ISSN: 2756-2638
Transactions on Engineering and Computing Sciences; Vol. 14 No. 04 (2026) (175-182)
https://doi.org/10.14738/tmlai.1404.12130

Mössbauer Spectroscopy Investigations on Terbium Oxide Ball Milled with Hematite Nanoparticles System

Monica Sorescu, Seth McGuire, John McNally, Jayden Connors

Duquesne University, School of Science and Engineering, Department of Physics, Pittsburgh, PA 15282, United States

Abstract: For the first time in literature we report a Mössbauer spectroscopy investigation on terbium oxide ball milled with hematite nanoparticles for molar concentrations of x=0.1, 0.3 and 0.5. The samples were synthesized by mechanochemical activation using high energy ball milling for milling times between 0-12 hours. The Mössbauer spectra were deconvoluted by using Lorentzian line shapes with 2 sextets and a quadrupole split doublet. The sextets corresponded to hematite and terbium-doped hematite and the doublet was assigned to terbium iron perovskite (terbium orthoferrite). It is known that Tb4O7 decomposes into Tb2O3 at high temperatures, as those involved in ball milling. Mössbauer spectroscopy proved to be a high resolution experimental technique to characterize the structural and magnetic properties of mixed-oxide nanoparticles systems.

Keywords: hematite, terbium oxide, nanoparticles, Mössbauer spectroscopy, milling.

INTRODUCTION

Mössbauer spectroscopy (especially ^{57}Fe Mössbauer) is uniquely suited for mixtures like Tb_2O_3+Fe_2O_3 because it probes hyperfine interactions at Fe sites, allowing to determine Fe oxidation state (Fe^{3+} versus Fe^{2+}), magnetic ordering (sextet versus doublet), superparamagnetic nanoparticles, phase evolution (hematite, maghemite, orthoferrites, amorphous) which arise from isomer shift (δ) which includes information on valence/electron density. Quadrupole splitting (ΔE_Q) which accounts for lattice symmetry and magnetic hyperfine field which is about magnetic order.

Ball milling reduces crystallite size and increases disorder. Coexistence of nanocrystalline and microcrystalline hematite phases occurs along with grain size reduction which lowers the hyperfine magnetic field (B_{hf}). With long milling, partial transformation to magnetite or metallic Fe may occur, which brings extra sextets in the Mössbauer spectra. Nanostructuring causes suppression of Morin transition, emerging of superparamagnetic (SPM) doublet component and broadening of lines due to structural disorder.

Typical Mössbauer features (ball milled hematite)

Component	Spectrum	Interpretation
Sextet (hematite)	B_{hf}~50-52 T	Fe^{3+} in α-Fe_2O_3
Broad sextet	reduced B_{hf}	nanosize/disorder
Doublet	ΔE_Q~0.5-1 mm/s	SPM or amorphous phase
Additional sextet	variable B_{hf}	Fe metal/magnetite

Rare earth ions promote distortion of FeO_6 octahedra, changes in B_{hf} and quadrupole splitting and possible formation of orthoferrites $REFeO_3$ and solid solution in hematite lattice.

Hematite (α-Fe_2O_3) has been at the center of various theoretical and experimental studies due to its usefulness as a magnetic, semiconductor and catalytic material. Doping hematite with multiple transition metal and rare earth elements was determined to introduce an enhancement of its electrochemical and photocatalytic properties.

Terbium oxide (Tb_4O_7/Tb_2O_3) is a compound that can be applied to functionalize hematite for multiple utilizations in sensing, catalysis and flexible electronics. In particular, the Tb^{3+} ion was observed to exhibit intriguing properties when introduced in different systems.

