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Formation of Oxide Phases in the System $Fe₂O₃$ -Sm₂ $O₃$

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Formation of oxide phases in the system $Fe₂O₃$ -Sm₂O₃ was investigated. The samples wore prepared by the solid state reactions et two molar ratios of Fe_2O_3 and Sm_2O_3 . The following oxide phases were detected by X-ray diffraction: C-Sm₂O₃, B-Sm₂O₃, α -Fe₂O₃, SmFeO₃ and Sm₃Fe₅O₁₂. For the molar ratio $Fe₂O₃$: $Sm₂O₃ = 1 : 1$, $SmFeO₃$ 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 $Fe₂O₃$: Sm₂O₃ = 5 : 3, SmFeO₃ was the intermediate phase up to 1200 °C, and Sm₃Fe₅O₁₂ was found as a single phase at 1300 °C. The oxide phases containing iron ions were characterized by ⁵⁷Fe Mössbauer spectroscopy. The formation of $SmFeO₃$ and $Sm₃Fe₆O₁₂$ phases, as end products of the solid state reactions in the system $Fe₂O₃$ -Sm₂O₃, was also investigated by IR spectroscopy.

INTRODUCTION

Rare earth ferrites with perovskite or garnet structures are generally considered to be reaction products between R_2O_3 and Fe_2O_3 , R being a rare earth. At high temperatures, R_2O_3 and Fe_2O_3 react to produce rare earth orthoferrite in the reaction:

$$
R_2O_3 + F\mathbf{e}_2O_3 \longrightarrow 2RF\mathbf{e}O_3 \tag{1}
$$

In the presence of additional $Fe₂O₃$, garnet type ferrite can be also produced at high temperatures:

$$
3\text{RFeO}_3 + \text{Fe}_2\text{O}_3 \longrightarrow \text{R}_3\text{Fe}_5\text{O}_{12} \tag{2}
$$

These mixed metal oxides can be prepared in laboratories by the use of different methods. The coprecipitation method involves precipitation of mixed metal hydroxides, $R(OH)_{\alpha}/F_{\alpha}(OH)_{\alpha}$, and thermal treatment of the hydroxide coprecipitate. The sol-gel procedure fa 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 \mathbb{R}^{3+} and $\mathbb{F}e^{3+}$ 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.

Bachiorrini¹ investigated the synthesis of yttrium iron garnet, $Y_3Fe_6O_{12}$, using the following procedure: a) denitration of the mixture $Y(NO₃)₃ \times 6H₂O + Fe(NO₃) \times 9H₂O$ with organic reducing agents, b) chemical coprecipitation of mixed hydroxides $Y(OH)_{3}/Fe(OH)_{3}$, and c) the solid state reaction between $Y_{2}O_{8}$ and $Fe_{2}O_{3}$ 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.*² described the preparation of yttrium aluminium garnet, $Y_3AI_5O_{12}$, by the combustion of a mixture of $Y(NO₃)₃ \times 6H₂O$, Al(NO₃)₃ \times 9H₂O and carbohydrazide, which were previously dissolved in a minimum quantity of water. They also prepared $Y_3A_6O_{12}$ by the combustion of a mixture of $Y(NO_3)_3 \times 6H_2O$, Al(NO₃)₃ \times 9H₂O and urea. The garnet, $Y_3A I_5O_{12}$, 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.³ YFeO₃ was detected by X-ray diffraction in all samples prepared at temperatures up to 1.300 \degree 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 technique⁴ 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 \approx 95% in weight.

