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Mössbauer effect characterization and thermal transformations of Fe(III) ions co-precipitated with praseodymium trihydroxide

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Mössbauer studies at + 27 and − 196° C on 5 wt % Fe(III) ions co-precipitated with praseodymium trihydroxide and subjected to annealing for 24 h at 100, 350, 600, 725, 825 and 1100° C are reported. Variations in Mössbauer spectral parameters and the results of thermal analysis, infra-red spectroscopy, electron microscopy and X-ray diffraction (XRD) studies on the samples have been used to follow and to gain insight into the nature of thermal and microstructural processes that occur during phase transitions. In the co-precipitate, Fe ions exist as ferric oxide hydrate gel-like species. In samples annealed at 100° C Fe ions exhibit an increase in dispersion strengthening in the lattice while in samples annealed at 350° C they become somewhat labile due to disruption of lattice planes on dehydroxylation. In samples annealed at 600° C magnetically split six-line Mössbauer spectra are observed, which in agreement with XRD analysis and electron paramagnetic resonance studies indicate the precipitation of $PrFeO_3$ microphases in Pr_6O_{11}. Annealing to higher temperatures finally leads to a pronounced agglomeration of iron microphases and the establishment of a better crystallized host lattice.

1. Introduction

The only Mössbauer resonance study found by us on iron-doped praseodymium oxide is that of Clifford [1]. In his study iron has been used, as dilute impurity probe, for examining the subtle differences in the electronic environment of host PrO_x ($1.5 < x < 2.0$) undergoing oxidation with changes in composition in a manner typical of hysteresis. These investigations indicated that Fe ions remain obdurately trivalent and it was postulated that the ions substitute for rare-earth ions in the oxide host lattice. Subsequent investigations [2–4] involving Mössbauer and electron paramagnetic resonance (EPR) studies on Fe(III) ion dispersions in rare-earth oxide-type host lattices, also interpreted their results postulating substitution of Fe ions for rare-earth ions in the oxide host lattice, forming some sort of solid solution.

However, contrary to these studies, recent observations made by us on some iron-doped rare earth oxide systems [5, 6] have indicated formation of discrete orthoferrite clusters. This paper deals with the reinvestigation of systems based on Fe ions co-precipitated with praseodymium hydroxide and with the products resulting from annealing it in terms of their valency, co-ordination and aggregation behaviour using Mössbauer spectroscopy. To obtain an insight into the processes occurring during phase transformations, the initial co-precipitate was subjected to differential thermal

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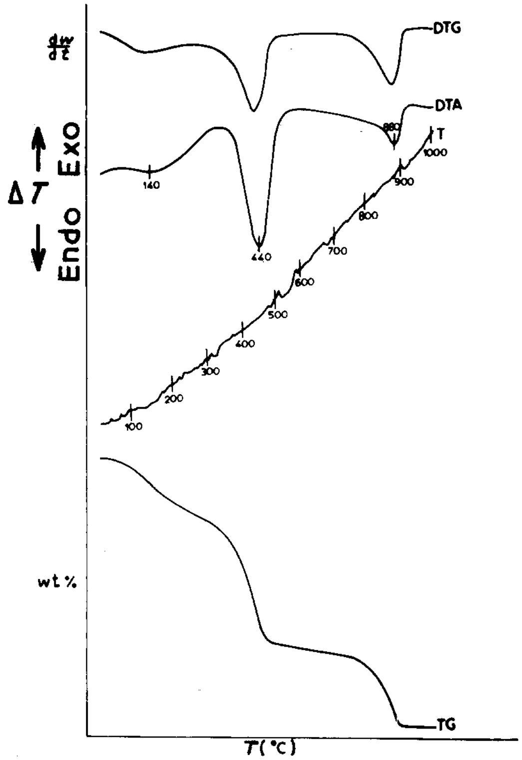

Figure 1 Thermal curves for 5 wt % Fe(III) co-precipitated with praseodymium hydroxide (heating rate 10° C min^{-1}).

analysis (DTA), thermal gravimetric analysis (TG) and differential thermal gravimetric analysis (DTG); the crystal forms and microstructure of the host lattices were examined by infra-red (i.r.) absorption spectroscopy, electron optical methods and powder X-ray diffraction.

