Fe^{4+} content and ordering of anion vacancies in partially reduced $AFe_xTi_{1-x}O_{3-y}$ (A = Ca, Sr; $x \leq 0.6$) perovskites. An ^{57}Fe Mössbauer spectroscopy study

Fe^{4+} content and ordering of anion vacancies in partially reduced AFe$_x$Ti$_{1-x}$O$_{3-y}$ (A = Ca, Sr; $x \leqslant 0.6$) perovskites. An ^{57}Fe Mössbauer spectroscopy study

J C Waerenborgh[1,5]**, F M Figueiredo**[2,3]**, J R Frade**[2]**, M T Colomer**[4]** and J R Jurado**[4]

[1] Departamento de Química, Instituto Tecnológico e Nuclear, P-2686-953 Sacavém, Portugal
[2] Departamento de Engenharia Cerâmica e do Vidro, UIMC, Universidade Aveiro,
3810-193 Aveiro, Portugal
[3] Departamento de Ciências Exactas e Tecnológicas, Universidade Aberta,
Rua da Escola Politécnica 147, 1269-001 Lisboa, Portugal
[4] Instituto de Ceramica y Vidrio, CSIC, 28500 Arganda del Rey, Madrid, Spain

E-mail: jcarlos@itn1.itn.pt

Abstract

CaFe$_x$Ti$_{1-x}$O$_{3-y}$ ($0.05 \leqslant x \leqslant 0.60$) and SrFe$_xTi_{1-x}O_{3-y}$ ($0.20 \leqslant x \leqslant 0.60$) perovskites were prepared by solid state reaction and subjected to different heat treatments in different atmospheres. Mössbauer spectroscopy of the CaFe$_x$Ti$_{1-x}$O$_{3-y}$ could detect Fe^{4+} in all the samples, even in those heated at 1000 °C in Ar atmosphere for 10 hours. Fe^{3+} coordinated by six, five and four anions were also identified and the estimated hyperfine parameters were consistent with those previously reported for the CaFe$_x$Ti$_{1-x}$O$_{3-x/2}$ oxides where all the Fe cations were present as Fe^{3+}. The Fe^{4+}/Fe^{3+} ratios estimated from Mössbauer data are in agreement with coulometric titration data. The absence of tetracoordinated Fe^{3+} in SrFe$_x$Ti$_{1-x}$O$_{3-y}$ suggests that in contrast to CaFe$_x$Ti$_{1-x}$O$_{3-y}$ no ordering of anion vacancies takes place even for $x = 0.60$ and explains the differences in the Fe concentration dependence of the electric transport properties of these materials.

1. Introduction

CaFe$_x$Ti$_{1-x}$O$_{3-y}$ and Sr$_{0.97}$Fe$_x$Ti$_{1-x}$O$_{3-y}$ with the perovskite-type structure have been the subject of extensive studies. The interest of these compounds is due to their ability to accomodate anion vacancies to keep electric neutrality when Ti^{4+} is replaced by Fe^{3+}. These vacancies are related to the high ionic and electronic conductivities of these oxides, which

[5] Corresponding author.

are suitable for materials for high-temperature electrochemical applications such as ceramic membranes for oxygen separation and partial oxidation of hydrocarbons, sensors, electrodes for solid oxide fuel cells etc (Kharton *et al* 2001).

The ionic conductivity depends both on the concentration and mobility of oxygen vacancies. Concentration of anion vacancies are directly related to the Fe^{3+} content of the oxide. Ordered vacancies however lose their mobility. Therefore, ^{57}Fe Mössbauer spectroscopy, being sensitive to the oxidation state and coordination of Fe, has been often used in the study of $SrFeO_{3-y}$ (Gibb 1985, Fournès *et al* 1987, Wißman and Becker 1996) and $SrFe_xTi_{1-x}O_{3-y}$ (Zheng *et al* 1990), $CaFeO_3$ (e.g. Takano *et al* 1977) as well as $CaFe_xTi_{1-x}O_{3-y}$, where all the Fe is in the 3+ oxidation state i.e. where $y = x/2$ (Grenier *et al* 1977, McCammon *et al* 2000). The analysis of the $CaFe_xTi_{1-x}O_{3-x/2}$ spectra by McCammon *et al* (2000) has shown that it is possible to detect not only octahedral and tetrahedral Fe^{3+}, but also pentacoordinated Fe^{3+}, hereafter referred to as CN6-Fe^{3+}, CN4-Fe^{3+} and CN5-Fe^{3+}, respectively. The presence of CN4-Fe^{3+} already detected by Grenier *et al* (1977) in $CaFe_xTi_{1-x}O_{3-x/2}$ has shown that short-range ordering of anion vacancies occurs for all compositions. Transmission electron microscopy further revealed for $x > 0.5$ the formation of fully ordered structures, with regular sequences of octahedrally and tetrahedrally coordinated Fe and Ti layers.

Comparison between Mössbauer and thermogravimetric data showed that in $SrFeO_{3-y}$ electrons created during the anion vacancy formation are trapped by the Fe cations forming Fe^{3+}, rather than by single ionized anion vacancies. The same seems to occur in $CaFe_xTi_{1-x}O_{3-x/2}$ oxides according to the number of vacancies deduced from the composition and the fractions of Fe^{3+} in different coordinations (McCammon *et al* 2000).

In practical applications, Ca and Sr perovskites are subjected to relatively high temperatures in atmospheres where the oxygen fugacity is higher than in those used to prepare the totally reduced $CaFe_xTi_{1-x}O_{3-x/2}$. Ionic transport and thermal gravimetric analysis data suggest that Fe^{4+} is most likely present in these conditions (Kharton *et al* 2001), as in the cases of $SrFe_xTi_{1-x}O_{3-y}$ (Zheng *et al* 1990) or $CaFeO_{3-y}$ (Takano *et al* 1977). Besides lowering the concentration of vacancies, the presence of Fe^{4+} may also have an influence in vacancy ordering and therefore affect the transport properties. In this article we present a ^{57}Fe Mössbauer spectroscopy study of Fe^{4+} containing $CaFe_xTi_{1-x}O_{3-y}$ with $0.05 \leqslant x \leqslant 0.60$ (which as far as we know was never reported before) and $SrFe_xTi_{1-x}O_{3-y}$ with $0.20 < x < 0.60$, annealed at different temperatures and in different atmospheres. The effect of lattice ordering and Fe oxidation degree on the physical properties of both the Ca and Sr perovskites is reported elsewhere (Figueiredo *et al* 2001, Kharton *et al* 2001).

