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## Formation of Oxide Phases in the System $\text{Fe}_2\text{O}_3\text{--Sm}_2\text{O}_3$

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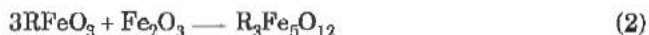
Formation of oxide phases in the system  $\text{Fe}_2\text{O}_3\text{--Sm}_2\text{O}_3$  was investigated. The samples were prepared by the solid state reactions at two molar ratios of  $\text{Fe}_2\text{O}_3$  and  $\text{Sm}_2\text{O}_3$ . The following oxide phases were detected by X-ray diffraction:  $\text{C--Sm}_2\text{O}_3$ ,  $\text{B--Sm}_2\text{O}_3$ ,  $\alpha\text{--Fe}_2\text{O}_3$ ,  $\text{SmFeO}_3$  and  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$ . For the molar ratio  $\text{Fe}_2\text{O}_3 : \text{Sm}_2\text{O}_3 = 1 : 1$ ,  $\text{SmFeO}_3$  was detected as one of the oxide phases at temperatures up to 800 °C and as a single phase at 1000 °C and higher temperatures. For the molar ratio  $\text{Fe}_2\text{O}_3 : \text{Sm}_2\text{O}_3 = 5 : 3$ ,  $\text{SmFeO}_3$  was the intermediate phase up to 1200 °C, and  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$  was found as a single phase at 1300 °C. The oxide phases containing iron ions were characterized by  $^{57}\text{Fe}$  Mössbauer spectroscopy. The formation of  $\text{SmFeO}_3$  and  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$  phases, as end products of the solid state reactions in the system  $\text{Fe}_2\text{O}_3\text{--Sm}_2\text{O}_3$ , was also investigated by IR spectroscopy.

### INTRODUCTION

Rare earth ferrites with perovskite or garnet structures are generally considered to be reaction products between  $\text{R}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , R being a rare earth. At high temperatures,  $\text{R}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  react to produce rare earth orthoferrite in the reaction:



In the presence of additional  $\text{Fe}_2\text{O}_3$ , garnet type ferrite can be also produced at high temperatures:



These mixed metal oxides can be prepared in laboratories by the use of different methods. The coprecipitation method involves precipitation of mixed metal hydroxides,  $R(OH)_3/Fe(OH)_3$ , and thermal treatment of the hydroxide coprecipitate. The sol-gel procedure is very useful for the preparation of oxide particles with a narrow size distribution and defined morphology. However, when two or more metal cations are hydrolyzed simultaneously from their corresponding alkoxides, it is difficult to monitor the particle size distribution and morphology because of different hydrolysis rates of metal cations. Rare earth ferrites with a perovskite or garnet structure can be also prepared by simple thermal decomposition of proper mixtures of inorganic or metal-organic salts, or by pyrolysis of aerosol droplets containing  $R^{3+}$  and  $Fe^{3+}$  cations. Solid state reactions of the corresponding metal oxides, crystal growth from the melt and film growth on different substrates have been also used to produce mixed metal oxides.

Bachiorri<sup>1</sup> investigated the synthesis of yttrium iron garnet,  $Y_3Fe_5O_{12}$ , using the following procedure: a) denitration of the mixture  $Y(NO_3)_3 \times 6H_2O + Fe(NO_3)_3 \times 9H_2O$  with organic reducing agents, b) chemical coprecipitation of mixed hydroxides  $Y(OH)_3/Fe(OH)_3$ , and c) the solid state reaction between  $Y_2O_3$  and  $Fe_2O_3$  at 1300 °C. The reaction products obtained by procedures (a) and (b) crystallized at 730 °C. The best reproducibility of the particle size and morphology was achieved by chemical coprecipitation, as an experimental method.

Kingsley *et al.*<sup>2</sup> described the preparation of yttrium aluminium garnet,  $Y_3Al_5O_{12}$ , by the combustion of a mixture of  $Y(NO_3)_3 \times 6H_2O$ ,  $Al(NO_3)_3 \times 9H_2O$  and carbonyldrazide, which were previously dissolved in a minimum quantity of water. They also prepared  $Y_3Al_5O_{12}$  by the combustion of a mixture of  $Y(NO_3)_3 \times 6H_2O$ ,  $Al(NO_3)_3 \times 9H_2O$  and urea. The garnet,  $Y_3Al_5O_{12}$ , is isostructural with  $Y_3Fe_5O_{12}$ .

The mixture of  $Y_2O_3$  and  $Fe_2O_3$  with molar ratio 3 : 5 was sintered and heated at a 800 to 1400 °C temperature range for 3 to 12 hours in air.<sup>3</sup>  $YFeO_3$  was detected by X-ray diffraction in all samples prepared at temperatures up to 1300 °C. The final product was  $Y_3Fe_5O_{12}$ . The relative amounts of oxide phases depended on the final temperature of heating and, to a much smaller extent, on the time of heating.