Moasbauer spectroscopy found an important application in the characterization of rare earth orthoferrites and garnets.⁵ The Mössbauer spectra of the rare earth orthoferrites appeared as far back as in the sixties. $6-10$ The Mössbauer spectra of the lantanide orthoferrites show hyperfine magnetic splitting at room temperature. The hyperfine magnetic field, HMF, extrapolated to 0 K, decreases regularly with the atomic number of lantanide cation from 564 kOe for LaFeO₃ to 545.5 kOe for LuFeO₃.¹¹

Michalk and Thiel¹² used Mössbauer spectroscopy to investigate the substitution of Fe³⁺ with Al³⁺ ions in the ytrium iron garnet. $Y_3Fe_{5-x}Al_xO_{12}$, $x = 0$, 0.25 or 0.65. Mössbauer spectroscopy was also used¹³ in the study of the double-substituted yttrium iron garnet, $Y_{3-x}Gd_xFe_{5-x}Al_xO_{12}$ (x = 0.60 to 1.2, y = 0.10 to 0.85).

On the basis of Conversion Electron Mossbauer Spectra (CEMS), Okuda *et.* al.1' 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

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bubble films, $(Y, Sm, Ca, Tm)_{3}$ (Fe,Ge)₅O₁₂, grown on GGG (gadolinium gallium garnet) substrate and irradiated with 60 keV H_2^* ions, showed changes in the corresponding CEMS.¹⁵

The formation of the oxide phases in the system $(1-x)Fe₂O₃ + xGd₂O₃$, $0 \le x \le 1$, was investigated by XRD and Mössbauer spectroscopy.¹⁶ The samples were prepared using the chemical coprecipitation procedure. By XRD measurements, the distribution of oxide phases, α -Fe₂O₃, GdFeO₃, Gd₃Fe₅O₁₂ and Gd₂O₃, was determined as a function of *x*. New accurate crystallographic data for $Gd_3Fe_5O_{12}$ were obtained. The temperatures of the formation of $GdFeO_3$ and $Gd_3Fe_6O_{12}$ were higher in the case of solid state synthesis¹⁷ than in the case of chemical coprecipitation.¹⁶ The formation of oxide phases in an analogous system, $Fe₂O₃$ -Eu₂O₃, was also investigated.¹⁸

Physical properties of gamets, with rare-earth sites fully or partially occupied by Sm³⁺ ions, were previously subjected to several investigations^{19,20} because of their possible application in advanced technologies. In this study, we focussed our attention on the formation of oxide phases in the system $Fe_2O_3-Sm_2O_8$. The characteristic properties of the samples were investigated by combined use of X-ray diffraction, $57Fe$ Mössbauer spectroscopy and IR spectroscopy.

EXPERIMENTAL

The chemicals were obtained from Ventron. The content of $Sm₂O₈$ in the starting chemical was determined after its calcination and removal of H_2O 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, $Fe₂O₃$: Sm₂O₃ = 1 : 1 and 5 : 3, were used for the preparation of the $Fe₂O₃-Sm₂O₃$ mixed oxides.

X-ray diffraction (XRD) powder patterns were taken at room temperature using a counter diffractometer with monochromatized Cu Ka radiation (Philips diffractometer, proportional counter and graphite monochromator).

The ⁵⁷Fe 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 $(cm⁻¹).$

RESULTS AND DISCUSSION

The results of XRD phase analysis of the samples are given in Table II and the crystallographic data for $Sm(OH)_{3}$, C-Sm₂O₃ (body-centered cubic), B-Sm₂O₃ (monoclinic), α -Fe₂O₃, SmFeO₃ and Sm₃Fe₅O₁₂ are given in Table III. XRD analysis of the Sm_2O_3 , supplied by Ventron, showed that this chemical was actually a mixture of $\text{Sm}(\text{OH})_3$ and B-Sm₂O₃ (sample S₁). After heating this mixture at 900 °C for 2 hours, a mixture of $B-Sm_2O_3$ and $C-Sm_2O_3$ was obtained (sample S_2), as illustrated in Figure 1. $C-Sm₂O₃$ was also obtained by oxidation of samarium metal in a dynamic vacuum at temperatures of 200 to 350 °C. C-Sm₂O₃ recrystallized on further heating into crystals of B-Sm₂O₃.^{21,22}

Heating of a mixture of $Fe₂O₃$: Sm₂O₃ = 1 : 1 up to 700 °C did not cause formation of samarium orthoferrite, $SmFeO₃$ (samples $S₃$, $S₄$ and $S₅$). Figure 2 shows the characteristic X-ray diffraction powder pattern of sample S_3 . SmFeO_s was de-