2. Experiment

Powders of nominal $Sr_{0.97}Ti_{1-x}Fe_xO_{3-y}$ ($x = 0.20$–0.60) and $CaTi_{1-x}Fe_xO_{3-y}$ ($x = 0.05$–0.60) materials were obtained by solid state reaction of high purity $SrCO_3$, $CaCO_3$, TiO_2 and Fe_2O_3. The reactants were wet-mixed in Nylon$^©$ containers with zirconia balls for 2 hours, dried in a stove at $60\,°C$ and calcined at $1100\,°C$ for 10 hours with heating/cooling rates of $4\,°C\,min^{-1}$. The resulting powder was wet-milled, again dried, sieved through a 30 μm mesh and uniaxially pressed at 200 MPa into 1 mm thick discs with a diameter of 10 mm. Sintering was carried out in air at temperatures ranging from 1320 to $1500\,°C$, increasing with decreasing Fe content, for 2 hours with heating/cooling rates of $5\,°C\,min^{-1}$. The sample density was above 95% of the theoretical value. The samples of each composition were separated in different sets according to the final heat treatment: $Sr_{0.97}Ti_{1-x}Fe_xO_{3-y}$ samples were (A) annealed in air at $900\,°C$ for 10 hours and slowly cooled ($5\,°C\,min^{-1}$) in order to obtain oxygen nonstoichiometry close to the equilibrium at room temperature; (B) annealed in air at $1450\,°C$ for 10 hours and

quenched; $CaTi_{1-x}Fe_xO_{3-y}$ samples were (C) annealed in air at 1000 °C for 10 hours and slowly cooled down (5 °C min^{-1}), (D) annealed in air at 1000 °C for 10 hours and quenched and (E) annealed in argon at 1000 °C for 10 hours and slowly cooled (5 °C min^{-1}) in the same atmosphere. Hereafter the samples with different final heat treatments will be identified by (A), (B), (C), (D) and (E).

The final samples were characterized by x-ray diffraction (XRD). All the $Sr_{0.97}Ti_{1-x}Fe_xO_{3-y}$ compounds crystallize in a single cubic perovskite phase. Slowly cooled $CaFe_xTi_{1-x}O_{3-y}$ (C) oxides in the composition range $0.05 \leqslant x \leqslant 0.40$, as well as those quenched (D) and those annealed in argon (E) in the composition range $0.05 \leqslant x \leqslant 0.20$, crystallize in the orthorhombic structure of pure $CaTiO_3$. As shown in figure 1 in the case of the (C) samples, in the powder x-ray diffractograms of the $CaFe_{0.60}Ti_{0.40}O_{3-y}$ oxides some of the weaker peaks observed for the orthorhombic structure have disappeared. In the case of the (D) and (E) samples these weaker peaks are already absent for the $CaFe_{0.40}Ti_{0.60}O_{3-y}$ compositions. The remaining peaks are relatively broad and all of them can be indexed on a cubic perovskite-type unit cell as in the case of the $CaFe_xTi_{1-x}O_{3-y}$ ($0.3 \leqslant x \leqslant 0.5$) prepared by Iwahara *et al* (1988) or the $Ca_xLa_{1-x}FeO_{3-y}$ ($0.66 \leqslant x \leqslant 0.9$) prepared at 1400 °C in air by Alario-Franco *et al* (1983). Based on a transmission electron microscopy study, the cubic XRD patterns were explained for the latter samples by the formation of three-dimensional microdomains where long-range ordering of oxygen vacancies along the ($0k0$) planes takes place. These microdomains consist of ordered sequences of octahedral and tetrahedral layers as in the $CaFe_xTi_{1-x}O_{3-x/2}$ perovskites with $x > 0.5$ reported by Grenier *et al* (1977).
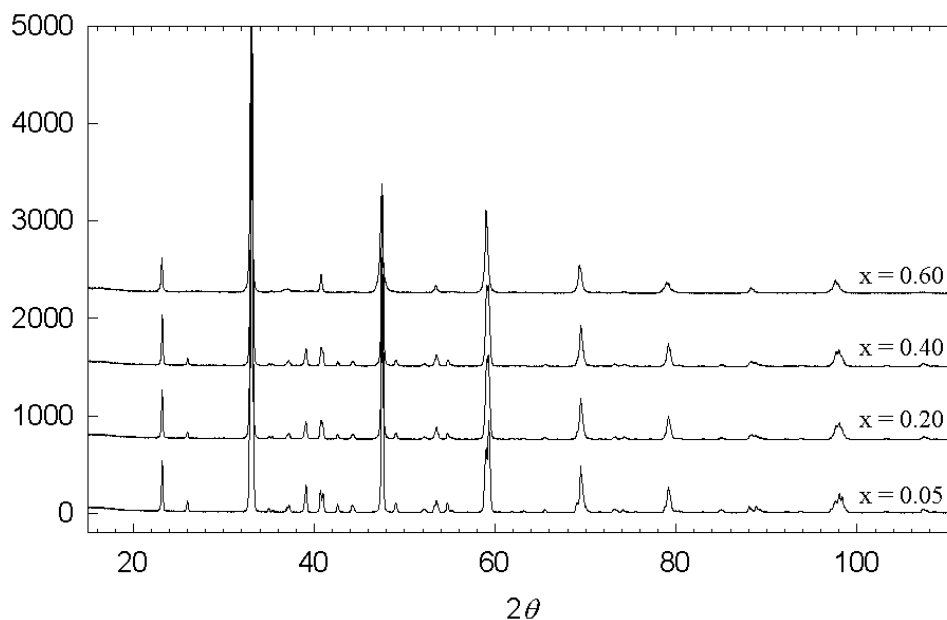
Figure 1. Powder x-ray diffractograms of the (C) $CaFe_xTi_{1-x}O_{3-y}$ samples (heat treatment explained in the text) showing that the weaker peaks disappear with increasing Fe content. The diffractogram of the $x = 0.6$ sample may be indexed on a cubic perovskite-type unit cell.

Mössbauer spectra were measured in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi ^{57}Co source in a Rh matrix. The velocity scale was calibrated using an α-Fe foil at room temperature. Absorbers were obtained by pressing the

sample powder (5 mg of natural Fe cm^{-2}) into a Perspex holder. Spectra collected at 10 K were obtained using a flow cryostat with temperature stability of ± 0.5 K. Mössbauer spectra were analysed using a modified version (Waerenborgh *et al* 1994) of a non-linear least-squares computer method. Isomer shifts are given relative to metallic α-Fe at room temperature. Relative areas and line widths of each peak in a quadrupole doublet were kept equal during the refinement procedure. Except where otherwise stated these were the only constraints used.

3. Results and discussion

3.1. Mössbauer spectra of $CaFe_xTi_{1-x}O_{3-y}$ taken at room temperature

Mössbauer spectra of the totally reduced $CaFe_xTi_{1-x}O_{3-x/2}$ perovskites, i.e., perovskites where all the Fe was present in the 3+ oxidation state, show three quadrupole doublets corresponding to CN6-Fe^{3+}, CN5-Fe^{3+} and CN4-Fe^{3+} (McCammon *et al* 2000). The spectra of our samples (figures 2–4), which are expected to contain Fe^{4+}, should be more complex and at least four quadrupole doublets should be considered in their analysis. Due to the high degree of overlap of these doublets a careful analysis is necessary. At least two refinement stages were performed for each spectrum.

In the first stage, three quadrupole doublets were fitted to the spectra. The initial values attributed to the corresponding isomer shifts, δ, and quadrupole splittings, Δ, were those published for the CN6-Fe^{3+}, CN5-Fe^{3+} and CN4-Fe^{3+} in $CaFe_xTi_{1-x}O_{3-x/2}$ (McCammon *et al* 2000).

