Research Letter

Synthesis and Characterization of Ceramic Nanoparticles System Based on Anatase-Doped Hematite

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The $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ ceramic nanoparticles system has been obtained by mechanochemical activation for $x = 0.1$ and 0.5 and for ball milling times ranging from 2 to 12 hours. Structural and morphological characteristics of the anatase-doped hematite system were investigated by X-ray diffraction (XRD), Mössbauer spectroscopy, and transmission electron microscopy (TEM) combined with electron diffraction (ED). In the XRD patterns, we could evidence the dissolution of anatase in hematite, more pronounced for $x = 0.1$. The Rietveld structure of the XRD patterns yielded the dependence of the particle size and lattice constants on the amount x of Ti substitutions and as function of the ball milling time. For $x = 0.1$, we observed line broadening of the Mössbauer resonances and corresponding fit with several subspectra. For $x = 0.5$, it can be observed that the central doublet corresponding to superparamagnetic particles becomes more prominent. The ball milling route allowed us to reach nanometric particle dimensions, which would make the materials very promising for catalytic and gas sensing applications.

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1. INTRODUCTION

During the past several years considerable research effort has been directed towards the synthesis and investigations of ceramic oxides due to their interesting properties [1–4]. The aim of the present paper was to obtain mixed oxides and nanometric solid solutions based on TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$, such that we could also follow the enhancement of the solubility limits of this system [5, 6].

For this purpose, we synthesized $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ ceramic nanoparticles system (anatase-doped hematite) using the ball milling method and characterized its structural and magnetic properties using XRD, Mössbauer spectroscopy, and TEM-ED. One success of this route is the occurrence of particles at the nanoscale.

In this paper, we report for the first time on the successful synthesis of ceramic nanoparticles based on anatase-doped hematite and their characterization using complementary techniques. Applications of the anatase-doped hematite nanoparticles are expected in gas sensing and catalysis.

2. EXPERIMENTAL

Powders of hematite and titanium dioxide were milled at different molar concentrations ($x = 0.1$ and 0.5) in a hardened steel vial with twelve 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 periods ranging from 2 to 12 hours. The ball/powder mass ratio was 5 : 1 and all experiments were performed in a glove box under protective argon atmosphere. XRD measurements were performed using a Rigaku D-2013 diffractometer with $\text{Cu K}\alpha$ radiation. Room temperature transmission Mössbauer spectra were recorded using an MS-1200 constant acceleration spectrometer with a 10 mCi ^{57}Co source diffused in an Rh matrix. Least-squares fitting of the Mössbauer spectra was performed with the NORMOS program. JEOL 200 CX electron microscope was used for the electron microscopy analyses.

3. RESULTS AND DISCUSSION

Figures 1(a)–(e) and 2(a)–(e) represent the XRD patterns of anatase-doped hematite, $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ for $x = 0.1$

FIGURE 1: XRD patterns of $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ nanoparticles system at $x = 0.1$ and ball milling time of (a) 0 hour; (b) 2 hours; (c) 4 hours; (d) 8 hours; (e) 12 hours.

and 0.5, corresponding to milling times between 2 and 12 hours. Both spectra are consistent with the gradual dissolution of anatase into hematite, which is more rapid for the case with $x = 0.1$. For $x = 0.5$, traces of anatase are still present in the XRD patterns up to 4 hours of ball milling. In this case, the anatase-doped hematite phase coexists with small amounts of rutile, $\alpha\text{-Fe}$, and brookite as an intermediate phase. The peaks associated with $\alpha\text{-Fe}$ in the XRD patterns occur due to the contaminations from balls and vial walls, known to occur in these systems at long milling times. The peaks do not appear in the Mössbauer spectra due to the low value of the recoilless fraction for this phase. For $t = 12$ hours the only phase present is $\text{Ti:Fe}_2\text{O}_3$.

FIGURE 2: XRD patterns of $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ nanoparticles system at $x = 0.5$ and ball milling time of (a) 0 hour; (b) 2 hours; (c) 4 hours; (d) 8 hours; (e) 12 hours.

Table 1 presents the Rietveld refinement parameters for the $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ system ($x = 0.1$ and 0.5) as a function of ball milling time, for each molar concentration involved. The refinement was carried out in the hypothesis that the interstitial and substitutional positions of iron are equally populated by Ti^{4+} . It can be seen that the lattice parameters generally increase for longer milling times. Moreover, it can be seen in Table 1 that the particle dimensions decrease down to 10 nm, demonstrating the occurrence of nanoparticles in the anatase-hematite system.

Figure 3(a)–(c) shows the room-temperature transmission Mössbauer spectra of the $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ system ($x = 0.1$), after milling for 0, 8, and 12 hours, respectively.

FIGURE 3: Room temperature transmission Mössbauer spectra of the $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ nanoparticles system for $x = 0.1$ and ball milling time of (a) 0 hour; (b) 8 hours; (c) 12 hours.

In general, the Mössbauer spectra of hematite can be fitted with one or two sextets, depending on the emphasis on the antiferromagnetic and weak ferromagnetic phases [7]. The room temperature Mössbauer spectrum of hematite was fitted with one sextet (Figure 3(a)). It can be seen that the spectra exhibit line broadening as the ball milling time increases, in agreement with the model of local atomic environment. For instance, the linewidth increases with the ball milling time, which means there are possible other resonances to occur, with lower numbers of Fe nearest neighbors. Because of this reason, we obtained line broadening and the Mössbauer spectrum for 8 milling hours had to be fitted with 3 sextets, corresponding to 51.3, 46.4, and 47.2 T, with populations of

FIGURE 4: Room temperature transmission Mössbauer spectra of the $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ nanoparticles system for $x = 0.5$ and ball milling time of (a) 2 hours; (b) 4 hours; (c) 12 hours.