Pyrolysis of aerosol droplets containing metal cations is a relatively simple technique for rapid preparation of mixed metal oxides. This technique<sup>4</sup> was used in the preparation of gadolinium iron garnet,  $Gd_3Fe_5O_{12}$ . Polydispersed solid spheres of 0.05 – 2 µm in size were obtained. The  $Gd_3Fe_5O_{12}$  yield was ≈ 95% in weight.

Mössbauer spectroscopy found an important application in the characterization of rare earth orthoferrites and garnets.<sup>5</sup> The Mössbauer spectra of the rare earth orthoferrites appeared as far back as in the sixties.<sup>6-10</sup> The Mössbauer spectra of the lanthanide orthoferrites show hyperfine magnetic splitting at room temperature. The hyperfine magnetic field, HMF, extrapolated to 0 K, decreases regularly with the atomic number of lanthanide cation from 564 kOe for  $LaFeO_3$  to 545.5 kOe for  $LuFeO_3$ .<sup>11</sup>

Michalk and Thiel<sup>12</sup> used Mössbauer spectroscopy to investigate the substitution of  $Fe^{3+}$  with  $Al^{3+}$  ions in the yttrium iron garnet,  $Y_3Fe_{5-x}Al_xO_{12}$ ,  $x = 0, 0.25$  or  $0.65$ . Mössbauer spectroscopy was also used<sup>13</sup> in the study of the double-substituted yttrium iron garnet,  $Y_{3-x}Gd_xFe_{5-y}Al_yO_{12}$  ( $x = 0.60$  to  $1.2$ ,  $y = 0.10$  to  $0.85$ ).

On the basis of Conversion Electron Mössbauer Spectra (CEMS), Okuda *et al.*<sup>14</sup> calculated the HMF values for  $Bi_3Fe_5O_{12}$  (421 kOe for 24 d-sites and 491 kOe for 16 a-sites) and for  $Y_3Fe_5O_{12}$  (391 kOe for 24 d-sites and 486 kOe for 16 a-sites). Garnet

bubble films,  $(\text{Y,Sm,Ca,Tm})_3(\text{Fe,Ge})_5\text{O}_{12}$ , grown on GGG (gadolinium gallium garnet) substrate and irradiated with 60 keV  $\text{H}_2^+$  ions, showed changes in the corresponding CEMS.<sup>15</sup>

The formation of the oxide phases in the system  $(1-x)\text{Fe}_2\text{O}_3 + x\text{Gd}_2\text{O}_3$ ,  $0 \leq x \leq 1$ , was investigated by XRD and Mössbauer spectroscopy.<sup>16</sup> The samples were prepared using the chemical coprecipitation procedure. By XRD measurements, the distribution of oxide phases,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{GdFeO}_3$ ,  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$  and  $\text{Gd}_2\text{O}_3$ , was determined as a function of  $x$ . New accurate crystallographic data for  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$  were obtained. The temperatures of the formation of  $\text{GdFeO}_3$  and  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$  were higher in the case of solid state synthesis<sup>17</sup> than in the case of chemical coprecipitation.<sup>16</sup> The formation of oxide phases in an analogous system,  $\text{Fe}_2\text{O}_3\text{-Eu}_2\text{O}_3$ , was also investigated.<sup>18</sup>

Physical properties of garnets, with rare-earth sites fully or partially occupied by  $\text{Sm}^{3+}$  ions, were previously subjected to several investigations<sup>19,20</sup> because of their possible application in advanced technologies. In this study, we focussed our attention on the formation of oxide phases in the system  $\text{Fe}_2\text{O}_3\text{-Sm}_2\text{O}_3$ . The characteristic properties of the samples were investigated by combined use of X-ray diffraction,  $^{57}\text{Fe}$  Mössbauer spectroscopy and IR spectroscopy.

## EXPERIMENTAL

The chemicals were obtained from Ventron. The content of  $\text{Sm}_2\text{O}_3$  in the starting chemical was determined after its calcination and removal of  $\text{H}_2\text{O}$  and carbonates. Proper weights of oxide powders were mixed and mechanically activated in a planetary mill (Fritsch). The obtained powder was pressed into tablets (Carver press) and heated in air. An LKO II furnace with Kanthal heaters was used for temperatures above 1000 °C. Experimental conditions for the preparation of samples are given in Table I. Two molar ratios,  $\text{Fe}_2\text{O}_3 : \text{Sm}_2\text{O}_3 = 1 : 1$  and  $5 : 3$ , were used for the preparation of the  $\text{Fe}_2\text{O}_3\text{-Sm}_2\text{O}_3$  mixed oxides.

X-ray diffraction (XRD) powder patterns were taken at room temperature using a counter diffractometer with monochromatized  $\text{Cu K}\alpha$  radiation (Philips diffractometer, proportional counter and graphite monochromator).

