Effects of Molybdenum Concentration and Valence State on the Structural and Magnetic Properties of $\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$ Hexaferrites

G.H. Dushaq¹⁾, S.H. Mahmood^{1)†}, I. Bsoul²⁾, H.K. Juwhari¹⁾, B. Lahlouh¹⁾ and M.A. AlDamen³⁾

1) Physics Department, The University of Jordan, Amman 11942, Jordan

2) Physics Department, Al al-Bayt University, Mafraq 13040, Jordan

3) Chemistry Department, The University of Jordan, Amman 11942, Jordan

[Manuscript received 20 January 2013, in revised form 27 April 2013]

© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg

Barium hexaferrites $\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$ ($x = 0.1, 0.2, 0.4$) were prepared by precipitation of the precursors using wet chemical mixture method and then sintering the dried powders at 1100 °C. The properties of the prepared samples were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), vibrating sample magnetometer, and Mössbauer spectroscopy. XRD patterns revealed that all prepared samples had $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite structure as a majority phase. SEM images demonstrated that the samples consisted mainly of hexagonal platelet-like grains with diameters ranging from 100 to 500 nm. Mössbauer spectra revealed that Zn^{2+} ions occupy $4f_1$ sites leading to the splitting of the $12k$ component. However Mo^{6+} ions occupy $2b$ sites while Mo^{4+} prefer $4f_1$ and $12k$ sites. For the sample with $x = 0.4$, Mo^{6+} and Mo^{4+} ions were found to have preference for $2b$ and $12k$ sites, respectively, and to induce the development of Fe^{2+} ions in the hexaferrite, leading to noticeable changes in the magnetic properties of the system. The observed magnetic properties were found to be consistent with the preferential site occupation of metal ions, and the hyperfine fields derived from Mössbauer spectra of these samples.

KEY WORDS: Coercivity; Barium Hexaferrites; Mössbauer spectroscopy; Magnetic properties; Hyperfine Interactions

1. Introduction

Hexagonal ferrites have attracted much attention owing to their excellent characteristics such as high coercivity, high Curie temperature, large saturation magnetization, high magnetocrystalline anisotropy, excellent chemical stability and low cost. M-type ferrites, such as $\text{BaFe}_{12}\text{O}_{19}$ (BaM or barium ferrite) and $\text{SrFe}_{12}\text{O}_{19}$ (SrM or strontium ferrite) are of much current scientific and technological interest due to their potential for a wide range of applications in permanent magnets, magnetic recording and data storage media, and components in microwave and high frequency devices^[1,2].

The structure of BaM is built up from cubic spinel (S) blocks having the spinel-type structure, and hexagonal (R) blocks containing the Ba ions. The structural stacking of $\text{BaFe}_{12}\text{O}_{19}$ layers is of the type RSR^*S^* , where R^* and S^* are rotated by 180° around the hexagonal c -axis. The unit cell contains two formula units, with the ferric ions arranged in five different interstitial sites: three octahedral sites ($12k$, $4f_2$ and $2a$), one tetrahedral site ($4f_1$) and one trigonal bipyramidal site ($2b$)^[3]. The spin-up Fe^{3+} ions are distributed with one ion at the $2a$, one at the $2b$, and six at the $12k$ sites, while the spin-down Fe^{3+} ions are distributed with two at the $4f_1$ and two at the $4f_2$ sites. Accordingly, the magnetic moment per formula (m) can be expressed as follows:

$$m = 6m_{12k} + m_{2a} + m_{2b} - 2m_{4f1} - 2m_{4f2} \quad (1)$$

A number of researchers had prepared and investi-

† Corresponding author. Prof., Ph.D.; Tel.: +962 796709673; E-mail address: s.mahmood@ju.edu.jo (S.H. Mahmood)

gated barium M-type hexaferrites with Fe^{3+} ions substituted by different cations or combination of cations, such as Al-Cr^[4], Co-Ti^[5], Ti-Ru^[6], Al^[7], Co-Zr^[8], and Ga^[9]. Furthermore, investigators had used various chemical and physical techniques to prepare their samples, such as citrate precursor method^[10], sol-gel method^[11], chemical co-precipitation^[12], combustion method^[13], and high-energy ball milling (HEBM)^[6,9]. These studies had demonstrated critical dependence of the properties of the ferrites on the chemical composition, type of substitution, and preparation method.