2. Experimental procedure

Ammonium hydroxide was added in excess to freshly prepared and vigorously stirred mixed solutions of ferric and praseodymium chloride (AR) containing 5 wt % Fe(III) and 95 wt % Pr(III) ions. The precipitate formed was washed repeatedly, filtered and dried in air at room temperature. Starting from the original, air-dried co-precipitate, annealed samples were obtained by heating the sample for 24 h each at different temperatures ranging from 100 to 1100° C in a muffle furnace followed by cooling down slowly to room temperature.

Thermal curves (DTA, TG and DTG) of the original co-precipitate were recorded on a Paulik Erdey Derivatograph model 1969 manufactured by MOM, Budapest. The i.r. spectra were obtained for samples in KBr discs using a Beckman model IR-20 spectrophotometer operated in the double beam mode in the range 4000 to 250 cm^{-1}. For electron microscopy experiments specimens were mounted onto a film of carbon black deposited on 200 mesh copper grids and were examined with a Phillips EM 300 electron microscope using a 40 kV beam. The powder X-ray diffraction (XRD) patterns at room temperature and EPR spectra at − 193° C at the X-band were also recorded for samples annealed at 600° C.

Mössbauer effect spectra of samples were obtained at 27 and − 196° C using a constant acceleration velocity transducer coupled to a source of 25 mCi cobalt-57 in a copper matrix in standard transmission geometry. Velocity calibrations were made using thin (1.9 mg $^{57}Fe\ cm^{-2}$) iron foil and isomer shifts are referred to natural iron as the zero point.

3. Results and discussion

3.1. Characterization and thermal transformations of co-precipitate

Fig. 1 gives the thermal curves obtained from the co-precipitate. The DTA curve shows a slow descent starting at about 140° C continuing up to about 300° C, followed by sharp endothermic effects which peak at 440 and 880° C. Associated with these effects, a pronounced weight loss takes place in steps, as may be distinctly seen on the TG and DTG curves.

Infra-red spectra of the original co-precipitate show several bands due to a $Pr(OH)CO_3$ phase which is formed due to interaction of atmospheric CO_2 with the praseodymium hydroxide precipitate. Also present are bands due to structural hydroxyls and water present in co-precipitated hydroxide. In i.r. spectra of samples annealed at 250 and 300° C, features identifiable with the dehydroxylation of $Pr(OH)_3$ to PrOOH phase are discernible. In samples annealed at 500° C, bands characteristic of the formation of Pr_6O_{11} were observed. Additional bands due to an iron oxide component and incorporation of CO_3^{2-} in the lattice, however, complicate the i.r. spectra of these samples. Samples annealed at 600° C and above show similar i.r. features except that samples annelaed to 900 and 950° C are devoid of absorptions due to CO_3^{2-} species.

Fig. 2 a to d, show some transmission electron micrographs (TEM) of samples annealed at different temperatures. Unheated samples are comprised

