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Research Article

Long Time Stability Investigation for Structural and Magnetic Properties of Ti-doped Barium Ferrite

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ABSTRACT

Barium hexaferrite (BHF) ($BaFe_{12}O_{19}$) and its substituted derivatives have been considered as the most potential magnetic candidates with considerable chemical stability and physiochemical characteristics. BHF with x ferrite ions substituted by titanium (Ti-doped BTHF) ($BaTi_xFe_{12-x}O_{19}$) (x=1 and x=3) was prepared from ferric oxide (Fe_2O_3), barium oxide (BaO), and titanium oxide (TiO_2) of purity >98%. The materials were mixed with deionized water and then dried at 1100°C and 1200°C overnight. For the formation of $BaFe_{12}O_{19}$ phase, the mixture was annealed at a rate of 10°C/min in static air atmosphere until reaching 1200°C and then maintained for 10 h. Structural properties of these samples were measured using X-ray diffraction (XRD) and scanning electron microscopy, while magnetic properties were measured using vibrating sample magnetometer (VSM) device. Magnetic and structural characteristics are investigated after preserving Ti-doped BHF samples at room temperature and ambient conditions for 12 years. The samples are characterized using the same previous techniques to find out the possible effect of long period storage on their properties. The results showed that the storage process has little effect on these properties where the granular size increased due to increased oxidation. XRD tests also showed the absence of Ti at low ratios due to increased oxidation of ferrite. VSM results showed increased magnetic properties after storage due to increased iron oxide.

Keywords: Material, electromagnetic, microwave, ferrite

INTRODUCTION

The ferrites are homogeneous ceramic materials dark gray or black color which is made up of a blend of different types of oxides with iron oxide and have different crystalline structures.[1] It is also considered as ionic compounds and its magnetic properties due to the magnetic ions they contain. The high permeability due to the distribution of the wall of the field controlled by the sintering density and by increasing the size of particleboard.[2] Barium hexaferrite (BHF) and its substituted derivatives have been considered as candidates with the most potential due to their chemical stability and suitable magnetic characteristics.[3]

Ferrites are ideally suited for making device such as inductor cores, circulators, memory devices, and also for various microwave application. A reduction in size and weight of power supplies can be achieved using switched-mode or resonant concepts. For the voltage conversion, several circuit designs are in use with ferrites as transformer core materials. Transformer ferrites must show low-energy losses at high induction levels at higher and higher frequencies; this requires the development of new ferrite materials with constantly improving loss characteristics.[4] Although the saturation magnetization of ferrites is less than that of ferromagnetic alloys, they have advantages such as applicability at higher frequency, lower price, and greater electrical resistance. Ferrites are classified into two groups, namely, magnetically soft and hard. Furthermore, depending on their crystal symmetry, they may be cubic, hexagonal, or orthorhombic.[5]

Ti, a tetravalent element, is well known candidate to cosubstitute Fe^{3+} ions. The ionic radius of Ti^{4+} ion is 0.605 Å, which is smaller than Fe^{3+} ion (0.645 Å). Furthermore, the electronegativity of Ti (1.54) is small compared with Fe (1.83). Hence, Ti^{4+} ions may easily substitute Fe^{3+} ions in the structure with minimal impact on the intrinsic structure of the ferrite.[6]

The main applications of these materials intend to reduce the human exposure to microwaves by means of absorbing coatings.[2,7] Ti-doped BHF powder is an efficient absorber of electromagnetic waves in the microwave spectrum. To

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optimize the Ti-doped BHF microwave absorption properties increase in the saturation magnetization (M_S) and a decrease in the coercivity (JH_C) are required.[8,9] These properties depend on the localization of the Ti^{4+} in BHF structure. According to literature,[10,11] the Ti^{4+} ions preferentially occupy the octahedral $4f_2$ sites of the BHF structure when the Ti-doped BHF is synthesized using the ceramic route, especially at low doping rates.[12]

BHF in powder form is one of widely implicated magnetic ceramic materials by both researchers and manufacturers in many applications such as permanent magnets, microwave absorber devices, and recording media. BHF is attractive due to its high stability, excellent high-frequency response, narrow switching field distribution and its temperature coefficient of coercivity in various applications, fairly large magnetocrystalline isotropy, high Curie temperature and relatively large magnetization, corrosion resistivity as well as chemical stability.[1-13]

In this paper, BHF substituted by Ti^{4+} (chose cosubstitution non-magnetic Ti^{4+} ions for Fe^{3+} at different levels to obtain a wide range of coercivity and high magnetic permeability) using conventional ceramic techniques is investigated by differential thermal analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), and magnetic measurements by vibrating sample magnetometer (VSM). The approach to saturation law was used to determine zero-field saturation magnetization M_s and anisotropy field H_a.