The type and level of substitution for Fe ions, and the preparation method of M-type hexaferrites was found to influence the magnetic properties of the hexaferrites substantially. In a previous study^[14] it was found that Sn^{2+} - Ru^{4+} substitution for Fe^{3+} kept the saturation magnetization at a relatively high value and reduced the coercivity with increasing the concentration of the substituent. Mössbauer studies revealed that Sn^{2+} ions replaced Fe^{3+} ions on octahedral sites ($4f_2$, $2a$), while Ru^{4+} ions preferred the tetrahedral $4f_1$ and bipyramidal $2b$ sites. Aluminum substitution for Fe in barium hexaferrite, however, was found to reduce the saturation and remnant magnetization^[13]. Further, Mn^{3+} substitution was reported to induce a drop in saturation magnetization and an increase in coercivity as Mn ions preferentially occupy $12k$, $4f_2$ and $2a$ sites^[15]. Also, the substitution of Fe^{3+} ions by Cr^{3+} ions was reported to decrease the saturation magnetization and increase the coercivity with Cr^{3+} ions preferentially occupying the $2a$, $12k$, and $4f_2$ sites^[16]. However, the substitution of Fe ions by Zn-Nb mixture in Sr-hexaferrites was found to increase the saturation magnetization and reduce the coercivity, resulting in material with potential applications in magnetic recording^[17].

In the current study the wet chemical mixture method was used to prepare samples of BaM hexaferrite ($\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$ with $x=0.1, 0.2, 0.4$). The variation of Mo-Zn ratio allowed for obtaining different valence states of Mo in the hexaferrite lattice. Then, preferential site occupation of the different valence states and their effects on the structural and magnetic properties of the hexaferrite system were investigated.

2. Experimental

The precursors of $\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$ ($x=0.1, 0.2, 0.4$) were synthesized by wet chemical mixture method. The atomic ratios of Mo/Zn were chosen to select the valence state of Mo ions which compensates for the charge of the removed Fe^{3+} ions and ensures chemical neutrality of the unit cell. Thus in the sample with $x = 0.1$, we have Mo^{6+} ions, while in the sample with $x = 0.2$, we have Mo^{4+} ions. The required molarities of at least 99% pure Fe_2O_3 , BaCO_3 , ZnO and MoO_3 were dissolved in distilled water and mixed together in a beaker with continuous stirring

on a magnetic stirrer. The mixture was refluxed at 150 °C for 24 h, and then filtered and left to dry in air. The powders were collected, pressed into pellets 1.5 cm in diameter, and sintered in air atmosphere at 1100 °C for 2 h.

The structure of the samples was investigated by X-ray diffraction (XRD) using Philips X'Pert PRO X-ray diffractometer (PW3040/60) with $\text{CuK}\alpha$ radiation ($\lambda=0.154$ nm). XRD diffraction patterns for the samples were recorded over the angular range $15^\circ < 2\theta < 75^\circ$ with scanning step of 0.017° . A powder diffraction software package which includes the standards of international center of diffraction data (ICDD) was used to identify the observed structural phases. The morphology of the particles in the prepared samples was examined using the scanning electron microscope (SEM FEI-Inspect F50/FEG).

Samples for Mössbauer studies were prepared by gently grinding parts of the sample disks, and pressing thin layer of the powder between two circular Teflon desks with a diameter of 2 cm. ^{57}Fe Mössbauer spectra were collected using a standard constant acceleration Mössbauer spectrometer over 512 channels. The spectrum of iron metal at room temperature was used to calibrate the system and the experimental spectra were fitted using routines based on the least squares analysis.