Sensitive luminescent determination of DNA using the terbium (III)-difloxacin complex was achieved in [1]. Synthesis, characterization and thermoluminescence of MgO:Li, Tb, Sm phosphor for high dose gamma dosimetry applications were accomplished in [2]. In [3] the tailored microstructures, optical and magnetic qualities of strontium hexaferrites were developed. Fabrication of Tb doped ZnO nanoparticles via co-precipitation technique for multifunctional applications was developed in [4]. The effects of terbium oxide on phase transition and electronic properties of potassium-sodium niobate-based ceramics were studied in [5]. Electrolytic synthesis of $TbFe_2$ from Tb_4O_7 and Fe_2O_3 powders in molten $CaCl_2$ was accomplished in [6]. In [7] the spin-glass behavior of mechanically milled CuO_2 was described. Exploration of crystal structure and luminescence behaviors of terbium-activated CaWO4 phosphor was performed in [8]. In [9] the structural and optical properties of terbium oxide nanoparticles were described. A review on the cracking, baking and leaching process rare earth element concentrates was published in [10]. In [11] the ultrasonic synthesis, magnetic and optical characterization of Tm^{3+} and Tb^{3+} ions co-doped barium hexaferrites were developed. The structural and photoluminescence properties of Tb-doped $CaMoO_4$ nanoparticles with sequential surface coatings were described in [12]. A novel synthesis of phase-pure YAG:Tb phosphor with different Tb concentrations was developed in [13]. Tb-doped $BiFeO_3$ nanostructure and its composites with CNTs to improve the light-harvesting properties were described and published in [14]. Anhydrous oxygen-free rare earth material preparation and characterization were performed in [15]. Fine milling in applied mechanochemistry was summarized in [16]. In [17] it was reported the development of a terbium-lithium glass for slow neutron detection. The effects of Tb^{3+} on the properties of luminescent calcium sulfate cement were identified in [18]. Ball milling and sintering of neutron absorber Mo-based Tb_2O_3-Dy_2O_3 composite and its characterization were reported in [19]. Photoluminescence and afterglow of Tb^{3+} doped $BaAl_2O_4$ were observed in [20].

MATERIALS AND METHODS

Nanoparticles of xTb_2O_3-$(1-x)\alpha$-Fe_2O_3 (x=0.1, 0.3 and 0.5) were obtained by mechanochemical activation of precursor powders of hematite and terbium oxide (Alfa Aesar), with particle sizes in the tens of nanometer range. The powders were mixed manually using a mortar and pestle and introduced in a SPEX 8000 mixer mill. They were ground for time periods of 0, 2, 4, 8, and 12 hours. The powder to ball mass ratio was 1:5.

Transmission Mössbauer spectra were recorded at room temperature using a SeeCo constant acceleration spectrometer model W302. A 25 mCi ^{57}Co gamma ray source diffused in a Rh matrix was used. All spectra were deconvoluted by least square fitting using a WINORMOS package of programs and the spectra were depicted using the SigmaPlot package.

RESULTS AND DISCUSSION

Mössbauer spectroscopy relies on recoil-free γ-ray emission/absorption in solids, enabling extremely precise probing of the local environment of ^{57}Fe nuclei.

The three key hyperfine interactions in the spectra are isomer shift (IS) which is sensitive to Fe valence and electron density, quadrupole splitting (QS) which is sensitive to electric field gradient (symmetry distortion) and the magnetic hyperfine field (B_{hf}) which reflects magnetic ordering.

For α-Fe_2O_3 (hematite), the typical room-temperature Mössbauer signature is a six-line magnetic sextet due to ordered Fe^{3+} spins.

High-energy ball milling in oxide systems introduces grain size reduction to nanoscale, lattice strain and defects, and enhanced cation interdiffusion and solid solution formation.

Mössbauer studies show that grain size decreases with milling time, magnetic hyperfine fields change due to size and disorder effects and multiple Fe environments (nano vs bulk-like) may coexist. This is directly relevant to Tb_2O_3–Fe_2O_3 systems, where Tb^{3+} can diffuse into the hematite lattice or form new phases.

