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SERVICES FOR SCIENCE AND EDUCATION

Mössbauer Spectroscopy Investigation of Thulium Oxide-Hematite Magnetic Ceramic Nanoparticles

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ABSTRACT

Magnetic ceramic nanoparticles system xTm_2O_3-(1-x) α -Fe_2O_3 (x=0.1and 0.5) was synthesized by mechanochemical activation starting from hematite and thulium oxide precursors and characterized by transmission Mössbauer spectroscopy. The Mössbauer spectra were typically analyzed considering 1-3 sextets, corresponding to hematite (with and without thulium doping) and a doublet, representing thulium iron perovskite (thulium orthoferrite). The magnetic hyperfine fields (BHF) and doublet abundance were studied as function of the ball milling time (BMT) for both molar concentrations employed. The results are consistent with the formation of solid solutions in the investigated system. The mixed-oxide nanoparticle system synthesized may have important applications in displays, sensors and photovoltaics, and is paving the way for emerging utilizations related to mechanically flexible electronics.

Keywords: magnetic materials; nanocomposites; thulium oxide; Mössbauer spectroscopy

INTRODUCTION

Many branches of today's economies rely on applications of thulium oxide (Tm_2O_3) [1-14]. Thulium oxide represents the next generation of neutron absorbers [1, 2] and Tm_2O_3 thin films are developed as passive saturable absorbers for pulsed fiber laser generation [12]. Vitamin C detection of nanostructured Tm_2O_3 leads to applications in electrochemistry and bioelectronics [8]. Zirconia-doped thulium oxide (ZrO_2:Tm_2O_3) is highly transparent [5] and thulium vanadate-hematite nanocomposites ($TmVO_4$/Fe_2O_3) were demonstrated to show higher catalytic activity than the separate pure nanoparticles [7]. In order to obtain high resolution information on its properties, thulium oxide must be functionalized with an iron oxide, such as hematite α-Fe_2O_3). Hematite has various applications in scientific and industrial fields and can be used as a semiconductor compound, magnetic material, catalyst and gas sensor. In this study we propose to synthesize the mixed oxide system xTm_2O_3-(1-x) α -Fe_2O_3 at two molar

concentrations (x=0.1 and 0.5) and characterize its structural and magnetic properties by ^{57}Fe Mössbauer spectroscopy. A similar approach was used recently for the characterization of other related rare earths oxides-hematite nanocomposites [15, 16]. Semiconducting oxides have formed the basis for technological significant advancements in displays, sensors and photovoltaics, and are setting the stage for emerging applications related to mechanically flexible electronics.

MATERIALS AND METHODS

Nanoparticles of xTm_2O_3-(1-x) α -Fe_2O_3 (x=0.1and 0.5) were obtained by mechanochemical activation of precursor powders of hematite and thulium oxide with particle sizes of 50 and 90 nm, respectively (Alfa Aesar). The powders were mixed manually using a mortar and pestle and were introduced in a SPEX 8000 mixer mill and ground for 0, 2, 4, 8 and 12 h of BMT. The room-temperature transmission Mössbauer spectra were recorded using a SeeCo constant accelerator spectrometer equipped with a 25 mCi 57Co gamma ray source in a Rh matrix. Analysis of the Mössbauer spectra was performed by least-squares fitting in the assumption of Lorentzian lineshapes using the WinNORMOS package of programs.

RESULTS AND DISCUSSION

Figure 1 (a)-(e) and (f)-(j) shows the room-temperature transmission Mössbauer spectra of the xTm_2O_3-(1-x) α Fe_2O_3 series at milling times of 0-12 hours for molar concentrations x=0.1 and 0.5, respectively. The spectra corresponding to 0 hours of milling time were fitted with a sextet with the hyperfine magnetic field of 51.9 T, representing hematite. A small quadrupole-split doublet was added to these fits to account for the presence of ultrafine hematite nanoparticles, with the dimension less than 7 nm.

A second six-line pattern was introduced in the analysis of the Mössbauer spectra in Figure 1 (b)-(e) and (g)-(j), with the magnetic hyperfine field around 47 T (smaller than that of hematite) and assigned to thulium-doped hematite nanoparticles, Tm: Fe_2O_3. This sextet originates from substitutions of Fe atoms by nonmagnetic Tm atoms and is consistent with the model of local atomic environment. In addition, a third sextet, with a BHF of about 35 T, was necessary in the Mössbauer spectra of Figure 1 (c)-(e) and (i)-(j), demonstrating an increased level of Tm substitutions in the system subjected to milling. The dependence of the BHF values of these sextets on the ball milling time is depicted in Figure 2 and indicates the formation of a limited solid solution in the studied samples. A higher level of substitution is not possible due to the difference in the ionic radii of the Tm^{3+} ions (1.02 Å) and Fe^{3+} ions (0.645 Å). It may be noted that the formation of a solid solution was also observed for the system xGd_2O_3-(1-x) α -Fe_2O_3[15], but was not observed in the xNd_2O_3-(1-x) α -Fe_2O_3 system reported previously, due to the specific chemistry of the Nd ions [16].