The  $^{57}\text{Fe}$  Mössbauer spectra were recorded using a commercial spectrometer (WISSEL). Mathematical deconvolution of the spectra was performed using the SIRIUS program.

All IR spectra were recorded by an IR spectrometer 580B (Perkin-Elmer). The specimens were pressed into discs using spectroscopically pure KBr. The IR spectra are presented as relative transmittance versus the wave number ( $\text{cm}^{-1}$ ).

## RESULTS AND DISCUSSION

The results of XRD phase analysis of the samples are given in Table II and the crystallographic data for  $\text{Sm}(\text{OH})_3$ ,  $\text{C-Sm}_2\text{O}_3$  (body-centered cubic),  $\text{B-Sm}_2\text{O}_3$  (monoclinic),  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{SmFeO}_3$  and  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$  are given in Table III. XRD analysis of the  $\text{Sm}_2\text{O}_3$ , supplied by Ventron, showed that this chemical was actually a mixture of  $\text{Sm}(\text{OH})_3$  and  $\text{B-Sm}_2\text{O}_3$  (sample  $\text{S}_1$ ). After heating this mixture at 900 °C for 2 hours, a mixture of  $\text{B-Sm}_2\text{O}_3$  and  $\text{C-Sm}_2\text{O}_3$  was obtained (sample  $\text{S}_2$ ), as illustrated in Figure 1.  $\text{C-Sm}_2\text{O}_3$  was also obtained by oxidation of samarium metal in a dynamic vacuum at temperatures of 200 to 350 °C.  $\text{C-Sm}_2\text{O}_3$  recrystallized on further heating into crystals of  $\text{B-Sm}_2\text{O}_3$ .<sup>21,22</sup>

Heating of a mixture of  $\text{Fe}_2\text{O}_3 : \text{Sm}_2\text{O}_3 = 1 : 1$  up to 700 °C did not cause formation of samarium orthoferrite,  $\text{SmFeO}_3$  (samples  $\text{S}_3$ ,  $\text{S}_4$  and  $\text{S}_5$ ). Figure 2 shows the characteristic X-ray diffraction powder pattern of sample  $\text{S}_3$ .  $\text{SmFeO}_3$  was de-

TABLE I  
*Experimental conditions of the preparation of samples  
 in the  $\text{Fe}_2\text{O}_3$ - $\text{Sm}_2\text{O}_3$  system*

Sample	Molar ratio ( $\text{Fe}_2\text{O}_3$ : $\text{Sm}_2\text{O}_3$ )	Temperature of heating / °C	Time of heating / hours
$S_1$	$\text{Sm}_2\text{O}_3$ , as received by Ventron		
$S_2$	$\text{Sm}_2\text{O}_3$ , as received by Ventron	900	2
	1:1	200	1
	1:1	300	1
	1:1	400	1
$S_3$	1:1	500	24
	1:1	200	1
	1:1	300	1
	1:1	400	1
	1:1	500	1
$S_4$	1:1	600	5
	1:1	200	1
	1:1	300	1
	1:1	400	1
	1:1	500	1
	1:1	600	1
$S_5$	1:1	700	5
	1:1	200	1
	1:1	300	1
	1:1	400	1
	1:1	500	1
	1:1	600	1
	1:1	700	1
$S_6$	1:1	800	5
	1:1	200	1
	1:1	300	1
	1:1	400	1
	1:1	800	5
$S_7$	1:1	1000	2
$S_8$	1:1	1200	2
	5:3	200	1
	5:3	300	1
	5:3	400	1
$S_9$	5:3	800	5
$S_{10}$	5:3	1000	2
$S_{11}$	5:3	1100	2
$S_{12}$	5:3	1200	2
$S_{13}$	5:3	1300	2

