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XAS study of the local environment of impurities in doped TiO_2 thin films

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Abstract

In this work, we present an X-ray absorption spectroscopy (XAS) characterization of the local environment of the impurity in room temperature ferromagnetic (RTF) anatase TiO₂ thin films doped with Co, Ni, Cu, or Zn, deposited on LaAlO₃ substrate by pulsed laser deposition (PLD). It was found that there is a considerable amount of impurity atoms substituting Ti in TiO₂ anatase, although the presence of metal transition monoxide clusters can not be discarded. From our results, we infer that the observed RT ferromagnetism of the samples could be assigned to the metal transition atoms replacing Ti in TiO₂ anatase. \bigcirc 2007 Elsevier B.V. All rights reserved.

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1. Introduction

The discovery of room-temperature ferromagnetism (RTF) in Co-doped anatase [1] and rutile [2] TiO_2 has stimulated intense theoretical and experimental studies of these systems due to their potential applications in spintronic technology. In effect, dilute magnetic semiconductors (DMS), produced by doping non magnetic semiconductors with transition metals, combine their electric conductivity with ferromagnetism and optical transparency, thereby opening up the possibility of new device concepts. But, the site of the impurity is still under debate and while some authors claimed that the presence of ferromagnetic metallic clusters cannot be completely excluded, others have concluded that ferromagnetism is a consequence of atomic scale doping [3].

Recently, we reported the experimental observation of unexpected and significant RTF in Cu-doped TiO₂ films [4], equivalent to what would be expected if, on the average, each Cu atom bears a magnetic moment of about

*Corresponding author. *E-mail address:* torres@fisica.unlp.edu.ar (C.E. Rodríguez Torres). $1.5 \,\mu_{\rm B}$. This result indicates that the presence of impurity clustering is not necessary to obtain ferromagnetic order. A large magnetic moment was also obtained from *ab initio* calculations, but only if an oxygen vacancy in the nearest-neighbor shell of Cu is present [4].

To clarify the role of impurities in DMS on the presence of magnetism it is crucial to determine the local environment of magnetic and non magnetic impurities. In this work we present an extended X-ray absorption Fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) characterization of the local environment of transition metal (TM)-doped anatase TiO₂ thin films (TM = Co, Ni, Cu, and Zn).

2. Experimental

Thin films of 10 at% TM (Co, Ni, or Cu) and 5 at% Zndoped TiO₂ were deposited on LaAlO₃ (001) substrate by pulsed laser deposition (PLD) using a Nd:YAG laser operating at 266 nm. The substrate temperature, laser energy density, oxygen pressure, and pulse repetition rate were 800 °C, 2 J/cm², 20 Pa, and 10 Hz, respectively.

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X-ray absorption spectroscopy (XAS) measurements were taken at RT in fluorescence mode at the TM K-edge, using a Si (111) monochromator at the XAS beamline of LNLS (Campinas, Brasil).



Fig. 1. TM (TM = Co, Ni and Cu) K-edge XANES spectra of $TM_{0.1}Ti_{0.9}O_{2-\delta}$ and $Zn_{0.05}Ti_{0.95}O_{2-\delta}$ thin films on LaAlO₃ (001). The results obtained for TM monoxide reference samples are also shown for comparison.

3. Results and discussions

The structural and magnetic characterization of all these samples were already published elsewhere [4,5]. All films are RT ferromagnetic, transparent to visible light and strongly textured. XRD studies (not presented here) showed only the (001) reflection of the anatase structure for pure and TM-doped TiO₂ films.

Fig. 1 shows XANES spectra of the doped films. They are compared with those of the TM oxide references that present more similarities with the former ones. The agreement with these references (all monoxides) is excellent in the case of Cu, rather good in the Ni and Co ones, and poor in the case of Zn. These results indicate that the TMs in the films are in the 2+ formal oxidation state. These spectra are also very different from those of the metallic elements, allowing us to rule out the presence of TM precipitates.

In Fig. 2, the EXAFS results are summarized. The oscillations observed in the films and their corresponding Fourier transforms (FT) are compared with those of the same oxide references used in Fig. 1. In the case of the Co-doped film, major similarities between the films oscillations and any of the measured references (CoO, Co_2O_3 , and metallic Co) ones were not found. It may exist some correspondence with CoO. In the corresponding FT some coincidences with Co_2O_3 , not shown here, and with the CoO spectra were found (especially in peak positions of the first two layers). Also, the Co-environment, reflected in



Fig. 2. EXAFS oscillations and their corresponding Fourier transforms (inset) of: (a) Co-doped, (b) Ni-doped, (c) Cu-doped, and (d) Zn-doped TiO₂ thin films. In all cases the results for the respective TM monoxide are also shown for comparison. The FTs were performed in the range k = 1.5-12Å⁻¹ with k^2 weighting in the oscillation.

both oscillation and FT, is very similar to that of $CoTiO_3$, in agreement with the results reported in Ref. [6].

