



Tin-doped LuCrO_3 : A new type of material allowing the location of a ^{119}Sn Mössbauer spectroscopic probe on the gas–solid interface

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ABSTRACT

In situ ^{119}Sn Mössbauer measurements show that annealing in hydrogen atmosphere of co-precipitated chromium and lutetium hydroxides, doped with 0.2 at.% Sn^{4+} , results in the formation of Sn^{2+} cations on the surface sites of LuCrO_3 microcrystals. Such a distribution of dopant cations is consistent with the anomalously high concentration of tin revealed by X-ray photoelectron spectroscopy (XPS). The ^{119}Sn spectrum recorded above the Néel point of LuCrO_3 attests to the distribution of Sn^{2+} ions over two kinds of site. For both of them, the isomer shift and quadrupole splitting values agree with those previously reported for $^{119}\text{Sn}^{2+}$ on surface sites of several oxides other than the perovskite-type one. The instantaneous oxidation of tin upon contact with ambient air did not allow us to characterize the cationic surrounding of Sn^{2+} by measurements involving sample transfer into a liquid-helium cryostat. Relevant information is obtained for the $\text{Sn}^{2+ \rightarrow 4+}$ oxidized species located on the sites with unchanged cationic surroundings. The spectrum recorded at 4.2 K shows that nearly two-thirds of the $\text{Sn}^{2+ \rightarrow 4+}$ species are spin-polarized to different extents. Comparison with Mössbauer parameters reported for $^{119}\text{Sn}^{4+}$ ions sitting in the regular Cr-substitution site in the bulk of LuCrO_3 allows us to ascribe the diffuse magnetic contribution to a distribution of $\text{Sn}^{2+ \rightarrow 4+}$ species over Cr-substitution sites with lower (than in the bulk) number of neighboring Cr^{3+} ions. The presence of an additional non-magnetic component in the spectrum of $\text{Sn}^{2+ \rightarrow 4+}$ ions points to the location of the remaining Sn^{4+} ions and, very likely, the predecessor Sn^{2+} ones, on Lu-substitution sites with magnetically compensated ($2\text{Cr} \uparrow + 2\text{Cr} \downarrow$) surroundings.

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1. Introduction

At present, Sn^{2+} dopant cations have been successfully stabilized, as isolated impurity centres, on surface sites of several metal oxides having the corundum structure [1–3], the ilmenite structure (MgTiO_3) [4] or the rock salt structure (MgO) [5]. In such cases ^{119}Sn Mössbauer spectroscopy offers the unique possibility to study processes occurring at the gas–solid interface [6]. However, no material with a perovskite-related structure has so far been investigated as a substrate for a surface-located ^{119}Sn spectroscopic probe. Of the perovskites to be tested, RCrO_3 antiferromagnetic rare-earth (R) orthochromites seem to be particularly suitable. In fact, most of them are stable upon annealing in hydrogen atmosphere (needed for stabilization of Sn^{2+} on surface sites of previously studied oxides [1–5]). Besides, Cr^{3+} ($3d^3$) cations strongly prefer an octahedral oxygen

surrounding; to retain their coordination number upon annealing in hydrogen, surface-located Cr^{3+} ions are expected to prohibit the neighbouring Sn^{2+} species from reducing to metallic $\beta\text{-Sn}$ [1, 2]. Another advantage of the orthochromites is due to the spin polarization of tin by neighbouring Cr^{3+} cations, revealed by the appearance of hyperfine splitting patterns in ^{119}Sn Mössbauer spectra recorded at low temperatures ($T < T_N$). The occurrence of such a spectrum thus unambiguously demonstrates the insertion of the dopant into the host structure, even though the doping level is as low as 0.1 at.%. Moreover, the value of the magnetic hyperfine field H transferred at ^{119}Sn becomes a parameter specifically sensitive to the cationic surrounding of the diamagnetic dopant. In order to begin studying the behaviour of tin in RCrO_3 perovskites we have chosen LuCrO_3 . In this compound, with a Néel temperature $T_N = 112$ K [7], Sn^{4+} ions are known to possess the largest saturation value of $H = 85$ kOe [8] and thus provide better resolution of ^{119}Sn Zeeman splitting patterns as compared to those reported for other rare-earth orthochromites. It is noteworthy that such perovskite-type oxides are utilized in practice for gas sensing and are known to display catalytic activity in oxidation reactions (e.g. combustion of CO or C_3H_4) [9]. This should make possible the elucidation of the eventual impact of the tin-dopant on the relevant surface properties.

