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Ceramics International 35 (2009) 1539–1544
CERAMICS INTERNATIONAL
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Preparation and characterization of some ferromagnetic glass–ceramics contains high quantity of magnetite

S.A.M. Abdel-Hameed [a,*], M.M. Hessien [b], M.A. Azooz [a]

[a] Glass Research Department, National Research Center, Dokki, Cairo 12622, Egypt
[b] Electronic Materials Lab, Advanced Materials Department, Central Metallurgical Research and Development Institute (CMRDI), Helwan, Cairo, Egypt

Received 29 May 2008; received in revised form 18 June 2008; accepted 24 August 2008
Available online 8 October 2008

Abstract

Ferrimagnetic glass–ceramics are promising candidates for magnetic induction hyperthermia, which is one form of inducing deep-regional hyperthermia, by using a magnetic field. The aim of this work was to study the effect of increasing the amount of crystallized magnetite on the magnetic properties of glass–ceramic samples. Two different ferrimagnetic glass–ceramics with the composition based on wollastonite or hardystonite with high quantity (~60%) of magnetite were prepared by melting the starting materials at 1450 °C for 2 h. The influences of chemical composition, amount of crystallized magnetite and microstructure of ferrimagnetic glass–ceramics on magnetic properties of ferromagnetic glass–ceramics were investigated using differential thermal analysis (DTA), X-ray diffraction (XRD), transmission electron microscope (TEM) and scanning electron microscope (SEM). The X-ray diffraction patterns show the presence of nanometric magnetite crystals in a glassy matrix after cooling from melting temperature. The amount of crystallized magnetite varies as a function of the chemical composition and heat treatment schedule. The presence of ZnO in the glass–ceramics was found to decrease the viscosity and so cases higher degree of mobility of ions leading to higher degree of crystallinity. The higher heat treatment parameters and so the lower viscosity of the glass containing ZnO are assumed to allow the magnetite to grow to larger crystallite size. Glass transition temperature and thermal stability were found to be functions of chemical composition. Magnetic hysteresis cycles were analyzed using a vibrating sample magnetometer (VSM) with a maximum applied field of 15 kOe at room temperature in quasi-static conditions. From the obtained hysteresis loops, the saturation magnetization (Ms), remanance magnetization (Mr) and coercivity (Hc) were determined. The results showed that these materials are expected to be useful in the localised treatment of cancer.

Keywords: Glass–ceramic; Ferrimagnetic; Hyperthermia; Cancer; Nanomagnetite

1. Introduction

Hyperthermia destroys cancer cells by raising the tumour temperature to a ''high fever'' range, similar to the way that the body naturally uses to combat other forms of disease [1]. Generally, tumours are more easily heated than the surrounding normal tissues, since blood vessels and nervous systems are poorly developed in the tumour, and cancer cells are easily killed by heat treatment, since oxygen supply via the blood vessels is not sufficient in the tumour. Hence hyperthermia is expected to be a most useful treatment of cancer which has no side effects [2]. On the contrary, these temperatures are safe for surrounding healthy tissues with normal and efficient blood cooling systems [3].

Bioactive and ferromagnetic glass–ceramics are expected to be useful as thermoseeds for hyperthermia treatment of cancer, especially deep-seated cancers such as bone tumours. When ferromagnetic glass–ceramics are implanted around tumours in granular form, they are bonded to each other so as not to be moved by forming biologically active bone-like apatite on them [4], and stably fixed around the tumours if they are located near bones. Moreover, when they are placed under an alternating magnetic field, they generally heat effectively cancer cells to be necrotized by magnetic hysteresis loss. After the heating, they can also reinforced weakened tumorous bone by bonding to bone.

Several materials that generate heat by hysteresis loss have been developed [5–10]. Among them, bioactive ferro and

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* Corresponding author. Fax: +20 02 33370931.
E-mail address: salwa_nrc@hotmail.com (S.A.M. Abdel-Hameed).

