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Effect of heterovalent substitutions in yttrium chromite on the hyperfine interactions of $^{119}\text{Sn}^{4+}$ studied by Mössbauer spectroscopy

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Abstract : In order to develop the ^{119}Sn Mössbauer spectroscopic probe technique to study magnetically ordered materials, three Ca-substituted yttrium chromites, *i.e.* $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$, $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Ti}_{0.2}\text{O}_3$, doped with 0.3 atom-% Sn^{4+} , were for the first time investigated. ^{119}Sn Mössbauer spectra, recorded at 4.2 K, have allowed, through analysis of the magnetic hyperfine field values, probed by ^{119}Sn nuclei, to gain insight into the local magnetically active surrounding of different Sn^{4+} ions. In all of these compounds, partial segregation of Sn^{4+} ions is revealed. In the case of $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$, neither highly oxidized Cr^{4+} nor Cr^{6+} species, expected to compensate for the Ca^{2+} positive charge deficit, is found in the vicinity of the $^{119}\text{Sn}^{4+}$ probe. In the case of both studied Ti-containing chromites, ^{119}Sn Mössbauer spectra have provided the original indirect evidence for the statistical distribution of Cr^{3+} and Ti^{4+} ions over the octahedral sites and permitted characterization of the occurring associates of Sn^{4+} .

1. Introduction

Mössbauer spectroscopy of ^{119}Sn diamagnetic dopant cations, introduced as resonant probes into a magnetically ordered compound, can provide particularly valuable information about their magnetically active surrounding [1]. This becomes possible due to the spin polarization of the ^{119}Sn electronic shell by neighboring cations giving rise to a Zeeman splitting of ^{119}Sn energy levels. Analysis of the observed hyperfine pattern thus permits to characterize changes in the local surrounding of the probe and relate them to the studied process. As an example, we can mention our results recently reported in [2] for tin-doped perovskites RECrO_3 (RE =rear earth element or Y) exhibiting a G-type AF arrangement [3]. In these compounds, $^{119}\text{Sn}^{4+}$ probe ions were located on the Cr^{3+} site and their spin polarization was created by six Cr^{3+} neighbors with parallel spins. In order to develop the ^{119}Sn Mössbauer spectroscopic probe technique to study such perovskite-type antiferromagnetics, we have attempted to investigate the mechanisms of heterovalent substitution in an isostructural compound $\text{RE}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ containing charge-deficient Ca^{2+} ions within the dodecahedral substructure. According to previous

studies, the Ca^{2+} charge deficit compensation, under oxidative conditions, can involve the stabilization of both Cr^{4+} ($3d^2$) and Cr^{6+} ($3d^0$) ions [4,5], whereas, under reducing conditions, the instability of these high oxidation states of chromium is expected to result in the loss of oxygen along with the concomitant creation of oxygen ion vacancies (V_{O}) [6]. ^{119}Sn doping and Mössbauer spectroscopy should thus allow to discern different charge compensation species in the neighborhood of the resonant probe and, consequently, gain insight into the local composition of the studied compound. Mössbauer spectrum of $^{119}\text{Sn}^{4+}:\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ sample, containing 0.3 atom-% Sn^{4+} substituted for Cr^{3+} [7], have revealed the presence of an additional magnetically split component which was not observed for $^{119}\text{Sn}^{4+}:\text{YCrO}_3$ [8]. The relevant value of the magnetic hyperfine field, probed by ^{119}Sn at 4.2 K, was found to be consistent with the lack of one of the six Cr^{3+} ions in the nearest magnetic surrounding of the concerned $^{119}\text{Sn}^{4+}$ ion. Because of the much higher content of Ca^{2+} substituent ions, as compared to that of Sn^{4+} , this new spectral component could not be explained by the specific charge compensation mechanism involving the formation of a Cr^{3+} vacancy in the vicinity of a $^{119}\text{Sn}^{4+}$ probe. On the contrary, the lack of one of its magnetic neighbors, *a priori*, might reflect the formation of diamagnetic Cr^{6+} ions to electrically compensate the Ca^{2+} -charge deficit. Nevertheless, taking into account other results obtained in [7], it was finally concluded that this spectral component could not be assigned to a

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$\text{Sn}^{4+}-\text{Cr}^{6+}$ pair, but rather, to an associate of two Sn^{4+} dopant ions. Interestingly, analysis of the ^{119}Sn Mössbauer spectra of $\text{Sn}:\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ did not reveal the presence of Cr^{4+} in the Sn^{4+} ion vicinity although the formation of Cr^{4+} in $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$ perovskites has been evidenced by other techniques [4]. In the present work, to obtain more information about the local surrounding of the ^{119}Sn probe, we have investigated three Ca-substituted yttrium chromites with a different Ca/Y ratio or containing different amounts of Ti^{4+} introduced to prevent the formation of chromium in higher than +3 oxidation states.

