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Studies on thermally treated lanthanum–iron (atomic ratio 1:9) oxyhydroxide

I. P. SARASWAT, G. S. RAO, C. L. SHARMA
Department of Chemistry, University of Roorkee, Roorkee 247 667, Uttar Pradesh, India
V. K. GARG
Departmento de Fisica e Quimica, Universidade Federal do Espirito Santo, 29 000 Vitoria, Brazil
A. C. VAJPEI
Laboratoire de Chimie des Materiaux Inorganiques, Universite Paul Sabatier, 31062 Toulouse, France

Mössbauer spectral (MS) and magnetic investigations on the products obtained by annealing coprecipitated La(III) and Fe(III) (atomic ratio 1:9) oxyhydroxide gel to different temperatures in the range 100 to 1250° C are reported. The annealing temperatures were chosen on the basis of thermal analysis data. It is observed that the thermal behaviour of the bulk ferric gel is significantly influenced by La(III) incorporation. A quadrupole split doublet observed in the MS of the gel annealed from 100° C persists up to 570° C and for samples annealed from 850° C and above it is not discernable. However, a six-fingered hyperfine split pattern emerges even for the gel heated to 150° C indicating the onset of short-range ordering. H_n values ranging from 495 to 519 kOe for the samples heated to 570° C are in agreement with that for α-Fe_2O_3, however, their magnetic susceptibility per gram (χ_g) of the order of 10^{-3} e.m.u. appears to be high for such systems. Annealing the gel from 850° C and above results in an H_n of about 526 kOe which is in better agreement with that of $LaFeO_3$, but the χ_g value falls to about 10^{-5} e.m.u.

1. Introduction

Iron–rare earth mixed oxides, which form multisublattice systems have provided magnetic materials of technological relevance, e.g., orthoferrites and garnets. Their properties are not only a sensitive function of the ionic radius and valency state of their constituents but are also dependent on the method of their formation. Recently anomalous magnetic behaviour of 10 at % yttrium (III) in ferric oxyhydroxide gel annealed to 850° C was reported [1]. In continuation of this work, the effect of incorporation of the same amount of larger cations, La(III), in ferric oxyhydroxide gel annealed to different temperatures, is reported in this paper.

2. Experimental details

Appropriate aliquots of standardized solutions of $LaCl_3$ and $FeCl_3$ were mixed to obtain an atomic ratio 1:9 of La(III) and Fe(III) ions. To this mixture, thermostatted at 55° C, 10% ammonia was added with constant stirring until the pH was 7. The precipitate thus obtained was separated by filtration and washed free of ammonia, dried in an air oven and stored in a desiccator. The filtrate was tested for residual metal ions to determine whether precipitation was complete. Starting from the gel, samples annealed at 150, 320, 570, 850, 1000 and 1250° C were obtained for investigation.

Thermal analysis of the gel was performed using an STA-780 series Thermal Analyser (Stanton Redcroft, London). X-ray diffraction (XRD) of the powdered sample, mixed with 10% KCl and sieved through a BSS 350 mesh were recorded on a PW 1140/90 (Philips) X-ray diffraction instrument using nickel-filtered Cu$K\alpha$ radiation, KCl was used as an internal standard. The Mössbauer data were recorded in transmission geometry mode on a constant acceleration velocity transducer coupled to ^{57}Co in a rhodium matrix source. Iron metal foil was used for velocity calibration and as a standard for the isomer shifts. Magnetic moments were recorded from room temperature to 800 K and back to room temperature on a vibrating sample magnetometer (VSM model 155, Princeton Applied Research) using a boric nitrate sample holder. The VSM was calibrated with a high-purity nickel standard, showing a saturation moment of 55 e.m.u. g^{-1} with a saturation flux 5 kG.