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doi:10.1016/j.ceramint.2008.08.021

ferrimagnetic glass–ceramics have been investigated [11–14]. Preparation of magnetite-containing glass ceramics has been reported by several workers [2,15,16] where ferrimagnetic bioglass-ceramics containing maximum 45 %wt of magnetite were prepared [17]. They also showed that a ferromagnetic glass–ceramic containing 45 wt% of magnetite has a saturation magnetisation of 34 emu/g and a coercive force of 85 Oe. The estimated heat generation of this glass–ceramic using a magnetic field of 40 kA/m and a frequency of 440 kHz was 25 W/g. This material showed a bioactive behavior, as after 2 weeks of soaking in a simulated body fluid the formation of a hydroxylapatite layer on their surface was observed on their surface. Ebisawa et al. [2] prepared glass ceramic contains 36% magnetite in a matrix of $CaO \cdot SiO_2$-based glass and β-wollastonite which show ferrimagnetisms and no bioactivity [18]. In general, the heat generation depends mainly on the magnetic properties of the implant, the magnetic field parameters and the characteristics of the tissue [17].

According to the importance of Zn ions in the human body, as reported to be involved in bone metabolism, it could stimulate bone formation and increase bone protein, calcium content, and alkaline phosphatase activity in humans and animals [19], Hardystonite ($Ca_2ZnSi_2O_7$) might be biocompatible and used as biomaterials. The hardystonite phase possesses improved bending strength and fracture toughness as compared to hydroxyapatite so it may possess good biocompatibility [19].

This work aims at prepare ferromagnetic glass ceramics based on wollastonite or hardystonite with high quantity (~60%) of magnetite. The influences of chemical composition, the amount of crystallized magnetite and the microstructure of ferrimagnetic glass–ceramics on magnetic properties of ferromagnetic glass–ceramics were also investigated.

2. Experimental procedures

2.1. Preparation of glasses

The chemical compositions of the examined glasses are shown in Table 1. About 100 g powder mixtures of these compositions were prepared from reagent grade Ca_2CO_3, SiO_2, Fe_2O_3, ZnO and H_3BO_3. Our target was to obtain a glass–ceramic, not a ceramic material, so a melting step was necessary to achieve the nucleation of magnetite in a liquid-derived amorphous phase. The batches were placed in a platinum crucible and melted in an electric furnace at 1350 °C for 2 h. The melts were poured on to a stainless steel plate at room temperature and pressed into a plate 1–2 mm thick by another cold steel plate.

2.2. Crystallization of glasses

Glass samples were thermally examined using differential thermal analysis (DTA). According to the DTA results the glass plates obtained were covered with active carbon powders, to ably reducing atmosphere to prevent ferrous ions from oxidation and heated up to various temperatures at a rate of 3 °C/min for crystallization in a SiC electric furnace. It is noticed that the synthesis process parameters (such as temperature, time, heating rate, and atmosphere) plays a fundamental role for magnetite crystallization.

2.2.1. Characterization

The heat-treated glasses were subjected to powder X-ray diffraction (XRD) using Ni-filled Cu Kα rays for determination of the types and contents of the crystalline phases precipitated in the glasses. The crystallite size of the heat treated and untreated glass samples for the most intense peak of magnetite (1 1 4) was determined from the XRD data using Debye–Scherrer formula. The heat treated glasses were crushed and sonically suspended in ethanol and few drops of the suspended solution were placed on an amorphous carbon film held by a copper microgrid mesh and then observed under a transmission electron microscope. The surfaces of glass–ceramics samples were examined with a scanning electron microscope (SEM), after coating with 5 μm thickness gold layers sputtered over the surfaces.

The magnetic properties of the as prepared samples (FH & FW) and the heat-treated samples were measured at room temperature using a vibrating sample magnetometer (VSM; 9600-1 LDJ, USA) in a maximum applied field of 15 kOe. From the obtained hysteresis loops, the saturation magnetization (Ms), remanance magnetization (Mr) and coercivity (Hc) were determined.

3. Results and discussions

The DTA traces of the investigated glasses are shown in Fig. 1. DTA analysis show endothermic effect at 680 and 662 °C for glass FW & FH, respectively. This endothermic reaction is believed to be caused by an increase in heat capacity due to transformation of glass from rigid to plastic structure [20]. This endothermic effect is followed by strong intense and sharp exothermic peak at 824 °C for FW and at 838 °C for FH glass which corresponds to crystallization of magnetite as identified by X-ray latter. Increasing the peak height and sharpness may be related to increase the tendency of bulk crystallization. It is noticed that the exothermic effect is shifted to slightly higher temperature while glass transition temperature (Tg) is shifted to lower one in glass FH than FW. The

Table 1
Chemical composition of the studied glasses in wt%.

