

# The High Temperature Properties of Tin-Doped Magnetite

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Materials of composition  $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$  ( $x = 0.1$  and  $0.2$ ) have been prepared. The  $^{119}\text{Sn}$  Mössbauer spectra show a magnetic hyperfine field demonstrating an interaction between  $\text{Fe}^{3+}$  ions on the tetrahedral A sites and  $\text{Sn}^{4+}$  ions on the octahedral B sites of  $\text{Fe}_3\text{O}_4$ .  $^{57}\text{Fe}$  Mössbauer spectroscopy shows the Curie temperatures of the materials to be lower than those of magnetite and related titanomagnetites. The  $^{57}\text{Fe}$  and  $^{119}\text{Sn}$  Mössbauer spectra also show the exsolution of tin from the tin-doped magnetite after prolonged treatment at elevated temperatures. © 1996 Academic Press, Inc.

## INTRODUCTION

Minerals known as titanomagnetite,  $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ , may be considered as a solid solution series between  $\text{Fe}_3\text{O}_4$  (magnetite) and  $\text{Fe}_2\text{TiO}_4$  (ulvöspinel) and are common constituents of a wide variety of igneous rocks. These oxides are of considerable interest because of their magnetic properties and also the time–temperature-dependent phase transformations which they undergo, such as the subsolvus exsolution of  $\text{FeTiO}_3$  (ilmenite) from titanomagnetite, which results in thin lamellae of ilmenite being formed at the boundaries of nearly titanium-free magnetite domains. The dynamics of the exsolution process are poorly understood. However, recent studies of both magnetite and  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite) with low titanium concentrations have provided evidence for the influence of titanium impurities on the stability of maghemite at high temperatures (1).

To examine the magnetite system with low levels of impurities in more detail we have investigated the material in which tin is substituted for iron. Some initial studies of tin-doped magnetite (2, 3) described the materials as ferrimagnets; the materials of composition  $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$  ( $x < 0.58$ ) were considered to adopt the same inverse spinel structure as that observed in titanomagnetite. Assuming a similarity between the titanium and tin species, there are some advantages in using tin, since both iron and tin have a Mössbauer isotope such that the phase transformations and magnetic properties at high temperature are amenable

to examination *in situ* by both  $^{119}\text{Sn}$  and  $^{57}\text{Fe}$  Mössbauer spectroscopy.

## EXPERIMENTAL

Compounds of composition  $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$  were prepared by heating stoichiometric quantities of powdered tin(IV) oxide, iron(III) oxide, and metallic iron in sealed evacuated quartz ampoules at  $900^\circ\text{C}$  for 24 hr and allowing the product to cool in the furnace.

The furnace designed for the *in situ* study of phase transitions has been described in detail elsewhere (4). The central part of the furnace consists of a highly polished internal surface of an aluminum elliptical cylinder. The semiaxes of the ellipse are 60 and 70 mm and the height of the chamber is 40 mm. The heat source, a 250 W halogen lamp, is placed at one focal point of the ellipse and a cylindrical black-painted copper tube acting as a heat absorber is placed at the other focal point. The main principles are illustrated schematically in Fig. 1, which shows a section along the major axis of the ellipse parallel to the cylindrical axis. The copper tube is 30 mm long and has an outer diameter of 20 mm. The sample is placed inside the copper tube between two 0.5 mm thick disks of beryllium oxide. The gamma rays enter and leave the chamber through aluminized Mylar windows. The temperature of the tube is monitored by a thermocouple with an electronic zero-point reference. The signal from the thermocouple controls the temperature by modulating the cycle of the power of the lamp. The power regulation maintains the sample at constant temperature within  $\pm 0.3\text{K}$  over a 24 hr run.

The  $^{57}\text{Fe}$  Mössbauer spectra were recorded from powdered samples with a constant acceleration spectrometer and a ca. 400 MBq  $^{57}\text{Co}/\text{Rh}$  source. The sample thickness was 50–80  $\text{mg}/\text{cm}^2$ . The line width (FWHM) of the calibration spectrum was 0.24 mm/sec. The chemical isomer shift data are quoted relative to the centroid of the metallic iron spectrum at room temperature. The  $^{119}\text{Sn}$  Mössbauer spectra were recorded at 298 K using a  $\text{Ca}^{119}\text{SnO}_3$  source and a microprocessor controlled Mössbauer spectrometer. The chemical isomer shift data are quoted relative to tin(IV) oxide.