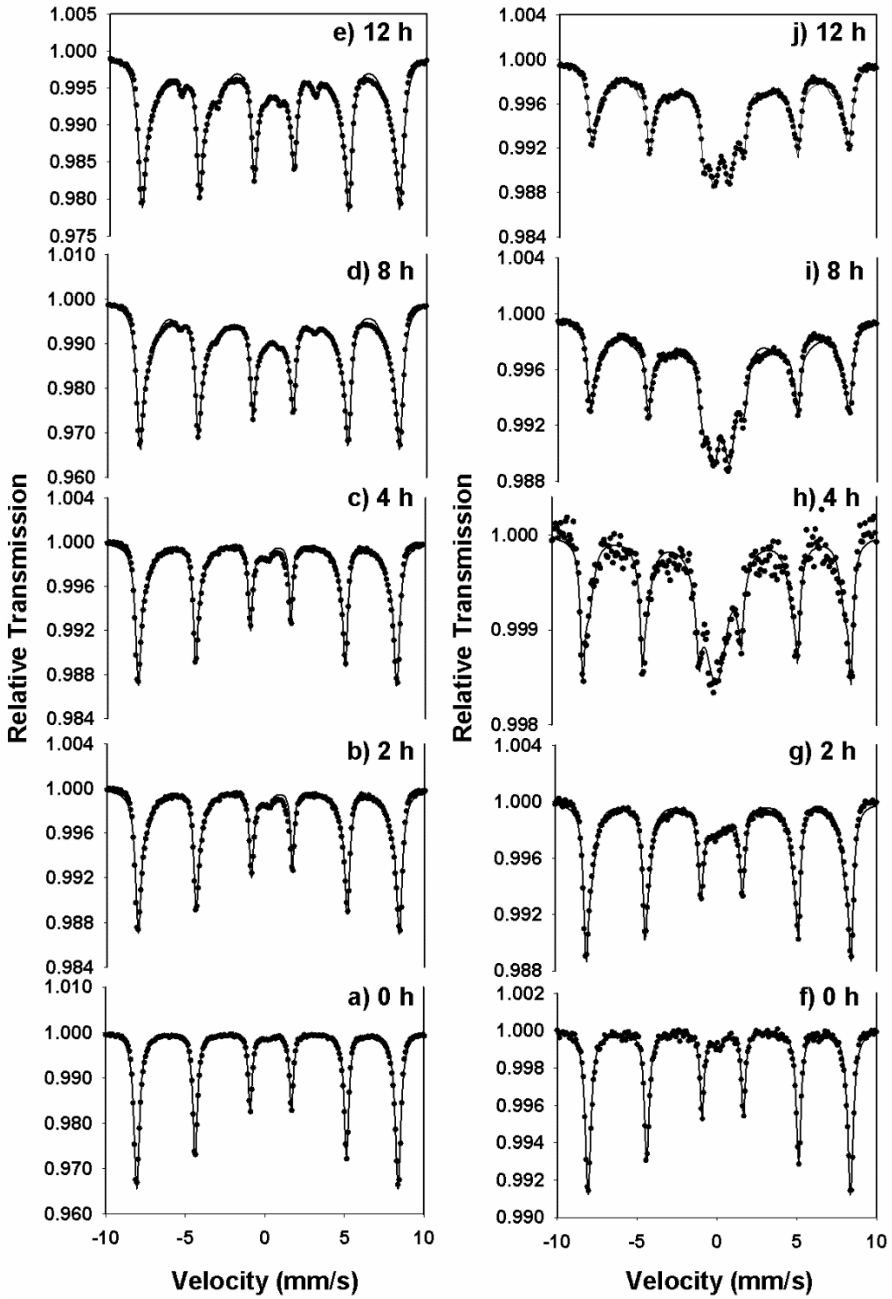

Fig. 1: Mössbauer spectra of xTm_2O_3-(1-x) α -Fe_2O_3 series at milling times of 0-12 hours