Sample	The designed phase percent	Fe_2O_3	CaO	ZnO	SiO_2	B_2O_3
FW	60% Magnetite: 40% wollastonite	60	19.31		20.69	3
FH	60% Magnetite: 40% hardystonite	60	14.3	10.37	15.32	3

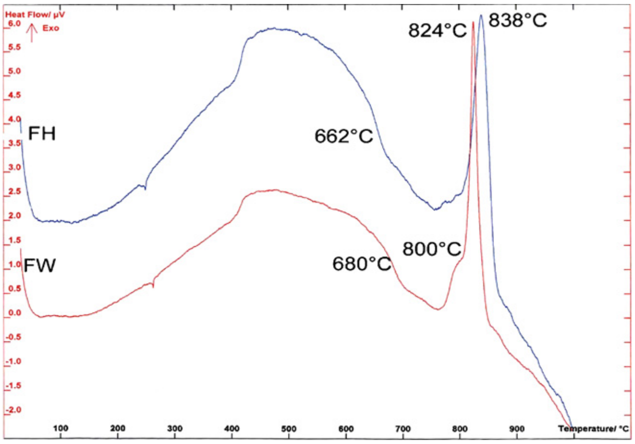

Fig. 1. DTA traces of FH and FW glasses.

decrease of the Tg temperatures in FH than FW can be attributed to the presence of ZnO in FH glass which leads to the decrease of the melt viscosity. The intense exothermic peak is exceeded by small shoulder at ~800 °C which is higher in FW than FH; it may correspond to the precipitation of hematite.

X-ray diffraction analysis (Figs. 2 and 3) revealed the precipitation of only magnetite phase in glassy phase in as prepared samples (without heat treatment). The amount of magnetite precipitated in FH glass sample is higher than that precipitated in FW without heat treatment. It is seemed that the presence of ZnO in FH, which leads to decrease in the viscosity, cases higher degree of mobility of ions leading to higher degree of crystallinity. This behavior describes the lowering in the exothermic peak height for FH than in FW where the amount of crystallinity in FH without heat treatment is higher than in FW.

Heat treatment at 800°/1 h with heating rate of 3 °C/min revealed the crystallization of magnetite with minor amount of hematite in FW and major magnetite with traces of hematite and wollastonite in FH (at the same heat treatment parameters). In general the amount of crystallization decreases in these samples (heat treated at 800°/1 h) than in as prepared glasses.

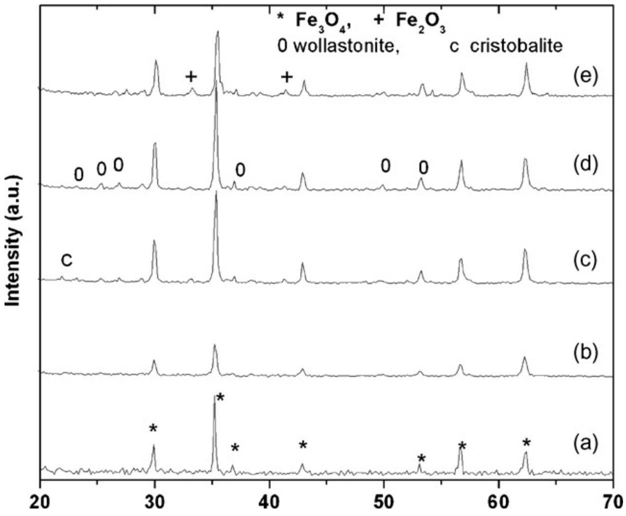

Fig. 2. XRD analysis of FH sample (a) without heat treatment (b) at 800 °C/1 h, (c) at 1000 °C/1 h, (d) at 1050 °C/1 h, and (e) at 1050 °C/3 h.