The magnetic measurements were carried out using a vibrating sample magnetometer (VSM Micro-Mag 3900, Princeton Measurements Corporation), with a maximum applied field of 796 kA/m. Samples for magnetic measurements were needle-shape cut from the sintered sample disks. All magnetic measurements were performed at room temperature and the system was calibrated using a nickel foil with a known moment.

3. Results and Discussion

3.1 X-Ray diffraction

Fig. 1 shows XRD patterns for the un-doped (pure $\text{BaFe}_{12}\text{O}_{19}$), and $\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$ ($x=0.1, 0.2, 0.4$) samples. XRD patterns for all samples show a major phase with reflections consistent with those for $\text{BaFe}_{12}\text{O}_{19}$ M-type hexaferrite ($a=(0.5892 \pm 0.0002)$ nm, $c=(2.3215 \pm 0.0005)$ nm) as demonstrated by comparison with the standard pattern (JCPDS 00-043-0002). In addition, weak reflections corresponding to traces of other phases were detected in the patterns for the pure and Mo doped samples. Specifically, the observed weak reflection at about $2\theta=28.2^\circ$ in the pattern for the pure sample indicates the presence of BaFe_2O_4 oxide as a minority phase. However, the pattern for $\text{BaFe}_{11.6}\text{Mo}_{0.4}\text{O}_{19}$ shows the presence of $\alpha\text{-Fe}_2\text{O}_3$ phase as evidenced by the weak reflections at $2\theta=24.2^\circ$, 32.2° , and 35.6° , and BaMoO_4 phase as evidenced by the weak reflections at $2\theta=26.5^\circ$ and $2\theta=27.8^\circ$. The most stable

Fig. 1 XRD patterns for the un-doped sample $\text{BaFe}_{12}\text{O}_{19}$ and for $\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$ ($x = 0.1, 0.2, 0.4$) samples, the standard JCPDS pattern for M-type hexagonal barium ferrite (No. 043-0002) is included for comparison

Mo^{6+} ion thus forms the BaMoO_4 oxide. This leaves deficient amount of Ba for the hexaferrite phase, resulting in the formation of $\alpha\text{-Fe}_2\text{O}_3$ phase.

The average crystallite sizes for the samples were calculated from the positions of the (107) and (114) peaks using the well-known Scherrer formula^[18]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where D is the crystallite size, k is the Scherrer constant, λ is the wavelength of radiation (0.154 nm), β is the peak width at half maximum, and θ is the peak position. The average crystallite sizes of all samples were found to range from 40 nm to 51 nm.

3.2 Scanning electron microscopy

SEM images in Fig. 2 were used to observe the morphology and average size of the particles in the investigated samples. It can be seen from Fig. 2, the particle size distributions and particle shapes for all samples are similar. Further, the images demonstrate that the prepared samples consisted mainly of hexagonal platelet-like particles with diameters ranging from 100 nm to about 500 nm and very few particles be-

Fig. 2 SEM micrographs for the hexaferrite samples: (a) $\text{BaFe}_{12}\text{O}_{19}$; (b) $\text{BaFe}_{11.6}\text{Mo}_{0.1}\text{Zn}_{0.3}\text{O}_{19}$; (c) $\text{BaFe}_{11.6}\text{Mo}_{0.2}\text{Zn}_{0.2}\text{O}_{19}$; (d) $\text{BaFe}_{11.6}\text{Mo}_{0.4}\text{O}_{19}$

yond this range.