TABLE I

Experimental conditions of the preparation of samples *in the Fe20rSm20a system*

Description: $C-Sm₂O₃ = cubic$, $B-Sm₂O₃ = monoclinic$

tected as one of the oxide phases in sample S_g , which was produced at 800 °C, and as a single phase at 1000 or 1200 °C (samples S_7 and S_8 respectively). The XRD powder pattern of $SmFeO₃$ produced at 1200 °C is shown in Figure 3. When the mixture $Fe₂O₃$: $Sm₂O₃ = 5 : 3$ was heated to 800 °C, formation of SmFcO₃ as the dominant component and of α -Fe₂O₃ as the minor component was detected (sample S_9). With increasing the temperature, the molar content of $\alpha-\mathrm{Fe}_2\mathrm{O}_3$ decreased (samples S_{10} and S_{11}). A mixture of $Sm_3Fe_5O_{12}$ and $SmFeO_3$ was generated at 1200 °C (sample S_{12}), and $Sm_3Fe_5O_{12}$ as a single phase (sample S_{13}) at 1300 °C. The XRD powder pattern of $Sm_3Fe_5O_{12}$, produced at 1300 °C, is shown in Figure 4.

The samples containing iron ions were also investigated by ⁵⁷Fe Mössbauer spectroscopy. The oxide phases α -Fe₂O₃, SmFeO₃ and Sm₃Fe₅O₁₂, show specific Mössbauer spectroscopic behavior, due to their different structural and magnetic properties.

TABLE ill

Crystallographic data• f0r Sm(OHJ& C-Sm2Ps. B-Sm20s. a-Fe20s, SmFeOa *and SmaFes012*

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. 0.8% greater than the ones in card 25--749.

 α -Fe₂O₃, which possesses the crystal structure of corundum (α -Al₂O₃), is characterized by a hyperfine magnetic splitting spectrum (one sextet) at room temperature. The shape of this spectrum depends on the crystallinity of α -Fe₂O₃, particle

 0 / \degree (Cu Ka)

Figure 1. X-ray diffraction powder pattern of sample S₂, recorded at room temperature $(\nabla B - \mathrm{Sm}_2\mathrm{O}_3, \blacktriangledown \mathrm{C} - \mathrm{Sm}_2\mathrm{O}_3).$

Figure 2. X-ray diffraction powder pattern of sample S₃, recorded at room temperature \forall C-Sm₂O₃, V B-Sm₂O₃, O α -Fe₂O₃).

sizes and partial substitution of Fe^{3+} ions by other metal ions. Due to these effects, the HMF of α -Fe₂O₃ can be significantly reduced. For instance, in the case of ultrafine α -Fe₂O₃ 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 S₈, recorded at room temperature (0 SmFeO_3) .

Figure 4. X-ray diffraction pattern of sample S_{13} , recorded at room temperature (\bullet Sm₃Fe₅O₁₂).

they are characterized by a hyperfine magnetic splitting spectrum. The Mössbauer spectrum of SmFeO₃ (sample S₈) is shown in Figure 5. The oxide phases, α -Fe₂O₃ and 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}Fe Mössbauer spectra of the mixed oxide phases α –Fe₂O₃–NdFeO₃,

Figure 5. 57 Fe Mössbauer spectrum of sample S_8 , recorded at room temperature, indicating hyperfine magnetic splitting of samarium orthoferrite, SmFeO₃.

Figure 6. 57 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.²⁸ Mathematical deconvolution of these spectra showed distinct regularities in the changes of Mössbauer parameters ΔE_o , Γ and HMF, indicating the presence of two ⁵⁷Fe subspectra of very similar spectral behavior.