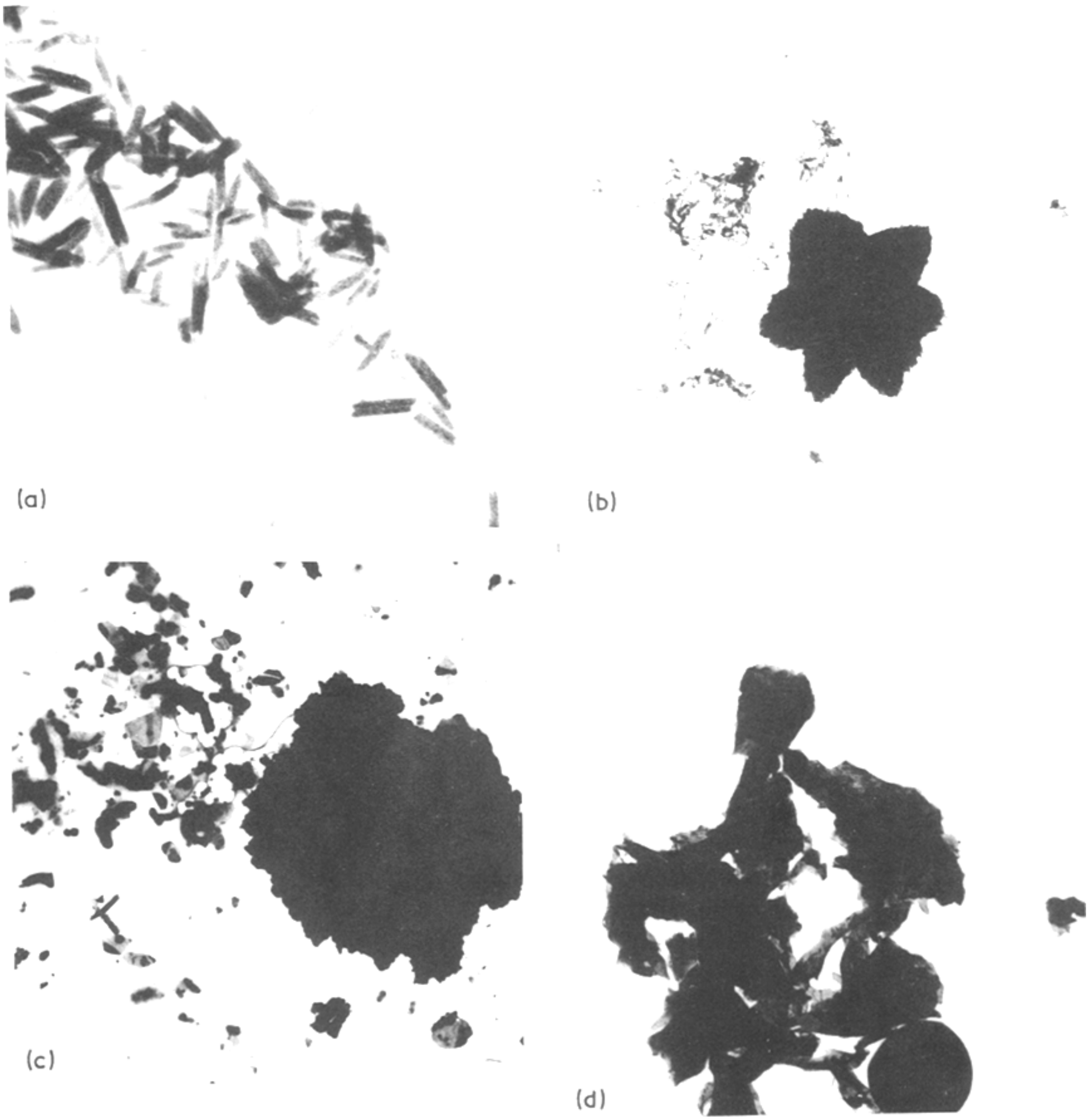

Figure 2 Crystal morphology and microstructure of co-precipitate subjected to heat treatment: (a) None, (b) 300° C, (c) 600° C (d) 1000° C for 24 h each at magnifications of (a) 70 000 (b) 42 000 (c) 33 000 and (d) 55 000.

of thin plates and hollow rods together with small amorphous particles. Samples annealed at 100 and 150° C show an increase in crystallinity with much the same microstructure and morphology as discerned in the initial precipitate. Annealing the sample at 250 and 300° C results in growth of large monoclinic to oblong-shaped crystalline sheets of PrOOH. Further dehydroxylation in samples annealed at 400° C and above showed an appreciable increase in lattice defects with lines having some definite crystal orientation in the microstructure of these samples. Samples annealed at 700° C show step dislocations with a complex lattice of curves, twinning with broad twinning boundaries and fringes parallel to them in different areas due to non-stoichiometry of the Pr–O system.