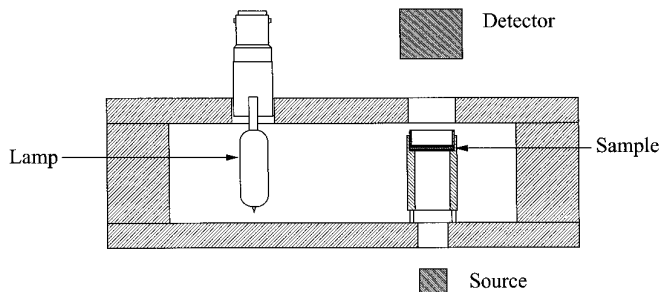


FIG. 1. A schematic representation of the elliptical furnace along the major axis of the ellipse.

## RESULTS AND DISCUSSION

The X-ray powder diffraction patterns recorded from materials of composition  $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$  ( $x = 0.1$  and  $0.2$ ) confirmed the formation of a monophasic product with a structure related to that of magnetite. No evidence for a discrete tin(IV) oxide phase was observed. The lattice parameters of materials of the type  $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$ , together with data on titanomagnetite (5), are collected in Fig. 2. The variation in the lattice parameters with increasing tin content is larger than that observed in the analogous titanomagnetite system and reflects the larger size of  $\text{Sn}^{4+}$  in sixfold oxygen coordination (69 pm) as compared to  $\text{Ti}^{4+}$  (61 pm).

The  $^{119}\text{Sn}$  Mössbauer spectrum recorded from the material of composition  $\text{Fe}_{2.9}\text{Sn}_{0.1}\text{O}_4$  (Fig. 3) showed a sextet pattern with a hyperfine field of 20.9 T at the  $\text{Sn}^{4+}$  ions (for the compound  $\text{Fe}_{2.8}\text{Sn}_{0.2}\text{O}_4$  the field is 19.1 T), which we interpret in terms of the supertransfer of spin density via oxygen from the  $\text{Fe}^{3+}$  ions on the tetrahedral A sites to the  $\text{Sn}^{4+}$  ions on the octahedral B sites of  $\text{Fe}_3\text{O}_4$  (6, 7).

Five  $^{57}\text{Fe}$  Mössbauer spectra recorded *in situ* from the material of composition  $\text{Fe}_{2.9}\text{Sn}_{0.1}\text{O}_4$  following heating over

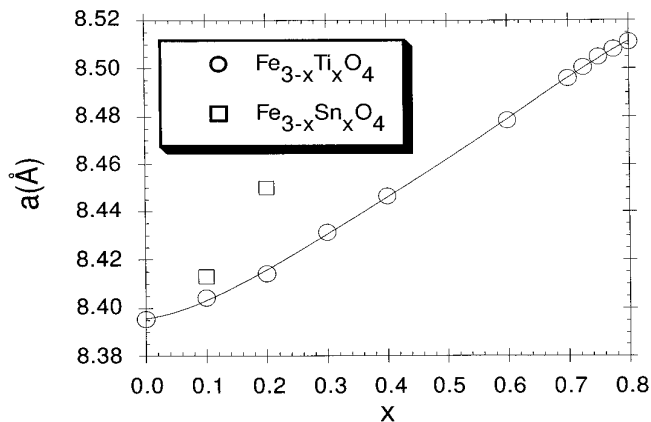


FIG. 2. Variation of unit-cell parameters with composition for titanomagnetite and tin-doped magnetite.

