Magnetic studies of $\text{Mn}_{0.2}\text{Cr}_{1.8-x}\text{Fe}_x\text{O}_3$ nano oxides prepared via hydrothermal route

Kalengay Mbela, T. Moyo, Nadir S. E. Osman, N. Akdoğan & M. Öztürk
Your article is protected by copyright and all rights are held exclusively by Springer Science + Business Media New York. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer’s website. The link must be accompanied by the following text: “The final publication is available at link.springer.com”.
Magnetic studies of Mn$_{0.2}$Cr$_{1.8-x}$Fe$_x$O$_3$ nano oxides prepared via hydrothermal route

Kalengay Mbela$^1$ · T. Moyo$^1$ · Nadir S. E. Osman$^1$ · N. Akdoğan$^2$ · M. Öztürk$^2$

Received: 15 December 2015 / Accepted: 6 May 2016

Abstract Manganese–iron chromium oxides (Mn$_{0.2}$Cr$_{1.8-x}$Fe$_x$O$_3$) with x varying from 0.3 to 1.3 have been produced by hydrothermal process in a stirred pressure reactor from pure metal chlorides. Single phase corundum structure and nanophase structure of the as-synthesized samples were confirmed by X-ray diffraction and by transmission electron microscope. The results show that the produced powders have an average size of 23 nm. The Mössbauer spectra recorded at about 300 K show transition from paramagnetic to ordered magnetic spin state. The shift in hysteresis loops observed along the magnetic field axis is associated with exchange bias effect. The exchange bias field increases as the particle size decreases with increased Fe content x. The loop shifts are different with different particle sizes suggesting that the materials at room temperature may be superparamagnetic.

1 Introduction

In recent years, magnetic nanoparticles have been the subject of intense research not only for their fundamental scientific interest but also for their potential applications in transformers, loading coils, magnetic storage media, biosensor device, catalysts and medical applications, such as targeted drug delivery [1]. It is well known that most of the physical properties of these nanoparticles strongly depend on size, shape, size distribution and interaction between the particles [2]. Their magnetic and structural properties are influenced by particle sizes [3, 4], degree of crystallinity [5], pressure [6] and doping [7, 8]. The effect of metal doping by titanium [9, 10], tin [11, 12], manganese [13], aluminium [14, 15], gallium [16] and indium [17] on the electrical, magnetic and other physical properties of α-Fe$_2$O$_3$ (hematite) has been investigated for some time. It is generally proposed that the dopant metal ions substitute for Fe$^{3+}$ in the corundum-related structure of α-Fe$_2$O$_3$ with the consequent formation of cationic and anionic vacancies. The difference in ionic radius between the dopant metal ion and that for Fe$^{3+}$ will influence the structural characteristics and phase behavior of the doped system. The tin-doped α-Fe$_2$O$_3$ system has attracted interest because of its sensing properties for gases such as methane and carbon monoxide [18–20]. The properties of α-Cr$_2$O$_3$ can also be drastically changed by varying their size and introducing dopants. Literature suggests that introducing dopants into the sensor material is an effective way to improve sensitivity and selectivity [21]. Formation of mixed oxides leads to the modification of the electronic structure of the system. Surface properties are expected to be influenced by new boundaries between grains of different chemical composition. It is anticipated that all these phenomena will contribute advantageously to the gas sensing mechanism [21]. The substitution of Cr$^{3+}$ by Fe$^{3+}$ to form solid solutions of the type α-Fe$_{2-x}$Cr$_x$O$_3$ has been known for some time [22]. Although there have been several studies of the α-Fe$_{2-x}$Cr$_x$O$_3$ [22–24] system, there appears to have been little activity in the doping of these materials. Berry et al. [25] initiated a study of tin-doped oxides of the type α-Cr$_2$O$_3$ and α-(FeCr)$_2$O$_3$ and reported on their structural properties. We have been interested in the doping and the examination of magnetic properties of these materials. Recently we observed the exchange bias phenomenon in Mn$_{0.2}$Fe$_2$Cr$_{1.8-x}$O$_3$ at low

$^1$ School of Physics, University of KwaZulu-Natal, Durban 4000, South Africa

$^2$ Department of Physics, Gebze Institute of Technology, 41400 Gebze, Turkey

Published online: 11 May 2016

DOI 10.1007/s10854-016-4953-z
temperature [26]. In this work we investigate the effect of doping with manganese due to its ability to exhibit variable oxidation states and negative interactions. We have made for this purpose Mn$_{0.2}$Fe$_x$Cr$_{1.8-x}$O$_3$ (0.2 ≤ $x$ ≤ 1.3, in steps of 0.2) fine powders and investigated magnetic properties.