2. Experimental

2.1. Synthesis method

Polycrystalline $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$ or $\text{Y}_{1-x}\text{Ca}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$ samples (with $x=0.1$ or 0.2), all of them containing 0.3 atom-% $^{119}\text{Sn}^{4+}$ on Cr^{3+} substitution sites in the bulk crystallites, were synthesized using a simplified citric acid method previously applied to prepare tin-free $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$ powder samples [6]. Accordingly, proper amounts of yttrium and calcium carbonates were dissolved in 1 M HNO_3 and the obtained solution was poured into the mixture of required volumes of chromium (III) nitrate solution and tin (IV) chloride solution, enriched up to 92% in the ^{119}Sn Mössbauer isotope. To obtain $\text{Y}_{1-x}\text{Ca}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$, the required volume of acidified titanium (IV) chloride solution was additionally poured into the reaction mixture. The concentration of tin was 0.01 mol L^{-1} and that of either main constituent metal 0.5 mol L^{-1} . Finally, citric acid monohydrate (used at a rate of $[\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}]:[\text{Cr}]=3:1$) was dissolved in the mixture of solutions heated to 80°C . The gel, formed upon evaporation of the resulting solution at 80°C , was heated in air for 3 h at 150°C . The obtained porous solid substance was then heated at a rate of *ca.* $3^\circ\text{C}/\text{min}$ up to 1050°C and kept at this temperature for 12 h. This operating procedure has allowed $^{119}\text{Sn}^{4+}$ probe ions to be located, as it was the case in unsubstituted YCrO_3 [8], on Cr sites in the bulk of both $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$ and $\text{Y}_{1-x}\text{Ca}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$ microcrystals.

2.2. Characterization techniques

XRD measurements were performed with a powder sample ARL X'TRA Thermo Scientific Diffractometer using $\text{Cu } K_\alpha$ radiation (wavelength $\lambda=1.5418 \text{ \AA}$).

Mössbauer spectroscopic measurements were carried out using a conventional spectrometer of the electromechanical type, operating in constant acceleration mode, with a $\text{Ca}^{119m}\text{SnO}_3$ source kept at room temperature. During the measurements the studied sample (absorber) was placed in an Oxford Instrument cryostat cooled down to 4.2 K. All spectra were analyzed by a least-squares fitting program. The isomer shift values quoted below are referred to a BaSnO_3 absorber at 295 K. The experimental value of the full width at half maximum, obtained with an optically thin ($5.6 \text{ mg}/\text{cm}^2$) BaSnO_3 absorber, $\Gamma_{ref}=0.83 \pm 0.04 \text{ mm s}^{-1}$, was assumed to characterize, in all studied chromites, a single absorption peak in the absence of any magnetic interaction.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a K-Alpha X-Ray photoelectron spectrometer (ThermoFisher Scientific Inc.) using monochromatic $\text{Al } K_\alpha$ radiation ($h\nu=1486.6 \text{ eV}$), spot size: $200 \mu\text{m}$, and charge compensation. Overview spectra were taken at a pass energy $E_p=200 \text{ eV}$ and high resolution spectra at $E_p=40 \text{ eV}$. Powder samples, analyzed in the as-prepared state, were pressed onto indium foil. High resolution spectra were fitted using the AVANTAGE software provided by ThermoFisher Scientific Inc.

3. Results and discussion

The X-ray diffraction patterns of all samples investigated in the present work were consistent with a rhombohedrally distorted perovskite structure (space group $Pbnm$) reported in [6] for the $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$ solid solutions. As an example, Fig. 1 shows an XRD pattern of a tin-doped $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ sample.

3.1. $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$

As evidenced by earlier measurements of the magnetic susceptibility [4], the antiferromagnetic ordering of Cr^{3+} moments in $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$, as well as in the unsubstituted YCrO_3 , occurs in the vicinity of $T_N=140 \text{ K}$. This means that the value of the hyperfine field $H(^{119}\text{Sn})$, determined from ^{119}Sn Mössbauer spectra recorded at 4.2 K, will correspond, in both compounds, to saturation values of the Cr-substructure magnetization.

A ^{119}Sn Mössbauer spectrum of the $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ sample is composed of a number of magnetically split components (Fig. 2a). The symmetrical shape of the spectrum is consistent with the value of the isomer shift ($\delta=0.12 \pm 0.05 \text{ mm s}^{-1}$) and the apparent quadrupole shift ε_Q (close to zero) which are the same for all components (Table 1). These hyperfine parameters are in good agreement with the tetravalent state of the tin atoms and data previously reported for $^{119}\text{Sn}^{4+}$ in bulk YCrO_3 [8]. Fitting of the spectrum shows that it can be represented by a superposition of the following components:

- (1) A major sextet (denoted hereafter as **ms**), corresponding to the hyperfine field $H_{ms}=80 \pm 1 \text{ kOe}$, with a relative area $A_{ms}=0.78$;
- (2) A less intense but particularly intriguing sextet (denoted as **xs**), corresponding to $H_{xs}=67 \pm 3 \text{ kOe}$, with $A_{xs}=0.14$; and
- (3) Several very weak unresolved sextets (denoted as **vws**), corresponding to $H_{vws} \leq 54 \text{ kOe}$, with a total relative area A_{vws} lower than 0.10.

