical milling (or alloying), the particle size can be controlled by factors such as type of mill, milling speed, milling time, and ball size and ball to powder mass ratio [13].

High energy mechanical milling is a suitable method for the preparation of spinel ferrite nanoparticles [14-17], because of the ferrites' fragile nature, which allows the milling process to take place in a shorter time than that of metal powders. If chemical reactions take place during of the milling process, it is known as "mechanochemical processing". Those chemical reactions may result in the formation of desired and/or intermediate phases [18-20]. In addition to this feature, some advantages of the mechanochemical processing are: the ability to use a lower calcination temperature than that needed in the conventional ceramic method; ease of nanoparticle preparation; and a lower cost [21, 22]. However, this method also has some disadvantages when compared with wet methods,

*Corresponding author: Tel: +98-31-3793-4741
Fax: +98-31-3793-4800, e-mail: mozafari@sci.ui.ac.ir

such as the possibility of forming a non-homogenous mixture of the constituents; the formation of contaminated phases; the possibility of introducing impurities of the milling medium in the course of milling, which affect the physical properties; and requiring more time and increased energy consumption [3, 23]. In this study, lithium ferrite nanoparticles were prepared by mechanochemical processing and their structural and magnetic properties were studied.

2. Experimental

Lithium ferrite nanoparticles with the stoichiometric formula $Li_{0.5}Fe_{2.5}O_4$ (or $LiFe_5O_8$) have been prepared by MCP. The starting materials used were Fe_2O_3 and Li_2CO_3, both from the Merck Co. Germany, with minimum purities of 99 %. A total of 4 g of the raw materials was weighed and mixed together in a hardened steel vial (125 cc) in air for 2, 10 and 20 h, using a SPEX 8000D mixer/mill with a ball to powder mass ratio of 7. Balls were made from hardened stainless steel and composed of two sizes, 9 and 12.6 mm in diameter. To obtain single phase lithium ferrite, the milled powders were calcined at temperatures of 500 and 600 °C for 5 h in air. The crystal structure of the powders was identified by an X-ray diffractometer (BRUKER, D8 ADVANCED model) before and after calcination, using CuKα radiation (λ = 1.5406 Å), and the mean crystallite size was estimated by Scherrer's formula: $d=0.9\lambda/B\cos\theta$, where d is the mean crystallite size, λ is the wavelength of the X-ray radiation, B is the full width at half maximum (FWHM) of the most intense peak (311), and θ is the Bragg angle [12].

A hydraulic press machine was used to form pellets of the calcined powders. Several drops of a 5% PVA (polyvinyl alcohol) solution were used as a binder. The powders were cold pressed for 30 seconds under a pressure of 2 tons/cm², using a die 10 mm in diameter and about 7 mm in height. After forming, the pellets were kept in an oven at 220 °C for 24 hours to be dried and strengthened for winding. Each sample was wound by 10 turns with a copper wire (0.12 mm) and placed in an electromagnet, which produces a magnetic field with a maximum of 1.2 T. The magnetic field was applied perpendicular to the flat surface of the pellets. B-H loops of the samples were obtained using a sensitive permeameter. To determine $4\pi M_s$ of the sample from B-H loops, high field parts of the loops were fitted linearly and extrapolated to zero field. In order to obtain saturation magnetization in emu/g, $4\pi M_s$ was divided by $4\pi\rho$, where ρ (g/cc) is the density of the sample [24].

Curie temperatures of the single phase sample were determined by recording self-inductance temperature (L-T) curves, using an LCR-meter (Fluke, 6303 model).

3. Results and Discussion

Figures 1 to 3 show XRD patterns of the as-milled samples for different milling times. As can be seen, the desired lithium ferrite phase is formed after 2 h milling. It is also apparent that by increasing milling time from 2 to 10 h, the amount of lithium ferrite phase increases, but there is still a small amount of hematite phase. Figure 3 shows that longer milling time (20 h) cannot result in a single phase lithium ferrite, because of the milling media wear, which in turn leads to an increase in unwanted α-Fe_2O_3 phase.