Powder X-ray diffraction and electron diffraction examination of samples annealed at 900° C show formation of fcc Pr_6O_{11}. X-ray analysis also indicates that iron is present in the form of PrFeO microphases. DTA, TG and DTG curves are in agreement with the i.r. spectroscopy electron microscopy and XRD studies and these suggest the complexity of the processes occurring during thermal decomposition of Fe(III) co-precipitated with $Pr(OH)_3$. Starting from 140° C a rapid drop in the TG curve corresponds with the early dehydration of the co-precipitate. Dehydroxylation to PrOOH at about 250° C and partial oxidation of Pr^{3+} to Pr^{4+} ions followed by recrystallization of the highly disorganized lattice to non-stoichiometric fcc structure having a composition close to Pr_6O_{11} and having a structure that can be regarded as a derivative of the fluorite lattice have been recorded both by distinct weight losses on TG and DTG curves and endothermic effects centred at 440° C in the DTA curve. The initially absorbed carbon dioxide was retained throughout these processes and was then evolved in the range 850 to 900° C indicated by a rapid fall in the TG curve and endothermic effect in this region of the DTA curve.

3.2. Mössbauer resonance studies

Mössbauer data are summarized in Table I. Typical Mössbauer spectra of some of the samples are shown in Fig. 3.

Mössbauer spectra of unannealed co-precipitate show a quadrupole split doublet with a $\delta/\mathrm{Fe} = 0.35 \pm 0.03$ mm sec^{-1} and $\Delta E_Q = 0.63 \pm 0.03$ mm sec^{-1} at 27° C and $\delta/\mathrm{Fe} = 0.38 \pm 0.03$ mm sec^{-1} and $\Delta E_Q = 0.65 \pm 0.03$ mm sec^{-1} at − 196° C. These values are quite close to those recorded for ferric oxide hydrate gels [5, 7, 8] and show a good agreement with those reported by Clifford [1] for 3 at% ^{57}Fe(III) co-precipitated with $Pr(OH)_3$. These values characterize Fe ions in the co-precipitate in the form of high spin ferric species with distorted octahedrally co-ordinated sites and apparently no magnetic ordering down to − 196° C.

Subtle variations in Mössbauer parameters of samples annealed at different temperatures reflect changes in local surroundings and in the structure and bonding of Fe ion microphases. An increased quadrupole splitting is also observed for samples annealed at 100 and 350° C. This may be accounted for by the creation of anion vacancies in the supercell due to the partial removal of water from the ferric oxide hydrate gel-like species resulting in increased distortion and a lowering of the site symmetry. An increase in the resonance effect magnitude is observed for samples annealed at 100° C. This results from stronger bonding between Fe ions and the host absorbers which achieve compactness on removal of sorbed water.

In samples annealed at 350° C, a broader doublet with a pronounced asymmetry in intensity of resonance lines and a considerable decrease in resonance effect magnitude is observed at 27 and − 196° C. These features indicate loosening of Fe ions, which still retain their gel character but become more labile on being held on or near the highly asymmetric surfaces of the host lattice which result from a pronounced dehydroxylation of praseodymium hydroxide.

Magnetically split spin-ordered spectra are observed both at 27 and − 196° C for samples annealed at, and above 600° C. A comparison of Mössbauer parameters of these samples with those of bulk $PrFeO_3$ [9] and the results of XRD studies confirm the presence of Fe ions precipitated in the form of $PrFeO_3$ micro-inclusions in Pr_6O_{11}. An X-band EPR examination at − 193° C

TABLE I Mössbauer parameters of 5 wt% Fe(III) co-precipitated with praseodymium hydroxide heated for 24 h at different temperatures

Heat treatment (° C)	Room temperature			Liquid nitrogen temperature		
	Isomer shift* δ† (mm sec^{-1})	Quadrupole splitting ΔE_Q‡(mm sec^{-1})	Hyperfine splitting H_n(kOe)‡	Isomer shift δ (mm sec^{-1})	Quadrupole splitting ΔE_Q(mm sec^{-1})	Hyperfine splitting H_n(kOe)*
None	0.35	0.63	0	0.38	0.65	0
100	0.33	0.65	0	–	–	–
350	0.30	0.68	0	0.41	0.85	0
600	0.42	0.06	506	0.50	0.02	551
725	0.44	0.01	507	0.50	0.02	557
825	0.38	0.03	512	–	–	–
1100	0.39	0.02	509	0.49	0.02	559

*Isomer shift values are with respect to iron.