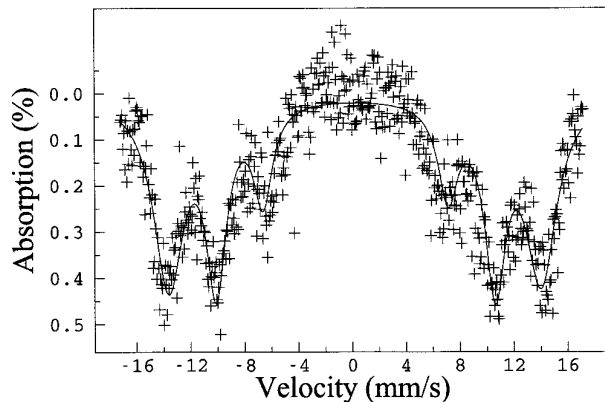


FIG. 3.  $^{119}\text{Sn}$  Mössbauer spectrum recorded from  $\text{Fe}_{2.9}\text{Sn}_{0.1}\text{O}_4$  at room temperature.

a range of temperatures *in vacuo* (pressure ca. 0.2 Pa) are collected in Fig. 4. The Mossbauer parameters are collected in Table 1. The spectrum recorded at 300 K (Fig. 4a) showed a magnetic splitting similar to that observed in the spectrum recorded from titanomagnetite of similar compo-

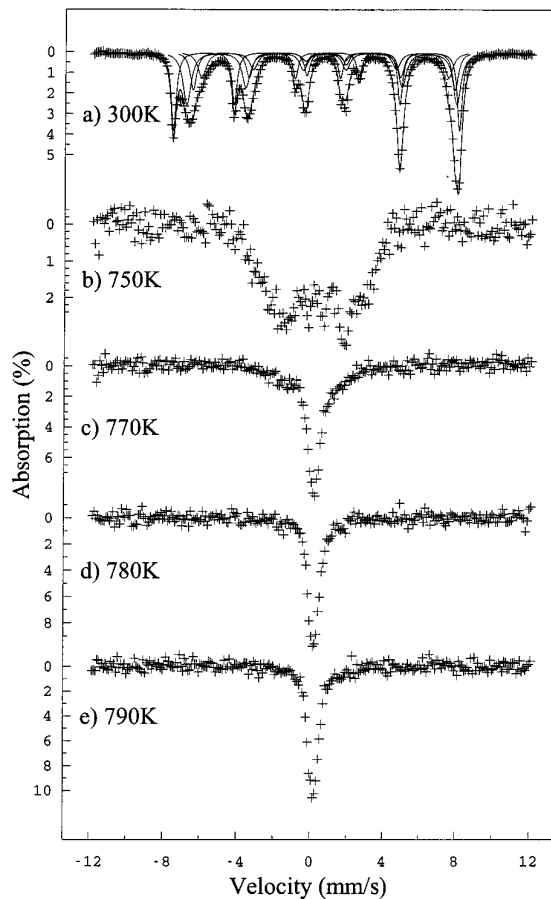


FIG. 4.  $^{57}\text{Fe}$  Mössbauer spectra recorded from  $\text{Fe}_{2.9}\text{Sn}_{0.1}\text{O}_4$  at different temperatures, *in vacuo*.

TABLE 1  
 $^{57}\text{Fe}$  Mössbauer Parameters for Each of the Four Sextets in Spectra Recorded from  $\text{Fe}_{2.9}\text{Sn}_{0.1}\text{O}_4$   
 and  $\text{Fe}_{2.8}\text{Sn}_{0.2}\text{O}_4$  at Different Temperatures

x	Temp. (K)	A sextet			B1 sextet			B2 sextet			C sextet		
		B (T)	$\delta$ (mm/sec)	Area (%)	B (T)	$\delta$ (mm/sec)	Area (%)	B (T)	$\delta$ (mm/sec)	Area (%)	B (T)	$\delta$ (mm/sec)	Area (%)
0.1	293	48.6	0.30	30	45.8	0.62	31	44.5	0.71	18	42.0	0.73	17
0.1	480	44.1	0.16	29	40.3	0.52	36	38.8	0.54	16	36.2	0.58	14
0.1	580	40.4	0.09	26	36.4	0.42	29	34.8	0.44	23	31.3	0.49	17
0.1	680	34.8	0.04	20	31.0	0.35	28	28.5	0.35	25	24.4	0.48	21
0.1	750	18			18			16			15		
0.1	770	11			11			10			9		
0.1	780	0			0			0			0		
0.2	293	47.9	0.30	23	45.2	0.58	31	43.4	0.75	24	40.2	0.78	19
0.2	480	42.3	0.16	21	38.6	0.48	30	36.6	0.49	22	34.1	0.60	24
0.2	573	38.4	0.09	20	34.7	0.40	30	32.0	0.44	21	28.9	0.45	25
0.2	630	30.4			27.5			24.0			20.2		
0.2	660	26.5			23.4			20			15.8		
0.2	670	24.7			21			18			13.5		
0.2	680	13			12			8			5		
0.2	690	7			6			5			4		
0.2	700	0			0			0			0		