The mere observation of the shapes of the spectra, particularly in the $x = 0.05$ (C) and $x = 0.20$ (C) cases (figure 2), reveals that there are significant differences between our samples and the totally reduced $CaFe_xTi_{1-x}O_{3-x/2}$ with similar Fe contents of McCammon *et al* (2000). The first stage of refinement clearly showed that these differences in shape could not be accomodated by only varying the relative areas of the three Fe^{3+} quadrupole doublets fitted to the spectra. Since the absorption close to the 0 mm s^{-1} Doppler velocity is much higher in our samples, a fourth doublet with the initial value of δ close to 0 mm s^{-1} was added in the second stage of refinement. A very good fit was thus obtained for the $x = 0.05$ (C) and $x = 0.20$ (C) spectra (figure 2). In the former case, however, the relative area of the doublet attributed to CN4-Fe^{3+} vanished during the refinement. A third stage was therefore performed considering only the other three doublets. The final refined values for the parameters of the quadrupole doublets with non-vanishing relative intensities are given in table 1.

The second stage of refinement with four doublets was also performed for all the other samples and a significant improvement in the quality of the fit was obtained. The final estimated values of the parameters are shown in table 1. Note that the CN4-Fe^{3+} doublet is not detected in the spectra of the $x = 0.05$ samples (figures 2–4).

In the case of the $x \geqslant 0.4$ samples, during refinement, δ of the doublets attributed to CN5-Fe^{3+} increased and became equal, within experimental error, to those of the CN6-Fe^{3+}. Frequently, when a large number of overlapping peaks are present and are refined, several χ^2 local minima may be found during the fitting procedure. If differences in these minima are lower than about 10%, it is often considered that they may be attributed to statistical fluctuations and, therefore, it is not possible to decide which is the correct solution from a statistical point of view. In order to test the reliability of the final solution proposed for the spectra of the $x \geqslant 0.4$ samples, attempts were made to refine the spectra imposing a constant difference between the δ values of the CN6- and the CN5-Fe^{3+} doublets, $\delta(6) - \delta(5)$, in the range 0.05–0.01 mm s^{-1}. For the refinements where $\delta(6) - \delta(5)$ were kept between 0.04 and 0.05 mm s^{-1} the final estimated parameters for the four quadrupole doublets were consistent with those obtained for

Table 1. Parameters estimated from the Mössbauer spectra, taken at 295 K, of CaFe$_x$Ti$_{1-x}$O$_{3-y}$ annealed in different conditions (C), (D) and (E) as explained in the text. δ (mm s^{-1}), isomer shift relative to metallic α-Fe at 295 K; Δ (mm s^{-1}) quadrupole splitting; Γ (mm s^{-1}) full width at half maximum, I, relative area. Estimated errors for δ, Δ and Γ of doublets with $I > 5\%$ are $\leqslant 0.02$ mm s^{-1} and for the others $\leqslant 0.04$ mm s^{-1}. Estimated errors for $I \leqslant 2\%$. N, number of anion vacancies per formula unit calculated assuming that each Fe^{3+} corresponds to $1/2$ anion vacancy.

| | CN4-Fe^{3+} | | | | CN5-Fe^{3+} | | | | CN6-Fe^{3+} | | | | Fe^{4+} | | | | |
Samples	δ	Δ	Γ	I	δ	Δ	Γ	I	δ	Δ	Γ	I	δ	Δ	Γ	I	N
$x = 0.6$																	
(D)	0.18	1.42	0.32	48%	—	—	—	—	0.33	0.51	0.38	26%	−0.01	0.47	0.22	4%	0.288(6)
									0.34	0.87	0.33	22%					
(C)	0.19	1.42	0.31	49%	—	—	—	—	0.34	0.47	0.36	22%	−0.01	0.43	0.22	4%	0.288(6)
									0.35	0.84	0.34	25%					
$x = 0.4$																	
(E)	0.18	1.48	0.31	46%	—	—	—	—	0.35	0.50	0.39	30%	−0.03	0.47	0.26	1%	0.198(4)
									0.35	0.87	0.36	23%					
(D)	0.18	1.51	0.32	43%	—	—	—	—	0.35	0.46	0.38	24%	−0.03	0.51	0.31	4%	0.192(4)
									0.35	0.82	0.39	29%					
(C)	0.19	1.53	0.33	39%	—	—	—	—	0.35	0.24	0.41	33%	−0.03	0.48	0.32	7%	0.186(4)
									0.34	0.88	0.37	22%					
$x = 0.2$																	
(E)	0.17	1.49	0.30	27%	0.32	0.91	0.42	34%	0.36	0.40	0.40	36%	−0.01	0.73	0.25	2%	0.098(2)
(D)	0.19	1.52	0.38	30%	0.31	0.94	0.34	25%	0.34	0.44	0.43	41%	−0.03	0.64	0.25	5%	0.095(2)
(C)	0.18	1.52	0.29	9%	0.31	0.73	0.53	62%	0.34	0.25	0.28	6%	−0.03	0.43	0.41	23%	0.077(2)
$x = 0.05$																	
(E)	—	—	—	—	0.30	0.97	0.62	68%	0.35	0.21	0.41	29%	−0.03	1.14	0.25	3%	0.024(1)
(D)	—	—	—	—	0.30	0.93	0.62	68%	0.33	0.21	0.37	27%	−0.03	1.28	0.31	5%	0.024(1)
(C)	—	—	—	—	0.32	0.87	0.56	57%	0.37	0.25	0.27	21%	−0.03	0.65	0.60	22%	0.020(1)

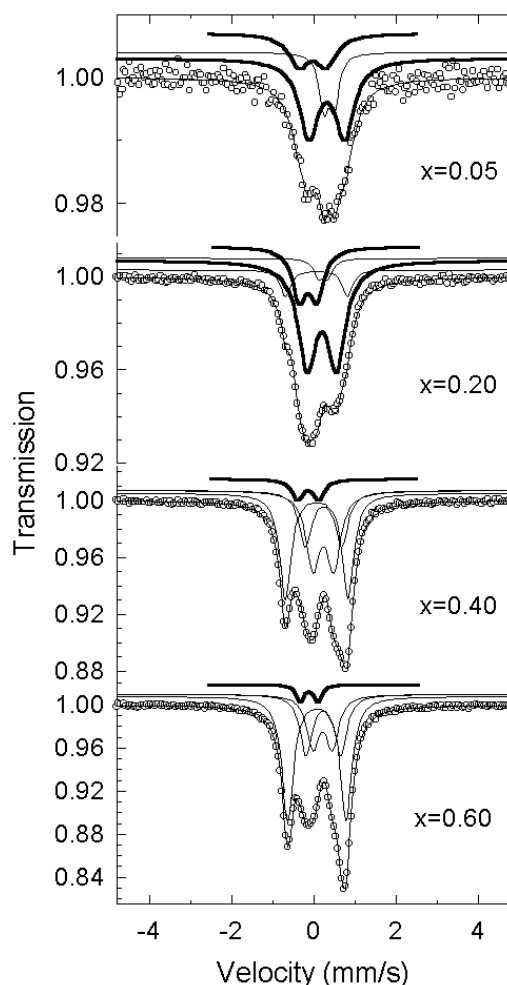**Figure 2.** Room temperature Mössbauer spectra of the $CaFe_xTi_{1-x}O_{3-y}$ (C) samples. Fits to the spectra with subspectral components are shown. Quadrupole doublets assigned to Fe^{4+} (thick line, shifted highest), CN4-Fe^{3+} (largest quadrupole doublet), CN5-Fe^{3+} (thick line) and CN6-Fe^{3+} are shown slightly shifted, for clarity.