Expected Mössbauer features in Tb_2O_3–Fe_2O_3 systems show a hematite component with a sextet (Fe^{3+} in α-Fe_2O_3), reduced B_{hf} with increasing milling time and line broadening due to size distribution and surface spin disorder.

The solid solution of Tb-doped hematite with the substitution of Tb^{3+} (non-Mössbauer active) modifies Fe environment and has effects to decrease the hyperfine field, increase in line width and slight shifts in IS/QS.

Paramagnetic/disordered components where doublets are observed due to superparamagnetic nanoparticles and amorphous or highly disordered regions are involved.

In nanoparticles, Mössbauer spectra often transition from sextet to broadened sextet and a doublet as particle size decreases and thermal fluctuations dominate.

Possible new phases which appear from mechanochemical synthesis that may lead to $TbFeO_3$ (terbium orthoferrite) formation are observed as a distinct doublet or sextet combination.

For size and magnetic effects critical for nanoparticles Mössbauer spectroscopy is particularly powerful because it captures superparamagnetism which appears as doublets at room temperature, caused by rapid spin relaxation in small particles.

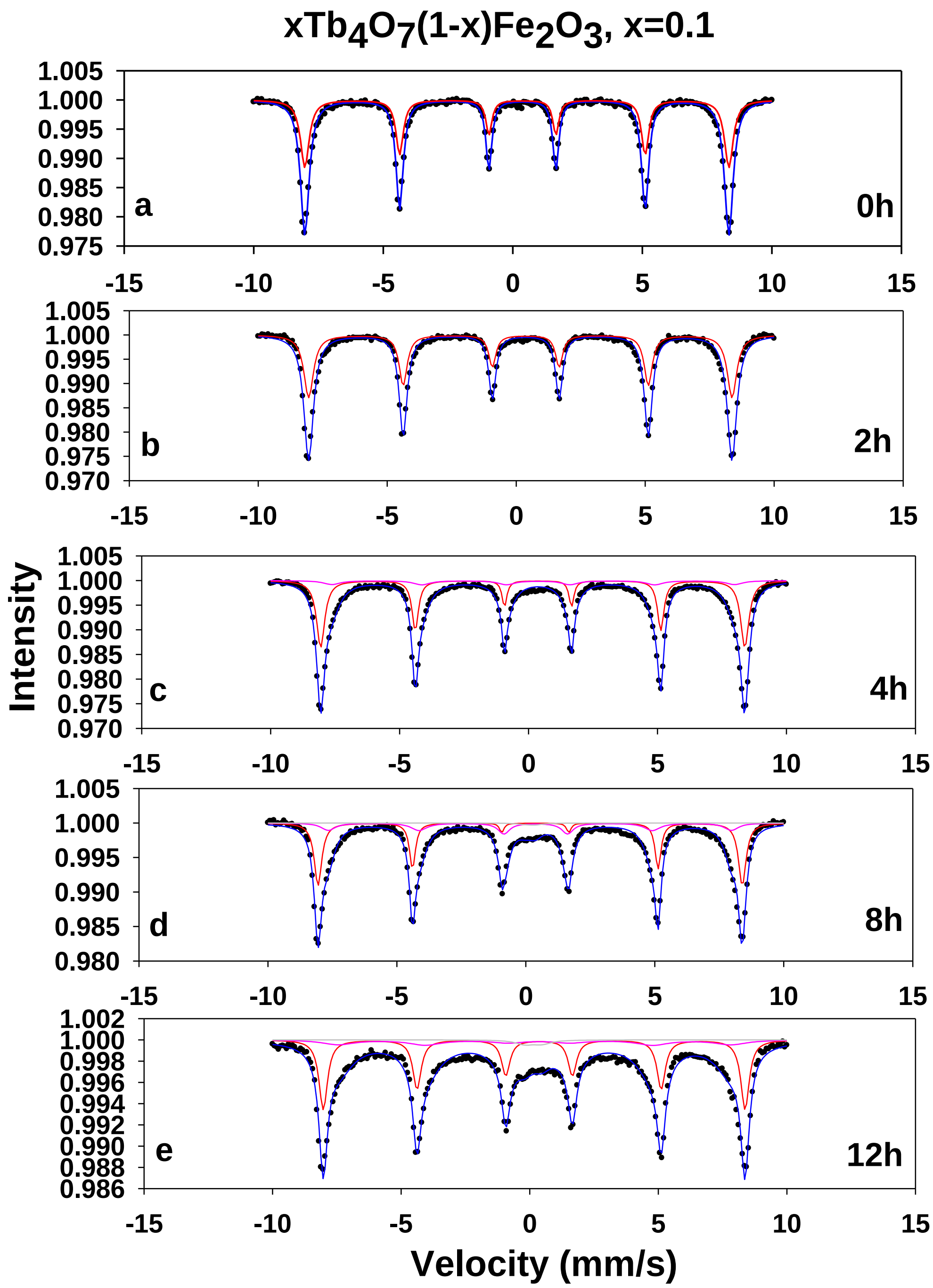

Figure 1: Mössbauer spectra for terbium oxide at a molar concentration of x=0.1.

In hematite nanoparticles a significant fraction can exhibit superparamagnetic behavior and magnetic transitions (e.g., Morin transition) may shift or disappear.

Surface spin disorder due to reduced coordination at nanoparticle surfaces leads to reduced B_{hf}, broadened lines and non-collinear spin structures. Interpretation strategy for Tb_2O_3–Fe_2O_3 systems in which a typical fitting model includes components such as sextet 1 (for bulk hematite), sextet 2 (for distorted/doped hematite) and a doublet (for superparamagnetic or orthoferrite phase) were developed.