4, 36, and 60%, respectively. The site with the highest hyperfine field is not necessarily the most populated. Each of the components in the Mössbauer spectra originates in a different number of Fe nearest neighbors, produced by an increasing number of Ti substitutions. For $t = 12$ hours, a small quadrupole split doublet had to be added, with a quadrupole splitting of 0.63 mm/s and an isomer shift of 0.35 mm/s.

Figure 4(a)–(c) shows the room-temperature transmission Mössbauer spectra of the $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ system ($x = 0.5$), after milling for 2, 4, and 12 hours, respectively. All spectra were fitted with 3 sextets and a doublet such that the relative abundance of the nonmagnetic phase increases from 5.2% for $t = 2$ hours to 32.5% for 12 hours of milling time.

TABLE 1: Rietveld parameters for $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ system ($x = 0.1$ and 0.5).

Milling time (h)	Molar content x	Lattice parameter a (Å)	Lattice parameter c (Å)	Particle dim. (nm)
0	0.1	5.0316	13.7391	57.2
2	0.1	5.0319	13.7398	28.4
4	0.1	5.0324	13.7402	17.1
8	0.1	5.0325	13.7474	16.7
12	0.1	5.0328	13.7559	16.5
0	0.5	5.0321	13.7458	58.0
2	0.5	5.0276	13.7109	49.1
4	0.5	5.0260	13.7162	27.5
8	0.5	5.0271	13.7422	18.0
12	0.5	5.0211	13.7524	10.1
Errors:	± 0.01	± 0.0015	± 0.0015	± 1.4

(a)

(b)

FIGURE 5: TEM image (a) and electron diffraction pattern (b) of the $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ nanoparticles system for $x = 0.5$ and ball milling time of 12 hours.

tion of the particles which remain non-superparamagnetic and give rise to a sextet; only very small nanoparticles collapse to a superparamagnetic doublet in the Mössbauer spectra.

Figure 5 shows the TEM image (a) and the ED pattern (b) of the $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ nanoparticles system for $x = 0.5$ and ball milling time of 12 hours. The TEM image presents small crystallite agglomerations, which usually appear aggregated with larger crystallites, exceeding tens of nanometers. For this reason, the transparent zones are located at the edges of the particle aggregates, where one could observe particles with nanometer dimensions.

We also performed particle size determinations on small particles (3–20 nm). The particles with dimensions of the order of 30–50 nm were not counted, but they are covered with particles having dimensions of 3–20 nm. Only these latter particles were counted and the average dimension calculated from the statistics is 10.4 nm, in good agreement with the XRD results.

4. CONCLUSIONS

In this paper, we prepared by ball milling and characterized by XRD, Mössbauer spectroscopy, and TEM-ED the structural and magnetic properties of the $x\text{TiO}_2-(1-x)\alpha\text{-Fe}_2\text{O}_3$ system ($x = 0.1$ and 0.5). It was observed that at low Ti content, Ti substitutes Fe in the hematite structure, creating vicinities with different numbers of Fe nearest neighbors. At high Ti content superparamagnetic particles occur. This work is a demonstration that the solubility limits can be extended in comparison with those in the bulk form by high-energy ball milling. We emphasize that rutile-doped hematite has a different behavior from anatase and will be reported in a separate paper.

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This quadrupole doublet can be assigned to the occurrence of superparamagnetic particles in the system. There is a distribution of particle sizes in the system such that there is a frac-

REFERENCES

- [1] J. Z. Jiang, R. Lin, S. Mørup, et al., "Mechanical alloying of an immiscible α -Fe₂O₃-SnO₂ ceramic," *Physical Review B*, vol. 55, no. 1, pp. 11–14, 1997.
- [2] J. Z. Jiang, R. Lin, W. Lin, et al., "Gas-sensitive properties and structure of nanostructured $(\alpha - \text{Fe}_2\text{O}_3)_x - (\text{SnO}_2)_{1-x}$ materials prepared by mechanical alloying," *Journal of Physics D*, vol. 30, no. 10, pp. 1459–1467, 1997.
- [3] O. K. Tan, W. Zhu, Q. Yan, and L. B. Kong, "Size effect and gas sensing characteristics of nanocrystalline $x\text{SnO}_2 - (1 - x)\alpha - \text{Fe}_2\text{O}_3$ ethanol sensors," *Sensors and Actuators B*, vol. 65, no. 1–3, pp. 361–365, 2000.
- [4] J. Tamaki, C. Naruo, Y. Yamamoto, and M. Matsuoka, "Sensing properties to dilute chlorine gas of indium oxide based thin film sensors prepared by electron beam evaporation," *Sensors and Actuators B*, vol. 83, no. 1–3, pp. 190–194, 2002.
- [5] M. Sorescu, L. Diamandescu, D. Tarabasanu-Mihaila, V. S. Teodorescu, and B. H. Howard, "Hydrothermal synthesis and structural characterization of $(1 - x)\alpha - \text{Fe}_2\text{O}_3 - x\text{SnO}_2$ nanoparticles," *Journal of Physics and Chemistry of Solids*, vol. 65, no. 5, pp. 1021–1029, 2004.
- [6] M. Sorescu, L. Diamandescu, and D. Tarabasanu-Mihaila, " α -Fe₂O₃In₂O₃ mixed oxide nanoparticles synthesized under hydrothermal supercritical conditions," *Journal of Physics and Chemistry of Solids*, vol. 65, no. 10, pp. 1719–1725, 2004.
- [7] M. Sorescu, R. A. Brand, D. Mihaila-Tarabasanu, and L. Diamandescu, "The crucial role of particle morphology in the magnetic properties of haematite," *Journal of Applied Physics*, vol. 85, no. 8, pp. 5546–5548, 1999.