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HYPERFINE AND STRUCTURAL PROPERTIES OF THE GOETHITE TO HEMATITE MECHANOCHEMICAL TRANSFORMATION

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RESUMEN

En este trabajo se estudia la transformación mecano-química goethita a hematita mediante la espectrometría Mössbauer y la difracción de rayos X. El experimento se llevó a cabo utilizando un molino planetario en el régimen de alta energía con tiempos de molienda entre 30 minutos y 20 horas. Los resultados muestran que a 30 minutos de molienda se inicia la transformación goethita a hematita con un aumento progresivo del área espectral de la hematita mientras el de la goethita disminuye. Los espectros Mössbauer revelan también la presencia de un doblete atribuido a goethita superparamagnética en conformidad con la reducción de tamaño de grano como consecuencia del proceso de molienda.

Palabras clave: Goethita, hematita, Mössbauer, molienda mecánica.

ABSTRACT

The mechanochemical-driven goethite to hematite transformation was addressed by means of Mössbauer spectroscopy and X-ray diffraction. The experiment was carried out using a planetary ball mill in the high energy regime with milling times between 30 minutes and 20 hours. Results show that at 30 minutes of milling the transformation goethite to hematite has already started with a progressive increase of the spectral area of hematite whereas that of goethite decreases. Mössbauer spectra reveal also the occurrence of a doublet attributed to superparamagnetic goethite accordingly with grain size reduction as a consequence of the milling process.

Key words: Goethite, hematite, Mössbauer, mechanical milling.

INTRODUCTION

The transformation goethite to hematite ($\alpha - FeOOH \rightarrow \alpha - Fe_2O_3$) has been the subject of different studies due to the wide interest in technological applications of iron oxides [1]. Most of the reported work on this subject deals with thermally driven transformations whereas a lot of work on solid-state reactions induced by mechanical milling is still lacking. Thus the increasingly importance of nanostructured systems makes the ball milling technique an alternative which is being widely employed to modify structural properties like grain size, morphology, crystallinity, etc. which in turn involve changes in the physical and chemical properties of these systems. Specifically the goethite dehydra-tion process by thermal treatment has been widely studied by X-ray diffraction (XRD), transmission electron microscopy (TEM) and infrared spectroscopy (FTIR) [2-3]. However, few works on the mechanochemical transformation have been reported [4-6]. When milling, several forces like impact, attrition, compression and friction give rise to diffusion at atomic scale, unit cell distortions and defects favoring the phase transformations. It is also interesting the connection between the high energy ball milling and those processes involved in the geological formation of rocks and iron oxides in nature. Hence the study of the mechanical transformation of goethite could be an approach to understand some geological aspects related to the formation of hematite. In this work, we present the effect of the high energy ball milling on the structural and hyperfine parameters of goethite for different milling times. The respective characteriza-tions were carried out by Mössbauer and a Rietveld analysis of X-ray diffraction data.

EXPERIMENTAL

The goethite precursor sample was obtained by following the procedure described by Schwertmann and Cornell [7]. The sample was milled in a Retsch S1000 planetary ball mill at 650 rpm with a Al_2O_3 vessel and balls of the same material. Milling times of 0.5, 3, 6, 12 and 20 hours were considered and the average powder to ball weight ratio was taken to be 1:10. The phase distribution was followed by XRD using a Bruker AXS D8 Advanced diffractometer with K_α-Co radiation, 0.014° of step in 2θ and 1 second of counting in the range 15°-80°. Rietveld refinement was carried out to some selected samples for which the respective diffractograms were recorded with 4 seconds of counting. Rietveld analysis was performed using the MAUD program (http://www.ing.unitn.it/~luttero/maud/). Mössbauer spectra were recorded at room temperature (RT=298K) in the transmission geometry with a Co^{57} source embedded in a Rh matrix. The Mössbauer fitting process was carried out with the Normos-Distri [8] program considering hyperfine field distributions accounting for the atomic disorder induced by milling in addition to some crystalline sites. A Mössbauer spectrum at 77 K was also recorded to one selected sample in order to understand the nature of the paramagnetic signal observed at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of the X-ray diffractograms for the considered milling times. Diffractograms are labeled with the nomenclature GOBM*t* which means “Goethite ball-milled *t* hours”. As is observed, the onset of hematite peaks is clearly evidenced at 3 hours of milling and they increase in magnitude as the milling time increases. The presence of goethite peaks even at 20 hours indicates that the transformation does not become completed at this milling time. Other related works [4] reveal that the goethite to hematite transformation is topotactic, for which the twining formation on basal planes of goethite is used as a substrate for the growing of hematite free of hydroxyl groups. The common planes are observed in the XRD patterns for the goethite peak (130) at 39° which is very similar to that of hematite (104). A broadening in goethite peaks with milling time is also observed, consistent with an increase in the degree of disorder and a reduction of the grain size. Table 1 shows the Rietveld fitting results of the samples corresponding to 3 and 20 hours of milling. On the other hand, the increase in the grain size of hematite can be understood in terms of the formation of this new phase as a consequence of the transformation. Figure 2 shows the Möss-bauer spectrum at room temperature and the corresponding hyperfine field distri-bution of the goethite sample before the milling process. The fitting process was carried out by using one sextet, one singlet and a hyperfine magnetic field distribution (HFD). The sextet is ascribed to a well-crystallized fraction of the goethite sample; the singlet is attributed to a fraction of superparamagnetic goethite with a broad distribution of relaxation times typical of this system [9], whereas the HFD is due to a fraction of poorly crystalline goethite.