TABLE II  
Results of the XRD phase analysis

Sample	Phase composition (approx. molar fractions)	Remarks
S <sub>1</sub>	$\text{Sm}(\text{OH})_3 + \text{B-Sm}_2\text{O}_3$	
S <sub>2</sub>	$\text{B-Sm}_2\text{O}_3 + \text{C-Sm}_2\text{O}_3$	
S <sub>3</sub>	$\text{C-Sm}_2\text{O}_3 + \text{B-Sm}_2\text{O}_3 + \alpha\text{-Fe}_2\text{O}_3$ (0.30) (0.20) (0.50)	Sharpening of diffraction lines
S <sub>4</sub>	$\text{C-Sm}_2\text{O}_3 + \text{B-Sm}_2\text{O}_3 + \alpha\text{-Fe}_2\text{O}_3$ (0.30) (0.20) (0.50)	
S <sub>5</sub>	$\text{C-Sm}_2\text{O}_3 + \text{B-Sm}_2\text{O}_3 + \alpha\text{-Fe}_2\text{O}_3$ (0.30) (0.20) (0.50)	
S <sub>6</sub>	$\text{C-Sm}_2\text{O}_3 + \text{B-Sm}_2\text{O}_3 + \alpha\text{-Fe}_2\text{O}_3 + \text{SmFeO}_3$ (0.25) (0.17) (0.43) (0.15)	
S <sub>7</sub>	$\text{SmFeO}_3$	
S <sub>8</sub>	$\text{SmFeO}_3$	Sharpening of diffraction lines of $\text{SmFeO}_3$
S <sub>9</sub>	$\text{SmFeO}_3 + \alpha\text{-Fe}_2\text{O}_3$ (0.05)	
S <sub>10</sub>	$\text{SmFeO}_3 + \alpha\text{-Fe}_2\text{O}_3$ (0.03)	
S <sub>11</sub>	$\text{SmFeO}_3 + \alpha\text{-Fe}_2\text{O}_3$ (0.02)	
S <sub>12</sub>	$\text{Sm}_3\text{Fe}_5\text{O}_{12} + \text{SmFeO}_3$ (0.15)	
S <sub>13</sub>	$\text{Sm}_3\text{Fe}_5\text{O}_{12}$	Sharpening of diffraction lines of $\text{Sm}_3\text{Fe}_5\text{O}_{12}$

Description: C- $\text{Sm}_2\text{O}_3$  = cubic, B- $\text{Sm}_2\text{O}_3$  = monoclinic

tected as one of the oxide phases in sample S<sub>8</sub>, which was produced at 800 °C, and as a single phase at 1000 or 1200 °C (samples S<sub>7</sub> and S<sub>8</sub> respectively). The XRD powder pattern of  $\text{SmFeO}_3$  produced at 1200 °C is shown in Figure 3. When the mixture  $\text{Fe}_2\text{O}_3 : \text{Sm}_2\text{O}_3 = 5 : 3$  was heated to 800 °C, formation of  $\text{SmFeO}_3$  as the dominant component and of  $\alpha\text{-Fe}_2\text{O}_3$  as the minor component was detected (sample S<sub>9</sub>). With increasing the temperature, the molar content of  $\alpha\text{-Fe}_2\text{O}_3$  decreased (samples S<sub>10</sub> and S<sub>11</sub>). A mixture of  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$  and  $\text{SmFeO}_3$  was generated at 1200 °C (sample S<sub>12</sub>), and  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$  as a single phase (sample S<sub>13</sub>) at 1300 °C. The XRD powder pattern of  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$ , produced at 1300 °C, is shown in Figure 4.

The samples containing iron ions were also investigated by  $^{57}\text{Fe}$  Mössbauer spectroscopy. The oxide phases  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{SmFeO}_3$  and  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$ , show specific Mössbauer spectroscopic behavior, due to their different structural and magnetic properties.

TABLE III  
*Crystallographic data\* for Sm(OH)<sub>3</sub>, C-Sm<sub>2</sub>O<sub>3</sub>, B-Sm<sub>2</sub>O<sub>3</sub>,  
 $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, SmFeO<sub>3</sub> and Sm<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>*

JCPDS PDF card No	Compound	Space group	Unit cell parameters at 25 °C/nm
6-117 <sup>(**)</sup>	Sm(OH) <sub>3</sub>	<i>Pb<sub>3</sub>/m</i> (176)	<i>a</i> = 0.6312, <i>c</i> = 0.359
15-813	C-Sm <sub>2</sub> O <sub>3</sub>	<i>Ia</i> 3(206)	<i>a</i> = 1.0927
25-749 <sup>(***)</sup>	B-Sm <sub>2</sub> O <sub>3</sub>	<i>C2/m</i> (12)	<i>a</i> = 1.418, <i>b</i> = 0.3633, <i>c</i> = 0.8847 $\beta$ = 99.97°
13-534	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	<i>R</i> 3c(167)	<i>a</i> = 0.50340, <i>c</i> = 1.3752 (hexagonal axes)
8-149	SmFeO <sub>3</sub>	<i>Pbnm</i> (62)	<i>a</i> = 0.5394, <i>b</i> = 0.5592, <i>c</i> = 0.7711
23-526	Sm <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	<i>Ia</i> 3d(230)	<i>a</i> = 1.2530

\* Source: International Centre for Diffraction Data, Joint Committee on Powder Diffraction Standards, Powder Diffraction File, 1601 Park Lane, Swarthmore, Pa. 19081, USA.

(\*\*) The present work: *a* = 0.6375(5), *c* = 0.367(1) nm.

(\*\*\*) The interplanar spacing (*d* values) found in this study are approx. 0.3% greater than the ones in card 25-749.

