Tin-doped $MgTiO_3$: A New Material for Studying the Solid-Gas Interface Making Use of the ^{119}Sn Mössbauer Spectroscopic Probe

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Dedicated to Professor Gérard Demazeau on the occasion of his 65th birthday

A co-precipitated hydroxide precursor containing equimolar quantities of Mg^{2+} and Ti^{4+}, doped by impregnation with *ca.* 0.1 at-% Sn^{4+}, after annealing in flowing H_2 at 600 °C, yields $MgTiO_3$ microcrystals containing Sn^{2+} ions. As attested by *in situ* ^{119}Sn Mössbauer spectroscopic measurements (at 295 K, isomer shift $\delta = 2.80 \pm 0.01$ mm s^{-1} and quadrupole splitting $\Delta = 1.80 \pm 0.02$ mm s^{-1}) the Sn^{2+} ions possess a low coordination number (CN < 6) and exhibit anomalously high resistance to be transformed to metallic β-Sn. Upon contact with air, at r. t., fast oxidation of Sn^{2+} to Sn^{4+} ($\delta = 0.03 \pm 0.01$ mm s^{-1} and $\Delta \leq 0.3$ mm s^{-1}) occurs. Quite a similar behavior was previously observed for the tin dopant located on the surface of Cr_2O_3, α-Al_2O_3 or MgO crystallites. Independent evidence for the presence of tin on surface sites of the $MgTiO_3$ substrate also is provided by XPS measurements. Whereas the Sn^{2+} Mössbauer spectrometric parameters are virtually unaffected upon further annealing in H_2 at higher temperature (900 °C), this treatment prevents the tin from reacting with ambient O_2. Such a passivation effect is imputed to itinerant t_{2g} electrons which inactivate absorbed oxygen. The high-temperature annealing is also responsible for the appearance of a minor single-line spectral component with $\delta = 1.6 \pm 0.1$ mm s^{-1}. This isomer shift value cannot be attributed to any known compound of tin that could be formed under the experimental conditions used. The puzzling spectral component is accounted for by the presence of residual Sn^{4+} ions immobilizing itinerant t_{2g} electrons on one of the neighboring Ti^{4+} cations in the bulk of the $MgTiO_3$ crystallites.

Key words: ^{119}Sn Mössbauer Probe, Surface Sites, $MgTiO_3$

Introduction

Up to now, Sn^{2+} dopant cations were successfully located as isolated impurity centers on the surface of Cr_2O_3 and some other oxides having the corundum structure [1 – 3] and, very recently, on surface sites of cubic MgO [4]. In the case of such oxide substrates, ^{119}Sn Mössbauer spectroscopy offered the unique possibility to study various processes occurring at the solid-gas interface [5]. However, information about the surface could be substantially extended if $^{119}Sn^{2+}$probe cations were stabilized on surface sites of a compound having the ilmenite structure. In fact, contrary to simple oxides having only cations of the same kind, in MTiO$_3$ ilmenite-type compounds, whose structure is closely related to the corundum type, two heterovalent cations, M^{2+} and Ti^{4+}, form individual (111) cation layers and then offer two possibilities for the Sn dopant to be accommodated. Similarly, the (111) facets of crystallites are expected to possess surface-adjacent cation layers constituted of either M^{2+} or Ti^{4+} ions. Therefore, location of Sn^{2+} on chemically non-equivalent facets of the same crystallite would allow, for instance, to examine the reactivity of the dopant depending on the composition of the facet concerned.