3.3 Mössbauer spectroscopy

Mössbauer spectra of all samples are shown in Fig. 3. Each spectrum shows complex structure consisting of a number of magnetically split sextet components corresponding to iron ions in the five crystallographic sites $4f_2$, $4f_1$, $2a$, $12k$, $2b$ of the BaM hexaferrite structure. Attempts to fit the spectrum of the pure sample with five components failed due to similarity of the hyperfine parameters for the $2a$ and $4f_1$ sites. Thus the spectrum was fitted with four sextet components having parameters as in Table 1. The first component with the highest hyperfine field is associated with Fe^{3+} ions in $4f_2$ sites in the R blocks. The second component is associated with the ($2a + 4f_1$) sites in the S blocks. The third component corresponds to iron ions in the $12k$ sites at the R-S interfaces, while the fourth component is associated with the $2b$ by-pyramidal sites in the R blocks. The hyperfine parameters for this sample are in excellent agreement with the results of previous studies^[19,20]. In our fitting procedure, the relative intensities for the components were not constrained to reflect the site

multiplicity in the hexaferrite lattice. The observed deviations of the relative intensities from the theoretical values of 16.7%, 25.0%, 50.0% and 8.3% could be due to differences in Mössbauer Lamb factors for the different sites, leading to different absorption efficiencies. The number of Fe ions at each site as derived by multiplying the corresponding relative intensity by the number of Fe ions in the unit cell (24 ions) is consistent with the results of lab A in Ref. [19] where the relative intensities were not constrained. The large quadrupole splitting for the last component is a consequence of the high electric field gradient at the $2b$, five-fold crystallographic sites.

The spectrum for the sample with $x=0.1$ ($\text{BaFe}_{11.6}\text{Mo}_{0.1}\text{Zn}_{0.3}\text{O}_{19}$) shows structure similar to that for the pure sample in addition to the evolution of a fifth component which is visually obvious at the inner shoulder of the $12k$ component. The spectrum was thus fitted with five sextet components, the first four of which correspond to those observed in the spectrum of the un-doped sample, with very much the same hyperfine parameters. The fifth component has hyperfine field of 37.6 T and isomer shift equals to that for the $12k$ component. Since Zn^{2+} ions have

Fig. 3 Mössbauer spectra for the hexaferrite samples: (a) $\text{BaFe}_{12}\text{O}_{19}$; (b) $\text{BaFe}_{11.6}\text{Mo}_{0.1}\text{Zn}_{0.3}\text{O}_{19}$; (c) $\text{BaFe}_{11.6}\text{Mo}_{0.2}\text{Zn}_{0.2}\text{O}_{19}$; (d) $\text{BaFe}_{11.6}\text{Mo}_{0.4}\text{O}_{19}$

Table 1 The hyperfine field (B_{hf}), isomer shift (CS), quadrupole splitting (QQ), and percentage relative intensities (I) of the components of the spectra for $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$ samples

Mössbauer parameter	Site	$\text{BaFe}_{12}\text{O}_{19}$	$\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$		
			$x=0.1$	$x=0.2$	$x=0.4$
$B_{\text{hf}1}$ (T)	$4f_2$	51.7	51.6	51.6	51.6
$B_{\text{hf}2}$ (T)	$2a + 4f_1$	49.3	49.3	49.4	49.3
$B_{\text{hf}3}$ (T)	$12k$	41.6	41.6	41.8	41.6
$B_{\text{hf}4}$ (T)	$2b$	40.5	40.4	41.1	40.2
$B_{\text{hf}5}$ (T)		-	36.7*	37.5*	
QQ ₁ (mm/s)		0.16	0.16	0.14	0.12
QQ ₂ (mm/s)		0.22	0.19	0.21	0.19
QQ ₃ (mm/s)		0.40	0.40	0.38	0.41
QQ ₄ (mm/s)		2.19	2.18	2.20	2.17
QQ ₅ (mm/s)		-	0.30*	0.31*	
CS ₁ (mm/s)		0.37	0.38	0.37	0.37
CS ₂ (mm/s)		0.25	0.27	0.27	0.27
CS ₃ (mm/s)		0.34	0.34	0.34	0.35
CS ₄ (mm/s)		0.29	0.30	0.30	0.31
CS ₅ (mm/s)		-	0.35*	0.35*	
I_1		16.4	17.0	17.2	16.6
I_2		28.6	26.6	26.7	29.4
I_3		50.0	47.1	47.0	50.5
I_4		5.0	4.6	5.2	3.5
I_5			4.7*	3.9*	