Figures 4 to 7 show XRD patterns of the milled powders for 10 and 20 h, which are calcined at 500 and 600 °C for 5 h. As can be seen, calcined powders at 600 °C are single phase lithium ferrite, which shows at this
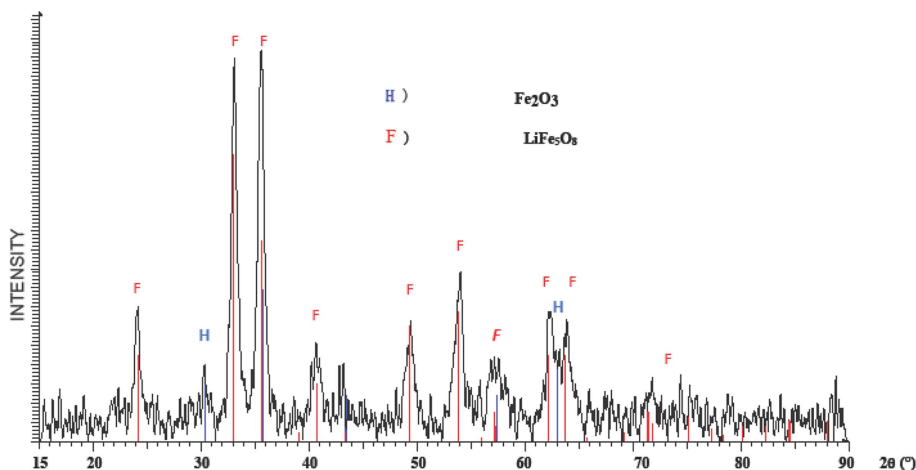

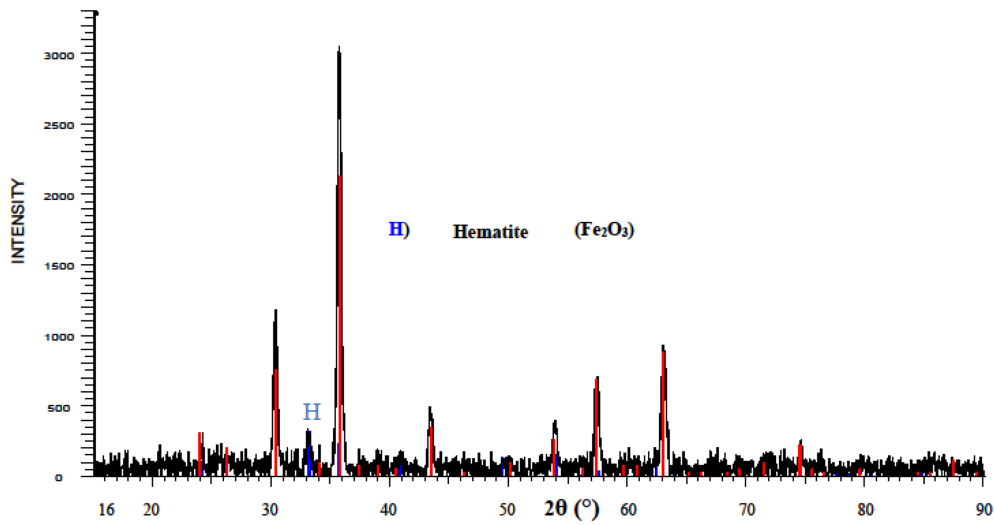**Fig. 1.** (Color online) XRD pattern of the milled sample for 2 h.

Fig. 2. (Color online) XRD pattern of the sample milled for 10 h. The unlabeled peaks are related to Li-ferrite.
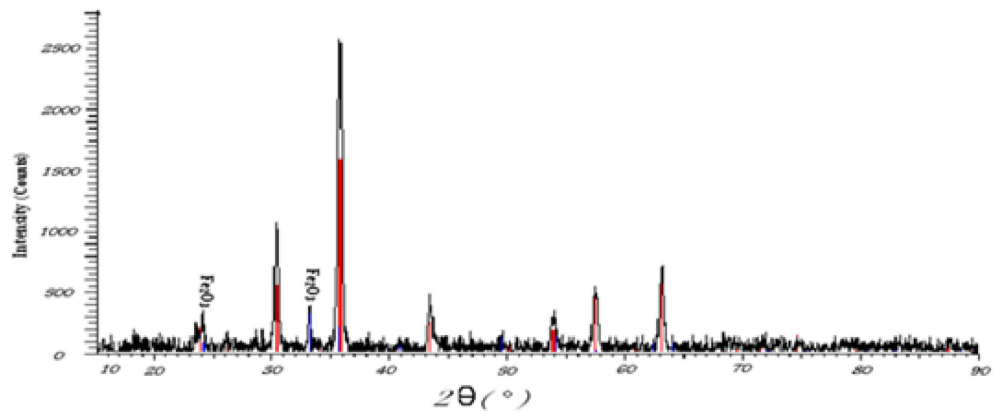