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which possesses the crystal structure of corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), is characterized by a hyperfine magnetic splitting spectrum (one sextet) at room temperature. The shape of this spectrum depends on the crystallinity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, particle

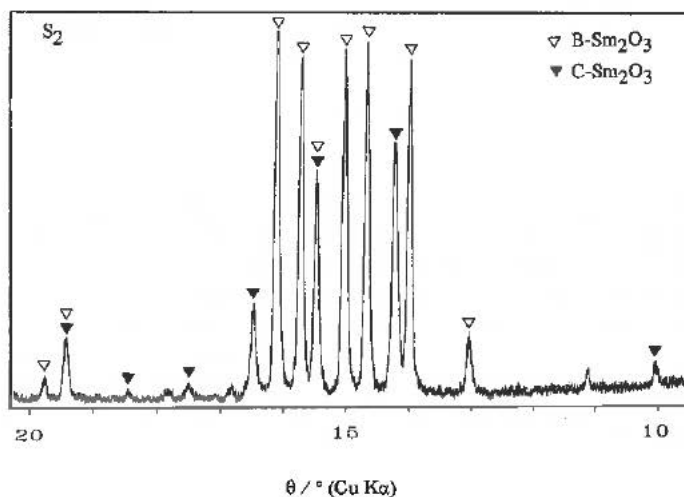


Figure 1. X-ray diffraction powder pattern of sample S<sub>2</sub>, recorded at room temperature (▽ B-Sm<sub>2</sub>O<sub>3</sub>, ▼ C-Sm<sub>2</sub>O<sub>3</sub>).

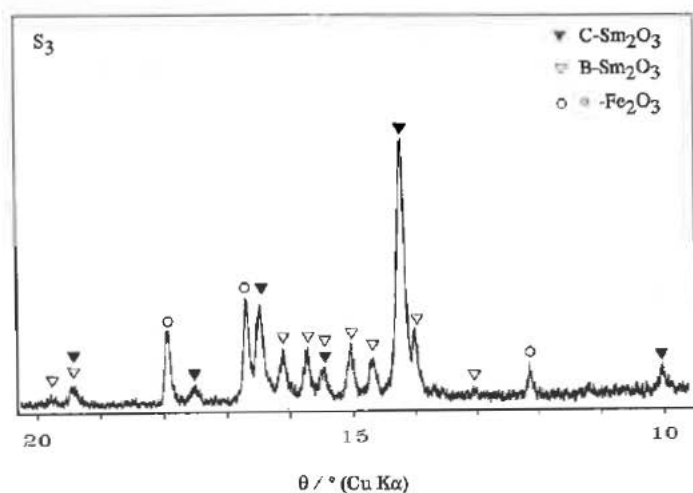


Figure 2. X-ray diffraction powder pattern of sample  $S_3$ , recorded at room temperature ( $\blacktriangledown$  C- $\text{Sm}_2\text{O}_3$ ,  $\triangledown$  B- $\text{Sm}_2\text{O}_3$ ,  $\circ$   $\alpha$ - $\text{Fe}_2\text{O}_3$ ).

sizes and partial substitution of  $\text{Fe}^{3+}$  ions by other metal ions. Due to these effects, the HMF of  $\alpha$ - $\text{Fe}_2\text{O}_3$  can be significantly reduced. For instance, in the case of ultrafine  $\alpha$ - $\text{Fe}_2\text{O}_3$  particles, six spectral lines may collapse into one doublet at room temperature.

The orthoferrites of lanthanide elements possess a distorted perovskite lattice with iron having the same environment throughout the lattice. At room temperature,

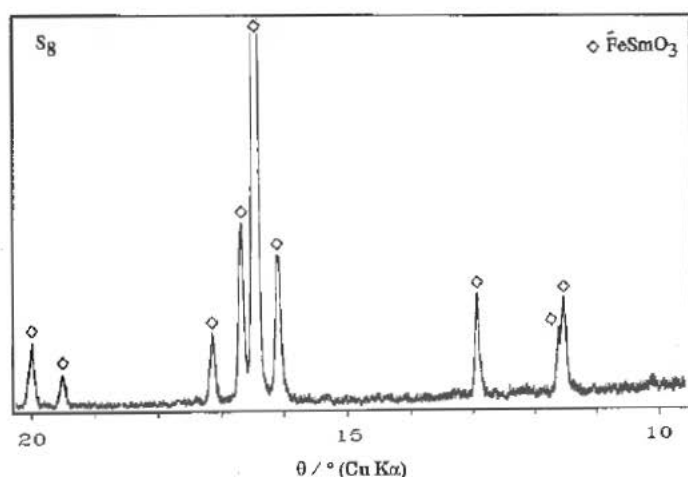


Figure 3. X-ray diffraction powder pattern of sample  $S_8$ , recorded at room temperature ( $\diamond$   $\text{SmFeO}_3$ ).