3. Results and discussion

The thermal behaviour of 10 at % La(III)-doped ferric oxide hydrate gel is quite different from that of the pure $Fe_2O_3 \cdot nH_2O$ or $La(OH)_3$ gel (Fig. 1). The most significant difference is that an exotherm between 350 to 500° C does not appear in the doped system and more features are shown in the 200 to 400° C range. The rate of weight loss also becomes sluggish because constant weight of the sample is reached only around

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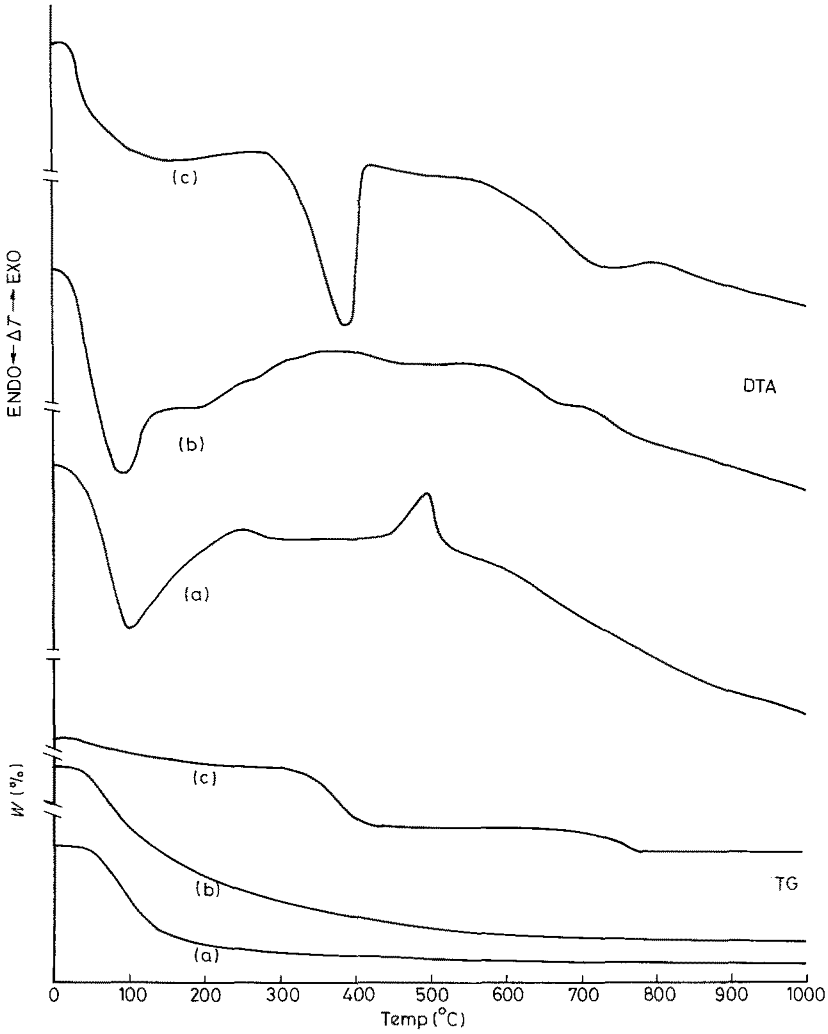

Figure 1 Thermal curves of (a) $Fe_2O_3 \cdot nH_2O$, (b) $La_{0.2}Fe_{1.8}nH_2O$ and (c) $La(OH)_3$.

580° C. No XRD lines were observed for the sample annealed to 150 and 320° C. Diffuse broad lines characteristic of α-Fe_2O_3 appeared in the sample annealed to 570° C, and sharp lines which appeared by annealing to 850° C and above were used for characterizing the products.

The room-temperature Mössbauer spectra (MS) of the gels annealed from varying temperatures are depicted in Fig. 2 and the data obtained from the plots are given in Table I. The MS of the gel shows only a doublet with isomer shift (IS) and quadrupole splitting (QS) values of 0.25 and 0.56 mm sec^{-1}, respectively. This indicates Fe^{3+} ions in distorted octahedral sites. On annealing the gel at higher temperatures this doublet persists up to 570° C and the hyperfine split (HFS) six-fingered pattern, which emerges at 150° C becomes sharper. However, Saraswat *et al.* [2] reported an unresolved almost featureless single broad band for the pure ferric gel annealed to 325° C, indicating motional narrowing of the magnetic spectra. A similar observation was made by Kaufman and Hazel [3].