Among the MTiO$_3$ ilmenites, the only one tested as a substrate for the ^{119}Sn probe was $MnTiO_3$ [6]. The choice of this titanate was motivated by the stability of Mn^{2+}, contrary to other $3d$ cations (*i. e.* Fe^{2+}, Co^{2+} or Ni^{2+}) upon annealing in H_2 (always utilized for stabilization of Sn^{2+}on surface sites of previously investigated oxides [1 – 4]). Another advantage of $MnTiO_3$ is related to the presence of magnetically active $3d^5$ Mn^{2+} cations (capable of inducing the hyperfine field at the nucleus of neighboring diamagnetic

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probe cations) that *a priori* could simplify the identification of the dopant sites. However, ^{119}Sn spectra showed that annealing in H_2 at 800 °C of a $MnTiO_3$ sample, doped with 0.5 at-% Sn^{4+}, instead of producing Sn^{2+} ions led to β-Sn cluster precipitation [7]. Under these conditions, Sn^{2+} ions thus appear to be unstable on either of the $MnTiO_3$ facets (including those formed by Mn^{2+}). Precipitation of β-Sn upon annealing in H_2, pointing to a weak stabilization effect produced by Mn^{2+} cations, was also observed in a MnO sample doped with 0.4 at-% Sn^{4+} [8]. On the contrary, on the surface sites of MgO crystallites Sn^{2+} ions preserve, as mentioned above, their oxidation state upon annealing in H_2 at least up to 1000 °C [4]. The capability of Mg^{2+} to stabilize divalent tin revealed in MgO impelled us to investigate ^{119}Sn Mössbauer spectra of the relevant titanate $MgTiO_3$.

Experimental Section

To achieve better homogeneity of the dopant distribution over the sample, the procedure of synthesis involved a co-precipitation stage. The use of a 2 M NaOH solution as the precipitating agent ensures the quantitative precipitation of both Ti^{4+} and Mg^{2+} cations [9]. On the contrary, when the precipitant is ammonia many Mg^{2+} cations remain in solution, and the precipitate composition no longer shows the stoichiometry required for $MgTiO_3$. However, the NaOH solution cannot be used for co-precipitation of Ti^{4+}, Mg^{2+} and Sn^{4+}, because of the formation of soluble sodium stannate. For this reason, the first stage in the synthesis of ^{119}Sn surface-doped $MgTiO_3$ consisted of the preparation of a co-precipitated hydroxide precursor, containing equimolar quantities of Ti^{4+} and Mg^{2+} ions, using a 2 M NaOH solution. The precursor was washed with water and dried in air at 100 °C. Prior to dropwise addition of an acidified solution of stannic chloride (enriched to 92 % in the ^{119}Sn isotope) the product was impregnated with ammonia. Upon contacting the precursor, fast neutralization of the impregnating solution occurred with formation of $SnO_2 \cdot xH_2O$. The tin-doped precursor was then calcinated under hydrogen at 900 °C for 3 h. XRD analysis of the resulting material revealed the presence of a single crystalline phase, rhombohedral $MgTiO_3$ [10]. ^{119}Sn spectra were recorded using a conventional Mössbauer spectrometer operating in constant acceleration mode with a $Ca^{119m}SnO_3$ source (isomer shift values refer to a $CaSnO_3$ absorber at 295 K). *In situ* Mössbauer spectroscopic measurements under H_2 were performed using a quartz reactor equipped with a lateral thin-window sample cell. Spectra were analyzed using standard computer software. XPS measurements were made using a Cratos Axis Ultra spectrometer (AlK_α exciting radiation, $h\nu$ = 1486.6 eV). Atomic concentrations were calculated from the integrated intensities of the $Sn3d_{5/2}$ (E_b = 486.6 eV), $Mg2p$ (E_b = 49.5 eV) and $Ti2p_{3/2}$ (E_b = 458.8 eV) lines. Prior to XPS measurements the sample was not subjected to any pretreatment. Spectra were analyzed using the CASA XPS program package.