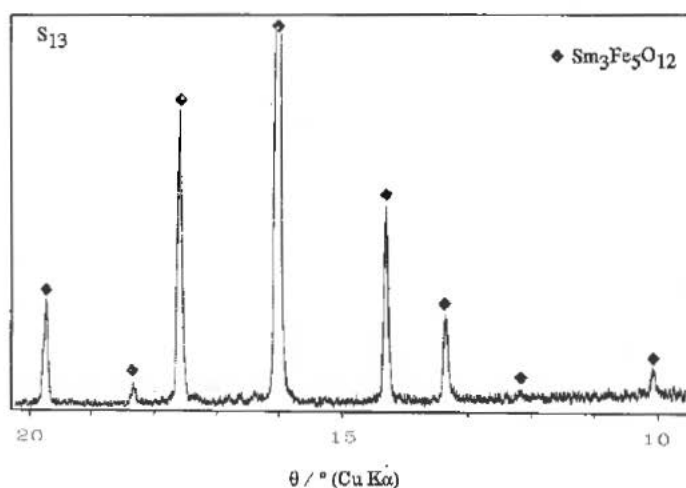


Figure 4. X-ray diffraction pattern of sample  $S_{13}$ , recorded at room temperature ( $\blacklozenge$   $\text{Sm}_3\text{Fe}_5\text{O}_{12}$ ).

they are characterized by a hyperfine magnetic splitting spectrum. The Mössbauer spectrum of  $\text{SmFeO}_3$  (sample  $S_8$ ) is shown in Figure 5. The oxide phases,  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{RFeO}_3$ , formed as a result of solid state reactions, may be characterized by similar Mössbauer parameters and, thus, the separation of two subspectra is not visible. For instance, the  $^{57}\text{Fe}$  Mössbauer spectra of the mixed oxide phases  $\alpha\text{-Fe}_2\text{O}_3\text{-NdFeO}_3$ ,

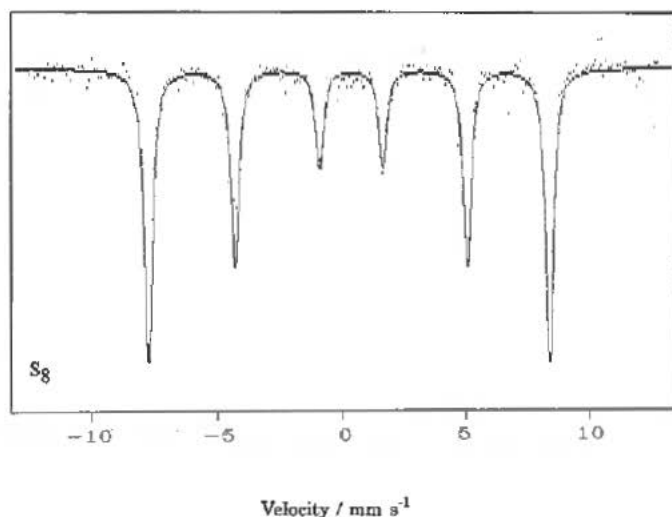


Figure 5.  $^{57}\text{Fe}$  Mössbauer spectrum of sample  $S_8$ , recorded at room temperature, indicating hyperfine magnetic splitting of samarium orthoferrite,  $\text{SmFeO}_3$ .

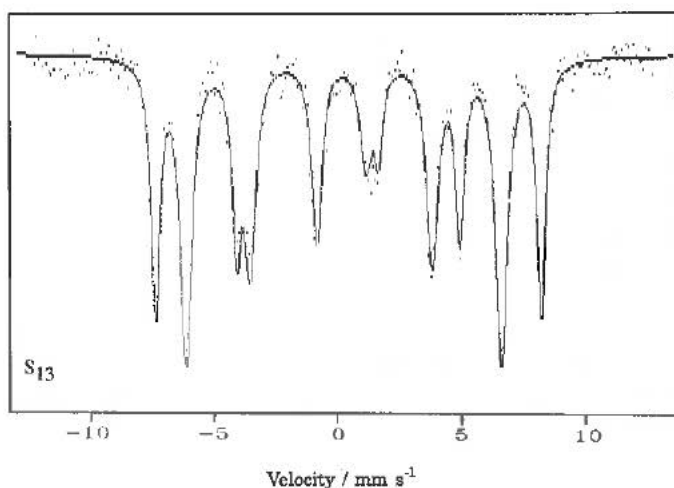


Figure 6.  $^{57}\text{Fe}$  Mössbauer spectrum of sample  $S_{13}$ , recorded at room temperature, indicating the superposition of two sextets of spectral lines corresponding to iron ions at a- and d-sites with hyperfine magnetic fields of 486 and 398 kOe, respectively.

were found to display one sextet of spectral lines at room temperature.<sup>23</sup> Mathematical deconvolution of these spectra showed distinct regularities in the changes of Mössbauer parameters  $\Delta E_Q$ ,  $\Gamma$  and HMF, indicating the presence of two  $^{57}\text{Fe}$  subspectra of very similar spectral behavior.

