

Structural and ^{57}Fe Mössbauer study of $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ nanocrystalline particles

H. M. Widatallah · T. M. H. Al-Shahumi ·
A. M. Gismelseed · Z. Klencsár · A. D. Al-Rawas ·
I. A. Al-Omari · M. E. Elzain · A. A. Yousif · M. Pekala

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Abstract A structural and Mössbauer study of mechanosynthesized $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ nanocrystalline particles ($\sim 20\text{--}30$ nm) is presented. The lattice parameters increase with increasing x -value leading to an increasingly distorted structure. The crystallite sizes range between 20 nm and 30 nm. Magnetic and ^{57}Fe Mössbauer measurements show the samples with $x < 0.7$ to be paramagnetic and those with $x \geq 0.7$ to be partially superparamagnetic at 298 K. The 78 K Mössbauer spectra of the samples with $x = 0.3\text{--}1.0$ are composed of well-resolved two sextets that are explicable in terms of the structural model that we recently have proposed for the EuCrO_3 nanoparticles according to which the transition metal ions and Eu^{3+} partly exchange their usual sites in the perovskite-related structure (Widatallah et al., *J Phys D Appl Phys* 44:265403, 2011). Consequently, the two sextets obtained at 78 K refer to Fe^{3+} ions at the usual B-octahedral site and the A-dodecahedral site usually occupied by Eu^{3+} .

Keywords Perovskite · Mössbauer spectroscopy · Milling · XRD · Magnetization

1 Introduction

EuCrO_3 and EuFeO_3 are useful materials in multiple fields of application that include, among others, solid oxide fuel cells, chemical sensing and optical

H. M. Widatallah (✉) · T. M. H. Al-Shahumi · A. M. Gismelseed · A. D. Al-Rawas ·
I. A. Al-Omari · M. E. Elzain · A. A. Yousif
Department of Physics, Sultan Qaboos University, P. O. Box 36, 123, Muscat, Oman
e-mail: hishammw@squ.edu.om

Z. Klencsár
Chemical Research Institute, Hungarian Academy of Sciences,
Pusztaszeri út 59-67, Budapest, 1025, Hungary

M. Pekala
Chemistry Department, University of Warsaw, 101, PL-02-089, Warsaw, Poland

communications [1–3]. The compounds crystallize in the space group $Pbnm$ with four distorted perovskite units in the true crystallographic orthorhombic cell [1–4] where Eu^{3+} and the transition metal ions occupy the dodecahedral A- and octahedral B-sites, respectively. Both solids are anti-ferromagnetic with only weak ferromagnetism due to spin canting below ~ 181 K and ~ 662 K respectively [3, 5]. Rather than using the term Néel temperature (T_N) to refer to these temperatures [3] we shall follow Gibb [4, 5] in referring to them as Curie temperature (T_C). They actually signify the transition from the weak ferromagnetic state to the paramagnetic one. Previous studies on the $\text{EuCrO}_3/\text{EuFeO}_3$ solid solutions were mainly performed on the $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ microcrystalline particles [2, 5]. Recently we have shown an unusual cationic site exchange to exist in EuCrO_3 nanocrystalline particles [1]. In the present study we report our preliminary studies on nanocrystalline $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ particles.

2 Experimental

Nanocrystalline $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ particles were prepared using mechanosynthesis starting from appropriate amounts of high purity Eu_2O_3 , Cr_2O_3 and $\alpha\text{-Fe}_2\text{O}_3$ in the 1: 1- x : x molar ratio ($x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$) using an identical milling and sintering regime to that reported by us recently [1]. X-ray powder diffraction (XRD) patterns were collected with a Philips PW1710 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406$ Å). The thermal variation of the magnetization was recorded with a Faraday balance under a 1.5 T external magnetic field. ^{57}Fe Mössbauer spectra were recorded in the transmission mode at 298 K and 78 K using a 50 mCi $^{57}\text{Co}/\text{Rh}$ source. The isomer shifts are quoted relative to iron foil.