Results and Discussion

A ^{119}Sn Mössbauer spectrum of a typical sample, recorded *in situ* after annealing in H_2 at 600 °C for 2 h (Fig. 1a) consists of a predominant doublet component (isomer shift $\delta = 2.80 \pm 0.01$ mm s^{-1}, quadrupole splitting $\Delta = 1.80 \pm 0.02$ mm s^{-1}, full width at half maximum $\Gamma = 1.04 \pm 0.02$ mm s^{-1}, spectral contribution $A = 95 \pm 3$ %) and a minor single-line component

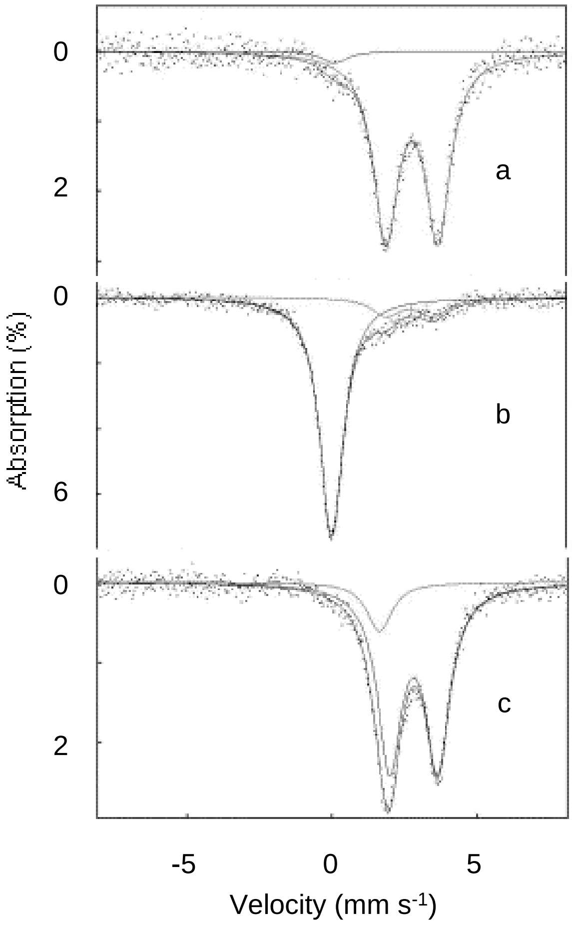

Fig. 1. Room-temperature ^{119}Sn Mössbauer spectra of $MgTiO_3$ doped with 0.1 at-% Sn^{4+}: (a) spectrum recorded *in situ* after annealing in H_2 at 600 °C for 2 h; (b) measurements after subsequent admission of air in the reactor cooled to r. t.; (c) spectrum recorded *in situ* after further annealing in hydrogen at 900 °C for 3 h.

($\delta = 0.20 \pm 0.15$ mm s^{-1}, $\Gamma = 1.20 \pm 0.04$ mm s^{-1} and A = 5 %). The spectrum thus clearly shows the major part of the tin to be present in the divalent state. No formation of β-Sn (single line with δ = 2.56 mm s^{-1}) was observed despite a rather elevated temperature of annealing in H_2. The minor spectral component characterized by δ = 0.20 mm s^{-1} reveals the presence of residual Sn^{4+} ions. The value of δ = 2.80 mm s^{-1}, characterizing the major component, implies a highly pronounced $5p$ character of the Sn^{2+} nonbonding (lone pair) electrons. According to [11], the relevant electronic configuration would be $5s^{1.2}5p^{0.8}$. Besides, the value of $\Delta = 1.80 \pm 0.02$ mm s^{-1} points to p_{zz} character of the lone pair which thus appears to be stereochemically active. This obviously rules out any hypothetical location of Sn^{2+} on metal sites in the bulk of $MgTiO_3$ (octahedral sites with the coordination number CN = 6). On the contrary, the stereochemical activity of the lone pair, implying a lower CN, is exactly what is expected for Sn^{2+} located immediately on the surface of crystallites. This conclusion agrees well with the fast oxidation of Sn^{2+} at r. t. upon admission of ambient air into the reactor, as demonstrated by the increase up to 85 % in the contribution of the center single-line component (Fig. 1b). The fast oxidation of Sn^{2+} thus unambiguously suggests easy accessibility of the dopant for oxygen molecules, as expected for surface-located species. Finally, the occurrence of the tin-on-surface sites is confirmed by XPS measurements: after annealing in H_2, the ratio of atomic concentrations $\frac{[Sn]}{[Mg]+[Ti]}$ is found to be 0.044. This value, relevant to a $2-3$ nm-thick surface-adjacent layer, is more than 40 times greater than the overall ratio calculated on the basis of the quantities of reagents involved in the synthesis $\left(\frac{[Sn]}{[Mg]+[Ti]} = 0.001\right)$.