EXPERIMENTAL

Ti-doped BHF ($BaTi_xFe_{12-x}O_{19}$) is prepared by conventional ceramic techniques (the conventional ceramic methods, i.e., high-energy ball milling was employed to obtain high quality of BHF)**.** The materials used were ferric oxide (Fe_2O_3), barium oxide (BaO), and titanium oxide (TiO_2) of purity greater than 98%. Ratios were calculated accurately by weighing of materials involved in the preparation of ferrite samples using an electronic balance its sensitive up to 0.0001 g. After grinding, the mixed oxides individually to obtain homogeneous size distribution and to facilitate the process of granule homogeneity between these compounds during the mixing. The powdered oxides were mixed with deionized water and then placed in the furnace. A time-temperature program was started in the furnace after placing the mixture sample. Heating rate was 10°C/min until it reaches the reaction temperature (Tc) (1100 or 1200°C) which remained for 10 h then cooling started before collecting the samples.

The crystallite phases present in the different samples were identified by XRD utilizing Bruker axis D8 diffract meter using Cu-Ka (λ=1.5406) radiation operating at 40 kV and 30 mA at a rate of 2°/min. The diffraction data were recorded for 2θ values between 20° and 80°. The particles morphology was observed using the SEM to study the surfaces micrographic appearance, to find out the effect of substitution on the structural properties, and to investigate the particle size measurements distribution of Ti-doped BHF samples.

The magnetic properties of the ferrites were measured at room temperature using a (VSM; 9600-1 LDJ, USA) in maximum applied field of 15 G. From the obtained hysteresis loops, the saturation magnetization (M_s), remanence magnetization (M_r), and the coercive field (Hc) were determined.

The same samples were marked and preserved on laboratory shelve in ambient conditions for 12 years and then the same above-mentioned characterization routines were employed for comparison and revealing the effect of long period storage.

RESULTS AND DISCUSSION

Structure and Morphology of Samples

XRD before 12 years

Figure 1 shows XRD patterns of Ti-doped BHF sintering at 1100°C–1200°C for 10 h. When comparing the XRD schemes of x=0, x=1, and x=3, we find that there is a significant correlation in the results. In addition to the appearance of Fe_3O_4 phase at x=3, indicating that the increased titanium ratio generated an increase in ion exchange iron; hence, the Fe_3O_4 phase will appear. It is also clear that increasing the amount of substitution of x gives a lower relative intensity and width peaks indicating a decrease in particle size.[8]

XRD after 12 years

Figure 2 shows the results of the same samples under the same conditions after 12 years. New and very well phases can be seen.

SEM before 12 years

Figure 3 shows the images of the surface of Ti-doped BHF. Image (a) shows that the interaction of this sample when x=1 at T=1100°C for 10 h did not complete and the large pores

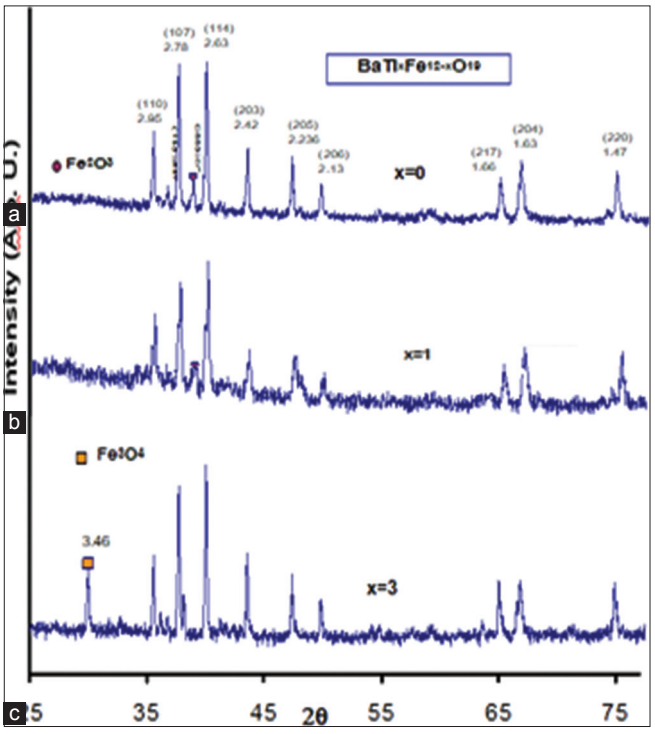

Figure 1: X-ray diffraction patterns of Ti-doped barium hexaferrite (a) x=0, (b) x=1, and (c) x=3 at T=1200°C for 10 h before 12 years