3 Results and discussion

Figure 1a shows the XRD patterns recorded from the pre-milled reactants' mixtures sintered (8 h) at the temperatures indicated. All patterns could be indexed to a single-phased perovskite-related $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ structure. The crystallite sizes were found to be in the range of 20–30 nm. Figure 1b shows the lattice parameters to generally increase with x . The increase in the b parameter becomes more pronounced at higher x . Consequently, a more distorted unit cell is to be expected at high x values. This unit cell expansion is expected as more of the larger Fe^{3+} ions (0.785 Å) replace the smaller Cr^{3+} ones (0.755 Å) [6]. Referring to our Rietveld refinement of the XRD pattern of the sample with $x = 0.0$ (EuCrO_3) [1], where the Eu^{3+} and Cr^{3+} ions were shown to partially exchange the A- and B-sites, a more pronounced site-exchange of Eu^{3+} and Fe^{3+} is anticipated in $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ nanoparticles on the basis of the higher ionic size of Fe^{3+} . Indeed initial analysis of ^{151}Eu data (not shown) suggests that a considerable amount of Eu^{3+} ions in the spectra of all samples exists at the transition metal B-sites. The T_C values were found to increase with increasing x from ~ 181 K, 172 K, 202 K, 425 K and 525 K for the $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ nanoparticles with $x = 0.0, 0.1, 0.3, 0.5$ and 0.7 respectively. The samples with $x = 0.9$ and 1.0 showed a similar T_C of ~ 625 K.

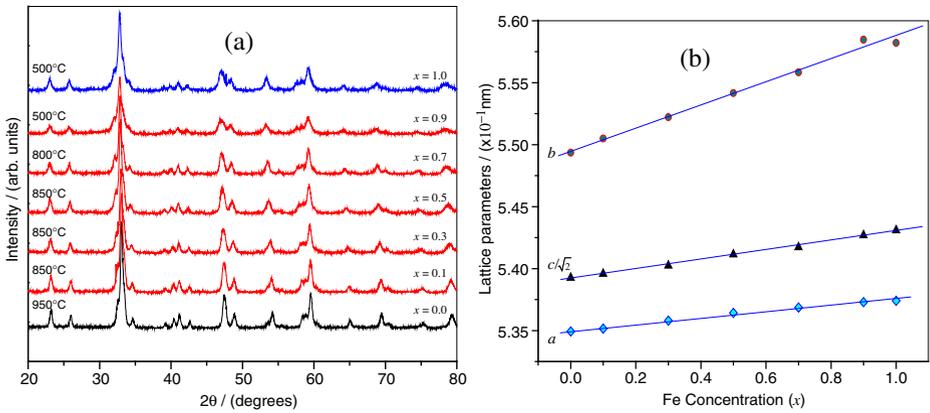


Fig. 1 **a** The XRD patterns of the $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ nanoparticles obtained at the temperatures indicated and **b** the variations with lattice parameters a , b and $c/\sqrt{2}$ with x

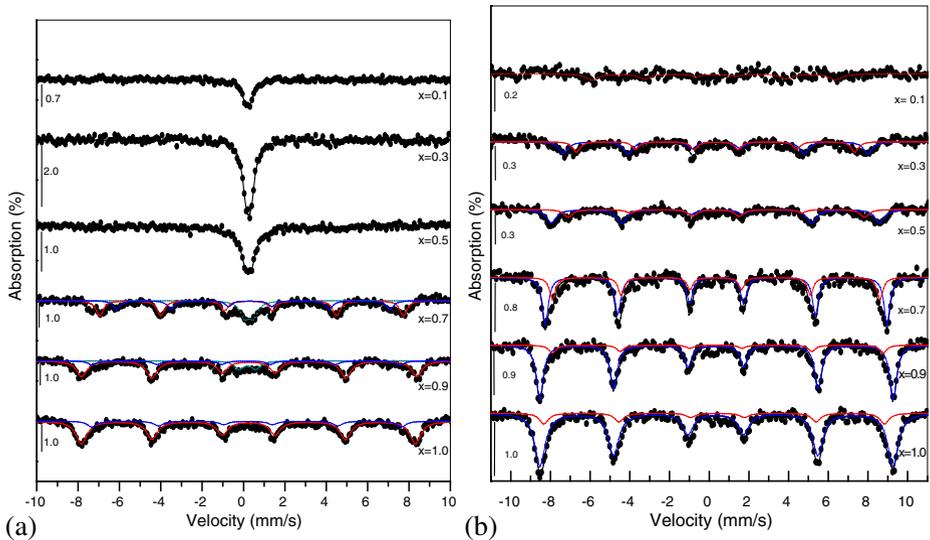


Fig. 2 The ^{57}Fe Mössbauer spectra recorded from the $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ nanoparticles at a 298 K, and **b** 78 K