2 Experimental details

We have prepared Mn$_{0.2}$ Cr$_{1.8-x}$ Fe$_x$ O$_3$ compound by hydrothermal technique. The starting materials were MnCl$_2$ (99.99 %) and FeCl$_3$·6H$_2$O (99 %) which were supplied by Sigma Aldrich. Suitable stoichiometric amounts of metal chlorides were mixed in deionized water by a magnetic stirrer for about 30 min. The precipitation reagent were added drop wise to the salt mixtures until complete precipitation. The precipitate was washed several times over Whatman GF/F microfiber filters by deionised water until all the chloride ions were removed as confirmed by using a standard solution of AgNO$_3$. The precipitate was finally dispersed in about 400 ml of deionised water. The samples were synthesized in a model 4843 PARR pressure reactor. The samples were heated for 3 h at 100 °C. The pressure in the reactor vessel was maintained at about 120 psi. After the hydrothermal treatment the samples were wash several times by deionized water and then finally in ethanol over Whatman GF/F microfiber filter. The synthesized oxides were dried under 250 W infrared light for 3 h. The ethanol drives out the water from the sample and is easier to remove from sample by drying. The dried powders were homogenized using agate mortar and pestle and sintered at 600 °C for 12 h in order to achieve single phase formation [26, 27]. The X-ray diffraction (XRD) patterns of the samples were obtained by using CoKα radiation (λ = 1.7903 Å) on a Philips diffractometer (type: PW 1710). The Mössbauer spectra were recorded at about 300 K using a conventional constant acceleration spectrometer with a $^{57}$Co source sealed in Rh matrix. The magnetization measurements were performed using two different systems, namely a Lakeshore model 735 vibrating sample magnetometer (VSM) for room temperature measurements and a Quantum Design MPMS SQUID magnetometer for magnetization measurements in applied magnetic fields of up 6 kOe in temperature range 2–400 K. These measurements included hysteresis loops, zero field cooling (ZFC) and field cooling (FC) magnetizations.

3 Results and discussions

Figure 1 shows the XRD patterns for the Mn$_{0.2}$Fe$_x$Cr$_{1.8-x}$O$_3$ compounds. The patterns confirm the formation of the basic corundum structure in all samples. No impurity phases were observed in the patterns. These XRD results are similar to those of Sn doped α-Fe$_2$O$_3$ compounds [25, 28] and which were interpreted in terms of tin occupying both octahedral, interstitial and substitutional sites. It appears that in solid solutions of the type of type α-(FeCr)$_2$O$_3$ manganese occupies similar sites as does tin and magnesium. The refinement of XRD data was performed by Rietveld analysis FullProfSuite for Windows using a model involving a combination of both interstitial and substitutional Mn$^{2+}$ ions in octahedral coordination [29].

The average particle sizes were obtained using the Debye–Scherrer formula [2]. Direct measurement of the grain size and powder morphology for the as prepared samples were also performed by transmission electron microscope (TEM). The TEM pictures in Fig. 2 show that the particles are small. The lattice parameters, the average particle sizes as calculated from XRD data ($D_{XRD}$) and observed by TEM measurements ($D_{TEM}$) are recorded in Table 1. The results from the different samples show that the calculated ($D_{XRD}$) and measured ($D_{TEM}$) are in good agreement. The Mössbauer spectra recorded for Mn$_{0.2}$Fe$_x$Cr$_{1.8-x}$O$_3$ samples at 300 K are shown in Fig. 3. It can be seen that the spectra for $x = 0.3$ and $x = 0.5$ are paramagnetic doublets. The spectrum for $x ≥ 0.9$ has a sextet component. The component with a larger...

