Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 333–343

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Nanostructured iridium oxide-hematite magnetic ceramic semiconductors

Julia Limongelli[a,b], Felicia Tolea[c], Mihaela Valeanu[c], Lucian Diamandescu[c], Tianhong Xu[a,d], Monica Sorescu[a,*]

[a]Duquesne University, Department of Physics, 309 B Fisher Hall, Pittsburgh, PA 15282-0321, USA
[b]BAE Systems, 130 Daniel Webster Highway, Merrimack, NH 03054, USA
[c]National Institute of Materials Physics, P.O. Box MG-7, Magurele, 077125 Bucharest, Romania
[d]FlexEl, LLC, 387 Technology Drive, College Park, MD 20742, USA

Received 11 July 2014; accepted 19 August 2014
Available online 28 August 2014

Abstract

xIrO$_2$–$(1-x)$α-Fe$_2$O$_3$ (x=0.1, 0.3 and 0.5) nanoparticle systems were successfully synthesized by mechanochemical activation of IrO_2 and α-Fe$_2$O$_3$ mixtures for 0–12 h of ball milling time. The study aims at exploring the formation of magnetic oxide semiconductors at the nanoscale, which is of crucial importance for catalysis, sensing and electrochemical applications. X-ray powder diffraction (XRD), Mössbauer spectroscopy, magnetic measurements and simultaneous differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were used to study the phase evolution of xIrO$_2$–$(1-x)$α-Fe$_2$O$_3$ nanoparticle systems under the mechanochemical activation process. Rietveld refinement of the XRD patterns yielded the values of the particle size and lattice parameters as function of composition and milling times and indicated the presence of Ir-substituted hematite and Fe-doped iridium oxide for large x values and long milling times. The Mössbauer studies showed that the spectrum of the mechanochemically activated composites evolved from a sextet for hematite to sextets and a doublet upon duration of the milling process with iridium oxide. Magnetic measurements recorded at 5 K in an applied magnetic field of 40,000 Oe showed that the saturation magnetization of the milled samples increased with ball milling time while preserving a multidomain magnetic structure. The unmilled sample at 5 K showed a spin-flop type metamagnetic transition around 30,000 Oe. The Morin transformation was evidenced by zero-field cooling–field cooling (ZFC–FC) measurements in 200 Oe and 1 T and the transformation characteristic temperatures were shifted to lower values.

Keywords: A. Milling; B. Spectroscopy; C. Magnetic properties

1. Introduction

Hematite has various applications in scientific and industrial fields and can be used as semiconductor compound [1], magnetic material [2], catalyst [3] and gas sensor [4]. Nanocrystalline hematite obtained by high-energy ball milling was found to exhibit decreased grain size, expansion of lattice parameters and two kinds of particles which coexist in the sample: nanostructured and micrometer hematite [5]. In [6] the magnetic properties of α-Fe$_2$O$_3$ antiferromagnetic nanoparticles of 5 nm mean diameter prepared by a sol–gel method were investigated by means of static magnetic measurements and ^{57}Fe Mössbauer spectrometry. The presence of 2 atomic thick surface magnetic layer estimated from a core–shell model was established. Nanostructured hematite samples synthesized using a chemical coprecipitation method [7] were found to exhibit open hysteresis loops at 10 K, a core–shell morphology and lower values of the recoilless fraction for smaller particles. Their Mössbauer spectra were fitted with two sextets, corresponding to core and surface layers of hematite nanoparticles.

Moreover, the incorporation of Ir^{3+} ions into the α-Fe$_2$O$_3$ structure [8] led to changes in unit-cell dimensions, crystallinity, particle size and shape, as well as in the magnetic, infrared and UV–vis properties. The effect of Ir crystallographic site on the catalytic performance of Ir-substituted barium hexaferrite for N_2O decomposition was studied in [9] and it was observed that Ir ions in the octahedral sites were

*Corresponding author. Tel.: +1 412 396 4166; fax: +1 412 396 4829.
E-mail address: sorescu@duq.edu (M. Sorescu).