Note: * Quantities corresponding to $12k'$ site

strong preference for tetrahedral $4f_1$ sites as evidenced by the noticeable drop in relative intensity for the corresponding component, the partial occupation of the $4f_1$ sites by Zn^{2+} ions weakens the hyperfine field in neighboring $12k$ sites due to the reduction of the $4f_1$ - $12k$ superexchange interactions. This results in the evolution of a new component ($12k'$) with lower hyperfine field corresponding to such $12k$ sites neighboring $4f_1$ sites occupied by Zn^{2+} ions. Such splitting of the $12k$ sites into two components was observed in other systems of hexaferrites^[21–23]. The sextet with hyperfine field of 37.6 T is thus associated with the $12k'$ sites at the R-S interfaces. The number of Fe^{3+} ions at each site is calculated by multiplying the corresponding relative intensity by the total number of Fe^{3+} ions in the unit cell (23.2 ions). The observed drop in the intensity of the second component corresponds to a 0.3 reduction in the number of Fe^{3+} ions per formula, which is consistent with 0.3 Zn^{2+} ions occupying the $4f_1$ sites. On the other hand, the drop in the intensity of the $2b$ component corresponds to a reduction of 0.1 in the number of Fe^{3+} ions in $2b$ sites, which is consistent with the 0.1 Mo^{6+} ions preferring the $2b$ sites. The number of Fe^{3+} ions in the $4f_2$ and ($12k + 12k'$) remains the same as in the undoped sample, which indicates that these sites are not affected by the doping with Mo-Zn ions. However, due to the weak intensity of the $2b$ component, which imposes significant uncertainty in determining its area to within our experimental uncertainty of about 0.5%, and the small variations in intensities due to low Mo concentration, we may not be able to have a decisive conclusion regarding the preferred sites of Mo^{6+} ions

from Mössbauer data alone.

The spectrum for the sample with $x = 0.2$ ($\text{BaFe}_{11.6}\text{Mo}_{0.2}\text{Zn}_{0.2}\text{O}_{19}$) was also fitted with five components in order to account for the asymmetry of the outer line of the $12k$ component. Comparing the hyperfine parameters for this sample with those of the $x=0.1$ sample we notice a slight increase in hyperfine fields beyond experimental uncertainties (0.5 T in B_{hf} , 0.01 mm/s in CS, and 0.02 mm/s in QQ). The last component with the smallest hyperfine field is associated with $12k'$ sites. The reduction in intensity for this component and the small increase in its hyperfine field compared with that for the sample with $x=0.1$ is attributed to the lower Zn^{2+} content in this sample which is responsible for lowering the hyperfine field and the development of this component. The drop in relative intensity of the second component corresponds to a 0.3 reduction in the number of Fe^{3+} ions per formula in the corresponding sites. Thus, the occupation of $4f_1$ sites by the 0.2 Zn^{2+} ions per formula does not account for the observed drop in relative intensity for the second component, which indicates that about half of the Mo^{4+} ions also occupy the ($2a + 4f_1$) sites. In addition, the relative intensity of the ($12k + 12k'$) component decreases by an amount corresponding to a reduction of the number of iron ions in these interfacial sites by 0.1, which indicates that Mo^{4+} ions are equally distributed between the ($12k + 12k'$) sites and the ($4f_1 + 2a$) sites. The relative populations of the $2b$ and $4f_2$ sites by iron ions in this sample are similar to that for the pure sample, indicating that Mo^{6+} and Mo^{4+} ions exhibit different preferential site occupations. This conclusion can be

further supported by the fact that Mo^{6+} ion is spherically symmetric with ^{36}Kr electronic configuration which makes it possible for such small ion (of radius 0.064 nm as compared to that of 0.079 nm for Mo^{4+}) to fit into the small space available in the 2b site.