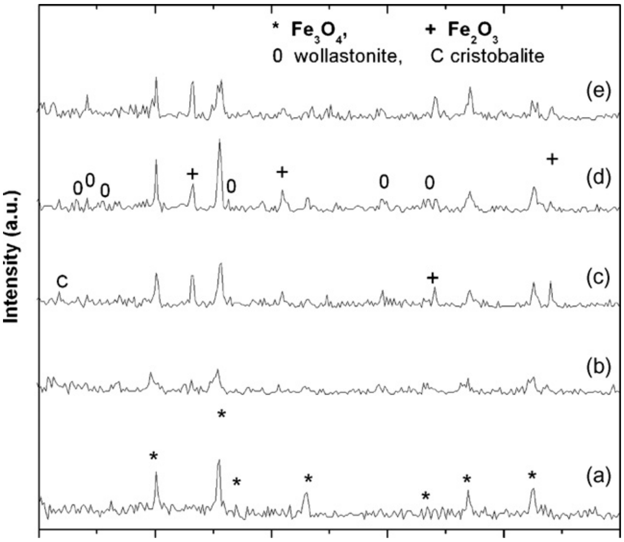

Fig. 3. XRD analysis of FW sample, (a) without heat treatment (b) at 800 °C/1 h, (c) at 1000 °C/1 h, (d) at 1050 °C/1 h, and (e) at 1050 °C/3 h.

Increasing heat treatment temperature to 1000 °C/1 h shows increasing in the amount of crystallization in both samples especially in FH. Major magnetite with traces of hematite, wollastonite and cristobalite appeared in FH while more development of hematite relative to the main magnetite phase and traces of wollastonite and cristobalite appeared in FW heat treated at 1000 °C/1 h.

At 1050 °C/1 h, FW & FH samples revealed the same crystallized phases as in the last heat treatment with relatively higher intensity of magnetite and absence of cristobalite.

The amount of crystallization slightly decreased by increasing time of heat treatment to 3 h at 1050 °C (due to slightly remelt of the samples) and the amount of hematite was more developed beside the major magnetite and traces of wollastonite in FH. While in FW hematite increased largely to be the main crystallized phase relative to magnetite while wollastonite disappeared.

The crystallite size calculated from XRD data for the most intense peak analysis of magnetite and hematite present in the heat treated and untreated glass ceramics are shown in Table 2 and Fig. 4. The results indicate the crystallization of nanoparticles from magnetite and hematite. The grain size of hematite is relatively larger than magnetite in general. It is

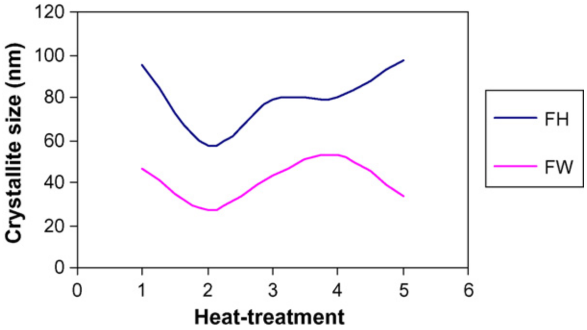

Fig. 4. The crystallite size with heat treatment (1) without heat treatment (2) at 800 °C/1 h, (3) at 1000 °C/1 h, (4) at 1050 °C/1 h, and (5) at 1050 °C/3 h.