have been shown in the surface, while the image (b) shows that the interaction will be integrated and homogeneous when T is increased to T=1200°C for 10 h. The interaction of the ferrite and particle size will be better than in the lower sintering, therefore, less porosity and better homogeneity of the sample, while image (c) shows the surface of Ti-doped BHF when x=3 at 1200°C for 10 h. It is expected that increasing of replacing of iron ions by Ti ions will decrease the diameter of the crystal; hence, the particle size and porosity will decrease, this is shown by the XRD (1) from the width and low height of the peaks.

The pictures above and the table below have shown that grain size decreased with increasing of x and it increased with increasing of Tc. The decreasing of x will be better than increasing it. Table 1 shows the grain size of the samples.

SEM after 12 years

Figure 4 and Table 2 show that the grain size decreased with increasing of x while it increased with increasing of Tc for the same reasons mentioned above, these granular sizes correspond to the results 12 years ago. However, we note from the results that granular size increases overtime due to increase of oxidation in samples.

Magnetic Properties of Prepared Samples

The hysteresis loop (B-H loop) is an important property of any magnetic material and it is a measure of the lost energy per volume during a magnet cycle. The density of the magnetic saturation is dependent on the composition of the ferrite structure and it increases when the Tc increases, and its effective values reduce due to the porosity of samples.[14]

Nanoparticles with a coercive field strength above 5 kOe derived BHF are convenient for permanent magnets, but the magnetocrystalline anisotropy is too large for recording media applications. Therefore, the partially substituted Fe^{3+} ions of the hexaferrite phase, for example, with metals CO_2^+, Mn^{2+}, Ni^{2+}, and Ti^{4+}, etc., were attempted to reduce anisotropy constant.

Before12 years

Figure 5 shows magnetic hysteresis loops of the Ti-doped BHF samples. Saturation magnetization (M_s) and coercivity

Table 1: Grain size of samples before 12 years

Number of samples	T (°C)	x	Grain size (μm)
a	1100	1	0.21
b	1200	1	0.38
c	1200	3	0.28

Table 2: Particle size of samples after 12 years

Number of samples	T (°C)	x	Grain size (μm)
A	1100	1	0.57
B	1200	1	0.76
C	1100	3	0.25
D	1200	3	0.59

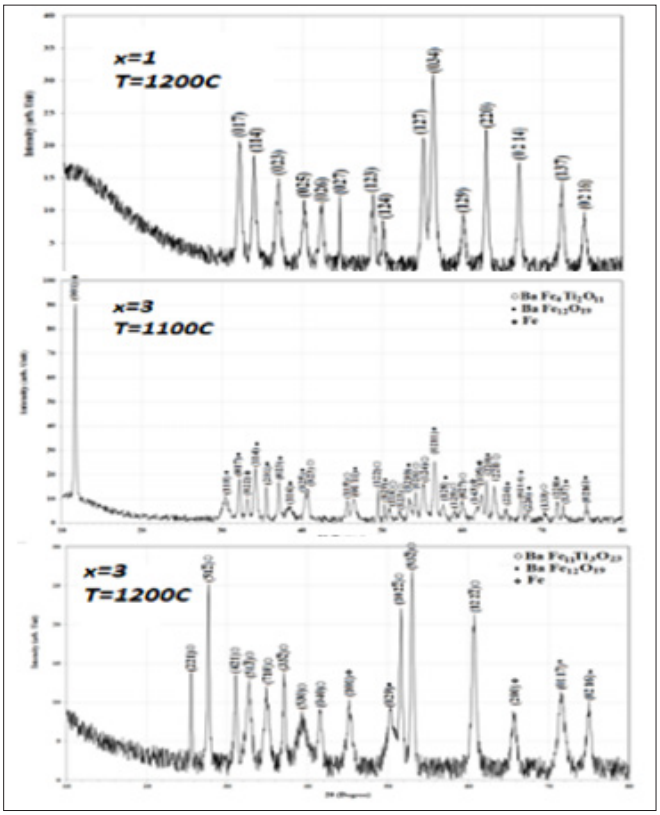

Figure 2: X-ray diffraction patterns of Ti-doped barium hexaferrite after 12 years