The spectrum of $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ is quite similar to that recently reported in [7] for $^{119}\text{Sn}^{4+}:\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$. In fact, in both cases the value of H_{ms} is equal within experimental error to the value of $H_6=80 \pm 3 \text{ kOe}$ which was previously assigned to Sn^{4+} on a regular Cr^{3+} site, with 6 Cr^{3+} nearest magnetic neighbors, in the bulk of the unsubstituted YCrO_3 [8].

Moreover, **xs**, which was not observed in the spectrum of

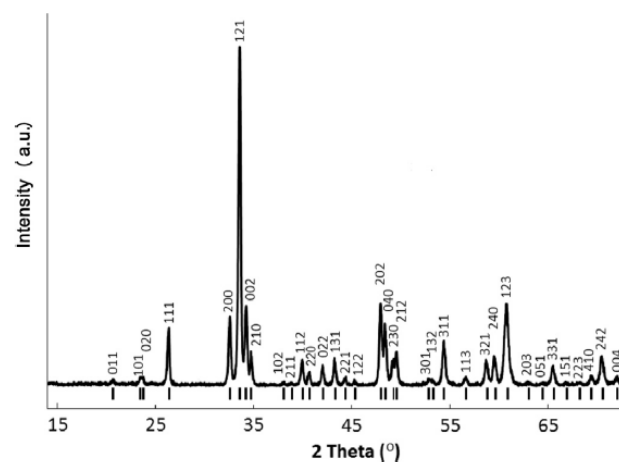


Fig. 1. XRD pattern of a tin-doped $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ polycrystalline powder sample exhibiting a single-phase orthorhombic perovskite structure (space group $Pbnm$ [6]).

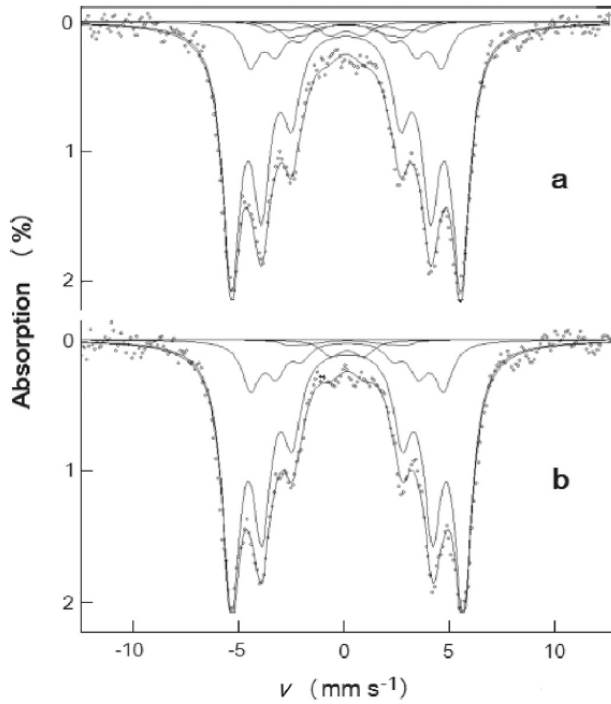


Fig. 2. ^{119}Sn Mössbauer spectra of tin-doped $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ recorded before (a) and after (b) H_2 annealing the sample at $700\text{ }^\circ\text{C}$.

Table 1
Mössbauer spectroscopic parameters of the $^{119}\text{Sn}^{4+}$ probe in the bulk of $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ at 4.2 K.

	δ (mm s $^{-1}$)	H (kOe)	e_Q (mm s $^{-1}$)	Γ (mm s $^{-1}$)	A
As synthesized					
ms:	0.12 ± 0.02	80 ± 1	~ 0	1.00 ± 0.05	0.78
xs:	0.12 ± 0.04	67 ± 3	–	1.00^*	0.14
vws: (1)	0.12 ± 0.05	54 ± 5	–	1.00^*	0.03
(2)	0.12 ± 0.05	40 ± 5	–	1.00^*	0.03
(3)	0.12 ± 0.05	13 ± 5	–	1.00^*	0.02
After subsequent H_2 annealing at $700\text{ }^\circ\text{C}$					
ms:	0.12 ± 0.02	80 ± 1	~ 0	1.00 ± 0.05	0.80
xs:	0.12 ± 0.04	67 ± 3	–	1.00^*	0.15
vws: (1)	0.12 ± 0.05	54 ± 5	–	1.00^*	0.00
(2)	0.12 ± 0.05	40 ± 5	–	1.00^*	0.02
(3)	0.12 ± 0.05	13 ± 5	–	1.00^*	0.03

The quoted fixed (*) values of Γ , somewhat higher than that obtained with our reference BaSnO_3 absorber ($\Gamma_{\text{ref}}=0.83\text{ mm s}^{-1}$), are assumed to reflect the relatively weak fluctuations in H values probed by different $^{119}\text{Sn}^{4+}$ ions with equal numbers of magnetic neighbors (formally considered as possessing "magnetically equivalent surroundings").