Note. The quadrupole splitting is less than  $\pm 0.01$  mm/sec for all the spectra and is not shown in the table. For the spectra near the Curie temperature only the hyperfine field can be accurately determined.

sition (8). The maintenance of charge balance resulting from the replacement of  $\text{Fe}^{3+}$  by  $\text{Sn}^{4+}$  is reflected in the increase in chemical isomer shift for the B<sub>2</sub> and C sextets as compared with the data recorded from pure magnetite. The spectrum recorded at 750 K (Fig. 4b) showed the magnetic hyperfine fields of the sextets to be smaller. The absence of the doublets characteristic of paramagnetic  $\text{Fe}^{3+}$  species confirmed magnetic order at this temperature. On further heating to 770 K the broad line  $^{57}\text{Fe}$  Mössbauer spectrum (Fig. 4c) showed the onset of the collapse of the sextet patterns indicative of most of the tin-doped magnetite being in the paramagnetic state and the material being within a few degrees of the Curie temperature. The  $^{57}\text{Fe}$  Mössbauer spectra recorded at 780 and 790 K (Figs. 4d and 4e) showed the material to be completely paramagnetic. The results demonstrate that the magnetic transition takes place over an interval of 30 K. By fitting the magnetic fields at different temperature (Table 1) to the relationship  $B(T) = B_0(1 - T/T_c)\beta$ , where  $B_0$  is the magnetic hyperfine field at  $T = 0$  K, and  $\beta$  is 0.3, the magnetic transition can be restricted to an interval of ca. 10 K. We conclude therefore that, for the compound  $\text{Fe}_{2.9}\text{Sn}_{0.1}\text{O}_4$ ,  $T_c$  is  $770 \pm 5$  K, 70 K lower than the Curie temperature of pure magnetite (9). The sharpness of the transition is consistent with the high degree of homogeneity of the sample as indicated by X-ray powder diffraction.

The  $^{57}\text{Fe}$  Mössbauer spectra recorded from the compound  $\text{Fe}_{2.8}\text{Sn}_{0.2}\text{O}_4$  showed the Curie temperature to be

$680 \pm 10$  K. The lowering of the Curie temperature with increasing tin content is somewhat greater than that recorded from related titanomagnetite systems (10).

Although the fitting procedure for the  $^{57}\text{Fe}$  Mössbauer spectra recorded from oxidic spinels has been considered in detail (11), the fitting of spectra recorded from tin-doped magnetite has received only limited attention (7, 12, 13). The general conclusion is that a single sextet should be assigned to the ferric iron at the tetrahedral site, which is usually called the A-site. For the octahedral B-site the matter is more complicated due to the unresolved system of lines. For pure magnetite the B-site magnetic interaction can be best interpreted in terms of two sextets of slightly different hyperfine fields (9). Spectra recorded from a titanomagnetite, analogous to the system described here, have been fitted with three sextets (8), with one sextet being attributed to the ferric iron at the A-site, a sextet of broader line-width being associated with the ferric/ferrous iron at the B-site, and finally a third sextet, the "C-sextet," of broad linewidth and smaller hyperfine field being attributed to the superposition of spectra from iron ions of locally varying energy states caused by the substitution of  $\text{Ti}^{4+}$ .

In the work presented here we have applied both the procedure involving three sextets (8) and the procedure where the B-sextet is split into two sextets (9). On the basis of superior chi-squared values, internal consistency between spectra at different temperatures, and visual fits