Taking into account the different behavior of tin in $MnTiO_3$ and $MgTiO_3$ samples upon annealing in H_2, the stability of Sn^{2+} in the case of $MgTiO_3$ indicates the location of the dopant on the sites whose neighborhood essentially consists of Mg^{2+} cations. This hypothesis implies that Sn^{2+} ions avoid Ti^{4+} facets where the formation of β-Sn would have occurred, as in the case of $MnTiO_3$. However, at first sight such a behavior might appear rather surprising. In fact, the striking stability of Sn^{2+} on the surface of corundum type sesquioxides in H_2 atmosphere was accounted for on the basis of the following assumption [1]. The presence of Sn^{2+} on sites with low coordination number allows the neighboring cations to retain their intrinsic coordination by O^{2-} anions, a coordination which is higher than that they would have possessed if the Sn^{4+} ions were reduced immediately to β-Sn. Therefore, Ti^{4+} ions, which strongly prefer an octahedral surrounding in oxides, would be expected to preserve this environment (and, consequently, to retain the neighboring tin in the divalent state) to a grater extent than Mg^{2+}cations which are known to be easily accommodated in both octahedral and tetrahedral oxygen surroundings. However, comparison of the spectra of ^{119}Sn in $MnTiO_3$ and $MgTiO_3$ clearly shows that the cationic surrounding of Sn^{2+} in the latter titanate cannot consist of Ti^{4+}. This contradiction can be resolved assuming that in hydrogen atmosphere at 600 °C certain surface-located Ti^{4+} ions are reduced to Ti^{3+}. If the reduction does not entail elimination of bulk oxygen (as H_2O molecules), only a partial hydroxylation of the oxygen anion layer covering the topmost Ti^{4+} cations will occur, without lowering the coordination number of the titanium. Formation of H^+ produces on the relevant facets an excessive positive charge prohibiting the facets from receiving Sn^{2+} ions. Contrary to Ti^{4+}, assuming a reduction of Mg^{2+} upon annealing in H_2 is not realistic, and therefore Sn^{2+} ions, filling the sites of low-coordination in the topmost Mg^{2+} layers of $MgTiO_3$, will complete the interface in the same way as it was observed in the case of tin-doped MgO.

Further annealing of the sample in H_2 at higher temperature (900 °C) does not change the spectral parameters of the divalent tin (Fig. 1c). This means that the dopant cations remain on their initial surface sites. Nevertheless, this treatment is found to prevent Sn^{2+} ions from being oxidized upon contact with ambient atmosphere. Such a behavior can be imputed to the formation at 900 °C of further amounts of Ti^{3+}, the electrons furnished to the titanate by hydrogen being accommodated in the empty t_{2g} orbitals of the titanium cations in the bulk of the crystallites. Subsequent extraction of these electrons by O_2 molecules adsorbed upon exposing the sample to air precludes the oxidation of neighboring Sn^{2+}. Similar electron extraction processes are generally assumed to occur in n-type semiconductor oxide gas sensors [12]. Hence, the passivation effect revealed by the ^{119}Sn probe shows that the failure in observation of a fast oxidation of Sn^{2+} upon contact with air is not a good probative evidence for dopant locations in the bulk sites.