†Error in δ and ΔE_Q is 0.03 mm sec^{-1} and the error in H_n is + 3 kOe.

‡1 Oe = 1000/4π Am^{-1}.

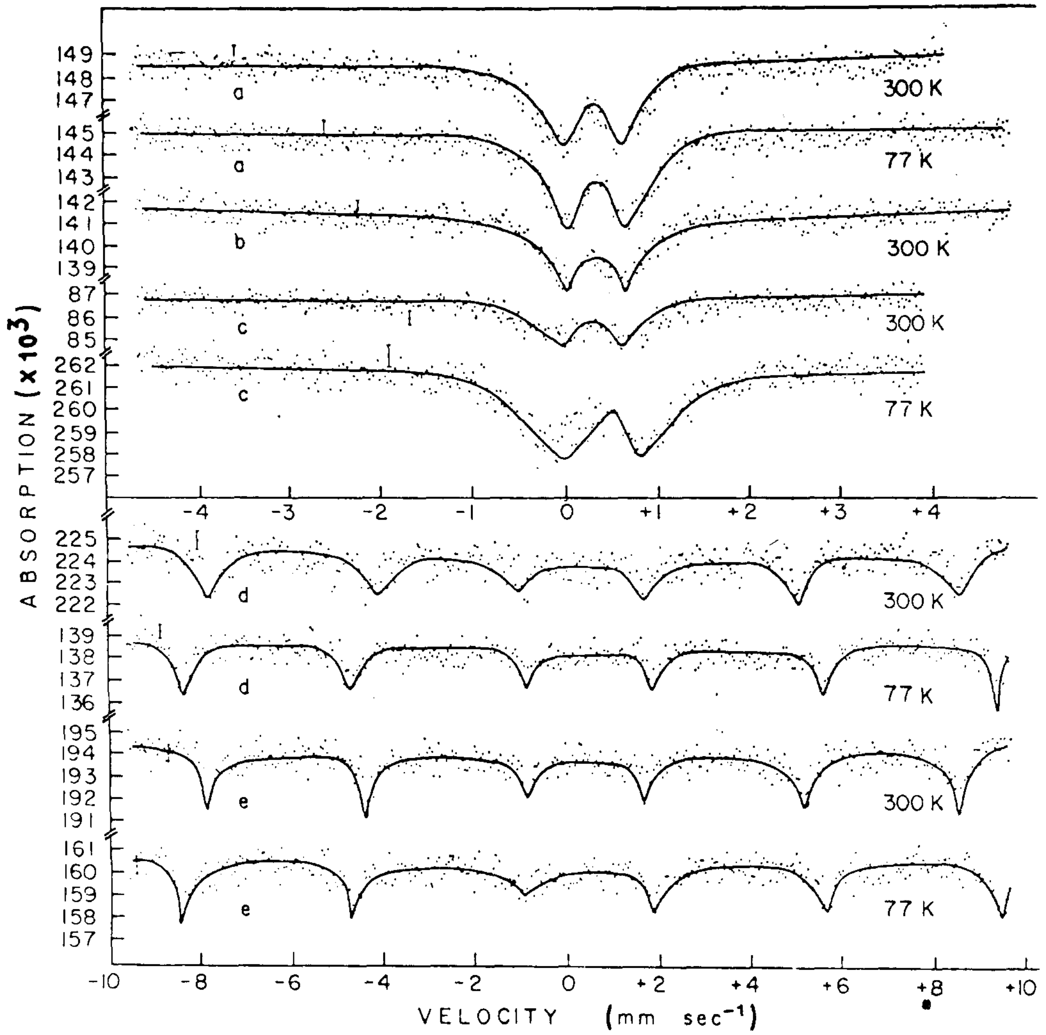

Figure 3 Mössbauer spectra at 27 and −196° C of 5 wt% Fe(III) with praseodymium hydroxide and annealed at different temperatures. Thermal treatment: (a) None (b) 100° C (c) 350° C (d) 600° C and (e) 725° C, each for 24 h.