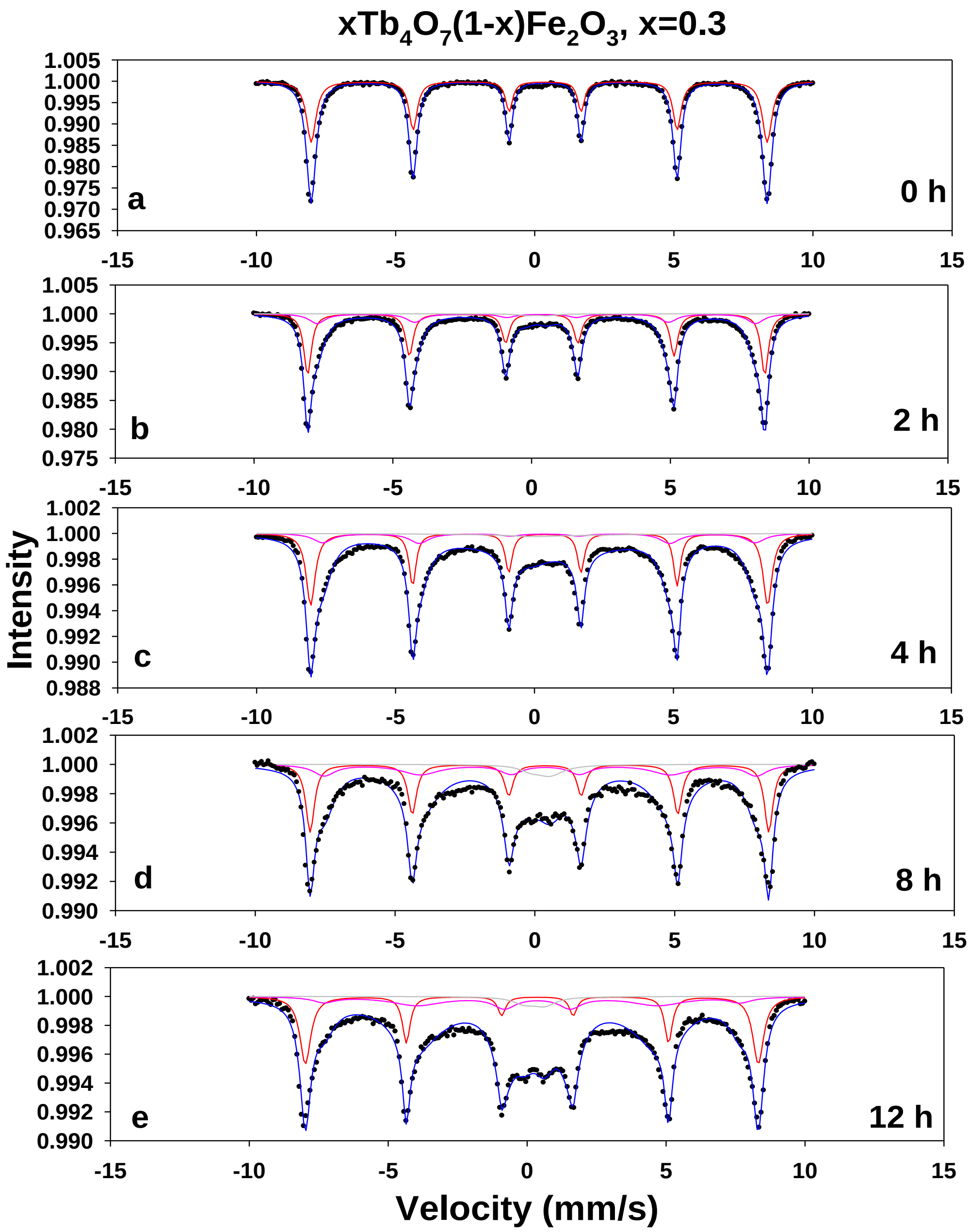

Figure 2: Mössbauer spectra of terbium oxide at a molar concentration of x=0.3.

Parameters to track vs milling time: B_{hf} decreases with increased milling, the relative sextet area decreases with more disorder, doublet area increases due to amorphization / superparamagnetism and the line width increases because of strain and size distribution.

Such systems are important because rare-earth oxides modify magnetic anisotropy, mechanochemistry enables solid solution formation at low temperature and Mössbauer spectroscopy uniquely reveals local Fe environment, phase evolution and magnetic ordering.

Also, these materials are relevant for spintronic materials, sensors and catalysts and magnetic ceramics.