all the other samples. However the final χ^2 obtained were about 10–20% larger than those obtained in the refinements where this constraint was not enforced. Furthermore, the final χ^2 obtained for sucessive refinements of the same spectrum decreased significantly with the value of $\delta(6) - \delta(5)$ imposed during the refinement. Therefore, estimated parameters from the refinements free of this constraint and leading to the lowest χ^2 were considered as those closest to the actual Fe^{3+} distribution in the sample (table 1). Since they lead to $\delta(5) \approx \delta(6)$ both doublets are very likely due to CN6-Fe^{3+}, which implies that no significant amounts of CN5-Fe^{3+} can be present in the $0.4 \leqslant x \leqslant 0.6$ samples. The reason why two doublets are necessary to analyse the CN6-Fe^{3+} contribution for these samples while only one is enough for the $x \leqslant 0.2$ samples will be discussed below.
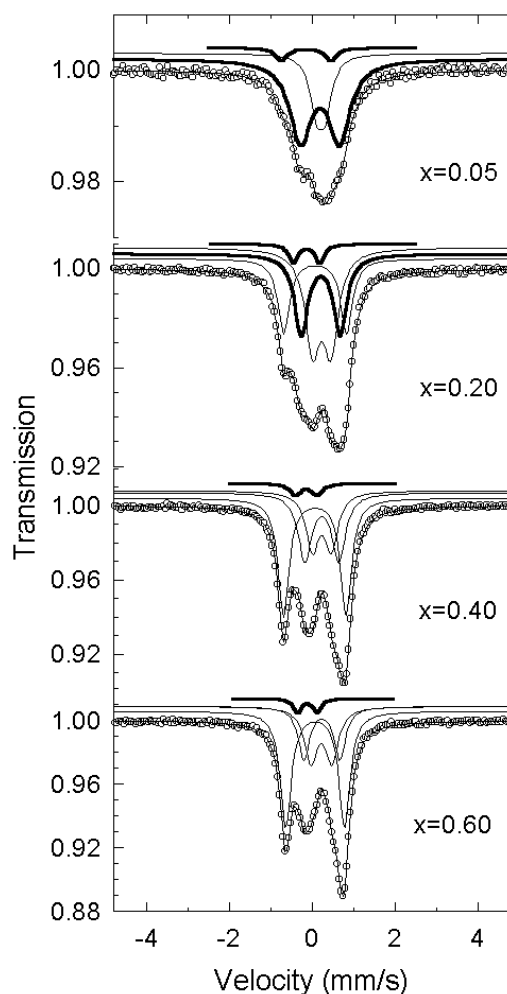
Figure 3. Room temperature Mössbauer spectra of the CaFe$_x$Ti$_{1-x}$O$_{3-y}$ (D) samples.

3.2. Low-temperature spectra

A spectrum of CaFe$_{0.6}$Ti$_{0.4}$O$_{3-y}$ (C) was taken at 10 K in order to confirm the absence of CN5-Fe^{3+}. This spectrum (figure 5) is similar to that obtained by McCammon *et al* (2000) for CaFe$_{0.67}$Ti$_{0.33}$O$_{2.67}$ at 4.2 K. The broader peaks observed in the CaFe$_{0.6}$Ti$_{0.4}$O$_{3-y}$ (C) spectrum may be explained by a greater disorder in this perovskite arising from the transformations occurring during slow cooling, namely those related to partial oxidation of Fe^{3+} to Fe^{4+}, to which CaFe$_{0.67}$Ti$_{0.33}$O$_{2.67}$ equilibrated at 1300 °C, and drop quenched, was not subjected. Furthermore no site with weak magnetic ordering similar to that observed for CaFe$_{0.38}$Ti$_{0.62}$O$_{2.81}$ by McCammon *et al* (2000) was observed in CaFe$_{0.6}$Ti$_{0.4}$O$_{3-y}$ (C), which is consistent with the absence of detectable amounts of CN5-Fe^{3+}. In a first approximation the spectrum of this sample may be fitted by two magnetic splittings (table 2) with magnetic hyperfine fields, B_{hf}, typical of CN6-Fe^{3+} and CN4-Fe^{3+} in perovskites or in brownmillerite (Grenier *et al* 1977, Wattiaux *et al* 1991). However, and as in the case of the room temperature
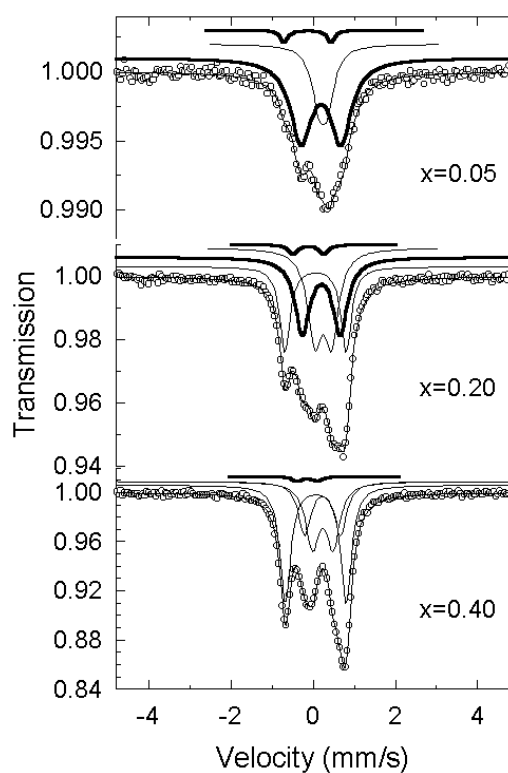
Figure 4. Room temperature Mössbauer spectra of the $CaFe_xTi_{1-x}O_{3-y}$ (E) samples.

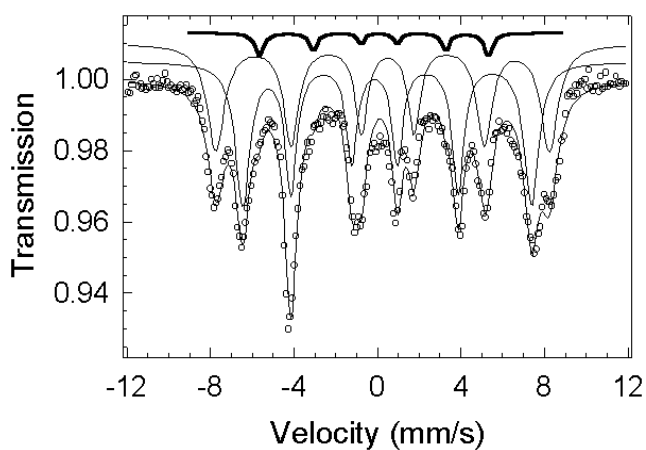**Figure 5.** Mössbauer spectra taken at 10 K of the $CaFe_{0.6}Ti_{0.4}O_{3-y}$ (C) sample. The magnetic sextets assigned to Fe^{4+} (thick line, shifted highest), CN4-Fe^{3+} and CN6-Fe^{3+} are shown slightly shifted, for clarity.

spectrum an additional component, in this case a third sextet with a lower $B_{hf} \approx 34.0$ T (table 2), improved significantly the quality of the fit.