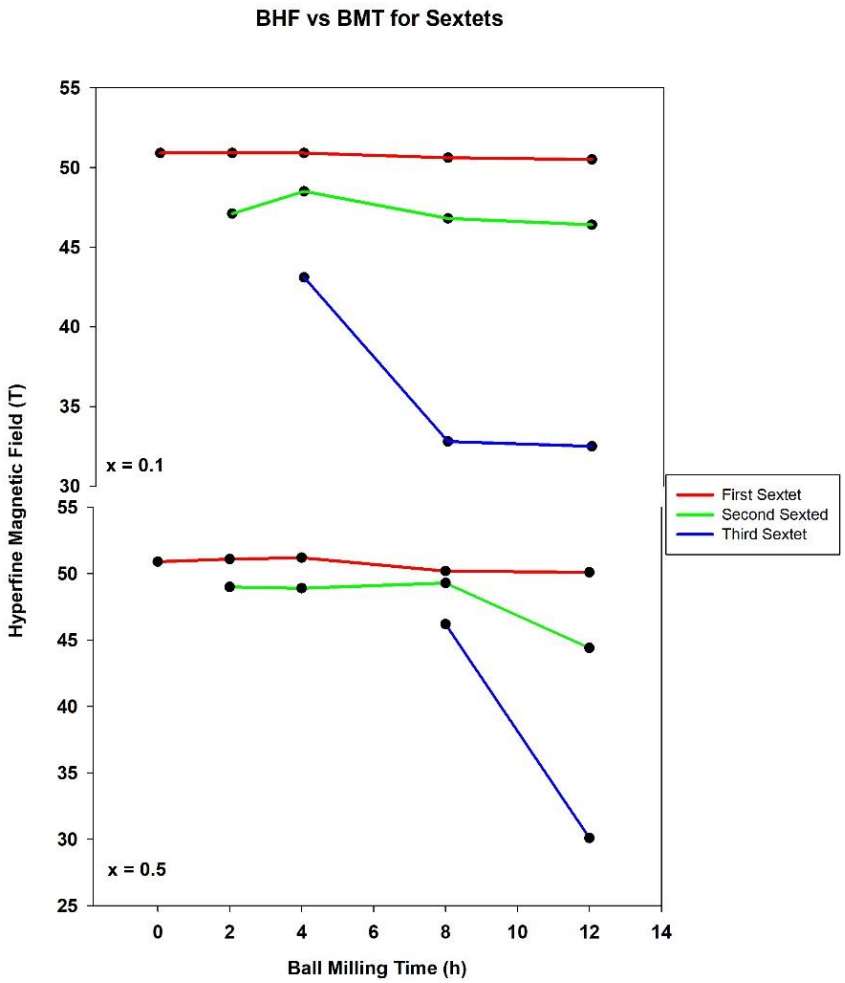

Fig. 2: Magnetic hyperfine fields as function of ball milling time for the three sextets involved at both molar concentrations.

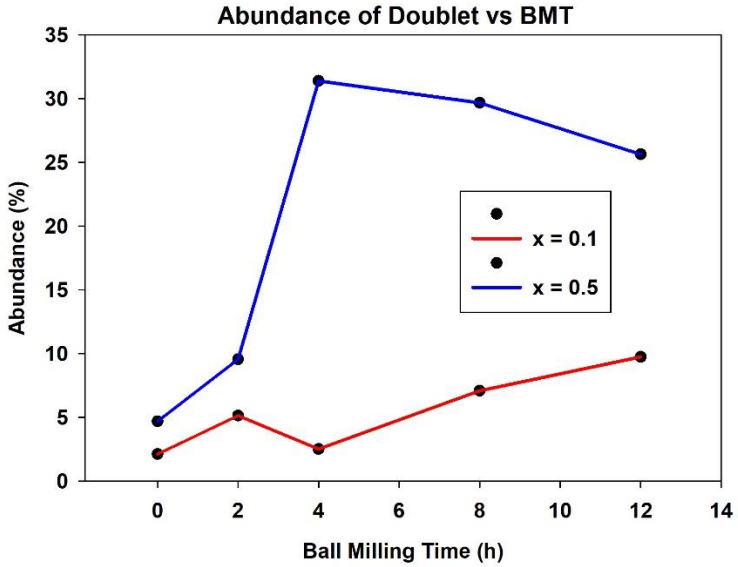

Fig. 3: Abundance of the quadrupole doublet as function of ball milling time for both molar concentrations.

In addition to the three sextets, a quadrupole-split doublet was introduced in the fitting of milled specimens, with a quadrupole splitting QS of ~0.25 mm/s and isomer shift IS of ~0.1 mm/s. As can be seen in Figure 3, its abundance as function of BMT increases up to 10% of the total spectral area for x=0.1 and to about 30% for the x=0.5 substitution level. The doublet can be assigned to the formation of thulium iron perovskite (thulium orthoferrite), which is believed to be governed by the reaction $Tm_2O_3+Fe_2O_3 \rightarrow 2TmFeO_3$, which occurs during the mechanochemical activation process [17]. The precipitation of thulium orthoferrite is more pronounced at the greater molarity employed and essentially increases as function of the ball milling time for both molar concentrations.

CONCLUSIONS

In this study we successfully synthesized the compositional series xTm_2O_3-(1-x) α -Fe_2O_3 at two different molarities (x=0.1and 0.5) and characterized its properties by ^{57}Fe Mössbauer spectroscopy. The phase outcome consisted of a solid solution of thulium-doped hematite and the formation of thulium orthoferrite. The fundamental microscopic mechanism explaining the phase sequence is related to the mutual substitutions of Tm ions in the hematite lattice and Fe ions in the thulium oxide lattice.

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Conflict of Interests

There are no conflicts of interests with this paper.

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