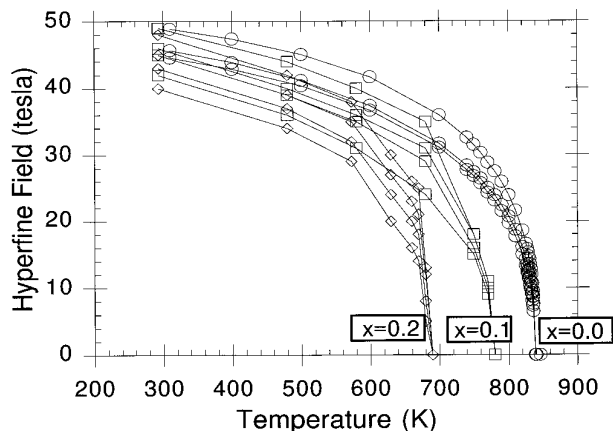


FIG. 5. Variation of the magnetic hyperfine fields with temperature for  $\text{Fe}_{2.9}\text{Sn}_{0.1}\text{O}_4$  and  $\text{Fe}_{2.8}\text{Sn}_{0.2}\text{O}_4$ . For comparison these data are plotted together with data on pure magnetite (9).

of the spectra, we conclude that the data recorded here are best fitted to four sextets. We associate these sextet patterns with (i) the interactions of  $\text{Fe}^{3+}$  on tetrahedral sites, assigned to the A-sextet; (ii)  $\text{Fe}^{2+}/\text{Fe}^{3+}$  hopping on octahedral sites which gives rise to two sextets (similar to the two B-sextets described previously) (9) and in this paper are assigned as B1 and B2; (iii) the interaction of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  on octahedral sites with tin ions, which gives the sextet pattern described as the C-sextet.

We therefore envisage the occupation by  $\text{Sn}^{4+}$  of the octahedral sites in  $\text{Fe}_3\text{O}_4$ . The magnitudes of the hyperfine magnetic fields for all the sextets in materials of composition  $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$  ( $x = 0.1$  and  $x = 0.2$ ) measured from room temperature to the Curie temperatures are collected with the other Mössbauer parameters in Table 1. The results are depicted graphically in Fig. 5, which shows the four hyperfine magnetic fields characterizing each sample to follow a similar pattern and, for each compound, all four sextets can be seen to collapse at the Curie temperature.

The spectra also show a doublet, accounting for a few percent of the total area, with Mössbauer parameters similar to the iron silicate of composition  $\text{Fe}_2\text{SiO}_4$  called fayalite which may result from reaction of the iron with the quartz ampoule.

It should be noted that the spectra used for determining the Curie temperature were recorded over minimal measuring times to avoid the effect of exsolution. In the absence of exsolution the fitting procedure is rather straightforward due to the well defined change from sextets to doublets at  $T_c$ . However, a different situation pertains when exsolution and magnetic phase transitions occur simultaneously in the sample. The stability of compounds of the type  $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$  at elevated temperatures was examined by recording each  $^{57}\text{Fe}$  Mössbauer spectrum over

28–48 hr at the higher temperatures *in vacuo*. The results recorded from the compound  $\text{Fe}_{2.9}\text{Sn}_{0.1}\text{O}_4$  are shown in Fig. 6.

The spectra recorded between 300 and 680 K were all amenable to fitting to four sextet patterns characteristic of tin-doped magnetite as described above. The variation of the magnetic hyperfine fields with temperature followed the same trend as shown in Fig. 5. The spectrum recorded at 730 K after 28 hr gave an additional sextet component in the Mössbauer spectrum with a magnetic hyperfine field of ca. 36 T which can be associated (9) with  $\text{Fe}^{3+}$  occupying the tetrahedral A sites of pure magnetite,  $\text{Fe}_3\text{O}_4$ . The spectrum recorded at 750 K showed a component similar to that of magnetite together with a component characteristic of the tin-doped magnetite but in which the field had collapsed to ca. 12 T. The X-ray powder diffraction pattern showed peaks attributable to tin dioxide. No evidence was found for the exsolution of  $\text{Fe}_2\text{SnO}_4$  or any other iron–tin oxide. The results are consistent with the segregation of tin from tin-doped magnetite at elevated temperatures.