TABLE I Mössbauer data (RT) of the gel annealed to different temperatures

Annealing temperature (° C)	HFS ($\pm$5 kOe)	IS ($\pm$0.03 mm sec^{-1})	QS ($\pm$0.03 mm sec^{-1})
100	0	0.25	0.56
150	495	0.38	0.60
320	514	0.53	0.00
570	519	0.53	0.14
850	525	0.55	0.18
1000	528	0.54	0.14
1250	530	0.54	0.18

From the above, it is evident that the short-range ordering of spins sets in even at 150° C, due to La(III)-doping, whereas this appears above 350° C in pure gels [2]. The MS data from HFS agrees with that of ferric oxide hydrate gel. The observed H_n values in the range 495 to 519 kOe and other parameters for the gel are in fair agreement with those reported for α-Fe_2O_3. Normally doublet peaks in the gel annealed at 320 to 570° C could have been assigned to α-Fe_2O_3 in the super paramagnetic state. But Yamamura *et al.* [4] have reported the formation of amorphous $LaFeO_3$ exhibiting a quadrupole split doublet even at 500° C. The doublet observed for the 570° C-annealed sample may be due to formation of very fine $LaFeO_3$ particles.

On annealing the sample to 850° C and above, the XRD lines for α-Fe_2O_3 and $LaFeO_3$ can be distinctly seen and the doublet in the MS disappears, indicating better crystallization. The observed H_n values in the range 525 to 530 kOe are in better agreement with those reported [5] for $LaFeO_3$ (521 kOe) than for α-Fe_2O_3 (517 kOe) which constitutes the bulk phase. But higher H_n values for α-Fe_2O_3 are also reported. The line shape and width indicate the presence of a mixture of α-Fe_2O_3 and $LaFeO_3$. Because defects (vacancies) persist in $LaFeO_3$ even up to an annealing temperature of 1000° C [4] and there is a lot of

