



Mixtures of iron and anatase TiO₂ by mechanical alloying

A.M. Calle^{a,*}, L.C. Sánchez^a, J.D. Arboleda^a, J.J. Beltrán^a,
C.A. Barrero^a, J. Osorio^a, K. Nomura^b

^aGrupo de Estado Sólido, Sede de Investigación Universitaria, Universidad de Antioquia, Colombia

^bDepartment of Applied Chemistry, School of Engineering, University of Tokyo, Japan

Abstract

Fe-doped TiO₂ powders were obtained by mechanical alloying. The starting materials were anatase TiO₂ and metallic iron (α -Fe) or hematite (α -Fe₂O₃). The influence of different milling conditions such as: ball to powder weight ratio, milling time, rotation velocity of supporting disc, and dopant concentration on the structural and magnetic properties were investigated. All experiments were performed in atmospheric conditions. The milled powders were characterized by X-ray diffraction (XRD) using Rietveld refinement and room temperature Mössbauer spectrometry. The XRD patterns of all samples show the coexistence of both anatase and rutile phases and also the high-pressure srilankite phase. Mössbauer spectra reveal the presence of Fe²⁺ and Fe³⁺ states in Fe-doped TiO₂ as well as α -Fe or α -Fe₂O₃ in samples obtained from metallic iron or hematite, respectively. The Fe³⁺ contribution could be attributed to Fe incorporated in the TiO₂ structure and the Fe²⁺ can be probably assigned to surface ferrous ions in the TiO₂.

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The development of functional ferromagnetic semiconductors is a key to the construction of spintronic like (or spin-based electronic) materials [1]. Wide gap oxide diluted magnetic semiconductors combine their electrical conductivity with ferromagnetism and optical transparency, thereby opening up the possibility of other device concepts. Transition metal-doped TiO₂ and SnO₂ belong to these class of materials [2–4]. In order to obtain iron-doped TiO₂ nanocomposites, a number of studies have been carried out, but many have the drawback of producing impurity phases and magnetic ion clustering. Therefore, the search for proper experimental conditions to successfully prepare these materials has become an important part of this research field. Ball milling is an alternative way of producing nanocrystalline materials, and few researchers have made attempt to use this technique [5–7]. In this work we studied the effect of different milling conditions on the formation of Fe-doped TiO₂ powders.

Mechanical alloying was performed in a planetary ball mill Fritsch Pulverisette 5. The starting materials were anatase TiO₂ and α -Fe or α -Fe₂O₃. Samples were milled for 6, 12, 18 and 24 h in air at atmospheric pressure, using Cr-based stainless steel jars and balls of 12 mm in diameter. Fe nominal concentrations of 0, 1, 4 and 8 at% were explored. The rotation velocity of the discs were of 100 rpm (low energy), 250 rpm (medium energy) and 390 rpm (high energy) and the ball to powder ratio were of 20:1 and 40:1. The crystalline structure was investigated by X-ray diffraction (XRD) using Rietveld refinement. Mössbauer spectra were measured at room temperature using a conventional Mössbauer spectrometer.

The XRD patterns of the precursor TiO₂ sample showed only the anatase phase, whereas the milled TiO₂ at high energy showed a mixture of anatase, high-pressure srilankite and rutile phases. High energy mechanical milling of anatase TiO₂ induces the anatase rutile transformation via high-pressure srilankite [7]. The XRD patterns of high energy milled TiO₂ mixed with α -Fe for different concentration of iron also shows the coexistence of these three TiO₂ phases (see Fig. 1).

*Corresponding author.

E-mail addresses: lsanchez@fisica.udea.edu.co (A.M. Calle), cbarrero@fisica.udea.edu.co (C.A. Barrero).