The spectrum for the sample with $x=0.4$ ($\text{BaFe}_{11.6}\text{Mo}_{0.4}\text{O}_{19}$) shows structure similar to that for the pure sample as far as splitting of the 12k component is concerned. The components of this spectrum are however not clearly resolvable due to complexity of the spectrum. The best fit of the spectrum for this sample was achieved with an additional component having hyperfine field of 52.2 T, center shift of 0.42 mm/s, and quadrupole splitting of -0.21 mm/s. These hyperfine parameters are characteristic of $\alpha\text{-Fe}_2\text{O}_3$ phase, which suggests the assignment of the additional component to the minority iron oxide phase observed in XRD pattern of this sample. The relative intensity for this component (8.4%) is in qualitative agreement with XRD relative intensity for the structural line of this phase. The relative intensities appearing in Table 1 for the various sub-spectra of this sample were normalized to 100%, and indicate that the Fe populations of the 2b and 12k sites were affected the most, suggesting partial substitution of Mo^{6+} and Mo^{4+} at these sites, respectively. Charge neutrality then suggests the development of the Fe^{2+} valence state in this sample. However, the Fe^{2+} valence state could not be resolved in the spectrum of this sample, since as in the standard spectrum of the spinel structure, the hyperfine parameters of Fe^{2+} and Fe^{3+} ions are similar as a consequence of electron hopping between the two valence states at room temperature.

3.4 Magnetic Measurements

The hysteresis loops for all samples are shown in Fig. 4. The curves do not saturate in an applied field up to 796 kA/m. The saturation magnetization was obtained from M vs. $1/H$ linear relation in the high field part of the curves. The linear fit in this region gave results with uncertainty better than 1%. The saturation magnetization ($71 \text{ A}\cdot\text{m}^2/\text{kg}$) for the pure sample is consistent with the bulk value at room temperature. The remnant magnetization for this sample of about $35 \text{ A}\cdot\text{m}^2/\text{kg}$, and the squareness ratio of about 0.5 are characteristic of single domain particles which have a critical size of 460 nm for BaM hexaferrites^[24]. This is consistent with the results obtained from SEM images.

Fig. 5 shows the saturation magnetization as a function of Mo concentration for the doped samples, together with that for the un-doped sample. The saturation magnetization for the sample $\text{BaFe}_{11.6}\text{Zn}_{0.3}\text{Mo}_{0.1}\text{O}_{19}$ increases by about 2.2% with respect to the un-doped sample. The spin-down ($4f_1$) sites occupation by Zn^{2+} ions and the spin-up (2b) sites occupation by Mo^{6+} ions as indicated

Fig. 4 Hysteresis loops for $\text{BaFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$ samples

Fig. 5 Saturation magnetization as a function of x of $\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$ ($x = 0.1, 0.2, 0.4$). The saturation magnetization of the $\text{BaFe}_{12}\text{O}_{19}$ sample is also plotted for comparison

by Mössbauer spectra would result in 5% increase in saturation magnetization according to the simple model in Eq. (1). This is more than double the value obtained from our magnetic data, and is explained on the basis of the weakening of the $2a - 4f_1$ superexchange interaction due to the reduction in the $4f_1$ spin-down magnetic moment resulting from the occupation of $4f_1$ sites by Zn^{2+} ions. Accordingly, the $2a - 12k$ superexchange interactions become dominant, resulting in a spin-flip or non collinear spin structure in the $2a$ sublattice, and a consequent reduction in net magnetization. The observed small, but detectable increase in magnetization is thus a result of the competition between the increase the magnetization due to the reduction of the $4f_1$ spin-down net moment, and the decrease due to the reduction of the spin-up $2a$ moment. On the other hand, the saturation magnetization for the sample $\text{BaFe}_{11.6}\text{Zn}_{0.2}\text{Mo}_{0.2}\text{O}_{19}$ increases by about 5.8%. This is consistent with our Mössbauer data which predict a 5% increase (0.2/4.0) in net magnetic moment as a result of the occupation of spin-down $4f_1$ sublattice by 0.2 Zn^{2+} ions and 0.1 Mo^{4+} ions, and of spin-up $12k$ sublattice by 0.1 Mo^{4+} ions. Further, the small increase in magnetization for

Fig. 6 Coercivity of $\text{BaFe}_{11.6}\text{Mo}_x\text{Zn}_{0.4-x}\text{O}_{19}$ as a function of x . The data point for the $\text{BaFe}_{12}\text{O}_{19}$ sample is included for comparison

this sample compared with that for the previous sample could be associated with the small increase observed in hyperfine field.