Fig. 3. (Color online) XRD pattern of the sample milled for 20 h. The unlabeled peaks are related to Li-ferrite.
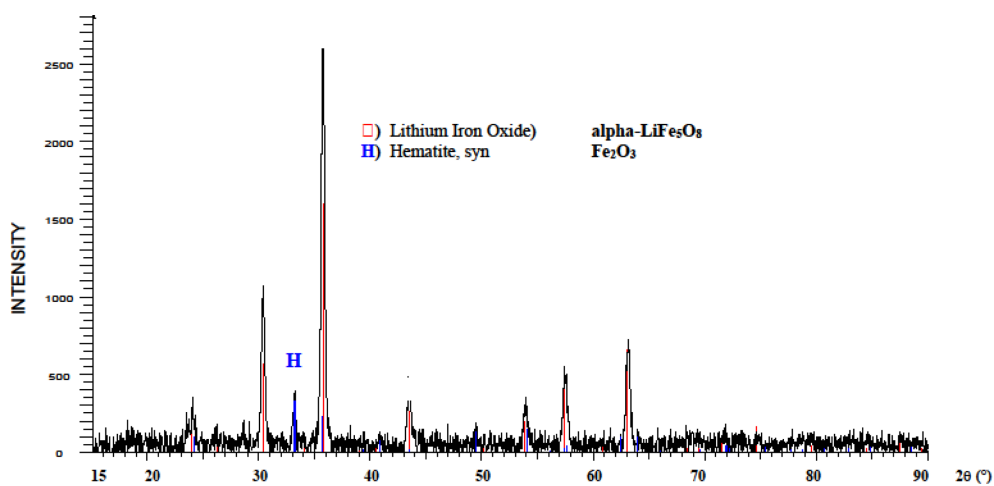

Fig. 4. (Color online) XRD pattern of sample milled for 10 h and calcined at 500 °C. The unlabeled peaks are related to Li-ferrite.

temperature the necessary activation energy is provided by heat. This temperature is much lower than that usually used in the conventional method, which is about 1200 ºC

[25]. The same results have been reported for Li ferrite prepared by MCP [26, 27]. In those works, the necessary temperature for formation of single phase sample is higher
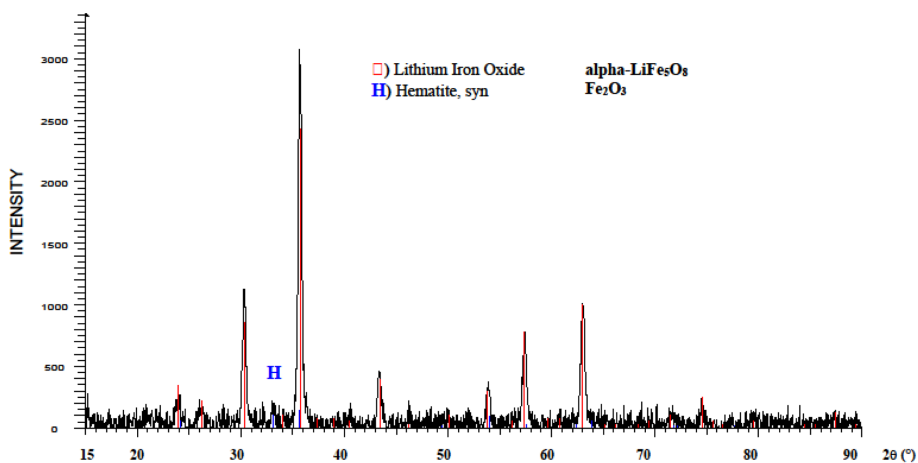
Fig. 5. (Color online) XRD pattern of the sample milled for 20 h and calcined at 500 °C. The unlabeled peaks are related to Li-ferrite.
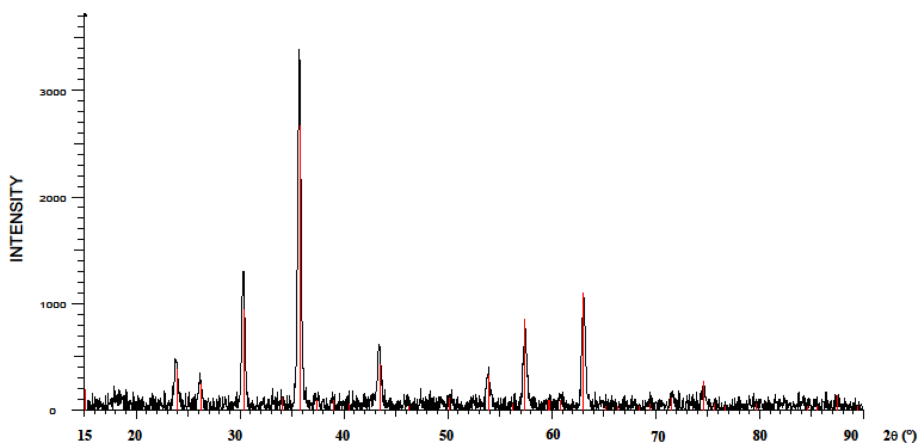