A spectrum of $CaFe_{0.2}Ti_{0.8}O_{3-y}$ (C) was also taken at 10 K. The Fe concentration in this oxide is too low to promote magnetic ordering at least down to this temperature. The spectrum

Table 2. Parameters estimated from the Mössbauer spectra of the CaFe$_x$Ti$_{1-x}$O$_{3-y}$ (C) samples taken at 10 K. Annealing conditions are explained in the text. δ, Δ, Γ and I are as defined in table 1. $\varepsilon = (e^2 V_{ZZ} Q/4)(3\cos^2\theta - 1)$, quadrupole shift, calculated from $(\phi_1 + \phi_6 - \phi_2 - \phi_5)/2$ where ϕ_n is the shift of the nth line of the magnetic sextet due to quadrupole coupling. B_{hf} (T), magnetic hyperfine field. Estimated errors for δ, Δ and Γ of doublets with $I > 5\%$ are $\leqslant 0.02$ mm s^{-1} and for the others $\leqslant 0.03$ mm s^{-1}. Estimated errors for $I \leqslant 2\%$ and for $B_{hf} \leqslant 0.2$ T for sextets with $I > 5\%$ and $\leqslant 0.4$ T for the other sextet.

Samples	CN4-Fe^{3+}					CN5-Fe^{3+}				CN6-Fe^{3+}					Fe^{4+}				
	δ	ε, Δ	B_{hf}	Γ	I	δ	Δ	Γ	I	δ	ε, Δ	B_{hf}	Γ	I	δ	ε, Δ	B_{hf}	Γ	I
$x = 0.6$																			
(C)	0.28	0.61	42.9	0.63	50%	—	—	—	—	0.47	−0.25	49.6	0.70	46%	0.07	−0.27	34.0	0.34	4%
$x = 0.2$																			
(C)	0.30	1.53	—	0.27	8%	0.44	0.75	0.56	64%	0.48	0.23	—	0.30	6%	0.05	0.43	—	0.40	22%

is very similar to that obtained at room temperature, but shifted to higher velocities. The analysis of the spectrum confirms that the four fitted doublets have similar Δ and I at both temperatures (tables 1 and 2). Only the δ have increased, as expected from the second order Doppler shift.

3.3. Isomer shift and magnetic hyperfine field of Fe^{4+}

Considering $\delta \approx -0.02 \pm 0.01$ mm s^{-1} of the additional doublet fitted to the spectra of the Ca perovskites prepared in this work, which was absent from the $CaFe_xTi_{1-x}O_{3-x/2}$ samples of McCammon *et al* (2000), it seems reasonable to attribute it to Fe^{4+}. These δ fall within the range of values published for Fe^{4+}, being larger than $\delta \approx -0.18$ mm s^{-1} for $SrLa_3LiFeO_8$ (Gibb 1985), similar to $\delta \approx -0.02$ mm s^{-1} for Sr_2FeO_4 (Adler *et al* 1995) and slightly smaller than those reported for Fe^{4+} in other perovskites, such as $SrFeO_3$ and $CaFeO_3$ ($\delta \approx 0.05$ mm s^{-1}, Nasu 1994, Adler *et al* 1995), $(La_{1-x}Sr_x)FeO_{3-y}$ ($\delta \approx 0.07$–0.10 mm s^{-1}, Dann *et al* 1994), $Sr(Fe_xZr_{1-x})O_{3-y}$ ($0 \leqslant x \leqslant 0.24$, $-0.07 \leqslant \delta \leqslant -0.04$ mm s^{-1}, Wyss *et al* 1997). In the case of $SrFeO_{3-y}$, and due to the complexity of the spectra, Gibb (1985) concluded that the spectral components could not be attributed to well defined oxidation states. Later, and based on a high-temperature Mössbauer study, Fournès *et al* (1987) reported that the room temperature δ of Fe^{4+} in $SrFeO_{2.75}$ is ≈ -0.13 mm s^{-1} and in $SrFeO_{2.83} \approx 0.03$ mm s^{-1}. Extensive discussions may be found concerning the typical values of δ and B_{hf} observed for Fe^{4+} (Gibb 1985). Particularly δ for this oxidation state is expected to be lower than the range of typical values measured for Fe^{3+} since the lower d-electron density corresponds to a weaker shielding effect of the inner s electrons and, consequently, an increase of the electron density at the Fe nucleus.

Values of B_{hf} within the range 53–40 T such as those found for $CaFe_{0.6}Ti_{0.4}O_{3-y}$ (C) at 10 K (table 2) are typical for high-spin Fe^{3+} with five unpaired electrons, the lower values being observed for Fe^{3+} in tetrahedral coordination. The increased covalency of Fe^{3+}–O bonds in tetrahedral cordination as compared to octahedral coordination is reflected in lower δ and B_{hf}. High-spin Fe^{4+} with only four unpaired electrons has lower magnetic moments than high-spin Fe^{3+}, with five unpaired d-electrons, and therefore also lower B_{hf}. Values of B_{hf} in the range 28–33 T have been reported for Fe^{4+} in $SrFeO_{3-y}$ or $La_{1-x}Sr_xFeO_{3-y}$ perovskites (Takano *et al* 1988, Dann *et al* 1994) or 25–33 T in Sr_2FeO_4 (Adler *et al* 1995). The assignment of the three magnetic splittings fitted to the $CaFe_{0.6}Ti_{0.4}O_{3-y}$ (C) at 10 K (figure 5 and table 2) to CN6-Fe^{3+}, CN4-Fe^{3+} and Fe^{4+} is confirmed by the excellent agreement of the estimated I with those of the corresponding quadrupole doublets in the 295 K spectrum (cf tables 1 and 2). The diversity of surroundings of CN6-Fe^{3+}, analysed by two quadrupole doublets in the 295 K spectrum, is reflected in the 10 K spectrum by the very large widths of the peaks of the corresponding magnetic sextet.

Both in this case and in the $CaFe_{0.2}Ti_{0.8}O_{3-y}$ (C) one, the increase in δ due to the second order Doppler shift is the same, within experimental error, for Fe^{3+} in the three different types of coordination but seems a little smaller for Fe^{4+}.

3.4. Comparison of δ and Δ of Fe^{3+} in the totally reduced and in the Fe^{4+}-containing $CaFe_xTi_{1-x}O_{3-y}$

The δ and Δ values for the Fe cations in the same oxidation state and with the same coordination number are either equal, within experimental error, or vary consistently with composition and heat treatment (table 1). For both samples for which spectra at 10 K were taken the estimated parameters at 295 K and 10 K (table 2) are consistent too.