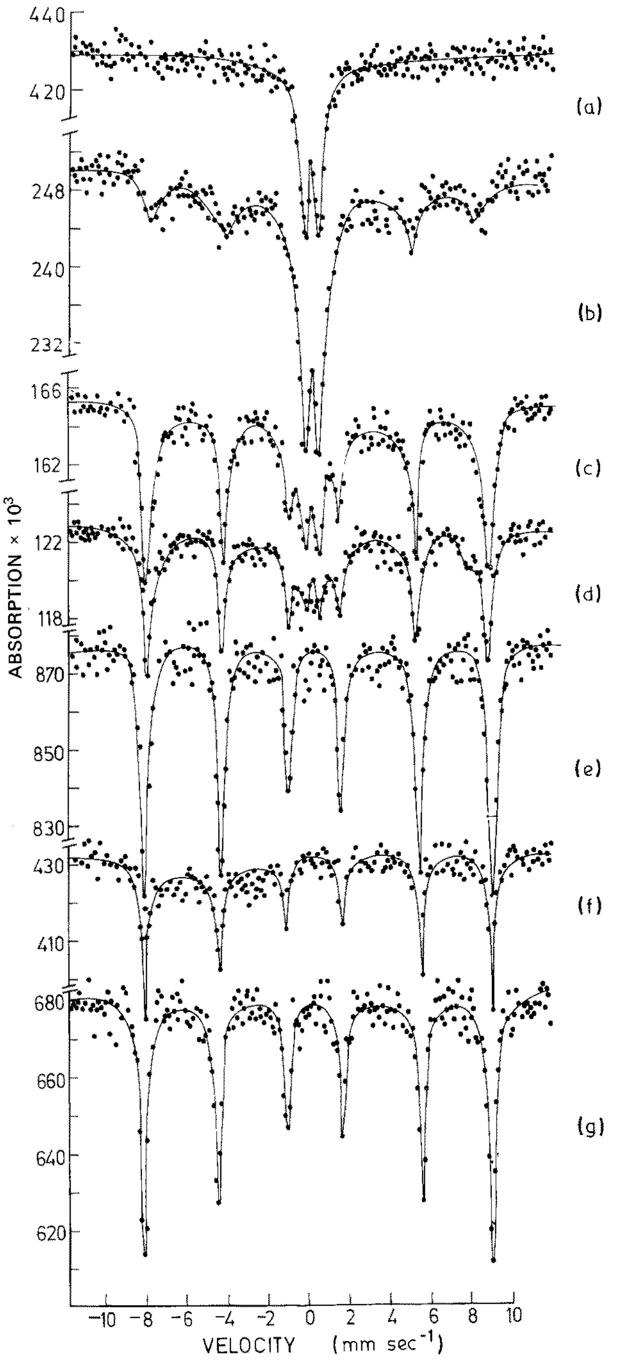

Figure 2 Mössbauer spectra of the gel annealed to (a) 100, (b) 150, (c) 320, (d) 570, (e) 850, (f) 1000 and (g) 1250° C.

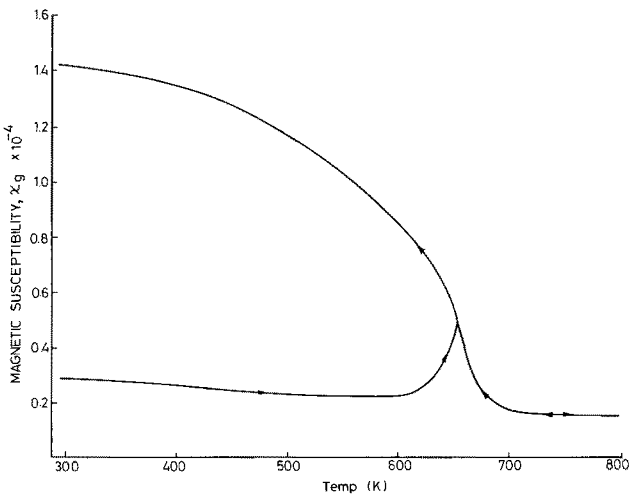

Figure 3 Magnetic susceptibility plotted against temperature (K) of the gel annealed to 850° C.

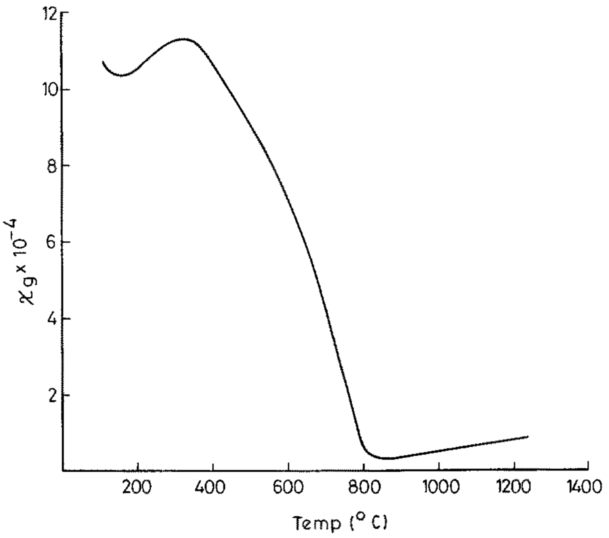

Figure 4 Magnetic susceptibility (RT) plotted against annealing temperature (° C) of the gel.

scattering in MS, it is not possible to resolve the main constituents.

The magnetic behaviour of gel annealed to 850° C (Fig. 3) is quite different from that of similarly treated 10% Y(III)-doped ferric oxide hydrate gel [1] in the sense that its χ_g value continues to increase up to 850 K, whereas in the present case the χ_g value increases up to 655 K and then it decreases. The ratio of χ_g at 800 K to χ_g(RT) is 0.55, whereas the same ratio for the Y(III)-doped system was 6.7; also the ratio of χ_g after cooling to room temperature under a magnetic field to χ_g(RT) is only 4.87 when the same ratio for the Y(III) system was 17.92. Further, from the plot of room-temperature χ_g gel against annealing temperature (Fig. 4) it is evident that the magnetic behaviour of the system is quite unusual in the sense that χ_g values of the gel annealed to 320° C are about ten times more than that of pure ferric hydrate gel and also of the gel annealed to 850° C and above. The La(III) ion with inert gas structure could make only a negative contribution to χ_g in the $La(OH)_3$, LaOOH or $LaFeO_3$ form. It appears that this may be due to short-range ordering of spins set up by incorporation of lanthanum.

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