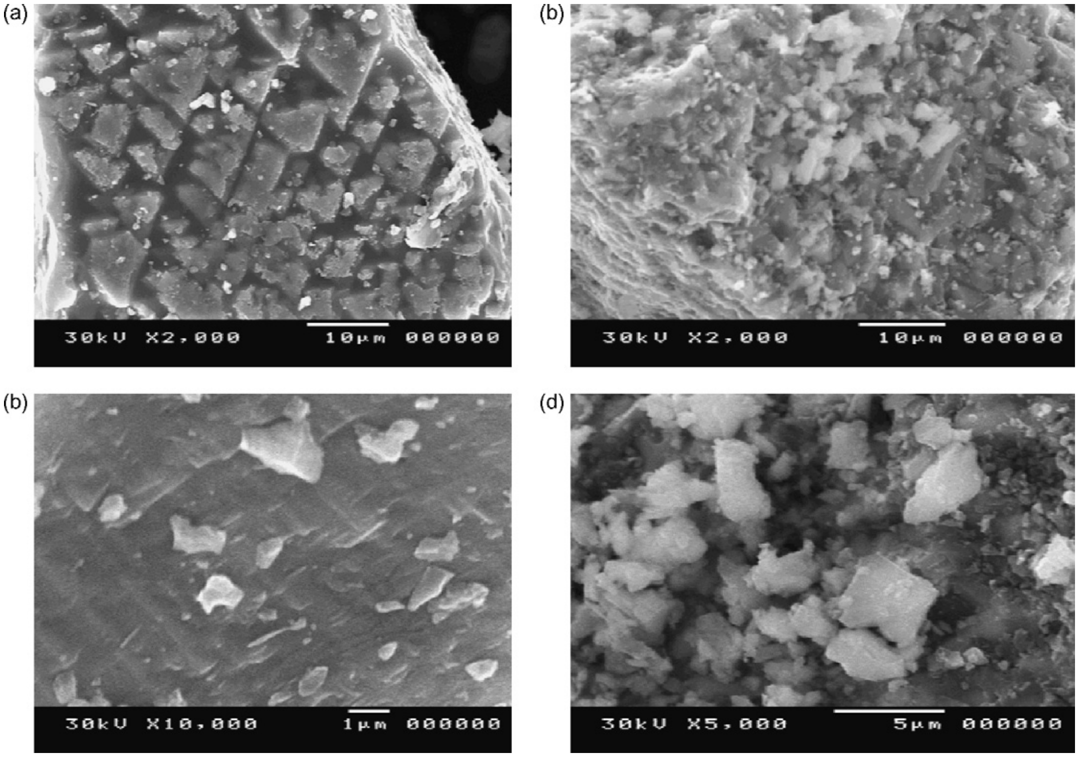

Fig. 5. SEM morphologies of (a) FH glass, (b) FH 1000 °C/1 h, (c) FW glass, and (d) FW 1000 °C/1 h.

noticed that the grain size is relatively bigger in as prepared glasses and decreased with heat treatment at 800 °C/1 h then start to increase again with heat treatment till reach maximum (97.2) at FH sample heat treated at 1050 °C/3 h while in FW heat treated at 1050 °C/3 h the crystallite size is decreased largely again, this may due to the small remelt of this sample cased by increasing the heat treatment time. It is seemed that the higher heat treatment parameter and so the lower viscosity of the glass contains ZnO are assumed to allow the magnetite to grow to larger sized crystallites. On the other hand, in FW less compact crystalline structure, as seen next in SEM results, leads to high chance for degradation of magnetite and formation of hematite and so relatively smaller size of magnetite were appeared in FW than in FH.

Fig. 5 presents the SEM morphologies of the samples FH, FH1000 °C/1 h, FW and FW1000 °C/1 h, respectively. For the FH glass ceramic, the photomicrograph (Fig. 5a) shows a uniform and homogenous magnetite grains dispersed in glass phase while interlocked crystallization of magnetite with little hematite crystals for FH heat treated at 1000 °C/1 h (Fig. 5b). The microstructure appeared hardly compact in FW glass while revealed bulk crystallization of less compact fine crystals of magnetite with relatively large crystal of hematite for FW heat treated at 1000 °C/1 h.

Table 2
The crystallite size of crystallized phases at different heat treatment in nm.

Samples	Magnetite	Hematite
FH	94.8	–
FH 800 °C/1 h	57.7	–
FH 1000 °C/1 h	78.4	186.9
FH1050 °C/1 h	80.3	
FH1050 °C/3 h	97.2	92.7
FW	46	
FW 800 °C/1 h	27.1	127.4
FW1000 °C/1 h	43.4	121.8
FW 1050 °C/1 h	52.6	71.8
FW 1050 °C/3 h	33.5	86

TEM (Fig. 6) studies (which confirm the previous XRD analysis) revealed a uniform precipitation of nanosized magnetite in FH & FW glasses and appearance of coagulation of hematite when samples heat treated at 1000 °C/1 h. It is noticed that the amount of crystallized magnetite in FH glass is higher than in FW glass on the contrary hematite appeared with heat treatment in higher quantity in FW than in FH.