The only Fe^{3+} parameters which vary significantly with composition and heat treatment are the Δ of CN5-Fe^{3+} and CN6-Fe^{3+}. The largest variations are observed for Δ of CN6-Fe^{3+} (figure 6). Since two quadrupole doublets were assigned to CN6-Fe^{3+} for $x \geqslant 0.4$, values plotted in figure 6 for these compositions are the weighted averages of the estimated Δ for each doublet (table 1). The very low Δ values found for samples with $x = 0.05$ may be explained by the fact that these samples are those where the Fe/Ti cation disorder and concentration of anion vacancies are the lowest. Since only 5% of the Ti cations are replaced by Fe, most of the CN6-Fe^{3+} cations may be in an environment similar to that of Ti in $CaTiO_3$. Although $CaTiO_3$ and $CaFeO_3$ crystallize in different space groups, their crystal structures are closely related and the environment of Ti and Fe should be very similar. Moreover, the point symmetry of Fe in $CaFeO_3$ is lower than cubic but the asymmetry of the electric charge distribution around Fe^{3+} is not very large since the observed Δ is virtually zero (Nasu 1994). Similarly the Fe^{3+} replacing one Ti cation in $CaTiO_3$ are also expected to have a very small Δ, as observed in the $CaFe_{0.05}Ti_{0.95}O_{3-y}$ perovskites.
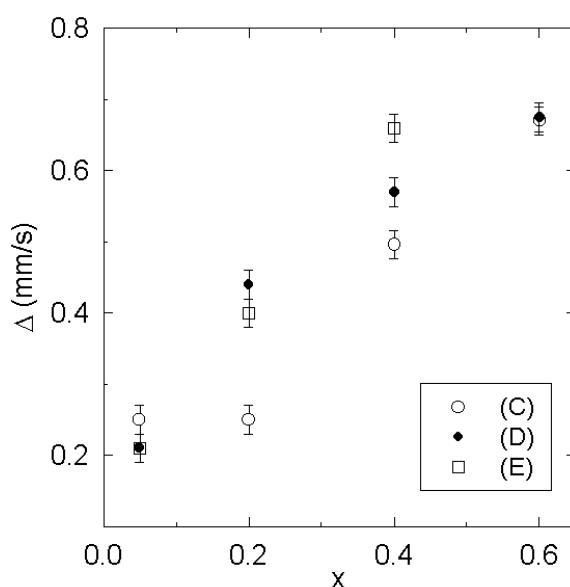

Figure 6. Dependence on composition and heat treatment of the quadrupole splitting of CN6-Fe^{3+} in the $CaFe_xTi_{1-x}O_{3-y}$ samples: (C) annealed in air at 1000 °C for 10 hours and slowly cooled down (5 °C min^{-1}), (D) annealed in air at 1000 °C for 10 hours and quenched, (E) annealed in argon at 1000 °C for 10 hours and slowly cooled (5 °C min^{-1}) in the same atmosphere.

It is well known that the hyperfine parameters of Fe are sensitive to differences in the second coordination sphere. This has been frequently observed and studied in spinel oxides (Osborne *et al* 1984, Waerenborgh *et al* 1990) and in silicates (Rancourt *et al* 1994), where different cations are present on the same crystallographic site, giving rise to different next-nearest (NN) neighbour cation arrangements. Fe cations with the same oxidation state and on the same crystallographic site but with different second coordination spheres show slightly different Δ. As already referred to by McCammon *et al* (2000) for the $CaFe_xTi_{1-x}O_{3-x/2}$, the probability of an octahedral site being adjacent to either a pentacoordinated or tetrahedral site increases with increasing number of oxygen vacancies. Since this produces a larger distortion of the charge distribution around CN6-Fe^{3+} a larger Δ should be observed as compared to the CN6-Fe^{3+} which only have octahedral sites as NN neighbours. Furthermore, the asymmetry of

the electric charge distribution around a CN6-Fe^{3+} with one or two Ti NN neighbours replaced by Fe cations should be larger than in the case where there are only Ti as NN neighbours. Therefore, the gradual replacement of Ti by Fe should also contribute to the increase of the CN6-Fe^{3+} Δ values as the Fe content in $CaFe_xTi_{1-x}O_{3-y}$ increases (figure 6).

A further effect is observed with increasing Fe content. Since the probability of the presence of CN6-Fe^{3+} with low Δ, similar to that measured for the $x = 0.05$ or 0.20 samples, is not yet negligible for $0.4 \leqslant x \leqslant 0.6$, a broadening of the peaks in the spectra is also observed when the average Δ increases with cation disorder. This broadening may increase with the Fe content until a distribution of unresolved quadrupole splittings has to be considered in the spectra analysis, as already described for spinel solid solutions (Osborne *et al* 1984, Waerenborgh *et al* 1990) where Fe cations have different NN neighbour cation arrangements. In the case of the $CaFe_xTi_{1-x}O_{3-y}$ ($x \neq 0$) perovskites the largest number of different cation arrangements with significant probabilities should be reached when the fraction Ti/Fe is close to unity in the second coordination sphere, i.e., when $x = 0.5$. As mentioned above, the coordination of the NN sites in these oxides also contributes to the differences in Δ and the probability of larger Δ also increases with x up to ≈ 0.4. This explains why considering two doublets for CN6-Fe^{3+} in the $0.4 \leqslant x \leqslant 0.6$ spectra significantly improves the fitting while for the $x \leqslant 0.2$ samples one doublet seems to be sufficient. For the Fe-richest samples the two doublets simulate the Δ distribution. For $x \leqslant 0.2$, where only the low Δ have a significant probability, the Δ distribution is narrow enough to be approximated by a single doublet with moderately broad peaks.

Differences among the average Δ of CN6-Fe^{3+} (figure 6) and CN5-Fe^{3+} for samples with the same composition but annealed in different conditions are either within experimental error or indicate larger Δ values for the samples with the higher Fe^{3+} contents. This is not surprising since the number of anion vacancies are expected to increase with Fe^{3+} content, and, as already referred to above, larger distortions of the charge distributions around the Fe^{3+} are expected with increasing number of anion vacancies.

Before concluding this section it should be emphasized that the present Fe^{3+} data are in agreement with those reported for the totally reduced $CaFe_xTi_{1-x}O_{3-x/2}$ samples with similar Fe contents (McCammon *et al* 2000). The main deviations between both data may be explained by different annealing temperatures or by the presence of Fe^{4+}.

The largest differences are found between the relative areas of the doublets of Fe^{3+} with different coordination in the totally reduced $CaFe_xTi_{1-x}O_{3-x/2}$ and in our (E) samples which have the lowest Fe^{4+} contents. The fact that the former $x = 0.05$ and $x = 0.20$ were equilibrated at 1000 °C and 1100 °C for more than 40 hours while the (E) samples were only kept at 1000 °C for 10 hours may explain these differences. The most striking disparity is however in the case of $x = 0.4$, where no CN5-Fe^{3+} was detected. The only sample from McCammon *et al* (2000) that has a similar Fe content, $x = 0.376$, was equilibrated at 1320 °C, a much higher temperature. Disorder of anion vacancies increases with temperature. Furthermore, referring to the phase diagram reported by McCammon *et al* (2000), while CN5-Fe^{3+} is expected to be found at 1320 °C for $x = 0.38$, at 1000 °C $x = 0.4$ samples already fall in the partially ordered domain where the number of CN5-Fe^{3+} is negligible.

In contrast to the totally reduced $CaFe_{0.05}Ti_{0.95}O_{2.97}$ (McCammon *et al* 2000) no CN4-Fe^{3+} was detected in our $x = 0.05$ samples. The peaks of the CN4-Fe^{3+} doublet should be observed at the low and high borders of the absorption envelope in the Mössbauer spectra (figures 2–4) due to the high Δ. Spectra of the $x = 0.05$ samples show no shoulders at those borders confirming that the fraction of CN4-Fe^{3+}, if different from zero, is below the detection limit. Our samples have Fe^{4+} and therefore a lower number of anion vacancies than the totally reduced ones. This may at least in part explain why in the totally reduced $CaFe_{0.05}Ti_{0.95}O_{2.97}$

samples 9–17% of the Fe^{3+}, depending on the heat treatment, are tetrahedrally coordinated (McCammon *et al* 2000).

3.5. Fraction of Fe in the 4+ state

In order to calculate the fraction of Fe in the Fe^{4+} state two issues have to be clarified: the relative values of the recoilless fractions of Fe^{3+} and Fe^{4+} and the possibility of different coordinations for Fe^{4+}.