Lanthanide iron garnets,  $\text{R}_3\text{Fe}_5\text{O}_{12}$ , possess the crystal structure of mineral grossular.  $\text{Fe}^{3+}$  ions occupy octahedral (a) and tetrahedral (d) sites, while  $\text{R}^{3+}$  ions are in dodecahedral (c) sites. Figure 6 shows the fitted Mössbauer spectrum of sample  $S_{13}$  corresponding to  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$ . It is characterized by two hyperfine magnetic fields at room temperature,  $\text{HMF(a)} = 486$  kOe and  $\text{HMF(d)} = 398$  kOe. The  $^{57}\text{Fe}$  Mössbauer parameters (RT) calculated for  $\text{SmFeO}_3$  and  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$  are given in Table IV.

TABLE IV

*Mössbauer parameters (RT) calculated for  $\text{SmFeO}_3$  and  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$*

Compound	Lines	$\delta_{\text{Fe}}/\text{mm s}^{-1}$	$\Delta E_Q/\text{mm s}^{-1}$	HMF/kOe
$\text{SmFeO}_3$	M	0.39	-0.07	500
$\text{Sm}_3\text{Fe}_5\text{O}_{12}$	Ma	0.40	0.08	486
	Md	0.19	0.10	398

Errors: HMF =  $\pm 1$  kOe,  $\delta$  and  $\Delta E_Q$  =  $\pm 0.01$  mm/s

The IR spectra of some selected samples are summarized in Figures 7, 8 and 9. The IR spectrum of sample  $S_6$  shows a very strong band at  $545\text{ cm}^{-1}$ , pronounced bands at  $415$ ,  $380$  and  $350\text{ cm}^{-1}$ , as well as shoulders at  $450$ ,  $305$  and  $285\text{ cm}^{-1}$ . With an increase in the temperature of preparation, the very strong band at  $545\text{ cm}^{-1}$  (sample  $S_6$ ) was shifted to  $555\text{ cm}^{-1}$  (sample  $S_8$ ). The IR spectrum of sample  $S_8$ , corresponding to  $\text{SmFeO}_3$ , is also characterized by two shoulders at  $440$  and  $415\text{ cm}^{-1}$ , bands at  $380$  and  $350\text{ cm}^{-1}$  and two shoulders at  $305$  and  $285\text{ cm}^{-1}$ .

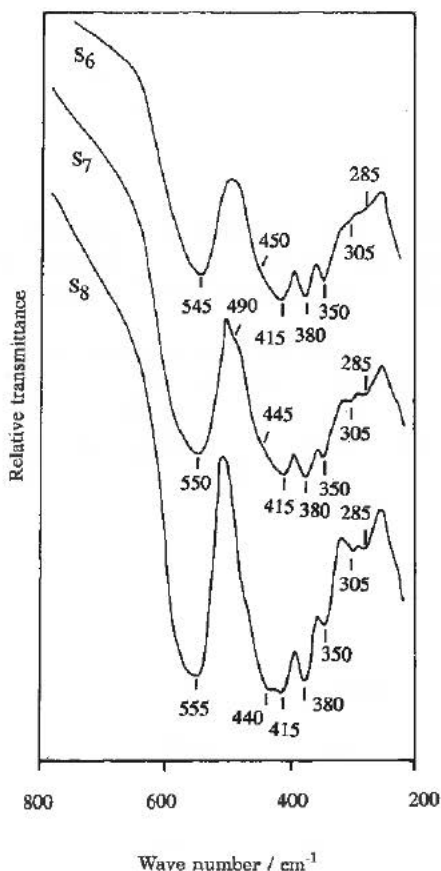


Figure 7. IR spectra of samples  $S_6$ ,  $S_7$  and  $S_8$ , recorded at room temperature.

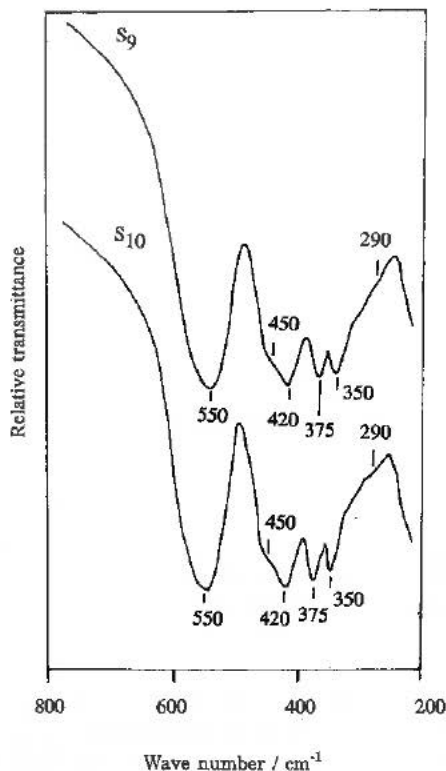


Figure 8. IR spectra of samples  $S_9$  and  $S_{10}$ , recorded at room temperature.