Fig. 6 shows that the coercivity of the prepared samples is in the range 158–180 kA/m, which is about half the value reported for pure BaM hexaferrites prepared by ball milling^[6,9]. These coercivities and the relatively high saturation magnetization place the prepared system in a class of materials having potential for applications in high density magnetic recording. The initial drop of the coercivity at low concentration of Mo is consistent with the preferred occupation of Mo^{6+} ions at $2b$ sites, which have the highest positive contribution to magnetocrystalline anisotropy. This observation is supported by the preferential site occupation of Mo^{6+} ions as determined from Mössbauer data. However, the observed increase in coercivity for $x = 0.2$ is associated with the difference in preferential site occupation of the Mo ions with different valence states, where Mo^{4+} ions in this sample prefer to occupy $4f_1$ and $12k$ sites as indicated by Mössbauer spectroscopy. The onset of occupation of $12k$ sites (with negative contribution to the magnetocrystalline anisotropy) by nonmagnetic ions is responsible for the observed rise in coercivity with respect to the sample with $x = 0.1$. However, the coercivity for this sample remained below that for the pure sample due to the fact that more nonmagnetic ions (all Zn ions and about half of Mo ions) are distributed at sites with positive magnetocrystalline anisotropy than at $12k$ sites.

The saturation magnetization for the sample $\text{BaFe}_{11.6}\text{Mo}_{0.4}\text{O}_{19}$ drops slightly below the value for the pure sample, and the coercivity increases appreciably. In this sample, the stable Mo^{4+} and Mo^{6+} ions partially occupy interstitial sites in the hexaferrite lattice, and partially segregate into a separate oxide phase, in accordance with the XRD patterns. The presence of these ions in the hexaferrite lattice leads to the development of Fe^{2+} ionic state in order to maintain chemical balance and electrostatic neutral-

ity. The observed drop in saturation magnetization could therefore be partially associated with the development of the Fe^{2+} valence state with lower magnetic moment per ion ($S = 2$ as compared with $S = 2.5$ for Fe^{3+}), in addition to the presence of impurity nonmagnetic phases. The magneto-crystalline anisotropy originates from dipole-dipole interaction which is enhanced by the presence of Fe^{2+} with high orbital angular momentum in comparison with Fe^{3+} . Since the impurity phases are nonmagnetic and are not expected to contribute to magnetic anisotropy in this sample, the observed 16% increase in the coercivity could be partially associated with the presence of ferrous ions in the hexaferrite.

4. Conclusions

The wet chemical mixture method was successful in synthesizing the precursors for pure and substituted hexaferrites with relatively high saturation magnetization and low coercivity. The substituted hexaferrites have a fixed number of iron ions (11.6 per formula unit) and the Mo ions substitute the Zn ions. This substitution induced a redistribution of Fe ions in the lattice resulting in changes of the magnetic properties and the relative intensities of Mössbauer subspectra. The saturation magnetization increased from 71.0 Am^2/kg for the un-doped sample to a maximum value of 75.1 Am^2/kg for the sample with $x = 0.2$ as a result of the preferential spin-down site occupation by the nonmagnetic ions. The observed changes in Mössbauer relative intensities and the sharp increase in coercivity for the sample $\text{BaFe}_{11.6}\text{Mo}_{0.4}\text{O}_{19}$ could be evidence of the development of Fe^{2+} ionic state to maintain electrostatic neutrality as Mo^{4+} and Mo^{6+} ions partially substitute Fe^{3+} ions in the hexaferrite lattice. However, further studies involving the transport properties of the system could be helpful in confirming the presence of the ferrous state in the hexaferrite lattice.