Considering the similarity of the *I* estimated from the analyses of the spectra of the same composition taken at 295 K and 10 K (tables 1 and 2), similar recoilless factors for Fe^{4+} and Fe^{3+} may be assumed. McCammon *et al* (2000) reached a similar conclusion for the recoilless fractions of Fe^{3+} in different coordinations.

If three coordinations are assumed for Fe^{4+}, the total number of overlapping doublets in the spectra would increase to six. To the best of our knowledge no spectra with resolved peaks due to Fe^{4+} coordinated by 5 or 4 O^{2-} are available. Refinement of six overlapping doublets is virtually hopeless without any information on typical differences in δ and Δ of Fe^{4+} in distinct coordinations. On the other hand, as the charge densities of Fe^{4+} or Ti^{4+} are larger than that of Fe^{3+}, coordination by six O^{2-} is more favoured for Fe^{4+} than for Fe^{3+}, as concluded by McCammon *et al* (2000) in the case of Ti^{4+}. Although it is not possible to ascertain that no Fe^{4+} is pentacoordinated, it is reasonable to assume that the main contributions to the Mössbauer spectra arise from Fe^{4+} coordinated by six O^{2-}. The minor contributions from the remaining Fe^{4+} are probably negligible and may be, at least in part, contributing to the area of the Fe^{4+} doublets whenever they are significant. In fact in the samples $0.05 < x < 0.20$ (C), which have the largest *I* for Fe^{4+}, the peaks of the Fe^{4+} doublets are broader, probably accomodating contributions with slightly different δ and Δ.

Thus, in a first approximation, *I* of the quadrupole doublets may be considered proportional to the amount of the corresponding Fe species. Assuming electroneutrality and that there are no electrons trapped by anion vacancies, the number of these vacancies per formula unit, *N*, may be calculated as in McCammon *et al* (2000), considering that each Fe^{3+} corresponds to 1/2 anion vacancy (table 1). A confirmation of the reliability of the fraction of Fe in the 4+ state estimated by the present analysis of the Mössbauer spectra is the fact that the *N* in table 1 are in excellent agreement with the oxygen coulometric titration data reported for the same samples (Figueiredo *et al* 2001).

Considering the larger standard deviations for the doublets with $I \leqslant 5\%$, the estimated δ for Fe^{4+} are the same, within experimental error, for all the samples. The estimated Δ are also similar for most of the samples except those of the (D) and (E) $CaFe_{0.2}Ti_{0.8}O_{3-y}$ samples and of all the $CaFe_{0.05}Ti_{0.95}O_{3-y}$ samples, which are significantly larger (table 1). The preparation of $CaFe_xTi_{1-x}O_{3-y}$ ($0.05 \leqslant x \leqslant 0.6$) samples annealed under high oxygen pressures is now being undertaken. The relative areas of the contributions of Fe^{4+} to the Mössbauer spectra of these samples are expected to be higher than in those reported in the present study, allowing a better investigation of the dependence of the Fe^{4+} parameters on heat treatment and composition of these perovskite oxides.

3.6. Mössbauer spectra of the $Sr_{0.97}Fe_xTi_{1-x}O_{3-y}$

Except for $Sr_{0.97}Fe_{0.60}Ti_{0.40}O_{3-y}$ (B) at least two quadrupole doublets are necessary to analyse the Mössbauer spectra of the $Sr_{0.97}Fe_xTi_{1-x}O_{3-y}$ ($x = 0.20, 0.50$) samples (figure 7). Two models may however be considered. If the four peaks corresponding to the two quadrupole doublets are labelled as 1, 2, 3 and 4 in the order of increasing velocity, in model (a)
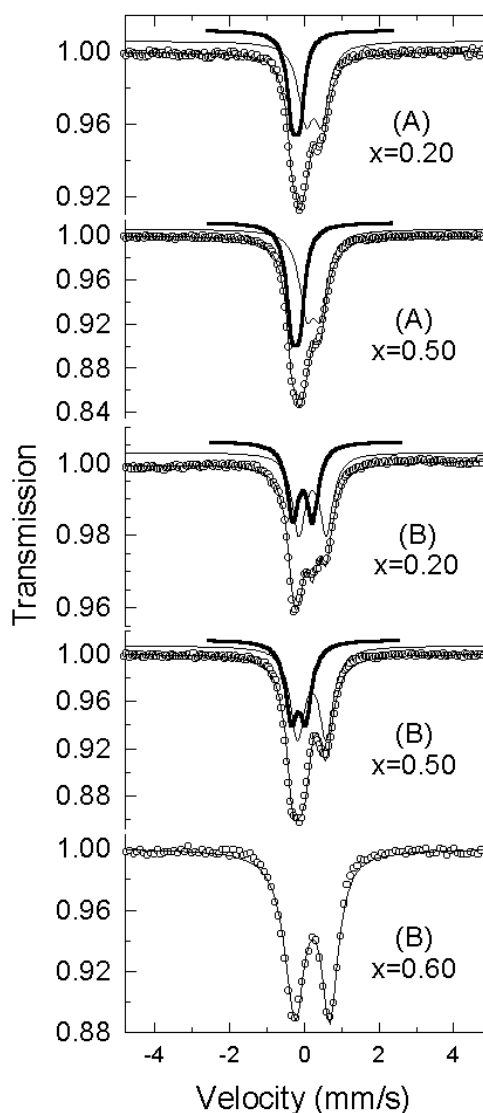
Figure 7. Mössbauer spectra taken at room temperature of the SrFe$_x$Ti$_{1-x}$O$_{3-y}$ (A) and (B) samples. Quadrupole doublets assigned to Fe^{4+} (thick line) and Fe^{3+} are shown slightly shifted, for clarity.

the quadrupole doublets are formed by coupling peaks 1–2 and 3–4 and in model (b) peaks 1–3 and 2–4. χ^2 values obtained for the final refined values are similar for both models.

Zheng *et al* (1990) obtained spectra for Sr$_{0.97}$Fe$_x$Ti$_{1-x}$O$_{3-y}$ (0.05 $\leqslant$ x $\leqslant$ 0.3) very similar to ours. They analysed them according to model (a) with a simplification: considering two single Lorentzians instead of two quadrupole doublets. Since the Δ we obtain from model (a) are always very small, this simplification does not significantly change the estimated δ. Therefore, our results obtained from model (a) agree with those reported by Zheng *et al* (1990) with estimated δ values for Fe^{3+} as high as 0.51 mm s^{-1} (it should be noticed that δ

reported by Zheng *et al* 1990 are given relative to the ^{57}Co source in Rh matrix). These values are very high for Fe^{3+} in oxides.

