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Ruthenium oxide–hematite magnetic ceramic nanostructures

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Abstract

$x\mathrm{RuO_2}$–$(1-x)$α-$\mathrm{Fe_2O_3}$ ($x=0.1$, 0.3, 0.5 and 0.7) nanoparticle systems were successfully synthesized by mechanochemical activation of $\mathrm{RuO_2}$ and α-$\mathrm{Fe_2O_3}$ mixtures for 0–12 h of ball milling. Mössbauer spectroscopy, X-ray diffraction (XRD), magnetic measurements, simultaneous differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were employed to investigate the phase evolution of $x\mathrm{RuO_2}$–$(1-x)$α-$\mathrm{Fe_2O_3}$ nanoparticle systems under the mechanochemical activation process. The Mössbauer studies showed that the spectrum of the mechanochemically activated composites evolved from a sextet for α-$\mathrm{Fe_2O_3}$ (hematite) to four sextets and a doublet upon duration of the milling process with ruthenium oxide. Rietveld refinement of the XRD patterns yielded the values of lattice parameters as function of composition and milling times. The presence of Ru-substituted hematite and Fe-doped ruthenium oxide was evidenced and correlated with differences between ionic radii of Fe^{3+} and Ru^{4+}. Magnetic measurements recorded at 5 and 300 K in applied magnetic fields of 50,000 and 100,000 Oe showed that the estimated saturation magnetization of the milled samples increased with ball milling time while preserving a multidomain magnetic structure. The Morin transformation was evidenced by zero-field cooling–field cooling (ZFC–FC) measurements in 200 Oe and 1 T, for samples milled for 0 and 8 h of mechanochemical activation. These results correlate well with the DSC–TGA measurements, which support the formation of mixed-oxide solid solutions in the system under investigation.

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

1. Introduction

Ruthenium oxides and ions play a significant role in basic and applied research and have been used to investigate iron–ruthenium catalysts by in-situ ^{57}Fe Mossbauer spectroscopy, the influence of ruthenium ions on the precipitation of α-FeOOH, α-$\mathrm{Fe_2O_3}$ and $\mathrm{Fe_3O_4}$ in highly alkaline media as well as ^{99}Ru Mossbauer spectroscopy of quaternary Ru(IV) oxides with the hexagonal barium titanate structure and the perovskite solid solution series $\mathrm{La_xSr_{1-x}RuO_3}$ and $\mathrm{La_xCa_{1-x}RuO_3}$ [1–4].

On the other hand, hematite can be used as semiconductor compound, magnetic material, catalyst and gas sensor [5–8]. In particular, thermal hysteresis of spin reorientation at the Morin transition was previously evidenced for 200 nm hematite nanoparticles [9]. Moreover, an anomalous decrease of the magnetic susceptibility at the Morin temperature was observed in [10] for hematite nanorods prepared by iron–water vapor reaction. In addition, magnetic transitions of hematite nanowires were comprehensively studied and the Morin temperature of the nanowires and hematite bulk reference powder were determined as 123 and 263 K, respectively [11].

Recently, the authors have performed several studies on mechanochemical activation of various oxide systems with hematite [12–20]. Our results ranged from demonstrating the

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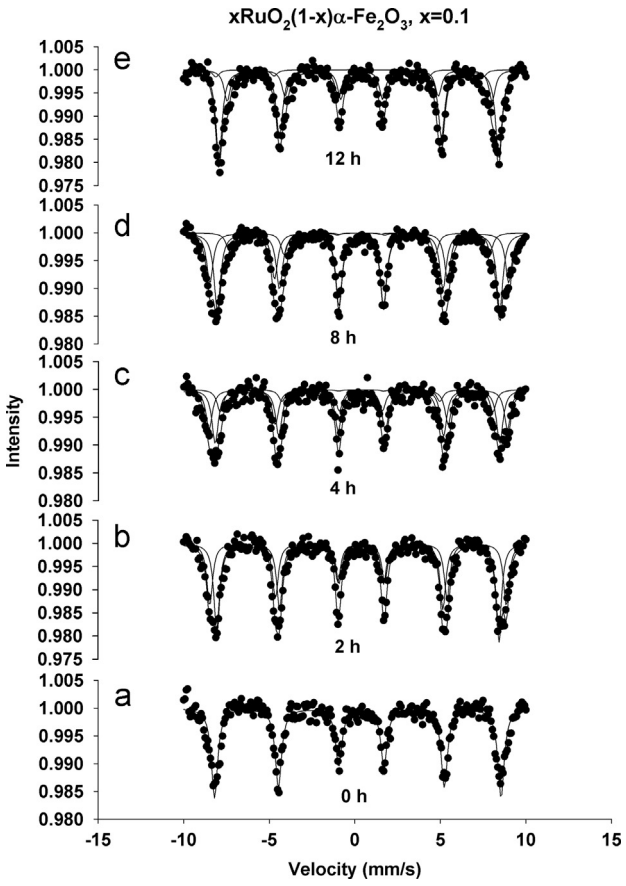