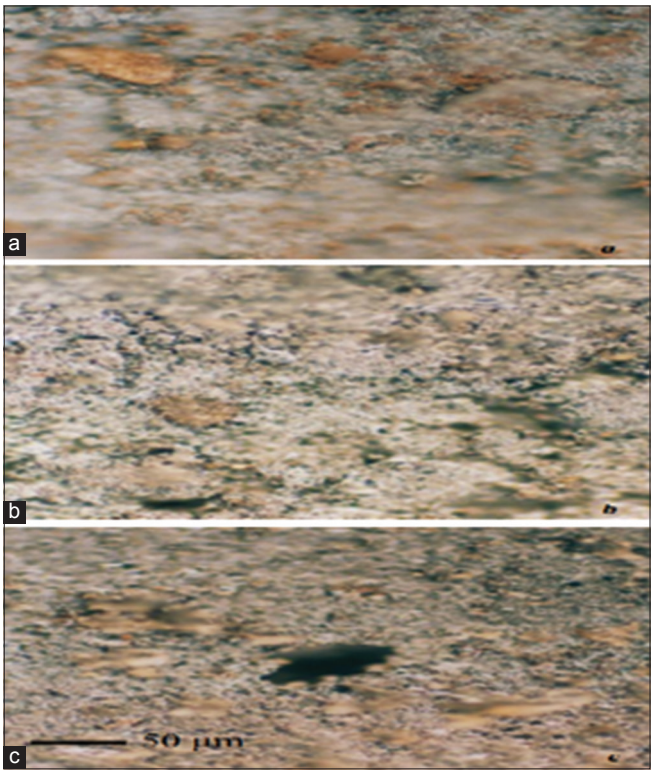

Figure 3: Scanning electron microscopy images and grain size of Ti-doped barium hexaferrite (a) x=1 at 1100°C, (b) x=1 at 1200°C, (c) x=3 at 1200°C