The magnetization of the produced powder glass–ceramic samples was performed at room temperature under an applied field of 15 KOe and the hysteresis loops of the powders were obtained. Plots of magnetization (*M*) as a function of applied field (*H*) for as prepared samples and that heat treated at 1000 °C for the FH and FW samples are shown in Fig. 7 and Table 3, respectively. It can be observed that all the samples exhibit magnetic behavior characteristic for soft magnetic particles, with small coercivity. As can be seen from this table, the saturation magnetization varies from 23.13 to 52.13 emu/g. In general, the saturation magnetization (MS) of powder glass–ceramic samples has a lower value with respect to magnetic data reported on magnetite in literature (MS = 92 emu/g) [1,21]. This fact can be explained considering the powder form in the measured samples and can be attributed in large part to

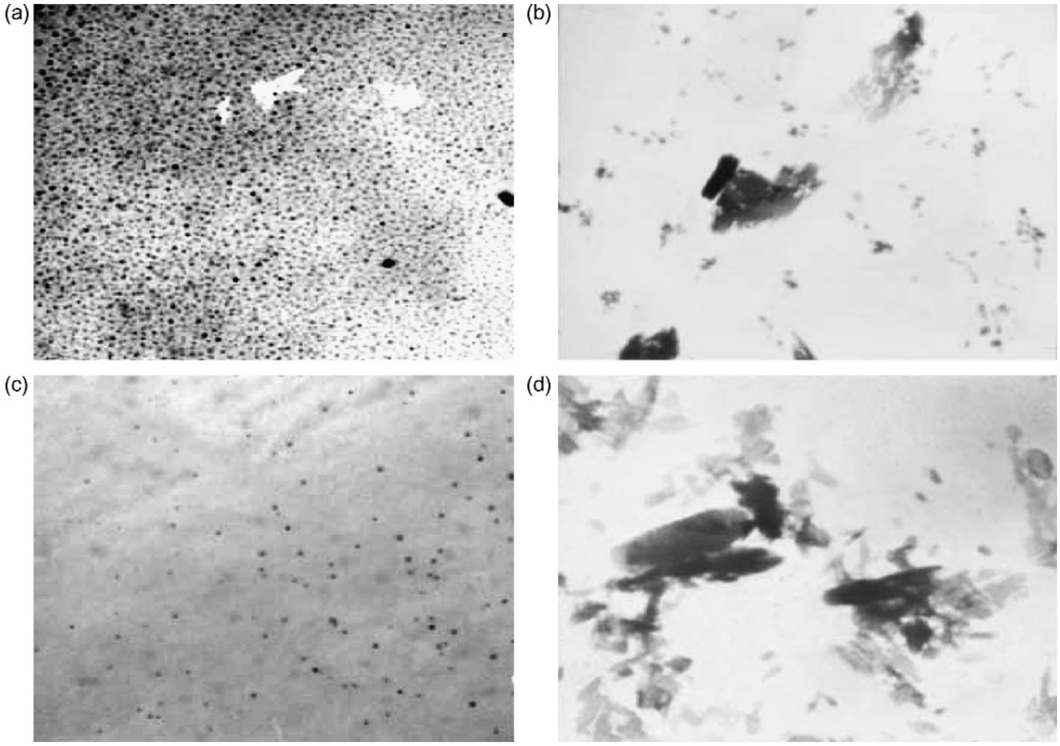

Fig. 6. TEM of (a) FH glass, (b) FH 1000 °C/1 h, (c) FW glass, and (d) FW 1000 °C/1 h (50,000×).