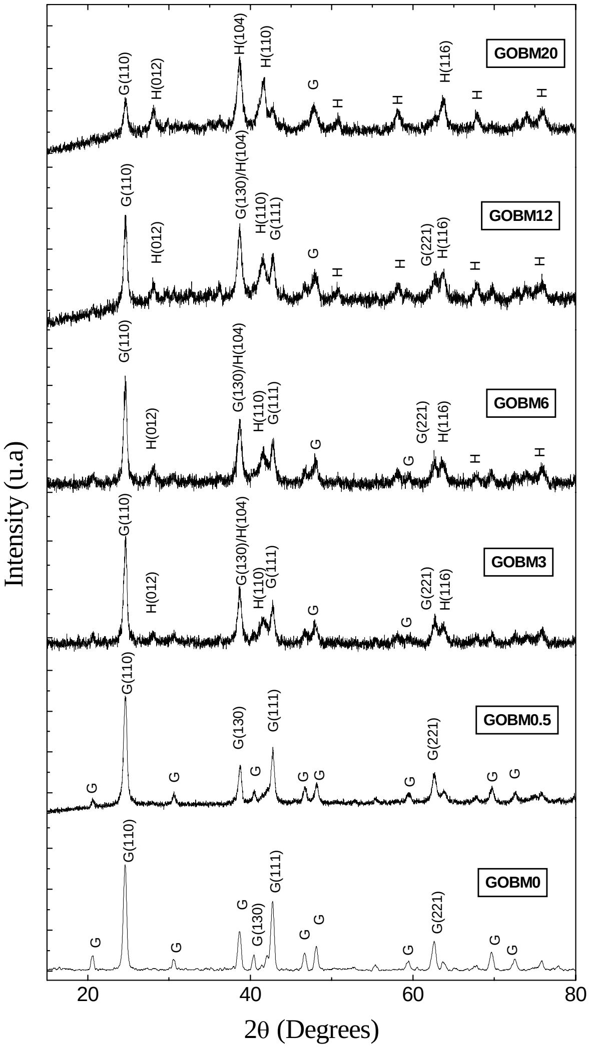

Figure 1. X-ray diffractograms for different milling times. Labels G and H correspond to Goethite and Hematite respectively.

Table 1. XRD results from Rietveld analysis for the samples with 3 and 20 hours of milling.

Sample	Component	*a* (Å)	*b* (Å)	*c* (Å)	Grain size (nm)
GOBM3	Goethite	4.609 (6)	9.976 (3)	3.026 (6)	19.2 (4)
	Hematite	5.038 (1)		13.779 (9)	8.5 (5)
GOBM20	Goethite	4.606 (2)	9.949 (8)	3.028 (1)	18.0 (1)
	Hematite	5.034 (6)		13.757 (3)	12.0 (2)

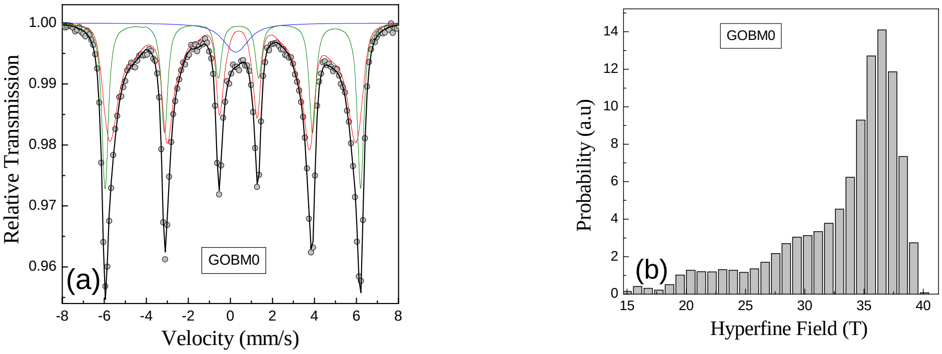

Figure 2. (a) Room temperature Mössbauer spectrum and (b) the corresponding hyperfine field distribution of the broadened magnetic component of the starting goethite sample.