YCrO_3 , exhibits relative areas of comparable magnitude in $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ ($A_{\text{xs}}=0.14$ and 0.19 [7], respectively).

Finally, as to the above-mentioned **vws**, their total contribution in $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ is also close to that in either $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ or YCrO_3 .

Analysis of Fig. 2a thus leads to the following conclusion: whereas **xs** is undoubtedly the only spectral component which can be thought of as a Mössbauer spectroscopic signature of the Ca^{2+} substitution for Y^{3+} , no obvious relation seems to appear between the atomic ratio Ca/Y and the relative area A_{xs} .

XPS measurements on the considered $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ powder have yielded, for yttrium and calcium, the binding energies E_b

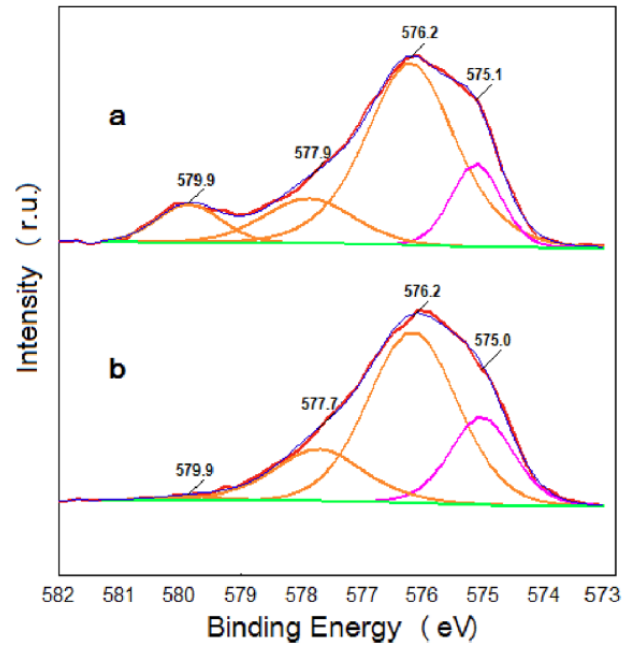


Fig. 3. Fitted $\text{Cr}2p_{3/2}$ XP spectra of tin-doped $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ recorded before (a) and after (b) H_2 annealing the sample at $700\text{ }^\circ\text{C}$. Cr^{6+} species are represented by the component centered at $E_b=579.9\text{ eV}$.

($\text{Y}3d$, $E_b=156.8\text{ eV}$ and $\text{Ca}2p$, $E_b=346.8\text{ eV}$) which were typically observed in Y and Ca oxides [9]. Hence, no specific information about charge compensation mechanisms in $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ could be extracted from XP spectra of these two constituent elements. By contrast, analysis of the composite $\text{Cr}2p_{3/2}$ peak ($E_b=572\text{--}582\text{ eV}$), appearing in the XP spectrum of this material, predominantly composed of trivalent chromium, has revealed the concomitant presence of Cr^{6+} ($3d^0$) diamagnetic surface species characterized by a single spectral component with a binding energy of 579.9 eV (Fig. 3a). As to the anticipated presence of Cr^{4+} ($3d^2$) species, possessing, like Cr^{3+} ($3d^3$) ions, unpaired electrons (that give rise, in both cases, to a complex unresolved multiplet splitting of the $\text{Cr}2p_{3/2}$ peak [10]), these species cannot be, for this reason, reliably detected by XPS in the considered compound.

Nevertheless, we could prove through complimentary ^{119}Sn Mössbauer spectroscopic measurements, that neither Cr^{6+} nor Cr^{4+} species were responsible for **xs**. In fact, this sextet was still present in the ^{119}Sn Mössbauer spectrum (Fig. 2b) recorded after H_2 annealing the sample at $700\text{ }^\circ\text{C}$, this chemical treatment being known to easily transform Cr^{6+} (as well as Cr^{4+}) into the most stable Cr^{3+} , as confirmed by the observed drastic decrease of the contribution at 579.9 eV in the $\text{Cr}2p_{3/2}$ XP spectrum (Fig. 3b).

Accordingly, these results lead us to believe that the most plausible origin of **xs** is the formation of an associate involving two neighboring Sn^{4+} dopant ions, as it was earlier suggested in the case of tin-doped $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ [7].