Acknowledgements

This work is supported by a generous grant from the Scientific Research Fund (SRF) in Jordan under grant number (S/1/21/2009). The financial support of the German Academic Exchange Program (DAAD), and the Deanship of Scientific research at the University of Jordan under contract number 1404 are also acknowledged.

REFERENCES

- [1] R.C. Pullar, Prog. Mater. Sci. **57** (2012) 1191.
- [2] U. Ozgur, Y. Alivov and H.J. Morkoc, J. Mater. Sci.: Mater. Electron. **20** (2009) 789.
- [3] E.W. Gorter, Proc. IEEE B **104** (1957) 255.
- [4] M.N. Ashiq, M.J. Iqbal and I.H. Gul, J. Magn. Magn. Mater. **323** (2011) 259.
- [5] D. Chen, Y. Liu, Y. Li, W. Zhong and H. Zhang, J. Magn. Magn. Mater. **323** (2011) 2837.

- [6] I. Bsoul, S.H. Mahmood and A.F. Lehlooh, J. Alloys Compd. **498** (2010) 157.
- [7] I. Bsoul and S.H. Mahmood, Jordan J. Phys. **2** (2009) 171.
- [8] Ch. Venkateshwarlu, Ch. Ashok, B. Appa Rao, D. Ravinder and B.S. Boyanov, J. Alloys. Compd. **426** (2006) 1.
- [9] I. Bsoul and S.H. Mahmood, J. Alloys. Compd. **489** (2010) 110.
- [10] N. Koga and T. Tsutaoka, J. Magn. Magn. Mater. **313** (2007) 168.
- [11] M. Han, Y. Ou, W. Chen and L. Deng, J. Alloy. Compd. **474** (2009) 185.
- [12] M.J. Iqbal, M.N. Ashiq and P.H. Gomez, J. Alloys. Compd. **478** (2009) 736
- [13] V.N. Dhage, M.L. Mane, A.P. Keche, C.T. Birajdar and K.M. Jadhav, Phys. B **406** (2011) 789.
- [14] A. González-Angeles, G. Mendoza-Suárez, A. Grusková, J. Sláma, J. Lipka and M. Papánová, Mater. Lett. **59** (2005) 1815.
- [15] P. Sharma, R.A. Rocha, S.N. Medeiros, B. Hallouche and A. Paesano Jr., J. Magn. Magn. Mater. **316** (2007) 29.
- [16] S. Ounnunkad and P. Winotai, J. Magn. Magn. Mater. **301** (2006) 292.
- [17] Q.Q. Fang, H.W. Bao, D.M. Fang, J.Z. Wang and X.G. Li, J. Magn. Magn. Mater. **278** (2004) 122.
- [18] B.E. Warren, X-ray Diffraction, Addison-Wesley, Reading, MA, 1969, p.253.
- [19] B.J. Evans, F. Grandjean, A.P. Lilot, R.H. Vogel and A. Gérard, J. Magn. Magn. Mater. **67** (1987) 123.
- [20] F. Gao, D. Li and S. Zhag, J. Phys.: Condens. Matter. **15** (2003) 5079.
- [21] B. Kaur, M. Bhat, F. Licci, R. Kumar, S.D. Kulkarni, P.A. Joy, K.K. Bamzai and P.N. Kotru, J. Magn. Magn. Mater. **305** (2006) 392.
- [22] A. González-Angeles, G. Mendoza-Suarez, A. Grusková, M. Papánová and J. Slama, Mater. Lett. **59** (2005) 26.
- [23] I. Bsoul, S.H. Mahmood, A-F. Lehlooh and A. Al-Jamel, J. Alloys Compd. **551** (2013) 490.
- [24] L. Rezlescu, E. Rezlescu, P.D. Popa and N. Rezlescu, J. Magn. Magn. Mater. **193** (1999) 288.