[5, 6] showed an evelope of absorptions smeared out into a broad band at *g*-values not measurably different from 2.0 and with no distinct magnetic hyperfine splitting. In conformity with the observation of magnetically split Mössbauer spectra, the broad EPR band identifies the presence of superexchange coupled Fe ions subject to strong nearneighbour interactions in $PrFeO_3$ microcrystals. These strong exchange interactions wash out the effects of hyperfine splitting of EPR absorptions and a broad band arises apparently from the superposition of different EPR signals with slightly different *g*-values. These features indeed, are attributable to fast spin relaxation effects and to the fluctuations of local crystalline fields due to microheterogeneity of the defect host lattice of Pr_6O_{11} [10].

Microheterogeneity of the Pr_6O_{11} host lattice, and distribution in dispersion profiles of iron microphases within the host lattice also results, on the other hand, in a range of electric field gradient values acting at Fe ions, thereby producing similar overlapping spectra as evidenced by the broadening of Mössbauer resonance lines. Variations observed in Mössbauer parameters and apparent differences in the broadening and intensity of resonance lines reflect the differences in the distribution of particle sizes of $PrFeO_3$ clusters, and change in oxygen uptake and in other microstructural features accompanying the heat treatment at different stages.

Thus, observation of an increase in the resonance effect magnitude and a decrease in the broadening of resonance lines for samples annealed at 725° C suggests some enlargement in the particle size of $PrFeO_3$ microcrystals and a more uniform particle size distribution in a rather more perfectly crystallized lattice. A diminution of resonance effect magnitude is noticed in Mössbauer spectra of samples annealed at 825° C, at the same time showing not much variation in the width of the resonance lines. These features are interpreted to suggest that even though the $PrFeO_3$ clusters are of quite uniformly distributed particle sizes, there is a weakening of the forces with which they are held in Pr_6O_{11}. According to thermal and microstructural evidence, in this region the Pr–O system (owing to evolution of CO_2) undergoes a series of complex phase changes resulting in a high surface area solid with defects and disorder distributed over the entire lattice. Concomittant to these variations, a loosening of iron sites in $PrFeO_3$ microphases held in Pr_6O_{11} is indeed expected in the vicinity of these lattice transformations. Finally, in samples annealed at 1100° C, sharpening of resonance lines takes place indicating a more uniform distribution and enlargement of particle size and an increased coupling of iron microphases with the host lattice formed as a result of sintering and grain growth at this temperature.

It is of obvious interest to note that though quadrupole splitting and hyperfine field values observed by us for Fe ions dispersed in praseodymium oxide lattices are in quite good agreement with those reported for bulk $PrFeO_3$ by Eibschutz *et al.* [9] a distinct increase in the isomer shifts in our samples is discerned. These differences may possibly be accounted for by the subtle dilational variations in iron–oxygen bonds in $PrFeO_3$ microcrystals and to different lattice contributions to the second-order Doppler shift. Further, it is noted that Mössbauer charactistics of Fe ions doped in $PrO_{1.83}$ [1] are very much different in both nature and magnitude compared with those observed in the present study for iron-doped Pr_6O_{11} lattice. To explain the observed features of the Mössbauer spectra, Clifford postulated the substitution of iron ions for praseodymium ions in the praseodymium oxide lattice. However, there is no need to assume this as in all likelihood Clifford's [1] observations appear to indicate Fe ions in the form of paramagnetic $PrFeO_3$ defect species in crystal fields of very low symmetry showing a variety of relaxation-broadened Mössbauer spectra. There appear to be more involved aspects of surface character and defect states of these microphases relating to their concentration and complex modes of distribution within the host lattices which merits further investigation.

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