Another change produced by annealing at 900 °C is the appearance in the ^{119}Sn spectrum, besides the Sn^{2+} quadrupole doublet, of a single-line minor component with $\delta \sim 1.6$ mm s^{-1}, $\Gamma = 1.1 \pm 0.1$ mm s^{-1} and $A = 12 \pm 5$ % (Fig. 1c). The observed value of δ, which is intermediate between those for Sn^{4+} ($\delta \sim 0$ mm s^{-1}) and Sn^{2+} ($\delta \sim 3$ mm s^{-1}) in oxide phases, cannot be attributed to micro-precipitates of any compound of tin capable to be formed under our experimental conditions in $MgTiO_3$. Therefore it may be suggested that an intermediate Sn^{x+} state arises from the Sn^{4+} ions which have allowed one of the neighboring Ti^{4+} to immobilize t_{2g} electrons injected in $MgTiO_3$. In other words, the formation of a localized "Ti^{3+}" state in the vicinity of a Sn^{4+} ion increases the $|\Psi(0)|^2$ value of the electron density at this nucleus which results in the queer isomer shift. The spectral contribution of the component with $\delta \sim 1.6$ mm s^{-1} is found to be little affected by temperature. The increase in the resonant absorption observed for Sn^{x+} upon cooling the sample to 100 K corresponds to a Mössbauer lattice temperature $\Theta_M \sim 300$ K, a value which is typical of oxostannates. This result is consistent with the location of the Sn^{x+} species essentially in the bulk of $MgTiO_3$ crystallites.

In this context we should mention the recent observation of an intermediate "Sn^{3+}" state in ^{119}Sn Mössbauer spectra of $Pb_{1-x}Sn_xS$ [13]. Formation of Sn^{3+} in this sulfide phase was attributed to ionization of Sn^{2+} donor centers upon heating the sample. No existence of similar tin species in oxide matrices was reported in the literature. Hence, further research is needed to elucidate the origin of signals with the intermediate isomer shift in tin-doped $MgTiO_3$.

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[1] P. B. Fabritchnyi, A. N. Protsky, V. P. Gorkov, T. M. Duc, G. Demazeau, P. Hagenmuller, *Sov. Phys. JETP* **1981**, *54*, 608 – 611.

[2] P. B. Fabritchnyi, *Zh. Vsesoyuznogo Khimicheskogo Obshestva im. D. I. Mendeleeva* **1985**, *30*, 143 – 152.

[3] M. I. Afanasov, P. B. Fabritchnyi, *Rossiysky Khim. Zh.* **1996**, *40*, 54 – 60.

[4] M. I. Afanasov, P. B. Fabritchnyi, M. V. Korolenko, T. M. Ivanova, *Russ. J. Inorg. Chem.* **2008**, *53*, in press.

[5] P. B. Fabritchnyi, M. I. Afanasov, M. Danot, *Rossiysky Khim. Zh.* **2007**, *51*, 44 – 51.

[6] P. B. Fabritchnyi, M. V. Korolenko, M. I. Afanasov, M. Danot, E. Janod, *Solid State Commun.* **2003**, *125*, 341 – 346.

[7] M. V. Korolenko, M. Danot, P. B. Fabritchnyi, I. S. Bezverkhy, M. I. Afanasov, *Russ. J. Inorg. Chem.* **2005**, *50*, 1423 – 1433.

[8] P. B. Fabritchnyi, E. V. Lamykin, A. M. Babeshkin, A. N. Nesmeyanov, *Sov. Phys. Solid State* **1972**, *13*, 2874 – 2876.

[9] H. Cheng, B. Hu, J. Ma, *J. Mater. Sci. Lett.* **1997**, *16*, 1570 – 1572.

[10] B. A. Wechsler, R. B. von Dreele, *Acta Crystallogr.* **1989**, *B45*, 542 – 549.

[11] P. A. Flinn in *Mössbauer Isomer Shifts* (Eds.: G. K. Shenoy, F. E.Wagner), North-Holland, Amsterdam **1978**, chapter 9.2, pp. 593 – 616.

[12] N. Barsan, U. Weimar, *J. Electroceramics* **2001**, *7*, 143 – 167.

[13] R. A. Castro, S. A. Nemov, P. P. Seregin, *Fizika i Tekhnika Poluprovodnikov* **2006**, *40*, 927 – 929.