In this context, it is noteworthy that the ^{119}Sn Mössbauer spectrum of the pristine $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$, which was not annealed in the reducing atmosphere (cf. Fig. 2a), has nevertheless provided no evidence for Cr^{4+} ions in the vicinity of the ^{119}Sn probe, either. In order to account for this finding we assume that the hole hopping between Cr^{4+} and Cr^{3+} , responsible for the electrical properties of $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$ observed in the temperature range $300\text{--}550\text{ K}$ [4], could be completely stopped upon Mössbauer spectroscopic measurements at 4.2 K, the hole being frozen on a Cr^{3+} ion, containing no Sn^{4+} dopant in its neighborhood. Accordingly, this allows the highly charged Cr^{4+} and Sn^{4+} ions to avoid location in

close proximity to one another. In other words, at 4.2 K, the magnetically active surrounding of $^{119}\text{Sn}^{4+}$, incorporated into $\text{Y}_{1-x}\text{Ca}_x\text{CrO}_3$, involves chromium only in its trivalent state, as it was the case in YCrO_3 .

Indeed, quite a different situation is expected when a chemically stable M^{4+} dopant, e.g. Ti^{4+} , was used to compensate the unbalance of charge created in the considered chromites by heterovalent Ca^{2+} ions. In order to elucidate this point we have investigated the spectra of the $^{119}\text{Sn}^{4+}$ probe introduced in the bulk of two relevant compounds with different titanium substitution levels.

3.2. The solid solution $\text{Y}_{1-x}\text{Ca}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$

XRD measurements, performed for both Ti^{4+} -containing materials discussed in the following two sections, proved that they contained only one phase consistent with the formation of the relevant solid solution exhibiting a distorted perovskite-type structure. Moreover, a slight shift of all the Bragg peaks to lower values of the diffraction angle was observed, in agreement with the larger ionic radius of Ti^{4+} (0.605 Å) with respect to that of Cr^{4+} (0.55 Å), which is believed to compensate for the charge deficit generated by Ca^{2+} in $\text{Y}_{1-x}\text{Ca}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$. However, our ^{119}Sn Mössbauer spectroscopic measurements, performed with the tin-doped samples of YCrO_3 , $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$, $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$, and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Ti}_{0.2}\text{O}_3$, have shown the value of $H(^{119}\text{Sn})$ for the regular Cr^{3+} site with 6 Cr^{3+} nearest magnetic neighbors, appearing clearly in the spectra all of these isostructural materials, to be the same within measurement error ($H=80 \pm 3$ kOe). This means that the spin polarization of the $^{119}\text{Sn}^{4+}$ ions is virtually unaffected by the crystallographic details which may therefore be neglected for following consideration.

3.2.1. $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$

XPS revealed the presence of Ti^{4+} ions through the $\text{Ti}2p_{3/2}$ peak (binding energy $E_b=458.4$ eV) which is commonly observed for Ti^{4+} -based oxides [9]. The presence of Ti^{4+} ions did not suppress the formation of Cr^{6+} at the surface (Fig. 4a). The relative amount (ca. 6%) of these surface species, characterized by the 579.9 eV peak, remained comparable to that in the as-prepared $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ (ca. 9%). This result was confirmed by further XPS characterization of a sample with a higher Ti^{4+} content (cf. Section 3.2.2). We assume that the hexavalent chromium has been essentially formed, in both cases, by the reaction between surface-located Cr^{3+} ions and O_2 molecules upon air annealing the samples. Accordingly, the Cr^{6+} content could only be slightly influenced by the different Ca^{2+} -charge compensation mechanisms in $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ and $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$. As expected, H_2 annealing the former chromite has also resulted in a drastic decrease in the Cr^{6+} spectral contribution (Fig. 4b).

As seen in Fig. 5, the ^{119}Sn Mössbauer spectrum of tin-doped $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ differs considerably from that of $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ (cf. Fig. 2a). In fact, it is clearly indicative of both the sharp decrease in the number of Sn sites, characterized by $H=81 \pm 1$ kOe, and the concomitant increase in the spectral contribution of all sextets related to lower values of H . This spectrum is thus qualitatively consistent with the expected fluctuation in the number of diamagnetic Ti^{4+} ions in the neighborhood of various Sn^{4+} ions distributed throughout the relevant solid solution. However, one can also see that most of the Sn^{4+} ions still exhibit the value of $H=81$ kOe which is close to those observed in the above three titanium-free chromites. Besides, the values of the isomer shift and the apparent quadrupole shift for all the ^{119}Sn constituent sextets of the spectrum in Fig. 5 are found to be equal, within experimental error, to those for Sn^{4+} in the bulk of the titanium-free chromites (cf. Table 1).

