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

Pavel B. Fabritchnyi, Mikhail I. Afanasov, and Mikhail V. Korolenko

Department of Chemistry, Moscow State University, Vorob'evy gory, 119992 Moscow V-234, Russia

Reprint requests to Prof. Pavel B. Fabritchnyi. Fax: (7)495 9393187. E-mail: pf@radio.chem.msu.ru

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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, $MgTiO_3$