Fig. 1. Mössbauer spectra of mechanochemically activated $x\mathrm{RuO_2}$–$(1-x)$α-$\mathrm{Fe_2O_3}$ ($x=0.1$) composites at ball milling time of: (a) 0 h; (b) 2 h; (c) 4 h; (d) 8 h; (e) 12 h, respectively.

formation of a single phase perovskite for $\mathrm{La_2O_3}$ [14] to the occurrence of multiple phases for $\mathrm{Li_2O}$ [20] and providing evidence for the effect of metallic species valence on the properties of the nanostructures formed for NbO, $\mathrm{NbO_2}$ and $\mathrm{Nb_2O_5}$ ball milled with hematite [18]. Indeed, mechanochemical activation by high-energy ball milling technique is a well-established method for the synthesis of nanostructured materials in which non-equilibrium phases, extended solid solutions or complex structures can be formed at moderate temperatures.

In this work, we report the successful synthesis of $x\mathrm{RuO_2}$–$(1-x)$α-$\mathrm{Fe_2O_3}$ nanoparticles ceramic system by the mechanochemical activation method through ball-milling of $\mathrm{RuO_2}$ and α-$\mathrm{Fe_2O_3}$ mixtures, with $\mathrm{RuO_2}$ molar concentrations of $x=0.1$, 0.3, 0.5 and 0.7. Mössbauer spectroscopy, X-ray powder diffraction, magnetic measurements and thermal analysis have been used to derive the phase evolution, structural and magnetic properties of ball-milled ceramic semiconductor oxides at different molar concentrations and ball-milling times. Evidence of mutual ionic substitutions during the formation of solid solutions at the nanoscale is provided.

2. Experimental

Ruthenium (IV) and iron (III) oxides were purchased from Alfa Aesar: ruthenium oxide (99% metals basis, average particle size about 90 nm), and hematite (α-$\mathrm{Fe_2O_3}$, 99% metal basis, average particle size about 49.2 nm). Powders of hematite and ruthenium 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

Table 1
Hyperfine parameters of the ruthenium oxide–hematite system.

x	BMT (h)	IS (mm/s)	QS (mm/s)	BHF (T)	Abundance (%)
0.1	0	0.27	−0.28	51.90	100
	2	0.28	−0.27	51.50	44.75
		0.28	−0.26	51.00	55.25
	4	0.31	−0.28	51.90	42.38
		0.27	−0.26	51.50	37.22
		0.28	0.01	49.50	20.40
	8	0.33	−0.15	51.60	28.40
		0.31	−0.01	50.80	59.67
		0.33	−0.13	46.30	11.93
	12	0.30	0.01	50.20	64.67
		0.50	0.03	46.80	4.81
		0.52	−0.02	44.80	30.52
0.3	0	0.27	−0.28	50.50	100
	2	0.28	−0.25	50.60	92.55
		0.14	−0.05	46.70	5.45
		0.26	0.10	–	2.00
	4	0.29	−0.02	50.70	71.83
		0.29	−0.06	48.30	17.10
		0.30	−0.13	44.90	8.69
		0.28	0.10	–	2.38
	8	0.28	−0.27	50.60	58.75
		0.28	−0.03	49.10	19.56
		0.29	−0.01	45.70	14.24
		0.25	0.10	–	7.45