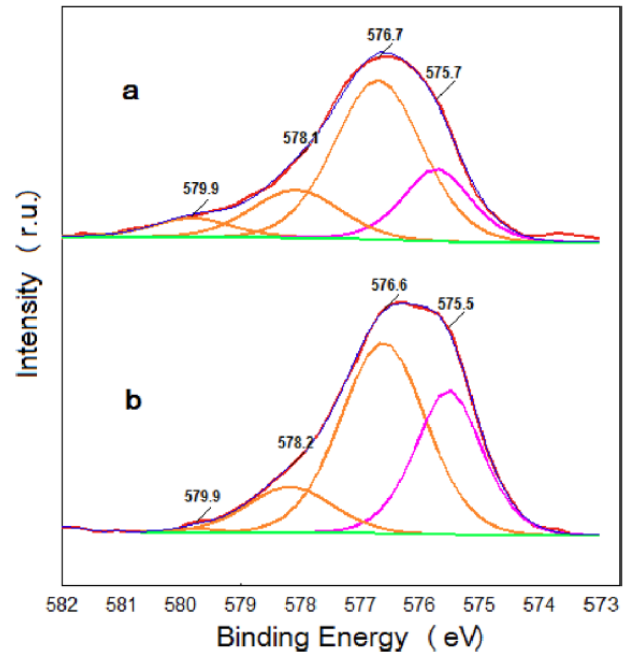


Fig. 4. Fitted $\text{Cr}2p_{3/2}$ XP spectra of tin-doped $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ recorded before (a) and after (b) H_2 annealing the sample at 700 °C. Cr^{6+} species are represented by the component centered at $E_b=579.9$ eV.

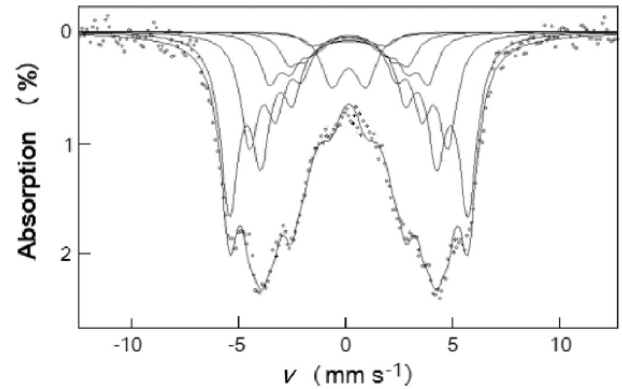


Fig. 5. ^{119}Sn Mössbauer spectrum of tin-doped $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$. For all the constituent sextets the values of δ and e_Q are assumed to be equal to those observed in the case of tin-doped $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ ($\delta=0.12 \pm 0.05$ mm s^{-1} and $e_Q \cong 0$ mm s^{-1}).

In an attempt to interpret the spectrum in Fig. 5, we have applied the Gilleo's model of randomly incomplete magnetic linkages [11]. This model has been successfully used by Lyubutin and Vishnyakov [12] to account for the evolution of ^{119}Sn Mössbauer spectra of $\text{RE}_{1-x}\text{Ca}_x\text{Fe}_{1-x}\text{Sn}_x\text{O}_3$ perovskites with increasing x value. According to [12], in these compounds, containing Sn^{4+} ions statistically distributed over the octahedral B-sites, the probability $P(k)$ to find k magnetic (Fe^{3+}) cations among six nearest neighboring B-cations, forming the magnetically active surrounding of the reference B-cation, can be defined as

$$P(k) = C_6^k (x)^{6-k} (1-x)^k \quad (1)$$

where $C_6^k = \frac{6!}{(6-k)!k!}$ is the binomial coefficient with $k=0, 1, 2, \dots, 6$.

A priori, the same relation can also be applied to the material, we are interest in, $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ($x=0.1$), assuming that the $^{119}\text{Sn}^{4+}$ probe ions are statistically distributed over the sites of the octahedral substructure. In this case, the following statistical

Table 2

Values of magnetic hyperfine fields H_k transferred to the $^{119}\text{Sn}^{4+}$ probe, located in the bulk of $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Ti}_{0.2}\text{O}_3$ on Cr sites with different magnetically active surroundings, and experimental values $A_{\text{exp}}(k)$ of the relevant spectral contributions at 4.2 K. Comparison of the statistical probabilities $P(k)$ with the adjusted $A^*(k)$ values allowing for the presence of the non-model spectral components. R_{model} is the ratio of the probabilities $\frac{P^*(k)}{P^*(6)}$ obtained using the relevant $P(k)$ values allowing for the formation of various $\text{Sn}^{4+}-\text{Sn}^{4+}$ associates, as explained in the text.

k	H_k (kOe)	$P(k)$	$\frac{P(k)}{P(6)}$	$A_{\text{exp}}(k)$	$A^*(k)$	$\frac{A^*(k)}{A^*(6)}$	R_{model}
$\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$							
6	81	0.531	1	0.441	0.488	1	1
5	67.5	0.354	0.67	0.272	0.301	0.62	0.62
4	54	0.098	0.19	0.119	0.132	0.27	0.27
3	40.5	0.015	0.03	0.071	0.079	0.16	0.16
2	27	0.001	$2 \cdot 10^{-3}$	0.024	–	–	–
1	13.5	$5 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	0.073	–	–	–
$\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Ti}_{0.2}\text{O}_3$							
6	81	0.262	1	0.230	0.253	1	1
5	67.5	0.393	1.5	0.317	0.348	1.38	1.38
4	54	0.246	0.94	0.227	0.249	0.99	1.04
3	40.5	0.082	0.31	0.137	0.150	0.60	0.47
2	27	0.015	0.06	0.043	–	–	–
1	13.5	0.0015	$6 \cdot 10^{-3}$	0.046	–	–	–

probabilities, related to $k=6, 5, 4, 3, 2, 1$, and 0, are expected:

0.531: 0.354: 0.099: 0.015: 0.001: 0.00005: 0.000001, respectively.