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2. Experimental

To achieve better homogeneity of the dopant distribution in the sample, the procedure of synthesis involved a co-precipitation stage. Aqueous ammonia solution was used to obtain a hydroxide precursor co-precipitated from a hot acidified solution containing Lu^{3+} , Cr^{3+} and Sn^{4+} (enriched to 92% in the ^{119}Sn isotope) ions in molar ratio 1:1:0.004. The precursor was filtered out, washed with distilled water and dried at 150 °C.

To obtain a LuCrO_3 sample containing ^{119}Sn probe cations in the bulk of crystallites (“the bulk-doped LuCrO_3 ”), the precursor was calcined in air at 700 °C for 2 h, pelletized and annealed at 950 °C for 36 h. To obtain a LuCrO_3 sample containing ^{119}Sn probe cations located immediately on the surface of crystallites (“the surface-doped LuCrO_3 ”), the hydroxide precursor was calcined under hydrogen flow, first at 300 °C for 1 h, and then at 900 °C for 21 h. In all cases, XRD analysis of the resulting material revealed the presence of a single crystalline phase, orthorhombically distorted LuCrO_3 perovskite [10–12].

^{119}Sn spectra were recorded using a conventional Mössbauer spectrometer operating in constant acceleration mode with a $\text{Ca}^{119\text{m}}\text{SnO}_3$ source (all the isomer shift δ values refer to a BaSnO_3 absorber at 295 K). Spectra at 4.2 K and 295 K were recorded using a regular variable-temperature cryostat. *In situ* Mössbauer measurements under H_2 were performed at 295 K only, using a quartz reactor equipped with a lateral thin-window sample cell [13]. Spectra were analysed using standard computer software.

XPS measurements were made using an ESCALAB VG 220i-XL spectrometer (non-monochromatic MgK_α exciting radiation, $h\nu = 1253.6$ eV) with powder samples pressed on indium plate supports. Atomic concentrations were calculated from the integrated intensities of $\text{Sn}3d5$ ($E_b = 486.6$ eV), $\text{Cr}2p3$ ($E_b = 576.3$ eV) and $\text{Lu}4d5$ ($E_b = 196.4$ eV). High-resolution spectra were fitted and quantified using the AVANTAGE software provided by ThermoFischer Scientific, each spectrum being referenced to the $\text{Sn}3d5$ maximum at 486.6 eV.

3. Results and discussion

3.1. ^{119}Sn Mössbauer spectra of the bulk-doped LuCrO_3

In the paramagnetic region at 295 K, the Mössbauer spectrum (Fig. 1a) could at first glance be reasonably fitted assuming the presence of a unique doublet. However, more careful analysis reveals the occurrence of very weak complementary absorption at positive velocities. The values of the isomer shift $\delta = 0.09$ mm/s and quadrupole splitting $\Delta = 0.46$ mm/s relative to the main spectral component (Table 1) thus show that the great majority of dopant atoms preserve their initial tetravalent state and occupy a slightly distorted site, as expected for a Sn^{4+} ion on the O_h substitution position in the LuCrO_3 lattice. As to the secondary doublet contribution ($\delta = 2.68$ mm/s and $\Delta = 0.22$ mm/s), it is assignable to trace amounts of divalent tin, exhibiting more pronounced temperature dependence of the recoil-free f fraction as compared to that for tetravalent tin.

In the antiferromagnetic region at 4.2 K ($T \ll T_N$), the Mössbauer spectrum (Fig. 1b) reveals the spin polarization of most of the dopant ions and thus ascertains their insertion in LuCrO_3 . The hyperfine parameters of various subspectra observed at 4.2 K are given in Table 1. The value of the hyperfine field for the main spectral component (59%), $H_{\text{bulk}} = 89$ kOe is in fair agreement with the value of $H = 85$ kOe quoted earlier [8] for a Sn^{4+} -doped LuCrO_3 sample prepared by the conventional ceramic method. According to [8], the sextet associated with H_{bulk} should, therefore, be assigned to a Sn^{4+} ion located on an O_h site of the LuCrO_3 lattice (Fig. 2). The presence of three other