As is shown in Fig. 3, the solid-state reaction at atomic level takes place during the first thirty minutes of milling for which the presence of hematite with a greater hyperfine magnetic field of 51.8(5) T becomes evident. Even though X-ray diffraction doesn't show any different phase that goethite, the local probe character of the Mössbauer technique reveals effectively that the reaction starts at 30 minutes of milling or even before. Such hematite phase, which is the dehydroxylated product of goethite, is confirmed from X-ray diffraction data for milling times above 3 hours. As the milling time increases the crystalline fraction of goethite (sextet) disappears at 3 hours of milling whereas the HFD attributed to goethite becomes broadened as well as that concerning to hematite. These features are attributed to an increase in the degree of disorder as a consequence of the milling process involving unit cell distortion and strain-stress effects. Such a disorder leads to a distribution of ionic environments corresponding for instance to Fe nucleus in a grain boundary, inside a grain, on a grain surface, or Fe nucleus near a vacancy or defect. After 20 hours of milling the fraction of magnetic goethite exhibits a spectral area of 34.0 %, whereas that of hematite corresponds to 43.2 %, and a 22.8 % belongs to the paramagnetic-type signal. Thus, the goethite-to-hematite transformation does not get to be completed at 20 hours of milling. Figure 4 shows the Mössbauer spectra of the 20 hours sample at room temperature and 77 K. In the room temperature spectrum the fitting process includes a second paramagnetic signal which remains as a doblet at 77K, and is attributed to nanometric hematite exhibiting superparamagnetic behavior. This behavior has been already reported to occur for grain sizes of the order of 8nm [5,9]. Finally, the negative value of –0.151(1) mm/s for the quadrupolar shift of the magnetic component of hematite at 77K and according to literature [5,6] suggests a weak ferromagnetic state. This fact suggests that at 77 K the Morin transition is not still evidenced. This feature agrees with other works for which the Morin transition can be modified or even suppressed due to the presence of OH groups in the structure of hematite, to grain size reduction or by particular morphologies of grains [10].

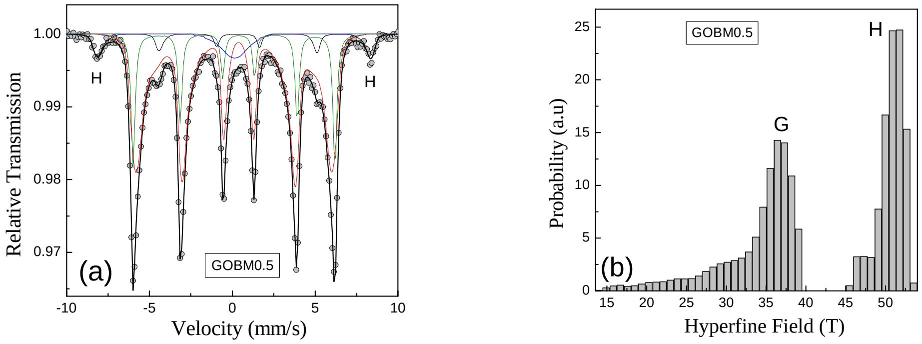

Figure 3. (a) RT Mössbauer spectrum and (b) the HFD for the sample of 30 minutes of milling.

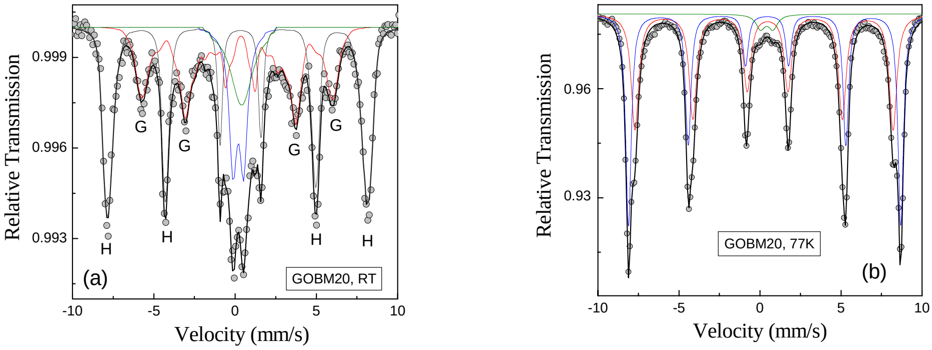

Figure 4. Mössbauer spectra of the 20 hours sample at (a) room temperature and (b) 77 K.

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