Accordingly, for $x=0.1$, only the first four sites of Sn^{4+} can actually influence the ^{119}Sn spectrum. Besides, the experimental value of the hyperfine field, assigned to six neighboring Cr^{3+} ($k=6$), $H_6=81$ kOe, allows the partial contribution of each Cr^{3+} cation to the resulting spin polarization of a Sn^{4+} ion to be quantified ($h=13.5$ kOe) and, consequently, all other H_k values to be determined.

To analyze the ^{119}Sn spectrum of a tin-doped $\text{Y}_{1-x}\text{Ca}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$, we thus assume that the presence of Ti^{4+} ions can only give rise to the sextets characterized by the following values of H :

$H_6=81$, $H_5=67.5$, $H_4=54$, $H_3=40.5$, $H_2=27$, $H_1=13.5$, and $H_0=0$ kOe.

The parameters determined from fitting the spectrum in Fig. 5, are gathered in Table 2. One can see that our approach yields a rather satisfactory representation of the experimental spectrum shape. However, the apparent contributions $A_{\text{exp}}(k)$ of the constituent sextets significantly differ from those expected from the $P(k)$ values related to the statistical distribution of Ti^{4+} . So, we attempted to verify, keeping in mind the above tentative assignment of \mathbf{xS} in ^{119}Sn spectra of both titanium-free Ca-substituted chromites, whether this discrepancy could also be accounted for by the formation of various Sn–O–Sn associates in the structure still preserving the statistical distribution of Cr^{3+} and Ti^{4+} within the B-substructure. Considering the constituent sextets in the fitted spectrum (cf. Fig. 5 and Table 2), we conclude that the sextets related to the lowest values of H_k (corresponding to $k < 3$), that were already observed in the titanium free samples, ought to be omitted from further discussion. In fact, their spectral contributions are obviously too high as compared to those expected for $x=0.1$ referred to $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ with statistically distributed Cr^{3+} and Ti^{4+} ions. Accordingly, to analyze the relative contributions of the model-consistent sextets (with $k=6, 5, 4$, and 3), the adjusted values of the relative areas $A^*(k)$, allowing for the total contribution of non-model components present in the spectrum ($A_{\text{exp}}=0.097$), should be used (Table 2). So, as can be seen in Table 2, the value of

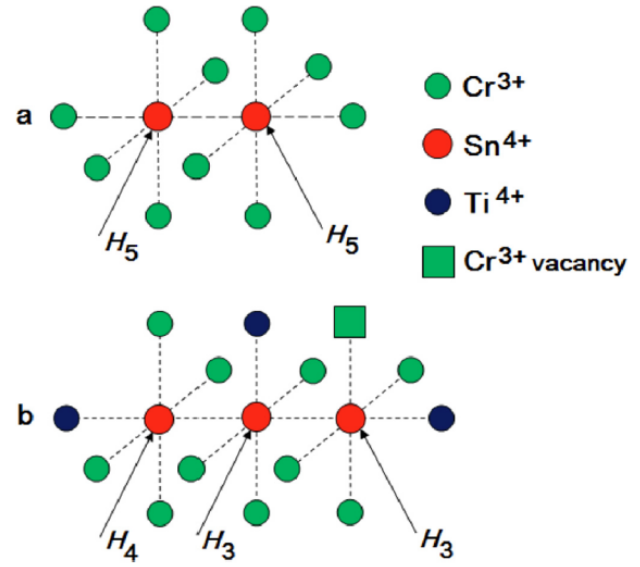


Fig. 6. Schematic representation of the Sn^{4+} associates allowing ^{119}Sn Mössbauer spectra of $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Ti}_{0.2}\text{O}_3$ to be accounted for: simple associate involving two neighboring Sn^{4+} (a); complex associate involving three Sn^{4+} together with a Cr^{3+} vacancy (b). Only relevant B-cations are shown.