On the other hand, a single doublet is enough to analyse the $Sr_{0.97}Fe_{0.60}Ti_{0.40}O_{3-y}$ (B) spectrum, suggesting that in this perovskite all the Fe is present in the same oxidation state. Considering the value of δ estimated for this doublet (table 3), similar to those estimated for CN5-Fe^{3+} or CN6-Fe^{3+} in the Ca perovskites, it is very likely that only Fe^{3+} is present in $Sr_{0.97}Fe_{0.60}Ti_{0.40}O_{3-y}$ (B). The δ and Δ of the Fe^{3+} doublets estimated for the $Sr_{0.97}Fe_xTi_{1-x}O_{3-y}$ ($x = 0.20, 0.50$) samples according to model (b) are also consistent with those deduced for $Sr_{0.97}Fe_{0.60}Ti_{0.40}O_{3-y}$ (B). This suggests that δ for Fe^{3+} in the Sr perovskites is not unusually high as deduced from model (a) and that model (b), although statistically allowing an equally good analysis of the spectra as model (a), is more adequate from a physical point of view. Results obtained considering model (b) are therefore summarized in table 3. Given the estimated values of δ, the doublet with the lowest δ in $Sr_{0.97}Fe_xTi_{1-x}O_{3-y}$ ($x = 0.20$, 0.40) is attributed to Fe^{4+} (table 3). Significant fractions of Fe^{4+} in Fe-doped Sr titanates were already reported, such as in the optical study of Bieger *et al* (1992).

Table 3. Parameters estimated from the Mössbauer spectra of the $Sr_{0.97}Fe_xTi_{1-x}O_{3-y}$ samples with different heat treatments (A) and (B), as explained in the text. δ, Δ, Γ, I and N are as defined in table 1.

	x	Fe^{3+}				Fe^{4+}				N
		δ	Δ	Γ	I	δ	Δ	Γ	I	
(B)	0.20	0.34	0.73	0.42	55%	0.06	0.53	0.37	45%	0.055(2)
	0.50	0.31	0.76	0.47	62%	−0.06	0.38	0.36	38%	0.155(5)
	0.60	0.32	0.94	0.58	100%	—	—	—	—	0.300(6)
(A)	0.20	0.27	0.59	0.45	61%	−0.03	0.33	0.36	39%	0.061(2)
	0.50	0.24	0.57	0.47	60%	−0.04	0.33	0.37	40%	0.150(5)

Although the d and Δ estimated by models (a) and (b) are significantly different, the differences in the I estimated for the Fe^{3+} and Fe^{4+} doublets are small, only in two cases above the corresponding standard deviations. The trends in I variation with composition or heat treatment are therefore also the same. Furthermore another important feature, independent of the model used in the analysis of the spectra of the $Sr_{0.97}Fe_xTi_{1-x}O_{3-y}$ perovskites (figure 7), is the absence of a doublet with Δ as large as 1.5 mm s^{-1}, which suggests that, in contrast to $CaFe_xTi_{1-x}O_{3-y}$ ($0.20 \leqslant x \leqslant 0.60$), no significant amounts of CN4-Fe^{3+} are present in the Sr perovskites.

4. Conclusion

Mössbauer data show that Fe^{4+} is present in all the $CaFe_xTi_{1-x}O_{3-y}$ samples, even when annealed in Ar atmosphere at temperatures as high as 1000 °C for 10 hours. This treatment reduces the samples prepared in air, as expected, but does not eliminate all the Fe^{4+}. The relative amounts of Fe^{4+} and Fe^{3+} obtained from the Mössbauer data are in agreement with the oxygen losses deduced from oxygen coulometric titration (Figueiredo *et al* 2001), which confirms the reliability of the analyses of the Mössbauer spectra reported in this work. The estimated amounts of Fe^{4+} in this study as well as in $SrFeO_{3-y}$ (Wißmann and Becker 1996) suggest that major ionic defects in the Fe containing Ca or Sr perovskites are fully ionized oxygen vacancies, since electrons are trapped by Fe cations forming Fe^{3+} rather than by single ionized anion vacancies.

For each composition, $CaFe_xTi_{1-x}O_{3-y}$ samples slowly cooled in air show a higher Fe^{4+} content than those quenched, in agreement with the expectation that equilibrium of these oxides in air favours the loss of oxygen as the temperature increases.

In general, the relative amount of $CN4$-Fe^{3+} increases with the number of oxygen vacancies deduced from the Fe^{3+} contents (table 1). In the $x = 0.05$ samples no $CN4$-Fe^{3+} was detected. Therefore, in these samples with a very low concentration of oxygen vacancies, no significant amounts of vacancy pairs coordinated to the same Fe^{3+} were observed, suggesting that no clustering takes place and that they are randomly distributed. For $x = 0.2$ there are already Fe^{3+} cations with two anion vacancies in the first coordination sphere. However the $CN4$-Fe^{3+} are randomly distributed, since the presence of significant amounts of $CN5$-Fe^{3+} suggest that no long-range ordering was yet established. This conclusion is consistent with the orthorhombic structure revealed by powder XRD data (figure 1) for all the $x = 0.2$ samples, typical of the disordered $CaFe_xTi_{1-x}O_{3-y}$ structures (Grenier *et al* 1977).

The concentration of $CN4$-Fe^{3+} still increases with $x > 0.20$ and when it reaches the highest values no $CN5$-Fe^{3+} is observed. The powder x-ray diffractograms of the (E) and (D) $CaFe_{0.4}Ti_{0.6}O_{3-y}$ and of all the $CaFe_{0.6}Ti_{0.4}O_{3-y}$ (figure 1) consist of the pseudo-cubic pattern, which suggests long-range ordering of anion vacancies (Iwahara *et al* 1988, Alario-Franco *et al* 1983). Furthermore, according to the phase transition boundaries established by McCammon *et al* (2000) for the totally reduced $CaFe_xTi_{1-x}O_{3-x/2}$, the $x = 0.4$ samples above $1150\,^\circ$C and the $x = 0.6$ oxides are expected to have long-range ordering of anion vacancies. The $CaFe_{0.6}Ti_{0.4}O_{3-y}$ and the (E) and (D) $CaFe_{0.4}Ti_{0.6}O_{3-y}$ oxides prepared by us have low amounts of Fe^{4+}. Equilibrium and kinetics of ion diffusion should not be very different from those in the totally reduced oxides and it would not be surprising that they also have long-range ordering of anion vacancies, thus explaining the absence of $CN5$-Fe^{3+}.

It should be noticed that the absence of $CN5$-Fe^{3+} cannot be taken as a sure sign of long-range ordering of vacancies. XRD data (figure 1) reveal that $CaFe_{0.4}Ti_{0.6}O_{3-y}$ (C) with the highest Fe^{4+} fraction among the samples with the same composition is still disordered, although no $CN5$-Fe^{3+} is detected by Mössbauer spectroscopy. $CaFe_{0.4}Ti_{0.6}O_{3-y}$ (C) is however on the brink of ordering since heating at $1000\,^\circ$C reduces the amount of Fe^{4+} and induces this transition, as suggested by the XRD data of the quenched samples. Transmission electron microscopy and diffraction are however necessary to clarify the complex structure of these materials.

The absence of a doublet with Δ as large as 1.5 mm s^{-1}, characteristic of $CN4$-Fe^{3+} in the Ca perovskites, strongly suggests that in the Sr perovskites no ordering of anion vacancies takes place. This is consistent with the fact that while for $Sr_{0.97}Fe_xTi_{1-x}O_{3-y}$ substitution of Ti by Fe leads to a higher ionic conduction, in $CaFe_xTi_{1-x}O_{3-y}$ this is only observed up to small Fe concentrations $x \leqslant 0.20$ (Kharton *et al* 2001, Figueiredo *et al* 2001). The effect of a further increase of Fe content in the Ca perovskites is counterbalanced by an increasing degree of ordering revealed by higher fractions of $CN4$-Fe^{3+}. Trapping of oxygen vacancies with increasing x eventually leads to lower ionic conductivities and higher activation energies for ionic transport.

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