Subba Rao *et al.*<sup>24</sup> published the IR spectra of several lanthanide orthoferrites. However, they did not publish the IR spectrum of  $\text{SmFeO}_3$ . They detected a very strong band at  $575\text{--}543\text{ cm}^{-1}$  for different lanthanide orthoferrites and ascribed it to the Fe-O stretching mode. Significant differences were observed in the region  $\approx 450$  to  $\approx 285\text{ cm}^{-1}$ , due to the nature of lanthanide ions. The present work indicates that the crystal ordering of  $\text{RFeO}_3$  also affects the corresponding IR spectrum, as illustrated by samples  $S_7$  and  $S_8$ .

The specific crystal structure of iron garnets has a strong reflection on their vibrational spectra. In spite of this fact, the changes in the corresponding IR

spectra, during the formation of iron garnets, were not extensively investigated.

Beregi and Hild<sup>25,26</sup> investigated the IR spectra of garnets,  $\text{R}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ ,  $\text{R} = \text{Y, Sm, Gd, Er, Yb, Lu}$ , and interpreted them as proposed by Tarte.<sup>27</sup> They assigned a broad and very strong band at  $\approx 600\text{ cm}^{-1}$  to the vibrations of isolated tetrahedra, and a very strong band at  $\approx 400\text{ cm}^{-1}$  to isolated octahedra. They observed a band at  $\approx 480\text{ cm}^{-1}$  in the IR spectra of all rare garnets containing Ga at the octahedral sites ( $x > 3$ ). The intensity of this IR band steadily increased with increasing Ga concentrations.<sup>25,26</sup> In their studies of the vibrational spectra of garnets,  $\text{Ln}_3\text{Sb}_5\text{O}_{12}$ ,  $\text{Ln} = \text{Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb}$ , Botto *et al.*<sup>28</sup> recorded a strong IR band at  $690\text{ cm}^{-1}$  for  $\text{Gd}_3\text{Sb}_5\text{O}_{12}$ , and ascribed it to the stretching of the shortest Sb-O band, i.e. the Sb(1)-O(1) band. The bands recorded at  $602/558$  and  $460/385\text{ cm}^{-1}$  were discussed in terms of Sb-O-Sb bridge vibrations, and the bands observed below  $350\text{ cm}^{-1}$  were ascribed to the  $\text{SbO}_2$  bending modes and Ln-O vibrations.

The IR spectrum of sample  $\text{S}_9$  is characterized by a very strong band at  $550\text{ cm}^{-1}$ , pronounced bands at  $420, 375$  and  $350\text{ cm}^{-1}$ , and shoulders at  $450$  and  $290\text{ cm}^{-1}$ . The IR spectra of samples  $\text{S}_{10}$  and  $\text{S}_{11}$  are similar to the spectrum of sample  $\text{S}_9$ . In these samples,  $\text{SmFeO}_3$  is the dominant phase. The IR spectra of samples  $\text{S}_{12}$  and  $\text{S}_{13}$  differ significantly from the previous spectra. The IR spectrum of sample  $\text{S}_{13}$ , corresponding to  $\text{Sm}_3\text{Fe}_5\text{O}_{12}$ , is characterized by a very strong IR band having peaks at  $630, 580$  and  $540\text{ cm}^{-1}$ . The second very strong IR band displays a weak band at  $420\text{ cm}^{-1}$ , two shoulders at  $370$  and  $355\text{ cm}^{-1}$ , and two shoulders at  $320$  and  $305\text{ cm}^{-1}$ .

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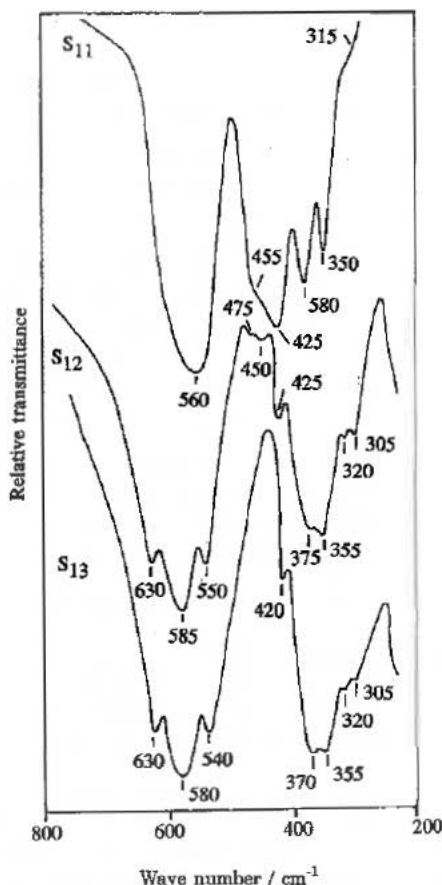


Figure 9. IR spectra of samples  $\text{S}_{11}$ ,  $\text{S}_{12}$  and  $\text{S}_{13}$ , recorded at room temperature.

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