the presence of glassy phases in the materials. The presence of nonmagnetic crystals among the amorphous glassy materials constitutes part of the overall sample mass used to calculate the saturation magnetization. Moreover, as a consequence, powders are characterized by a much higher surface/volume ratio than bulk materials whose saturation magnetization is reported in literature. Surface effects usually cause the lowering of the magnetization. From Fig. 7 and Table 3, the saturation magnetization of the FH was increased with the heat treatment at 1000 °C from 29.97 to 52.13 emu/g. While for FW samples, the saturation magnetization decreased with the heat treatment at 1000 °C from 35.25 to 23.13 emu/g. As expected, saturation magnetization increases with the amount of magnetic phases crystallized in the samples and with the increases of crystallization. It should be considered that magnetite is a ferrimagnetic material, while hematite is an antiferrimagnetic material. From experimental data it is seen that hematite and amorphous phases have a very low saturation magnetization. As a consequence, the variation of the saturation magnetization can be attributed to the modification of the quantity of magnetite crystals present in the glass–ceramic samples. Therefore, the saturation magnetization increases with increasing the crystallite size of magnetite phase in FH. The depressing in the magnetization value in the FW samples with the heat treatment can be attributed to the conversion of ferrimagnetic Fe_3O_4 into non-magnetic hematite that is evident in Fig. 2. Bretcanu et al. [1] found that, 1 g of ferromagnetic glass ceramic which has saturation magnetization 30 emu/g and coercitive force 220 Oe can increase the temperature of 20 ml distillate water after 2 min of applying magnetic field to about 40 °C. So, in this

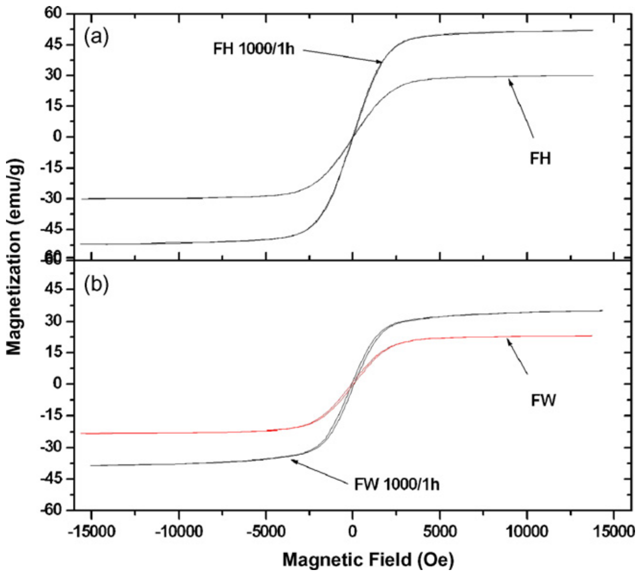

Fig. 7. Effect of heat treatment on the hysterersis loop of the prepared glass ceramic: (a) FH and FH1000/1 h and (b) FW and FW1000/1 h.

Table 3
Magnetic properties of the heat treated and untreated ferromagnetic glass ceramic.

Samples	Ms (emu/g)	Mr (emu/g)	Hc (Oe)
FH	29.967	0.074	7.21
FH 1000 °C/1 h	52.13	0.478	20.689
FW	35.247	1.36	75.86
FW1000 °C/1 h	23.13	1.0303	95.93

work, the studied ferromagnetic glass ceramic samples which have saturation magnetization reach 35.25 (for FW) and 52.13 emu/g (for FH) are expected to increase this temperature to higher than 40 °C, and this will be more effective for destruction of cancerous cells by hysteresis loss method.

4. Conclusion

Two different ferrimagnetic glass–ceramics with the composition based on wollastonite or hardystonite with high quantity (~60%) of magnetite were prepared. The influences of chemical composition, the amount of crystallized magnetite and the microstructure of ferrimagnetic glass–ceramics on magnetic properties of glass–ceramics were investigated. Nanometric magnetite crystals were precipitated in a glassy matrix after cooling from melting temperature. The amount of crystallized magnetite varies as a function of the chemical composition and heat treatment. It is seemed that the presence of ZnO in FH, which leads to a decrease in the viscosity, cases higher degree of mobility of ions leading to higher degree of crystallinity. Crystal size calculations shows precipitation of nanocrystals of magnetite size ranged from 27 to 95 nm depending on the heat treatment parameters. Magnetic hysteresis cycles were analyzed. From the obtained hysteresis loops, the saturation magnetization (Ms), remanance magnetization (Mr) and coercivity (Hc) were determined. It can be observed that all the samples exhibit magnetic behavior characteristic for soft magnetic particles, with small coercivity. The studied ferromagnetic glass ceramic samples which have saturation magnetization reach 35.25 (for FW) and 52.13 emu/g (for FH) were expected to increase the temperature of 20 ml distillate water by applying magnetic field to more than 40 °C, and this will be more effective for destruction of cancerous cells by hysteresis loss method.