The oscillations and the corresponding FT of Ni and Cudoped films have similarities with those of NiO and CuO, respectively. In the case of Cu-doped one, the agreement is better. In the FT of the Ni-doped film the attenuation experienced by peaks corresponding to the second and next neighbour layers is evident. No similarities between the Zndoped film and ZnO EXAFS oscillations were found. However, in the FT there are some coincidences, especially in the first coordination layer and in the position of the second one.

Then, from the comparison of XANES and EXAFS spectra of the doped films with those of the references, there are some coincidences with the corresponding TM monoxides. The agreement is excellent in the case of Cu, rather good for Ni and poor in the cases of Co and Zn (worst for the Zn one). However, in all cases there is a high degree of similarity between the FT of the doped films and those corresponding to their TM monoxides, especially in the first coordination layer.



Fig. 3. Fourier transforms of doped films and the corresponding to Ti in TiO_2 anatase.

In Fig. 3, it can be seen that there is also a strong similarity between the FT of Ti in TiO₂ anatase and those of TM in the films, in the fact that they present a second coordination peak smaller than the first one that corresponds to oxygen coordination. While CoO and NiO present the NaCl structure, CuO has the tenorite and ZnO the wurzite ones. All these oxides have oxygen nearest neighbours (NN) at similar distances to those of Ti-O in TiO₂ anatase (see Table 1). While the first two oxides have octahedral coordination (regular six-fold coordination for the cation) as Ti in TiO₂, the other two have their cations four-fold coordinated. In the case of CuO the 4 ONN are in the plane that contains the central Cu, as it is the case of the 4 ONN around Ti in TiO₂ anatase. In ZnO, the cation has a tetrahedral coordination with its ONN. Then, it is expected that the first FT peak of a TM atom substituting Ti in TiO₂ anatase be similar to the corresponding peak of the TM oxide. In the second coordination sphere of CoO and NiO, the TM has 12 TM NN at 2.95Å (Co) and 3.02 Å (Ni). In CuO, Cu has 4 Cu NN at 2.90 Å and 4 at 3.08 Å. In ZnO, Zn has 12 Zn NN at a mean distance of 3.23 Å. These distances (not the coordination numbers) are comparable with the Ti-Ti ones (4 Ti NN at 3.04 Å) in anatase. Then, it is presumed that the second FT peak of TM in anatase could be similar to that of TM in its oxide in the case of Cu and smaller in intensity but similar in position in the cases of Co, Ni and Zn. In our films the FT second coordination sphere peak coincides in position with the TM oxide one but with small intensity, suggesting that considerable amount of TM is substituting Ti in TiO₂ anatase, although the presence of TM oxide clusters can not be discarded. Since the TM oxides (at least in bulk) are paramagnetic at RT, from these results it is possible to ascribe the ferromagnetism found in these samples to the presence of TM substituting Ti in TiO₂ anatase, probably with the presence of one or two NN oxygen vacancies, in agreement with previous ab initio predictions [7].

4. Conclusions

In this work, we present an electronic and structural characterization by XAS of TM-doped anatase

Table I	
1st and 2nd shells of neighboring atoms around the cation in the oxides quoted	N is the number of A atoms located at a distance R from the cation

	CoO		NiO		CuO		ZnO		TiO ₂ anatase	
	N/A	<i>R</i> (Å)	N/A	<i>R</i> (Å)	N/A	<i>R</i> (Å)	N/A	<i>R</i> (Å)	N/A	<i>R</i> (Å)
1st layer	6 O	2.08	6 O	2.13	4 O	1.95	3 O 1 O	1.97 1.99	4 O 2 O	1.94 1.96
2nd layer	12 Co	2.95	12 Ni	3.02	2 O 4 Cu 4 Cu	2.78 2.90 3.08	6 Zn 1 O 6 Zn	3.21 3.22 3.25	4 Ti	3.04

 TiO_2 thin films (TM = Co, Ni, Cu, and Zn), ferromagnetic at RT, deposited by PLD. Metallic clusters were neither found in XRD patterns nor in XAS spectra. XANES and EXAFS spectra (performed at the K-edge of each impurity) show that the oxidation state of the impurities is 2+ and the oxygen NN local coordination is similar to that in their respective TM monoxides but, except in the Cu case, the similarity with these oxides only exists in the short range scale. The Fourier transform spectra of the doped films are similar to that of TiO₂ anatase suggesting that there is a considerable amount of TM substituting Ti in TiO₂ anatase, although the presence of TM-O clusters can not be discarded. Since the TM oxides are paramagnetic at RT, the magnetic signals present in the films could be assigned to the MT replacing cations in TiO₂ anatase.

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