Fig. 6. (Color online) XRD pattern of the single phase sample milled for 10 h and calcined at 600 °C.
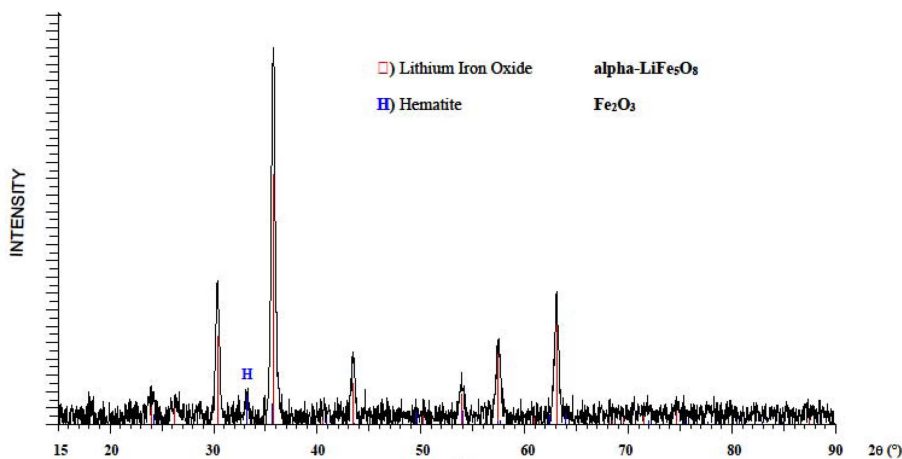

Fig. 7. (Color online) XRD pattern of the milled sample for 20 h and calcined at 600 °C.

than 600 ºC. However, we prepared the single phase sample at the temperature of 600 ºC and this avoids from lithium-loss due to a high temperature calcining temperature, which is used normally in the conventional ceramic method [9, 10].

Figure 8 shows B-H curve of the single phase sample milled for 10 h and calcined at 600 °C for 5 h. As can be seen, coercive force (H_C) and saturation magnetization
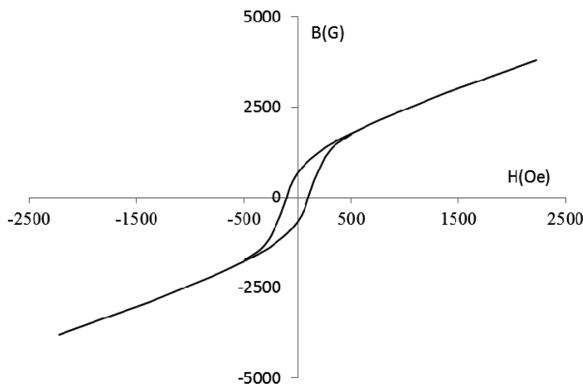
Fig. 8. B-H loop of the single phase sample.

Fig. 9. Variation of self-inductance with respect to temperature for the single phase sample.

$(4\pi M_s)$ of the sample are 100 ± 10 Oe and 1316 ± 20 G respectively.

Saturation magnetization, Curie temperature and mean crystallite size of the single phase lithium ferrite are tabulated in Table 1. These parameters related to lithium ferrite prepared by other methods are also tabulated in Table 1.