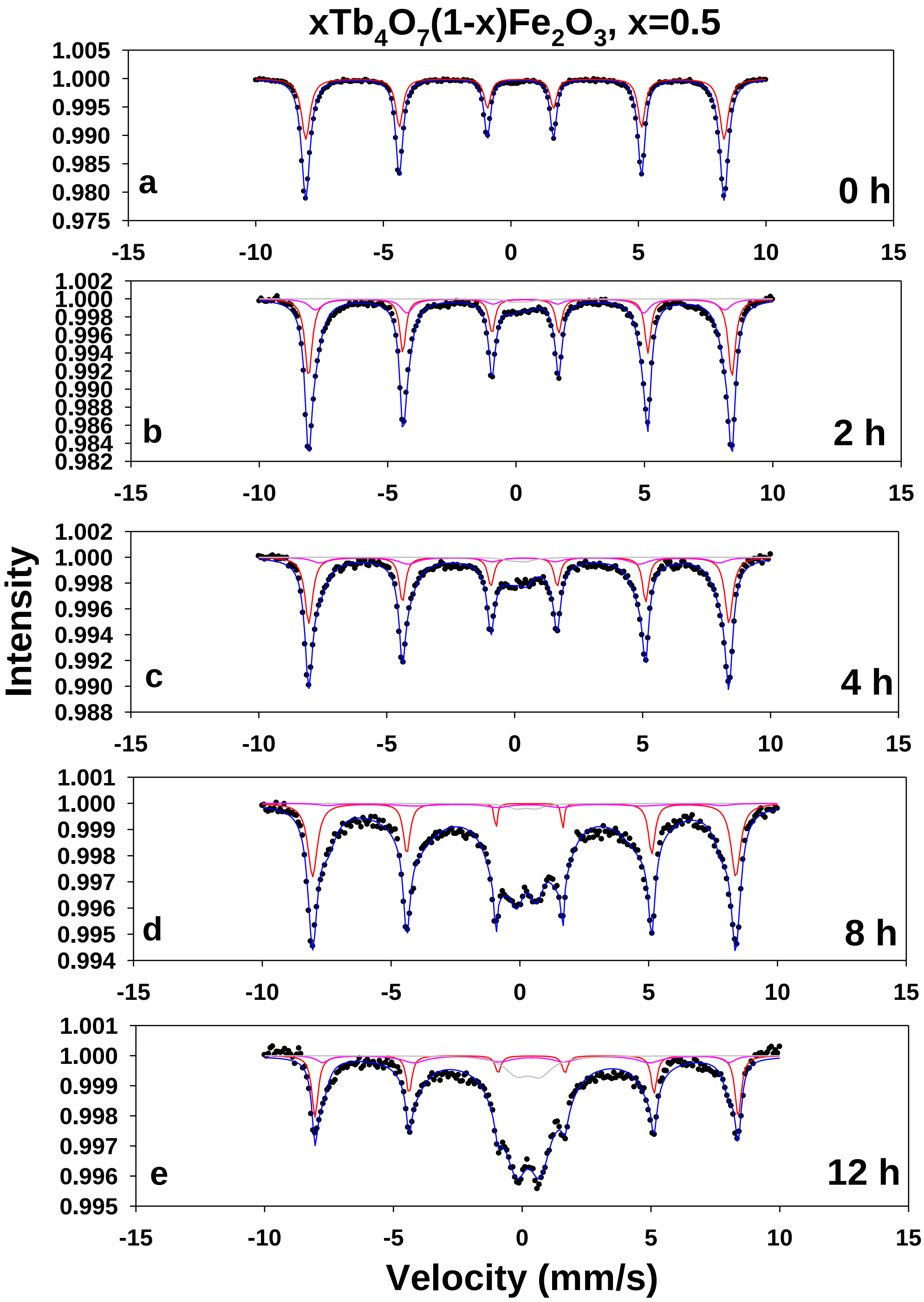

Figure 3: Mössbauer spectra of terbium oxide at a molar concentration of x=0.5.

Figure 1 reveals the Mössbauer spectra of terbum oxide ball milled with hematite nanoparticles for x=0.1 at different milling times. Figure 2 depicts the Mössbauer patterns of terbium oxide ball milled with hematite nanostructures for the molar concentration of x=0.3 at different ball milling times. Figure 3 presents the Mössbauer spectra for terbium oxide milled with hematite at x=0.5 at different ball milling times.

The Mössbauer spectra were deconvoluted by least square fitting with Lorentzian line shapes considering 2 sextets which correspond to hematite (B_{hf}~51.9 T) and terbium-doped hematite (B_{hf}~48.5 T). To obtain the best fit it was necessary to introduce a quadrupole split doublet with a splitting of about 0.4 mm/s which was assigned to terbium iron perovskite (terbium orthoferrite). Its abundance increased with ball milling time and molar concentration.