$A^*(6)=A_{\text{exp}}(6)/0.903=0.488$, assumed to be that $P^*(6)$ representing the actual probability to find, within this substituted chromite, a Sn^{4+} ion having six Cr^{3+} neighbors, is somewhat lower than the theoretical value $P(6)$. Assuming that the observed difference $P(6)-A^*(6)=0.043$ is due to the formation of an associate of two Sn^{4+} ions, each initially having six Cr^{3+} neighbors (Fig. 6a), it becomes possible to determine the increased spectral contribution of sites with $k=5$, probed by ^{119}Sn , i.e. $P(5)+0.043=0.397$. The latter value is higher than the adjusted experimental value $A^*(5)=0.301$, which we also assume to be that $P^*(5)$ representing the actual probability to find a Sn^{4+} ion with five Cr^{3+} neighbors. Hence, the difference observed ($0.397-0.301=0.096$) is suggestive of the concomitant formation of a more complex associate, involving several neighboring Sn^{4+} ions. In this way we reach, in the next step, a fair agreement of the values of $\frac{A^*(4)}{A^*(6)}$ and $\frac{A^*(3)}{A^*(6)}$, which seem at first glance surprisingly high, with those of $\frac{P^*(4)}{P^*(6)}$ and $\frac{P^*(3)}{P^*(6)}$, respectively (cf. Table 2). Such an associate, consistent with the above model's values of H , is shown in Fig. 6b. As can be seen, it involves a Cr^{3+} vacancy (\square_{Cr}). The formation of \square_{Cr} , caused by the charge compensation of the Sn^{4+} heterovalent dopant itself, has already been revealed by ^{119}Sn Mössbauer spectra of tin-doped chromium sesquioxide [13]. By contrast, in both $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ chromites Sn^{4+} dopant ions were involved, together with Cr^{4+} ions, in the charge compensation mechanism related to the Ca^{2+} -substitution for Y^{3+} . So, we can conclude that the spectrum of the ^{119}Sn probe in $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ is consistent with the statistical distribution of Cr^{3+} and Ti^{4+} , provided that partial segregation of Sn^{4+} dopant ions in the B-substructure took place. Despite their very low content, such segregations are thus proven capable of changing significantly the spectrum of the ^{119}Sn probe. Indeed, these results are in qualitative agreement with our above interpretation of the “intriguing” \mathbf{xS} sextet in the Mössbauer spectrum of titanium-free $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$.

3.2.2. $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Ti}_{0.2}\text{O}_3$

This chromite, characterized by the different Cr/Ti ratio and, consequently, by the different probability distribution $P(k)$, was used for further testing of the procedure described in Section 3.2.1.

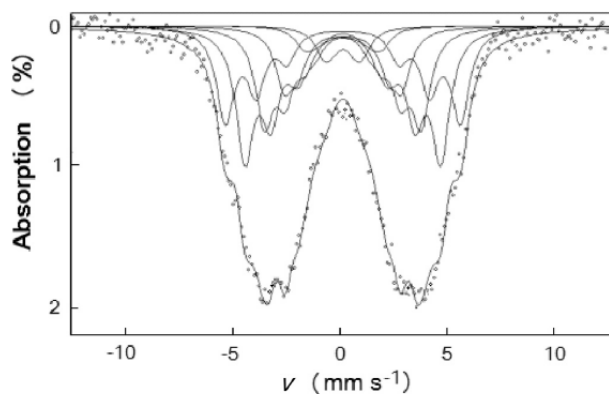


Fig. 7. ^{119}Sn Mössbauer spectrum of tin-doped $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Ti}_{0.2}\text{O}_3$.

In the present case, according to Eq. (1), the B-site with six Cr^{3+} neighbors is no longer the predominant one and the main contribution to the ^{119}Sn Mössbauer spectrum in Fig. 7 arises from the site with $k=5$. The results of analysis of this spectrum, gathered in Table 2, show that the procedure developed for interpreting the ^{119}Sn spectrum of the precedent chromite with $x=0.1$, remains valid in the case of $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Ti}_{0.2}\text{O}_3$ ($x=0.2$), provided that partial segregation of the Sn^{4+} dopant ions also took place. So, this furnished a further support for our interpretation of all other results reported in this paper.

4. Conclusions

Low-temperature Mössbauer spectra of $^{119}\text{Sn}^{4+}$ probe ions, located in the bulk of three Ca-substituted yttrium chromites, *i.e.* $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$, $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Ti}_{0.2}\text{O}_3$, have pointed out the occurrence of partial segregation of Sn^{4+} dopant ions in all of these compounds. In the case of $\text{Y}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$, neither highly oxidized Cr^{4+} nor Cr^{6+} species is found in the vicinity of the

bulk-located $^{119}\text{Sn}^{4+}$ probe. Although Cr^{4+} ions are distributed, like the ^{119}Sn probe, over B-sites in the bulk of crystallites, they are thought to be frozen, at 4.2 K, outside the magnetically active surrounding of Sn^{4+} , whereas Cr^{6+} ions are essentially located on the surface of crystallites, thus too far from the $^{119}\text{Sn}^{4+}$ probe. In the case of both studied Ti-containing chromites, ^{119}Sn Mössbauer spectra have provided the original indirect evidence for the statistical distribution of Cr^{3+} and Ti^{4+} ions over octahedral sites and allowed us to characterize the detected associates of Sn^{4+} .

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