The ^{57}Fe Mössbauer spectra recorded from the nanoparticles at 298 K and 78 K are given in Fig. 2a and b respectively. The fitted parameters are given in Table 1. In line with the magnetic measurements, the 298 K spectra of the particles with $x = 0.1$ – 0.5 depict paramagnetic doublets for $x = 0.1$ and 0.3 and a superparamagnetic doublet for $x = 0.5$ with very small quadrupole splitting that are presumably related to the distorted orthorhombic structure. For the samples with $x = 0.7$ and 0.9 , where $T_C > 298$ K, the spectrum is composed of a broad magnetic six-line pattern superimposed on a central doublet. The latter is due to superparamagnetic particles whose volumes are smaller than the critical (blocking) volume required for depicting

Table 1 The ^{57}Fe Mössbauer parameters for the $\text{EuCr}_{1-x}\text{Fe}_x\text{O}_3$ nanoparticles at 298 K, and 78 K (between brackets and in italics)

X	Component	δ (mm/s)	ε (mm/s)	Δ (mm/s)	H_{eff} (T)	A(%) ± 3
0.1	Doublet	0.34	0.22			100
	Doublet	0.36	0.22			100
0.3	Sextet I	<i>(0.46)</i>		<i>(-0.03)</i>	<i>(51.3)</i>	<i>(66)</i>
	Sextet II	<i>(0.47)</i>		<i>(0.03)</i>	<i>(46.4)</i>	<i>(34)</i>
	Doublet	0.36	0.30			100
0.5	Sextet I	<i>(0.47)</i>		<i>(-0.02)</i>	<i>(53.5)</i>	<i>(68)</i>
	Sextet II	<i>(0.45)</i>		<i>(0.03)</i>	<i>(51.2)</i>	<i>(32)</i>
	Doublet	0.37	0.43			23
0.7	Sextet I	0.40 <i>(0.47)</i>		0.04 <i>(-0.02)</i>	45.6 <i>(53.5)</i>	49 <i>(68)</i>
	Sextet II	0.48 <i>(0.45)</i>		0.04 <i>(0.03)</i>	41.1 <i>(51.2)</i>	28 <i>(32)</i>
	Doublet	0.31	0.79			12
0.9	Sextet I	0.39 <i>(0.48)</i>		0.01 <i>(0.03)</i>	50.3 <i>(55.3)</i>	74 <i>(87)</i>
	Sextet II	0.27 <i>(0.51)</i>		-0.01 <i>(0.02)</i>	46.3 <i>(51.8)</i>	14 <i>(13)</i>
1.0	Sextet I	0.36 <i>(0.47)</i>		-0.02 <i>(0.04)</i>	50.2 <i>(55.2)</i>	82 <i>(85)</i>
	Sextet II	0.38 <i>(0.46)</i>		-0.01 <i>(-0.09)</i>	46.5 <i>(53.3)</i>	18 <i>(15)</i>

δ : isomer shift, ε : quadrupole splitting, Δ : quadrupole shift, H_{eff} : magnetic hyperfine field, A: spectral area

the ferromagnetic nature. While the gradual increase in the quadrupole splitting values with x agrees with above XRD result that unit cell gets more distorted at higher x values, it also reflects an increasing cationic Eu-Fe site exchange. The magnetic part of the 298 K spectra, was fitted with two hyperfine-split sextets. These generally reflect Fe^{3+} in different environments. The gradual increase in the magnitude of H_{eff} for both sextets with increasing x clearly reflects enhanced exchange magnetic interactions. For the nanoparticles with $x = 1.0$, the 298 K spectrum is comprised of two sextets whose H_{eff} values are smaller than that reported for bulk EuFeO_3 (51.8 T) [5].

The Mössbauer spectrum recorded at 78 K, which is smaller than T_C for all samples, shows a very poorly resolved magnetic spectrum for the sample with $x = 0.1$. This is possibly due to the very small number of ^{57}Fe nuclei and the associated limited magnetic exchange interactions. Well resolved six-line magnetic patterns were attained for the rest of the samples ($x = 0.3 - 1.0$); each of which was fitted with two sextets (Table 1). We attribute the sextets with the higher magnetic fields in the above Mössbauer analysis with B-sites Fe^{3+} ions having a majority Fe^{3+} nearest cationic neighbors. The sextets with lower fields are associated with A-site Fe^{3+} as well as B-site Fe^{3+} with Eu^{3+} and/or Cr^{3+} nearest neighbors. A possibility that our initial analysis of ^{151}Eu Mössbauer data supports as indicated above.

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