---

**Fig. 1** XRD spectra recorded for Mn$_{0.2}$Cr$_{1.8-x}$ Fe$_x$O$_3$
The hyperfine magnetic field can be associated with the Fe$^{3+}$ ions without Mn$^{2+}$ ions in nearby lattice sites whereas the component with lower hyperfine magnetic field reflects the low spin density at Fe$^{3+}$ in the vicinity of Mn$^{2+}$ nearest cation neighbours. All the components in the spectra recorded at 300 K were characterized by a nearly constant chemical isomer shift of 0.32(3) mms$^{-1}$ confirming that the accommodation of manganese into the corundum-related structure did not induce a change in the Fe$^{3+}$ oxidation state [25]. Insignificant change in isomer shifts indicates that the s-electron density is not much affected by substitution of Cr by Fe atoms or by thermal relaxation of the lattice. Given that all the spectra recorded for $x > 0.5$ show evidence of magnetic splitting, it is evident that the second doublet at least represent the presence of small particles superparamagnetic oxides. The Mössbauer parameters are given in Table 2. The hyperfine magnetic fields appear to increase as the iron content $x$ increases, thus confirming a gradual transformation from paramagnetic to ordered magnetic phase of the compounds. The results confirm that manganese can also be accommodated in the corundum-related structure without inducing a change in the Fe$^{3+}$ state as demonstrated before for tin-doped samples [30].

The zero field cooling (ZFC) and field cooling (FC) magnetization curves are shown in Fig. 4. During FC, the oxides were cooled from 400 to 10 K in the presence of an external magnetic field of 50 Oe. For ZFC measurements, the samples were cooled to 10 K in zero field. The magnetizations were recorded during warming up to 400 K in the presence of the same external field. The magnetization for FC curves decrease continuously with increasing temperature. ZFC and FC magnetization coincide at a spin freezing temperature which depends on the applied field. ZFC curves increase gradually with increasing temperature and reach maximum values at blocking temperatures. The width of the peak in the ZFC curve is associated with particle size distribution [31]. The slow decrease in magnetization with further increase in temperature is associated with disordering of particle spins. One of the characteristic

![Fig. 2 Representative TEM micrograph for Mn$_{0.2}$Fe$_x$Cr$_{1.8-x}$O$_3$ ($x = 0.5$ and 0.9)](image)

![Fig. 3 Mössbauer spectra recorded for Mn$_{0.2}$Fe$_x$Cr$_{1.8-x}$O$_3$](image)

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a = b$ ($\text{Å}$) ±10$^{-3}$</th>
<th>$c$ ($\text{Å}$) ±10$^{-3}$</th>
<th>$D_{\text{NRD}}$ (nm) ±0.04</th>
<th>$D_{\text{TEM}}$ (nm) ±2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>4.989</td>
<td>13.621</td>
<td>32.84</td>
<td>31</td>
</tr>
<tr>
<td>0.5</td>
<td>4.986</td>
<td>13.643</td>
<td>28.99</td>
<td>27</td>
</tr>
<tr>
<td>0.7</td>
<td>5.004</td>
<td>13.622</td>
<td>26.89</td>
<td>26</td>
</tr>
<tr>
<td>0.9</td>
<td>4.976</td>
<td>13.586</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>1.1</td>
<td>4.989</td>
<td>13.778</td>
<td>15.35</td>
<td>15</td>
</tr>
<tr>
<td>1.3</td>
<td>5.024</td>
<td>13.768</td>
<td>14.20</td>
<td>14</td>
</tr>
</tbody>
</table>
The features of the plots in Fig. 4 are reduced magnetizations at low temperature for ZFC samples. Similar behavior of FC and ZFC magnetization has been considered to be spin-glass like behavior [32]. The ZFC curve for \( x = 0.9 \) shows a maximum in the magnetization at 82 K. Beyond this the magnetization reduces up to about 180 K before it further increases, touching the FC magnetization curve at about 330 K. This type of a double peak structure has been observed elsewhere [33] and was attributed to the bimodal distribution in particle size. At a lower temperature \( T_B \) called the blocking temperature the ZFC magnetizations reach a maximum where the moments of the FM clusters begin to freeze. The blocking temperature depends on the average particle size [34, 35]. In order to study the interactions within the alloys, we have plotted the temperature dependence of the inverse magnetization for \( x = 1.1 \) in Fig. 5. The linear fit shows that the sample exhibits a Curie–Weiss type behavior above 199 K. The corresponding extrapolated paramagnetic Weiss temperature is \( -175 \) K. The value of \( \theta_p \) shows that the antiferromagnetic interactions (AFM) are weaker in \( \text{Mn}_{0.2}\text{Fe}_x\text{Cr}_{1.8-x}\text{O}_3 \) compared to \( \text{Mg}_{0.2}\text{Fe}_x\text{Cr}_{1.8-x}\text{O}_3 \) where \( \theta_p = -722 \) K [26]. The variation of hysteresis curves of \( \text{Mn}_{0.2}\text{Fe}_x\text{Cr}_{1.8-x}\text{O}_3 \) as a function of \( x \) recorded at room temperature is shown in Fig. 6a. The amplified view of hysteresis loops at low fields is also shown in Fig. 6b. The magnetization increases rapidly to fields up to about 3 kOe and then vary almost linearly without reaching any saturation to a field of 14 kOe. This typical weak magnetic response confirms the antiferromagnetic interactions in the samples. This is similar to the main antiferromagnetic interactions in hematite particles responsible of a large magnetic susceptibility in high fields which is superimposed on a spontaneous ferromagnetic moment, coming either from true weak ferromagnetism for temperatures above the Morin transition, or from uncompensated moments mainly.

