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 $\beta$-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$_2$O$_3$, $\alpha$-Al$_2$O$_3$ 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$_2$O$_3$ 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 M$^{2+}$ 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 crystal lattice would allow, for instance, to examine the reactivity of the dopant depending on the composition of the facet concerned.

Among the M$^{2+}$ 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 3$d$ 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 3$d^5$ Mn$^{2+}$ cations (capable of inducing the hyperfine field at the nucleus of neighboring diamagnetic...
probe cations) that a priori could simplify the identification of the dopant sites. However, $^{119}\text{Sn}$ spectra showed that annealing in $\text{H}_2$ at 800 °C of a $\text{MnTiO}_3$ sample, doped with 0.5 at-% $\text{Sn}^{4+}$, instead of producing $\text{Sn}^{2+}$ ions led to $\beta$-Sn cluster precipitation [7]. Under these conditions, $\text{Sn}^{2+}$ ions thus appear to be unstable on either of the $\text{MnTiO}_3$ facets (including those formed by $\text{Mn}^{2+}$). Precipitation of $\beta$-Sn upon annealing in $\text{H}_2$, pointing to a weak stabilization effect produced by $\text{Mn}^{2+}$ cations, was also observed in a $\text{MnO}$ sample doped with 0.4 at-% $\text{Sn}^{4+}$ [8]. On the contrary, on the surface sites of $\text{MgO}$ crystallites $\text{Sn}^{2+}$ ions preserve, as mentioned above, their oxidation state upon annealing in $\text{H}_2$ at least up to 1000 °C [4]. The capability of $\text{Mg}^{2+}$ to stabilize divalent tin revealed in $\text{MgO}$ impelled us to investigate $^{119}\text{Sn}$ Mössbauer spectra of the relevant titanate $\text{MgTiO}_3$.

**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 $\text{NaOH}$ solution as the precipitating agent ensures the quantitative precipitation of both $\text{Ti}^{4+}$ and $\text{Mg}^{2+}$ cations [9]. On the contrary, when the precipitant is ammonia many $\text{Mg}^{2+}$ cations remain in solution, and the precipitate composition no longer shows the stoichiometry required for $\text{MgTiO}_3$. However, the $\text{NaOH}$ solution cannot be used for co-precipitation of $\text{Ti}^{4+}$, $\text{Mg}^{2+}$ and $\text{Sn}^{4+}$, because of the formation of soluble sodium stannate. For this reason, the first stage in the synthesis of $^{119}\text{Sn}$ surface-doped $\text{MgTiO}_3$ consisted of the preparation of a co-precipitated hydroxide precursor, containing equimolar quantities of $\text{Ti}^{4+}$ and $\text{Mg}^{2+}$ ions, using a 2 M $\text{NaOH}$ 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 $^{119}\text{Sn}$ isotope) the product was impregnated with ammonia. Upon contacting the precursor, fast neutralization of the impregnating solution occurred with formation of $\text{SnO}_2$·$\text{xH}_2\text{O}$. 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 $\text{MgTiO}_3$ [10]. $^{119}\text{Sn}$ spectra were recorded using a conventional Mössbauer spectrometer operating in constant acceleration mode with a $\text{Ca}^{119m}\text{SnO}_3$ source (isomer shift values refer to a $\text{CaSnO}_3$ absorber at 295 K). In situ Mössbauer spectroscopic measurements under $\text{H}_2$ 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$_\alpha$ exciting radiation, $h\nu$ = 1486.6 eV). Atomic concentrations were calculated from the integrated intensities of the Sn$^3d_{5/2}$ ($E_0 = 486.6$ eV), Mg$^{2p}$ ($E_0 = 49.5$ eV) and Ti$^{2p}_{3/2}$ ($E_0 = 458.8$ 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 $^{119}\text{Sn}$ Mössbauer spectrum of a typical sample, recorded in situ after annealing in $\text{H}_2$ 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 $^{119}\text{Sn}$ Mössbauer spectra of $\text{MgTiO}_3$ doped with 0.1 at-% Sn$^{4+}$: (a) spectrum recorded in situ after annealing in $\text{H}_2$ 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.](image-url)
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 $\beta$-$Sn$. 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 greater 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 $^{119}\text{Sn}$ spectrum, besides the $\text{Sn}^{2+}$ 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 $\delta$, which is intermediate between those for $\text{Sn}^{4+}$ ($\delta \sim 0$ mm s$^{-1}$) and $\text{Sn}^{2+}$ ($\delta \sim 3$ 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$^{3.5+}$” state in $^{119}\text{Sn}$ Mössbauer spectra of Pb$_{1-x}$Sn$_x$S [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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