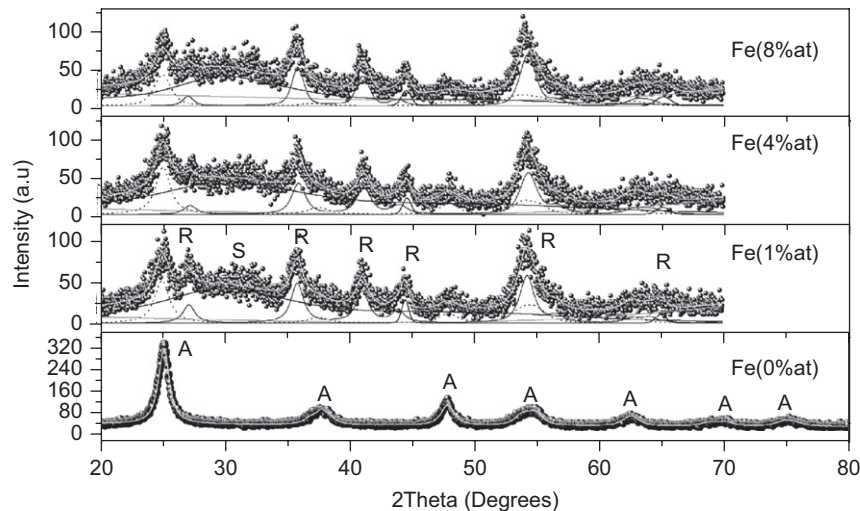


Fig. 1. XRD patterns for the mixture of anatase TiO_2 and metallic iron as a function of Fe concentration. The mixtures were milled at 390 rpm for 12 h. Ball to powder weight ratio was of 20:1. A—anatase, R—rutile and S—srilankite.

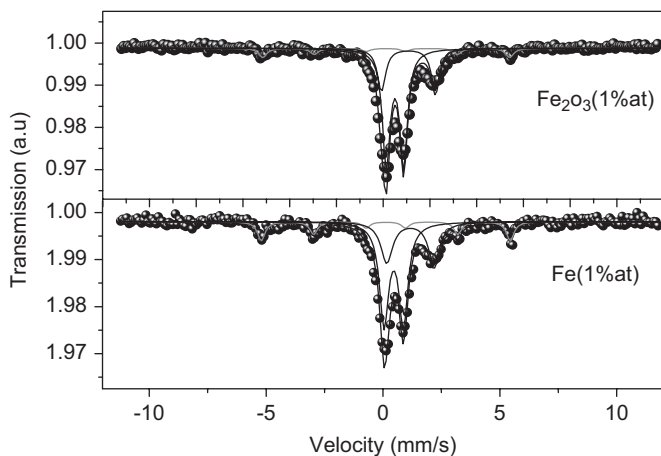


Fig. 2. Room temperature Mössbauer spectra for samples obtained from milling the mixture of anatase TiO_2 with hematite at 390 rpm during 18 h with the ball to powder weight ratio of 20:1.

Room temperature Mössbauer spectra for some selected Fe-doped TiO_2 powders are shown in Fig. 2. The spectra were fitted with three components: one sextet and two doublets. The hyperfine parameters of the sextet components are attributed to the presence of metallic iron or hematite for the samples obtained from α -Fe or α - Fe_2O_3 powders, respectively. These phases correspond to the starting iron materials that do not react with TiO_2 . The parameters of the two doublets are due to the presence of Fe^{2+} and Fe^{3+} states in octahedral sites. The Fe^{3+} doublet could be attributed to Fe incorporated in the TiO_2 structure and the Fe^{2+} can be assigned to surface ferrous ions in the TiO_2 or ions in the interstitial sites of TiO_2 [5,6].

Our results suggest that proper milling conditions for obtaining pure Fe-doped TiO_2 should consider: (i) hematite instead of metallic iron as an iron precursor; (ii) medium milling energy, because higher energies has the drawback of iron contamination coming from the balls and the jars, whereas lower energies do not promote appreciable Fe

incorporation into the TiO_2 lattice; and (iii) intermediate milling times and iron contents in order to avoid the possible formation of impurity phases and contamination. Chemical treatments with concentrated HCl can complement the procedure for improving the degree of purity in the samples.

Summing up, mechanical milling of undoped anatase TiO_2 at high energy proceeds via the transformation: anatase \rightarrow high-pressure srilankite \rightarrow rutile. On the other hand, the mechanical alloying of the mixture of anatase TiO_2 and α -Fe produces Fe-doped TiO_2 and α -Fe, whereas that of the mixture of anatase TiO_2 and α - Fe_2O_3 produces Fe-doped TiO_2 and α - Fe_2O_3 . The Fe-doped TiO_2 phases identified were anatase (major phase), srilankite (minor phase) and rutile (minor phase). The Fe-doped TiO_2 contains iron in two oxidation states: Fe^{2+} and Fe^{3+} . Fe^{3+} is attributed to iron incorporated in the TiO_2 structure, whereas Fe^{2+} is probably due to irons at the surface or interstitial sites of TiO_2 .

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