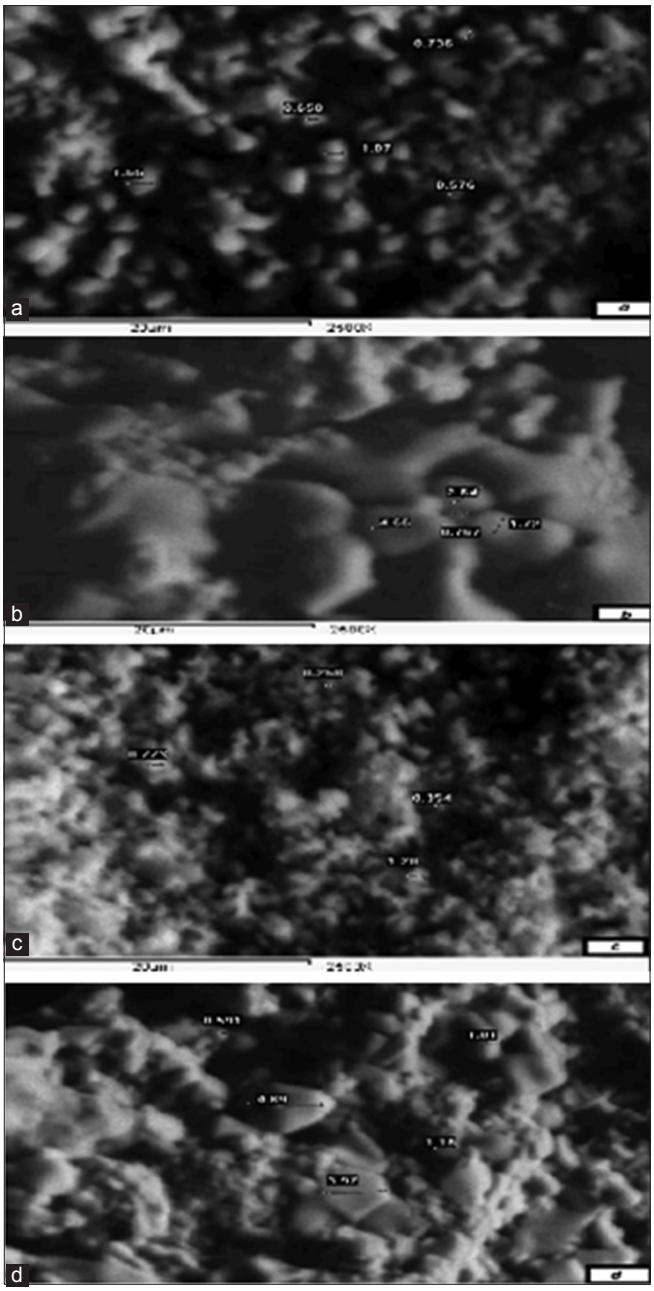

Figure 4: Scanning electron microscopy images and grain size of Ti-doped barium hexaferrite (a) x=1 at 1100°C after 12 years

(Hc) extracted from the loops are given in Table 3 as functions of the x and Tc values. It is seen that both M_s and Hc decreased with increasing x. Hc decreased more rapidly at lower x values, whereas M_s decreased more at higher x values.

Figure 5 shows the hysteresis loop of Ti-doped BHF at 1100°C and 1200°C, respectively, for 10 h. Figure 5 shows that Mr and Ms increased with increasing of Tc and they decreased with increasing of x,[4] while 11 Hc decreased with increasing of x and Tc; therefore, the samples will change from hard to soft material when the concentration and temperature increase. These parameters of all samples are shown in Table 3.

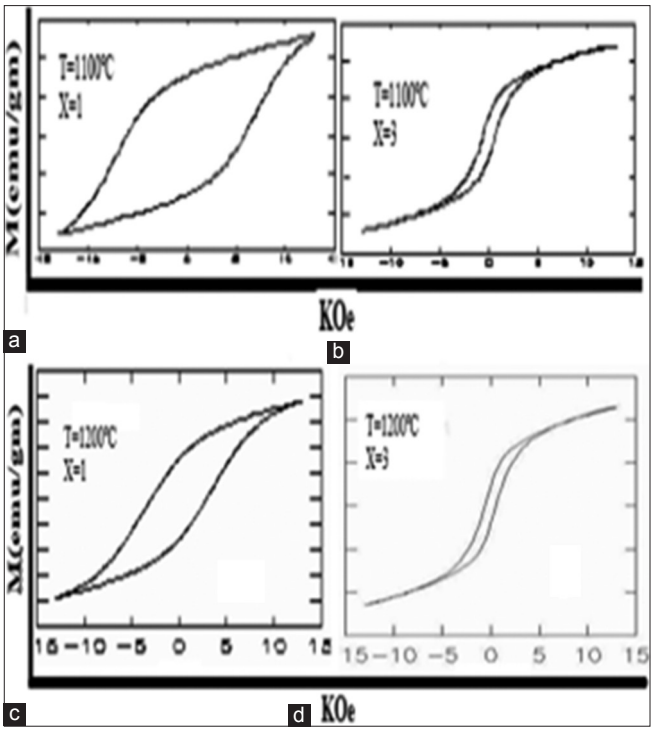

Figure 5: X-ray diffraction of Ti-doped BHF: (a) x=1 at 1100°C

Table 3: The magnetic parameters of Ti-doped barium hexaferrite before 12 years

X	T (°C)	Hc (KOe)	Ms (emu/g)	Mr (emu/g)	Type of material
0	1100	4.5	1.35	0.42	Hard
1	=	5.96	1.3	0.76	Hard
3	=	0.06	1.1	0.37	soft
0	1200	6.9	16.3	8.94	Hard
1	=	2.7	3.85	1.58	Hard
3	=	0.04	2.95	0.56	Soft

Table 4: The magnetic parameters of Ti-doped barium hexaferrite after 12 years

X	T (°C)	Hc (KOe)	Ms (emu/g)	Mr (emu/g)	Type of material
1	1100	1790 G	30	14.26	Hard
3	1100	168 G	20.7	3.25	Soft
1	1200	909.1 G	32.73	10.17	Hard
3	1200	145.5	17.87	2.45	Soft

After 12 years

It is known that magnetic property of ferrite is influenced by the chemical composition and ion distribution in the crystallographic sites. In the basic structure of M-type barium ferrite, Fe^{3+} ions occupy five different interstitial sites: One tetrahedral site 4f1 (↓), one bipyramidal site 2b (↑), and three octahedral sites12k (↑), 2a (↑), and 4f2 (↓). In addition to the reduction of the magnetocrystalline anisotropy due