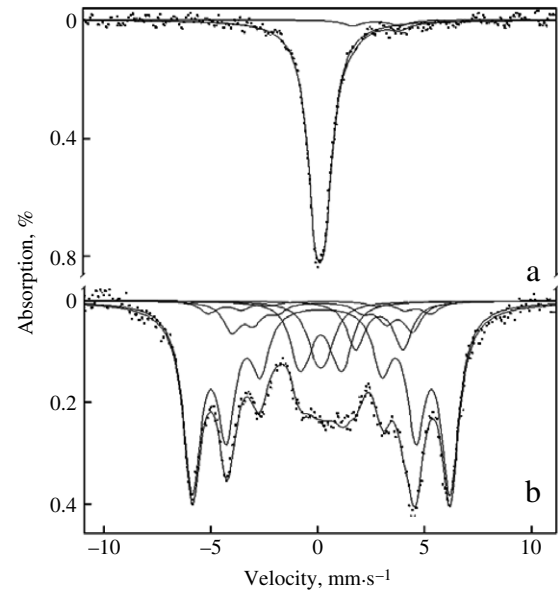


Fig. 1. Mössbauer spectra of $^{119}\text{Sn}^{4+}$ ions (0.04 at.%) in the bulk of LuCrO_3 polycrystals measured at 295 K (a) and 4.2 K (b).

Table 1

Mössbauer spectroscopic parameters of the ^{119}Sn probe located in the bulk and on the surface of LuCrO_3 polycrystals.

T (K)	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	H (kOe)	A (%)
Bulk-doped LuCrO_3					
295	0.09 ± 0.01	0.46 ± 0.02	0.95 ± 0.02	–	96
	2.68 ± 0.05	2.2 ± 0.1	0.95 ± 0.02	–	4
4.2	0.17 ± 0.05	–	0.98 ± 0.05	89 ± 1	59
	0.17 ± 0.05	–	0.9 ± 0.1	75 ± 3	5
	0.17 ± 0.05	–	0.9 ± 0.1	61 ± 3	9
	0.17 ± 0.05	–	0.9 ± 0.1	16 ± 2	12
	0.17 ± 0.05	0.46 ± 0.05	0.9 (fixed)	–	7
	2.84 ± 0.05	2.2 ± 0.1	0.9 (fixed)	–	8
Surface-doped LuCrO_3 (<i>in situ</i> measurements)					
295	2.74 ± 0.02	1.94 ± 0.18	0.85 (fixed)	–	70
	2.65 ± 0.03	2.38 ± 0.15	0.85 (fixed)	–	30
Surface-doped LuCrO_3 (<i>after exposure to air</i>)					
295	0.02 ± 0.01	0.9 ± 0.1	0.85 ± 0.02	–	53
	0.04 ± 0.01	0.4 ± 0.1	0.85 ± 0.05	–	43
	2.8 ± 0.1	2.0 ± 0.1	0.85 (fixed)	–	4
4.2	0.1 ± 0.1	–	1.1 ± 0.1	13	20
	0.1 ± 0.1	–	1.1 ± 0.1	25	7
	0.1 ± 0.1	–	1.1 ± 0.1	40	24
	0.1 ± 0.1	–	1.1 ± 0.1	65	14
	0.1 ± 0.1	0.6 ± 0.1	1.0 ± 0.1	–	29
	2.9 ± 0.1	2.1 ± 0.1	1.0 (fixed)	–	6

Note. The isomer shift at 4.2 K, $\delta_{4.2\text{K}} = \delta_{295\text{K}} + \delta_{\text{SDS}}$ (the second-order Doppler shift).

minor-contribution spectral components with $H < 89$ kOe could be indicative of the formation of $\{\text{Sn}^{4+}$ dopant- V_{Cr} chromium charge-balance vacancy} pairs and their agglomerates within the chromite lattice, as was, for instance, the case in Cr_2O_3 doped with 0.12 at.% Sn^{4+} [14]. No magnetically split ^{119}Sn components with $H < 85$ kOe were mentioned in [8], all studied RCrO_3 samples having been simultaneously doped with both Sn^{4+} (2 at.%) and charge-balance Ca^{2+} (2 at.%) cations. Analysis of the spectrum in Fig. 1b also reveals the presence of a quadrupole doublet ($\delta = 0.17$ mm s^{-1} , $\Delta = 0.46$ mm s^{-1} , $H = 0$) assignable to SnO_2 -like clusters and another doublet ($\delta = 2.84$ mm s^{-1} , $\Delta = 2.2$ mm s^{-1}) whose parameters point, as mentioned above, to reduction of small amount of Sn^{4+} to the divalent state during sample preparation.

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