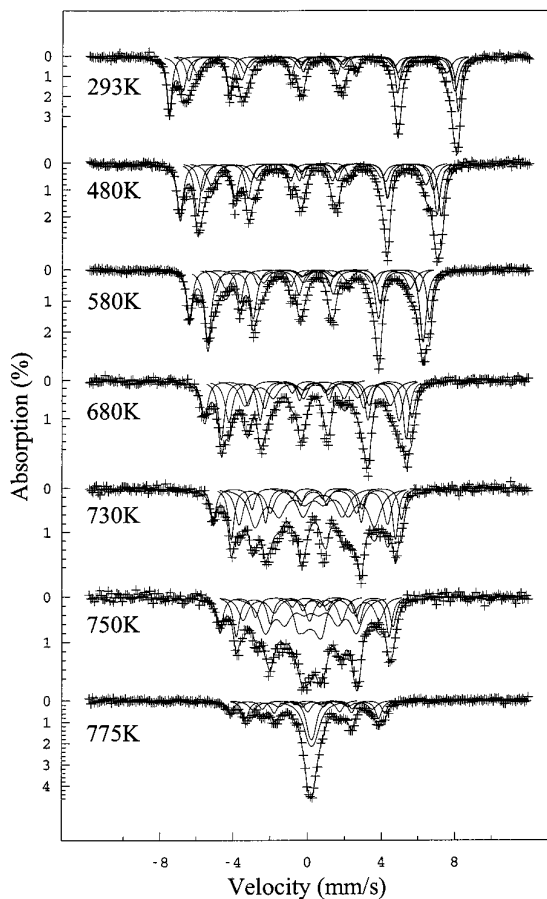


FIG. 6.  $^{57}\text{Fe}$  Mössbauer spectra recorded from  $\text{Fe}_{2.9}\text{Sn}_{0.1}\text{O}_4$  at elevated temperatures, *in vacuo*.

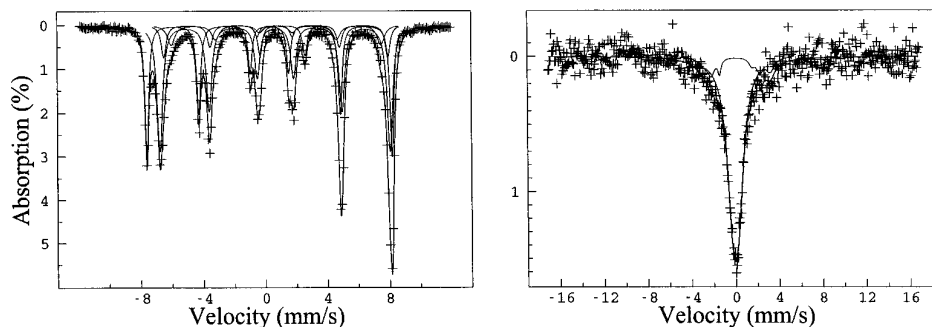


FIG. 7.  $^{57}\text{Fe}$  and  $^{119}\text{Sn}$  Mössbauer spectra recorded from  $\text{Fe}_{2.9}\text{Sn}_{0.1}\text{O}_4$  at room temperature after treatment at 800 K (24 hr).

We estimate an oxygen partial pressure of  $10^{-6}$  to  $10^{-7}$  atm, which would be sufficient to oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  during the exsolution process. The spectrum recorded at 775 K, i.e., 5 K above  $T_c$ , showed two distinct patterns, one corresponding to the paramagnetic tin-doped magnetite and the other to the double sextet pattern of pure magnetite. Finally, the  $^{57}\text{Fe}$  and  $^{119}\text{Sn}$  Mössbauer spectra recorded at room temperature from the sample after further heat treatment at 800 K (24 hr). (Fig. 7) are characteristic of magnetite and tin dioxide. A comparison of these spectra with those recorded before thermal treatment (Figs. 3 and 4a) clearly demonstrates the transformation of the tin-doped magnetite into magnetite and tin dioxide and confirms the X-ray diffraction evidence for tin dioxide being the exsolved phase.

### CONCLUSION

The structural and magnetic properties of  $\text{Fe}_{3-x}\text{Sn}_x\text{O}_4$  determined by  $^{57}\text{Fe}$  and  $^{119}\text{Sn}$  Mössbauer spectroscopy resemble those previously reported for titanomagnetite at least for low values of  $x$ . The high temperature properties of tin-doped magnetite investigated *in situ* by Mössbauer spectroscopy are characterized by a significant lowering of the Curie temperature which is greater than that observed in titanomagnetite with similar values of  $x$ . Long term treatment at elevated temperature results in the exsolution of tin dioxide from the tin-doped magnetite.

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