<table>
<thead>
<tr>
<th>Sample ( x )</th>
<th>1st Doublet</th>
<th>2nd Doublet</th>
<th>Sextet of max ( H )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \delta ) (mm/s)</td>
<td>( \Delta ) (mm/s)</td>
<td>( f(%) )</td>
</tr>
<tr>
<td>0.3</td>
<td>0.31 ± 0.01</td>
<td>1.15 ± 0.02</td>
<td>21</td>
</tr>
<tr>
<td>0.5</td>
<td>0.29 ± 0.01</td>
<td>0.22 ± 0.02</td>
<td>49</td>
</tr>
<tr>
<td>0.7</td>
<td>0.27 ± 0.01</td>
<td>0.32 ± 0.02</td>
<td>68</td>
</tr>
<tr>
<td>0.9</td>
<td>0.28 ± 0.01</td>
<td>0.81 ± 0.02</td>
<td>9</td>
</tr>
<tr>
<td>1.1</td>
<td>0.35 ± 0.01</td>
<td>1.14 ± 0.02</td>
<td>17</td>
</tr>
<tr>
<td>1.3</td>
<td>0.41 ± 0.01</td>
<td>1.13 ± 0.02</td>
<td>16</td>
</tr>
</tbody>
</table>
at the surface of the particles [36]. Evidence of displacement of hysteresis loops are also observed in Fig. 6. Asymmetric magnetic hysteresis loops exhibiting shifts both in the field and magnetization axis as well as an enhanced coercive field are observed which indicate the existence of exchange bias phenomenon. The exchange bias effect can be explained on the basis of a phenomenological core–shell model where the core shows AFM behavior and the surrounding shell possesses a net magnetic moment due to a large number of uncompensated surface spins [37, 38]. The variation of exchange bias \( H_{EB} \) with particle size \( D \) and iron content \( x \) are displayed in Figs. 7 and 8. We observed that the exchange bias increases as the particle size decreases with increased Fe content \( x \) (Table 3). The loops shifts are different with different particle sizes suggesting that the materials at room temperature may be superparamagnetic as observed from Mössbauer measurements. Strong correlations are also observed between the exchange bias \( H_{EB} \) with particle size \( D \) (Fig. 7) and with Fe content \( x \) (Fig. 8). The linear correlation between \( H_{EB} \) and \( D \) is particularly interesting. It suggests a collapse of \( H_{EB} \) to zero at a particle size of about 34 nm. This is a similar value as for the \( H_{EB} \) versus \( D \) curve for Mg-doped samples [18] for hysteresis loops at 10 K. The main difference in this case is that \( H_{EB} \) decreases with increase in \( D \). The exchange bias seems to disappear as the temperature is decreased. This fact is currently under investigation and shall be discussed elsewhere. The main difference between the present alloys series and previously referenced work are presented in Table 4.
4 Conclusions

Mn_{0.2}Cr_{1.8-x}Fe_{x}O_{3} fine powders have been successfully synthesized by hydrothermal process at low temperature (100 °C). We found much reduced magnetizations for the Mn-based samples compared to Sn-based samples [30]. The composition dependence of the loops is not very significant for Mn-based samples. Evidence successful Mn incorporation into the corundum structure is obtained. With an increased in Fe content, x, samples evolved from paramagnetic to ordered magnetic phase. The nanoparticle oxides have been found to exhibit exchange bias effects at room temperature. The exchange bias in the present case arises from the exchange interaction between the AFM host and ferrimagnetic clusters. Mn^{2+} ions which occupy interstitial and substitutional sites establish ferrimagnetic clusters inside an AFM background.

Acknowledgments We acknowledge the financial support from the DST/NRF (South Africa) and University of KwaZulu-Natal (UKZN). We are also grateful to the Electron Microscopy Unit at UKZN (WC) for TEM measurements. This work was was partially supported by DPT (State Planning Organization, Turkey) through the Project nos. 2009K120730 TÜBITAK-RFBRand209T061.

References