References

[1] O. Bretcanu, E. Verné, M. Coisson, P. Tiberto, P. Allia, Temperature effect on the magnetic properties of the coprecipitation derived ferrimagnetic glass–ceramics, J. Magn. Magn. Mater. 300 (2006) 412–417.
[2] Y. Ebisawa, F. Miyaji, T. Kokubo, K. Ohura, T. Nakamura, Bioactivity of ferromagnetic glass ceramics in the system FeO–Fe_2O_3–CaO–SiO_2, Biomaterials 18 (1997) 1277–1284.
[3] http://www.bsdmc.com/Hyperthermia.pdf.
[4] T. Kokubo, T. Hayashi, S. Sakka, T. Kitsugi, T. Yamamuro, Bonding between bioactive glasses, glass–ceramics or ceramics in a simulated body fluid, Yogyo-Kyokai-Shi 95 (1987) 785–791.
[5] T.C. Cetas, E.J. Gross, Y. Contractor, IEEE Trans. Biomed. Eng. 45 (1998) 68.
[6] A. Jordan, R. Scholz, P. Wust, H. Fähling, R. Felix, J. Magn. Magn. Mater. 201 (1999) 413.
[7] S.A. Gómez-Lopera, R.C. Plaza, A.V. Delgado, J. Colloid Interf. Sci. 240 (2001) 40.
[8] Y.K. Lee, D.H. Kim, Y.J. Lee, K.N. Kim, I.B. Shim, Ceramics, cells and tissues, in: Eighth Annual Seminar and Meeting, Faenza, 2003.
[9] K. Takegami, T. Sano, H. Wakabayashi, J. Sonoda, T. Yamazaki, S. Morita, T. Shibuya, A. Uchida, J. Biomed. Mater. Res. 43 (2) (1998) 210–214.
[10] Borrelli et al., US Patent 4,323,056, 1982.
[11] T. Kokubo, T. Yamamuro, Y. Ebisawa, K. Ohura, European Patent 361797, 1990.
[12] S.H. Oh, S.Y. Choi, Y.K. Lee, K.N. Kim, J. Biomed. Mater. Res. 54 (2001) 360.
[13] Y. Ebisawa, F. Miyaji, T. Kokubo, K. Ohura, T. Nakamura, J. Ceram. Soc. Jpn. 105 (1997) 947.
[14] D. Arcos, R.P. del Real, M. Vallet-Regi, Biomaterials 23 (2002) 2151.
[15] M. O'Horo, R. Steinitz, Characterization of devitrification of iron-containing glass by electrical and magnetic properties, Mater. Res. Bull. 3 (1968) 117–126.
[16] P. Auric, N.V. Dang, A.K. Bandyopadhyay, J. Zarzycki, Superparamegnetism and ferrimagnetism of the small particles of magnetite in a silicate matrix, J. Non-cryst. Solids 50 (1982) 97–106.
[17] O. Bretcanu, S. Spriano, E. Verné, M. Coisson, P. Tiberto, P. Allia, The influence of crystallised Fe_3O_4 on the magnetic properties of coprecipitation-derived ferrimagnetic glass–ceramics, Acta Biomater. 1 (2005) 421–429.
[18] Y. Ebisawa, Y. Sugimoto, T. Hayashi, T. Kokubo, K. Ohura, T. Yamamurao, Crystallization of (FeO, Fe_2O_3)–CaO–SiO_2 glasses and magnetic properties of their crystallized products, Seramikkusu Ronbunshi 1 (1991) 7–13.
[19] Chengtie Wu F, Chang Jiang, Zhai Wanyin, A novel hardystonite bioceramic: preparation and characteristics, Ceram. Int. 31 (2005) 27–31.
[20] A.W.A. El-Shennawi, M.M. Morsi, G.A. Khater, S.A.M. Abdel-Hameed, Thermodynamic investigation of crystallization behavior of pyroxenic basalt-based glasses, J. Therm. Anal. 51 (1998) 553–560.
[21] R.D. Cullity, Addison-Wesley, 1972.