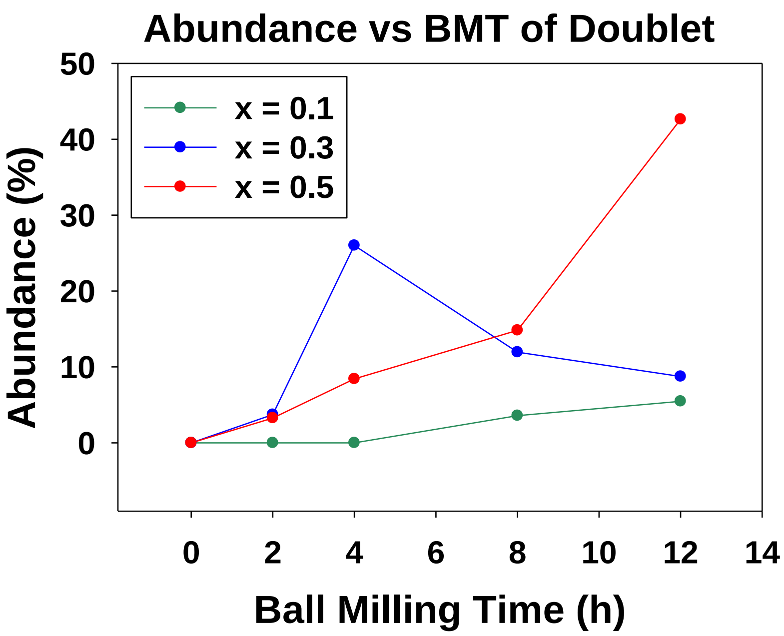

Figure 4: Abundance of the quadrupole split doublet on the ball milling time showing the production of terbium iron perovskite.

These results show that Mössbauer spectroscopy is a powerful technique to characterize the structural and magnetic properties of rare earth doped hematite nanoparticles.

CONCLUSIONS

Our investigations are the first in literature to report on the structural and magnetic properties of terbium oxide ball milled with hematite. Molar concentrations of x=0.1, 0.3 and 0.5 were used. The ball milling times selected were 0, 2, 4, 8 and 12 hours. The Mössbauer spectra were deconvoluted using Lorentzian line shapes with 2 sextets and a quadrupole split doublet. The sextets corresponded to hematite and terbium-doped hematite and the doublet was assigned to terbium iron perovskite (terbium orthoferrite).

Mössbauer spectroscopy proved to be a high resolution experimental technique to characterize the structural and magnetic properties of mixed-oxide nanoparticles systems.

Acknowledgment: This work was supported in part by the National Science Foundation, USA under grant DMR-1002627-1.

Conflicts of interest

There are no conflicts of interest regarding the work described in this paper.

REFERENCES

1) A.Yegorova et al., Analytica Chimica Acta 584 (2007) 260-267.
2) A.Jain et al., Applied Radiation and Isotopes 206 (2024) 111222.
3) M.A. Almessiere et al., Ceramics International 45 (2019) 21385-21394.
4) B.Shivaraj et al., Chemical Physics Letters 818 (2023) 140421.
5) Y.Zhai et al., Journal of Alloys and Compounds 776 (2019) 984-992.
6) G.Qui, Journal of Electroanalytical Chemistry 589 (2006) 139-147.
7) D.P. Rojas et al., Journal of Magnetism and Magnetic Materials 310 (2007) e506-e508.
8) R.Paikaray et al., Journal of Molecular Structure 1290 (2023) 135902.
9) G. Wakefield et al., Journal of Physics and Chemistry of Solids 60 (1999) 503-508.
10) F. Sadri et al., Journal of Rare Earths 35 (2017) 739.
11) M.A. Almessiere et al., Journal of Solid State Chemistry 286 (2020) 1213 10.
12) A.A. Ansari, Materials Chemistry and Physics 147 (2014)715-721.
13) J. Zhang, Materials Letters 57 (2003) 3077-3081.
14) M.F. Abu Taleb et al., Materials Science and Engineering B 299 (2024) 116916.
15) N.T. Hung et al., Materials Today Chemistry 22 (2021) 100608.
16) P. Balaz et al., Minerals Engineering 23 (2009) 681-694.
17) G. Zanella et al., Nuclear Instruments and Methods in Physics Research A 359 (1995) 547-550.
18) D.R. Khayrutdinova et al., Open Ceramics 18 (2024) 100587.
19) D. Lv et al., Powder Technology 331(2018) 226-235.
20) Y. Cai et al., Results in Physics 60 (2024) 107656.