http://dx.doi.org/10.1016/j.ceramint.2014.08.076
0272-8842/

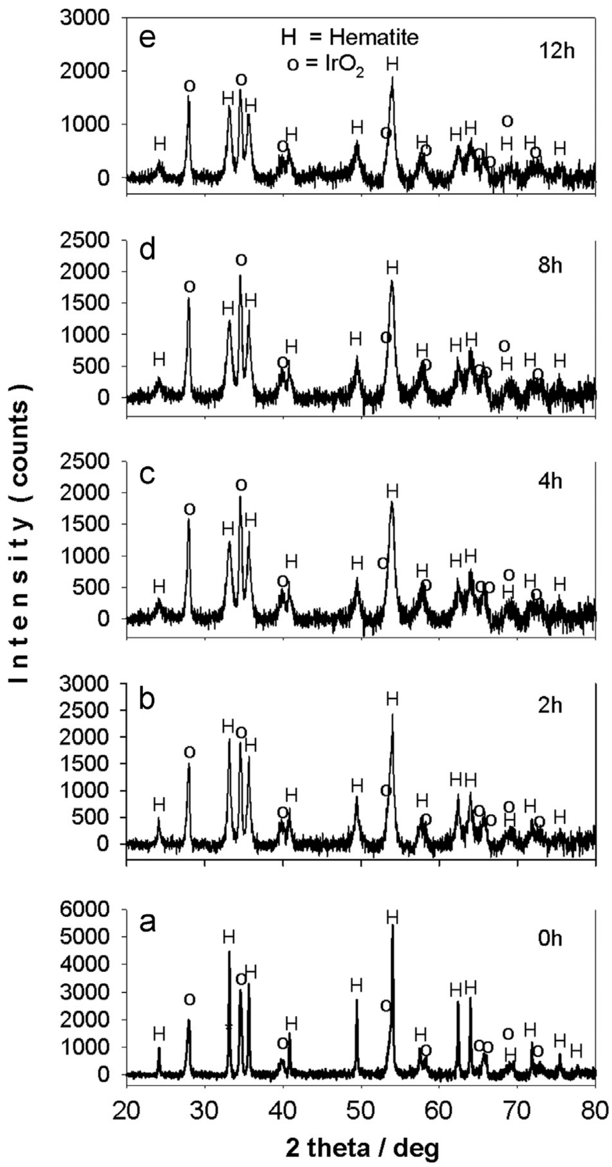

Fig. 1. XRD patterns of mechanochemically activated xIrO$_2$–$(1-x)$α-Fe$_2$O$_3$ (x=0.1) composites at ball milling time of: (a) 0 h; (b) 2 h; (c) 4 h; (d) 8 h; (e) 12 h, respectively.

highly active for the decompositions. In [10] it was observed that Ir^{3+} substitution for Fe^{3+} in the structure of α-Fe_2O_3 led to an increase in the temperature of the Morin transition, while Mössbauer spectroscopy showed the presence of α-Fe_2O_3 in the antiferromagnetically ordered state at 293 K. In addition, Ir is a Mössbauer isotope and ^{193}Ir Mössbauer spectroscopy of Pt-IrO_2 catalysts showed that iridium largely provides the dissociative O_2 adsorption sites, while CO adsorption occurs primarily at metallic Pt sites [11].

High-energy ball milling technique is a well-established method for mechanochemical synthesis of nanostructured or nanocomposite materials in which non-equilibrium phases, extended solid solutions or complex structures can be formed at fairly low temperatures. Recently, the authors have performed several studies on mechanochemical activation of various mixed oxide systems [12–20]. Our findings ranged from demonstrating the formation of a single phase perovskite [14] to the occurrence of multiple phases [20] and providing evidence for the effect of metallic species valence on the properties of the nanostructures formed [18].

In this work, we report the successful synthesis of xIrO$_2$–$(1-x)$α-Fe$_2$O$_3$ nanoparticles semiconductor system by a mechanochemical activation method through ball-milling of IrO_2 and α-Fe_2O_3 mixtures, with IrO_2 molar concentrations of x=0.1, 0.3 and 0.5 at room temperature. X-ray powder diffraction, Mössbauer spectroscopy, magnetic measurements and thermal analysis have been employed to investigate the phase evolution, structural and magnetic properties of ball-milled ceramic semiconductor oxides at different ball-milling times.

2. Experimental

Iridium and iron (III) oxides were purchased from Alfa Aesar: iridium oxide (99% metals basis, average particle size about 100 nm), and hematite (α-Fe_2O_3, 99% metal basis, average particle size about 49.2 nm). Powders of hematite and iridium oxides were milled in a hardened steel vial with 12 stainless-steel balls (type 440; eight of 0.25 in diameter and four of 0.5 in diameter) in the SPEX 8000 mixer mill for time

Table 1
Rietveld refinement of xIrO$_2$–$(1-x)$α-Fe$_2$O$_3$ at x=0.1.

Milling time (h)	*Lattice parameters* (Å)			*Crystallite size* (nm)	*Phase content* (wt%)
	a	***b***	***c***		
0	5.0359	–	13.7664	66.5	α-Fe_2O_3 (86.6)
	4.5145	–	3.1652	32.3	IrO_2 (13.4)
2	5.0368	–	13.7677	26.3	Ir: α-Fe_2O_3 (86.5)
	4.5165	–	3.1670	28.4	IrO_2 (13.5)
4	5.0383	–	13.7699	18.0	Ir: α-Fe_2O_3 (86.1)
	4.5145	–	3.1665	31.7	IrO_2 (13.9)
8	5.0409	–	13.7705	15.9	Ir: α-Fe_2O_3 (85.6)
	4.5149	–	3.1655	26.5	IrO_2 (14.4)
12	5.0422	–	13.7761	15.0	Ir: α-Fe_2O_3 (84.6)
	4.5153	–	3.1643	23.2	IrO_2 (15.4)
Errors	±0.0005	±0.0005	±0.0005	±1.5	±1.4