The results show that the saturation magnetization of lithium ferrite prepared by the mechanochemical method is lower than in those prepared by other methods, except the hydrothermal technique. The lower saturation magnetization of lithium ferrite nanoparticles prepared by mechanochemical processing in comparison with that of the bulk sample can be explained by the core-shell model [32]. This is due to the formation of a magnetic dead layer on the surface of the nanoparticles in the course of mechanical milling, and of course a high surface to volume ratio in nano scale.

Figure 9 shows variation of self-inductance (that is proportional to permeability) of the single phase sample with respect to temperature. The Curie temperature of the single phase sample is 578 ± 10 °C, which is lower than that of the samples prepared by the conventional ceramic method, as can be seen in Table 1. This is due to higher magnetic dipoles, which are on the surface of the nanoparticles [16].

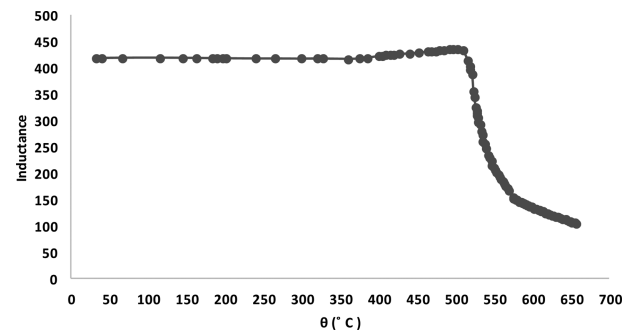The lattice constant and the mean crystallite size of the

lithium ferrites prepared by different conditions are tabulated in Table 2. As can be seen, increasing of the milling time from 10 to 20 h, resulted in a decrease in the mean

Table 2. Mean crystallite sizes and lattice constants of lithium ferrites prepared at different conditions.

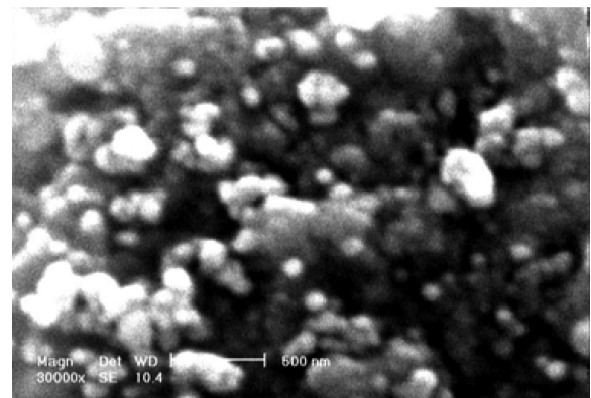| Sample preparation conditions	Mean crystallite size (nm)	Lattice constant (Å)
Milled for 10 h	21	8.37
Milled for 20 h	12	8.34
Milled for 10 h and annealed at 600 ºC	23	8.34

Fig. 10. SEM micrograph of the single phase Li ferrite nanoparticles.

Table 1. Saturation magnetization, Curie temperature and mean crystallite size of lithium ferrite prepared by various methods.

Preparation method	Saturation magnetization (emu/g)	The mean size of the particles (nm)	Curie temperature (º C)
Mechanochemical [present study]	44.6	23.5±1.5	578
Conventional ceramic [28]	65	-	670
Sol-gel [29]	75	12-32	-
Hydrothermal [30]	25.23	5	-
Microwave [31]	71.17	50-80	640

crystallite size from 21 to 12 nm. However, after annealing of the sample at a temperature of 600 ºC for 5 h, the mean crystallite size increased from 21 to 23 nm. The increase in mean crystallite size is related to heat energy due to annealing [12].

Figure 10 shows a SEM image of the single phase lithium ferrite and, as can be seen, sizes of the particles are in the range of 50 to 200 nm, with a mean particle size of about 90 nm. From a comparison between this and the mean crystallite size obtained from Scherrer's formula, it can be concluded that each particle is composed of several crystallites.

4. Conclusions

The results of this research show that:

1. It is possible to obtain single phase lithium ferrite nanoparticles by mechanochemical processing and subsequent heat treatment at a temperature much lower than that usually used in the conventional ceramic method.

2. It is possible to carry out both milling and calcination processing in air.

3. Longer milling times result in a higher amount of the desired phase, but because of the milling media wear, unwanted hematite phase is increased too. There is therefore an optimum milling time to obtain a single phase lithium ferrite by MCP.