Lanthanide iron garnets, $R_3Fe_5O_{12}$, possess the crystal structure of mineral grossular. Fe³⁺ ions occupy octahedral (a) and tetrahedral (d) sites, while R^{3+} ions are in dodecahedral (c) sites. Figure 6 shows the fitted Mossbauer spectrum of sample S_{13} corresponding to $Sm_3Fe_6O_{12}$. It is characterized by two hyperfine magnetic fields at room temperature, $HMF(a) = 486$ kOe and $HMF(d) = 398$ kOe. The 57 Fe Mössbauer parameters (RT) calculated for SmFeO₃ and Sm₃Fe₆O₁₂ are given in Table IV.

Compound	Lines	$\delta_{\rm Fe}/\rm{mm~s}^{-1}$	ΔE_c /mm s ⁻¹	HMF/kOe
SmFeO ₃	M	0.39	-0.07	500
$Sm_3Fe_6O_{12}$	Ma	0.40	0.08	486
	M_d	0.19	0.10	398

TABLE IV

Mössbauer parameters (RT) calculated for SmFeO₃ and Sm₃Fe₅O₁₂

Errors: HMF = \pm 1 kOe, δ and $\Delta E_0 = \pm$ 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_c shows a very strong band at 545 cm^{-1} . pronounced bands at 416, 380 and 350 cm-1, as well as shoulders at 450, 305 and 285 cm-1. With an increase in the temperature of preparation, the very strong band at 545 cm^{-1} (sample S_6) was shifted to 555 cm^{-1} (sample S_a). The IR spectrum of sample S_8 , corresponding to $SmFeO₃$, is also characterized by two shoulders at 440 and 415 cm^{-1} , bands at 380 and 350 cm^{-1} and two shoulders at 305 and 285 cm^{-1} .

Wave number / 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.*²⁴ published the IR spectra of several lanthanide orthoferrites. However, they did not publish the IR spectrum of $SmFeO₉$. They detected a very strong hand at 575-543 cm-1 for different lanthanide orthoferrites and ascribed it to the Fe-O stretching mode. Significant differences were observed in the region ≈ 450 to ≈ 285 cm⁻¹, due to the nature of lanthanide ions. The present work indicates that the crystal ordering of $RFeO₃$ 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 Hild²⁵.26 investigated the IR spectra of garnets, $R_3Fe_{5.7}Ga_2O_{12}$, $R = Y$, Sm, Gd, Er, Yb, Lu, and interpreted them as proposed by Tarte.²⁷ They assigned a broad and very strong band at ≈ 600 cm⁻¹ to the vibrations of isolated tetrahedra, and a very strong band at ≈ 400 cm⁻¹ to isolated octahedra. They observed a band at ≈ 480 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. 25·26 In their studies of the vibrational spectra of garnets, $Ln_3Sb_5O_{12}$, Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Botto et al.²⁸ recorded a strong IR band at 690 cm-1 for $Gd_3Sb_5O_{12}$, and ascribed it to the stretching of the shortest Sb-O band, *i.e.* the Sb(l)-0(1) band. The bands recorded at $602/558$ and $460/385$ cm⁻¹ were discussed in terms of Sb-O-Sb bridge vibrations , and the bands observed below 350 cm^{-1} were ascribed to the SbO₂ bending modes and Ln-0 vibrations.

The IR spectrum of sample $S₉$ is characterized by a very strong band at 550 cm-1, pronounced bands at 420, 375 and 350 cm-1, and shoulders at 450 and 290 cm⁻¹. The IR spectra of samples S_{10} and S_{11} are similar to the spectrum of sample S_9 . In these samples, SmFeO₃ is

Figure 9. IR spectra of samples S_{11} , S_{12} and 813, recorded at room temperature.

the dominant phase. The IR spectra of samples S_{12} and S_{13} differ significantly from the previous spectra. The IR spectrum of sample S_{13} , corresponding to $Sm_3Fe_6O_{12}$, is characterized by a very strong IR band having peaks at 630, 580 and 540 cm^{-1} . The second very strong IR band displays a weak band at 420 cm^{-1} , two shoulders at 370 and 355 cm^{-1} , and two shoulders at 320 and 305 cm⁻¹.

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