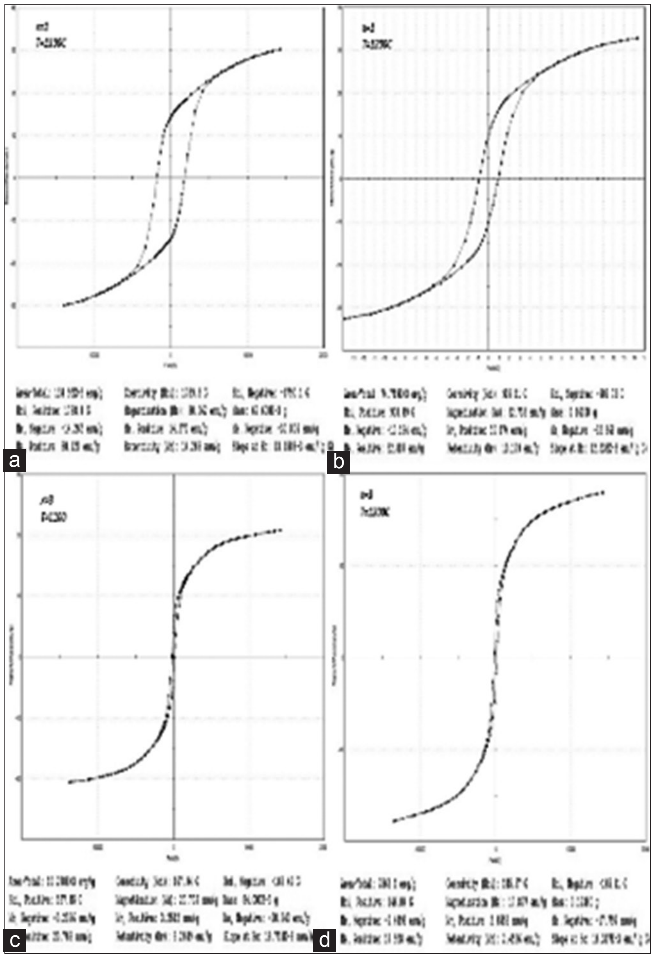

Figure 6: X-ray diffraction of Ti-doped barium hexaferrite: (a) x=1 at 1100°C, (b) x=1 at 1200°C, (c) x=3 at 1100°C, (d) x=3 at 1200°C

to the substitution of iron by titanium, a decrease in the Hc has resulted. This is in agreement with the magnetic results, Figures 5 and 6. The magnetic hysteresis curves show that the original hard magnetic behavior is shifted to soft magnetic by means of high doping content. In effect, it is clearly observed that Ti-doped BHF samples exhibit a decrease of Hc and Ms.

It is clear from the patterns below that samples were not significantly affected by the time factor, where they retained their properties. The hard sample remained hard and soft remained soft. Furthermore, we will see that Hc and Mr decreased with increasing of x and Tc, while Ms will decrease when x increases, but it will increase at x=1 when Tc increases while it will decrease at x=3 when Tc increases. The ratio of Ti is affected by the increasing of oxidation of ferrite due to the storage factor; hence, the samples with the low substitution ratio of x are close to the pure BHF. Figure 6 and Table 4 show B-H loop and the magnetic parameters of our samples after 12 years.

CONCLUSIONS

Ti-doped BHF ($BaTi_xFe_{12-x}O_{19}$) prepared by conventional ceramic techniques. In addition to the appearance of Fe_3O_4 phase at x=3, indicating that the increased titanium ratio generated an increase in ion exchange iron; hence, the Fe_3O_4 phase will appear. It is also clear that increasing the amount of substitution of x gives a lower relative intensity and width peaks indicating a decrease in particle size. The results show that the deviation in the value of d is very low, not exceeding 0.007, due to convergence of fixed network values between Fe^{3+} (0.63 A°) and Ti^{4+} (0.68A) ions.

The density of the magnetic saturation is dependent on the composition of the ferrite structure and it increases when the temperature increases, and its effective values reduce due to the porosity of samples. The magnetic parameters (Mr, Mrs, and Hc) are increasing with increasing temperature. BHF has been substituted by Ti^{4+} with formula ($BaTi_xFe_{12-x}O_{19}$), at different x and temperature. The forms of the B-H loop shown the material changes from the solid to the soft material at high concentrations as well as to all temperatures.

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