Acknowledgments

References

[1] J. Smit and H. P. J. Wijn, Ferrites, Philips Technical Library, Eindhoven (1959).

[2] S. Y. An, I. B. Shim, and C. S. Kim, J. Magn. Magn. Mater. **290-291**, 1551 (2005).

[3] A. Tavkoli, M. Sohrabi, and A. Kargari, Chem. Pap. **61**, 151 (2007).

[4] D. Segal, J. Mater. Chem. **7**, 1297 (1997).

[5] C. J. Brinker and G. W. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, Academic Press, San Diego (1990) pp 667-781.

[6] M. L. S. Teo, L. B. Kong, Z. W. Li, G. Q. Lin, and Y. B. Gan, J. Alloys Compd. **459**, 557 (2008).

[7] M. L. S. Teo, L. B. Kong, Z. W. Li, G. Q. Lin, and Y. B. Gan, J. Alloys Compd. **459**, 567 (2008).

[8] M. L. S. Teo, L. B. Kong, Z. W. Li, G. Q. Lin, and Y. B. Gan, J. Alloys Compd. **459**, 576 (2008).

[9] D. H Ridgley, H. Lessoff, and J. D. Childress, J. Am. Ceram. Soc. **53**, 304 (1970).

[10] H. Ueda, A. Matsui, Y. Miura, N. Minoru, and F. Minoru, Mater. Sci. **17**, 562 (1985).

[11] J. S. Benjamin, Metal Powder Rep. **45**, 122 (1997).

[12] C. Suryanarayana, Prog. Mater. Sci. **46**, 1 (2001).

[13] D. R. Maurice and T. H. Courtney, Metall. Trans. A **21**, 289 (1990).

[14] A. Hasanpour, M. Mozaffari, M. R. Azani, and A. Hassanpour, Russ. J. Phys. Chem. A **86**, 264 (2012).

[15] M. Mozaffari and Y. Zare, J. Supercond. Nov. Magn. **28**, 3157 (2015).

[16] M. Mozaffari, M. Eghbali Arani, and J. Amighian, J. Magn. Magn. Mater. **322**, 3240 (2010).

[17] M. Mozaffari and H. Masoudi, J. Supercond. Nov. Magn. **27**, 2563 (2014).

[18] M. Mozaffari, M. Gheisari, M. Niyaifar, and J. Amighian, J. Magn. Magn. Mater. **321**, 2981 (2009).

[19] A. Hasanpour, M. Mozaffari, and J. Amighian, Physica B **387**, 298 (2007).

[20] M. Mozaffari, F. Ebrahimi, S. Daneshfozon, and J. Amighian, J. Alloys Compd. **449**, 65 (2008).

[21] T. Tsuzuki, K. Pethick, and P. G. McCormick, J. Nanopart. Res. **2**, 375 (2000).

[22] Takuya Tsuzuki and Paul G. McCormick, J. Mater. Sci. **39**, 5143 (2004).

[23] K. Rama Krishna, K. Vijaya Kumar, and Dachepalli Ravinder, Adv. Mater. Phys. Chem. **2**, 185 (2012).

[24] B. D. Cullity and C. D. Graham, Introduction to Magnetic Materials, John Wiley & Sons, NJ (2009) p 7.

[25] S. Soreto Teixeira, M. P. F. Graça, and L. C. Costa, J. Non-Cryst. Solids **358**, 1924 (2012).

[26] Hisham M. Widatallah and Frank J. Berry, J. Solid State Chem. **164**, 230 (2002).

[27] S. A. Mazen and N. I. Abu-Elsaad, Appl. Nanosci. **5**, 105 (2015).

[28] J. Smit and H. P. J. Wijn, Ferrites, Philips Technical Library, Eindhoven (1959) p 157.

[29] M. George, S. S. Nair, A. M. John, P. A. Joy, and M. R. Anantharaman, J. Phys. D: Appl. Phys. **39**, 900 (2006).

[30] X. Wang, L. Gao, L. Li, H. Zheng. Z. Zhang, W. Yu, and Y. Qian, Nanotech. **16**, 2677 (2005).

[31] Y. P. Fu, S. Tsao, C. T. Hu, and Y. D. Yao, J. Alloys Compd. **395**, 272 (2005).

[32] M. Mouroi, R. Street, P. G. McCormick, and J. Amighian, Phys. Rev. B **63**, 184414 (2001).