

## II. CHEMISTRY

### Physical Chemistry

# MÖSSBAUER RESONANCE CHARACTERIZATION AND THERMAL TRANSFORMATION OF IRON(III) COPRECIPITATED WITH LANTHANUM TRIHYDROXIDE

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Mössbauer spectra at 300 and 77 K of Fe (III) 5 weight per cent ions coprecipitated with lanthanum trihydroxide and heated for 24 hours at 100, 350, 600 725 and 825 °C were investigated. According to thermal (DTA, TG and DTG) analysis, IR and electron microscopy studies, the transformation of lanthanum trihydroxide to lanthanum sesquioxide occurs on annealing, through an intermediate oxyhydroxide LaOOH phase. In electron microscopy examination, this phase is characterized by appearance of a spindle shaped monoclinic morphology with sharp crystal edges. On the basis of the Mössbauer spectral parameters of the initial coprecipitate, it is inferred that the coprecipitate consists of iron ions in high spin ferric form in distorted octahedral sites and show considerable semblance to those of iron ions in ferric oxide hydrate gels. The variations in Mössbauer features of annealed samples characteristically reflect the loosening of iron ions due to the dehydroxylation of the samples annealed upto 350°C. On increasing the annealing temperature to 600 °C, precipitation of iron as LaFeO<sub>3</sub> microphases takes place as has also been substantiated by X-ray diffraction analysis. The EPR spectra at 80 K give evidence for the existence of iron ions as isolated LaFeO<sub>3</sub> centres and as pairs or large groupings forming microcrystalline LaFeO<sub>3</sub> species in La<sub>2</sub>O<sub>3</sub>. An approach towards a more uniform distribution of iron microphases with an increased coupling with the host environment is discerned for samples annealed at 700 °C and above, but the features of growth inhibition of orthoferrite microcrystallites by the lanthanum oxide lattice are persistently retained altogether.

**Keywords:** Mössbauer Resonance; Thermal Transformation; Lanthanum Hydroxide.

### INTRODUCTION

MÖSSBAUER and EPR spectroscopy studies on paramagnetic iron impurity doped diamagnetic rare earth oxide type lattices have been made by several workers. Clifford (1967) reported <sup>57</sup>Fe<sup>3+</sup> Mössbauer spectroscopic parameters for iron ions doped in polycrystalline hexagonal A-La<sub>2</sub>O<sub>3</sub>. Bouysset *et al.* (1975) investigated room temperature EPR spectra of iron doped single crystals of lanthanum sesquioxide obtained by using solar furnace. In both these investigations, and also in those reported by Birchall and Reid (1973) on iron doped scandium oxide and by Vainer

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*et al.* (1974) on iron doped yttrium oxide, it was observed that iron ions remain obdurately trivalent and it was postulated that these iron ions substitute for rare earth ions in host oxide lattice forming some sort of solid solutions. However, contrary to the latter, recent observations made by us have revealed formation of discrete orthoferrite clusters in iron doped rare earth oxide systems.

The present paper in continuation to our previous studies, Vajpei (1978), Saraswat *et al.* (1979), aims at investigating the changes in the Mössbauer spectra recorded at 300 and 77 K, of samples annealed at different temperatures so as to infer the nature of the iron ions distributed in initially coprecipitated lanthanum trihydroxide and in its annealed products. For characterization and investigation of thermal transformations of the coprecipitate, the samples were initially examined with thermal analysis (DTA, TG and DTG), IR spectroscopy, electron microscopy, powder X-ray diffraction and EPR spectroscopy studies and an attempt is made to correlate the results so obtained with the data obtained  $^{57}\text{Fe}$  Mössbauer spectroscopy measurements on these systems.

#### MATERIALS AND METHODS

Excess of ammonia was added to mixed solutions of ferric and lanthanum chloride containing 5 weight per cent of Fe (III) and 95 weight per cent of lanthanum (III) ions. The precipitate formed was repeatedly washed, filtered and dried at room temperature. Starting from this original coprecipitate, samples annealed for 24 hours each at 100, 350, 600, 725 and 825 °C were obtained.

Thermal analysis of original coprecipitate was performed on a Paulik Erdey Derivatograph model 1969 manufactured by MOM, Budapest. The IR spectra were obtained for samples in KBr discs using a Beckman model IR-20 spectrophotometer operated in double beam mode in the range 4000–250  $\text{cm}^{-1}$ . For electron optical observations, specimens were mounted on to a thin film of carbon black deposited on the 200 mesh copper grids and were examined with a Philips EM 200 electron microscope using 40 kV beam. The powder XRD pattern at room temperature and EPR-spectrum at 80 °K at X-band were also recorded for samples annealed at 600 °C.

Mössbauer spectra of samples were recorded in transmission geometry on a constant acceleration velocity transducer coupled to  $^{57}\text{Co}$  in Cu-matrix. Iron metal was used for velocity calibration and as the standard for the central shift data.

#### RESULTS AND DISCUSSION

##### *Characterization and Thermal Transformations of Coprecipitate*

Differential thermal curve of the original coprecipitate in Fig. 1 exhibits endothermic effects peaked at 140, 400, 680 and 780 °C. The latter two effects are contained in a closely spaced doublet. TG curve shows distinct steps for the weight losses associated with these effects, as is also being indicated by the coincidence of DTG and DTA-curve peaks.

IR spectra of original coprecipitate indicated presence of small amounts of  $\text{La}(\text{OH})\text{CO}_3$  which may result from interaction on the surfaces of highly basic lanthanum hydroxide with atmospheric  $\text{CO}_2$ . Samples annealed at 200 and 250 °C show

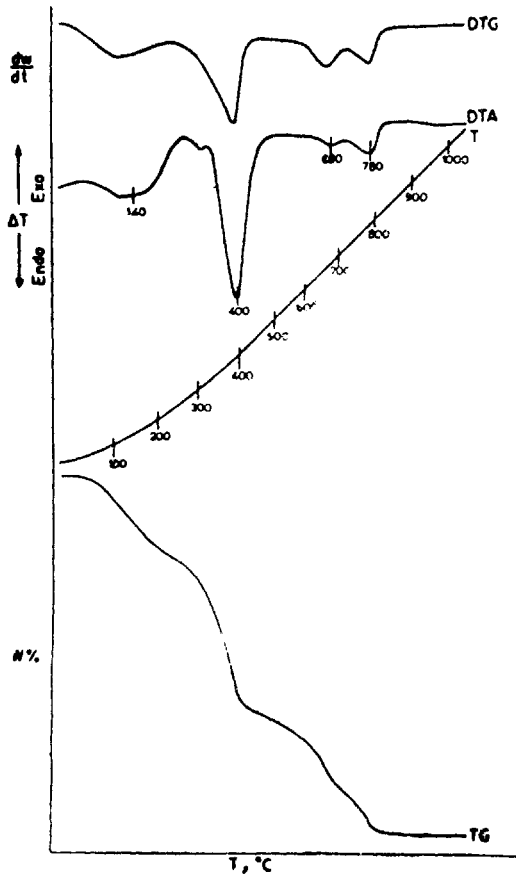


FIG. 1. Thermal curves for Fe(III) 5 weight per cent coprecipitated with Lanthanum hydroxide (heating rate  $10\text{ }^{\circ}\text{C min}^{-1}$ ).

processes of dehydroxylation of lanthanum hydroxide and samples annealed at  $600\text{ }^{\circ}\text{C}$  in their IR-spectra show features identifiable with those reported for  $\text{La}_2\text{O}_3$ . Surface carbonation and additional features due to iron oxide component complicate however, the interpretation of IR spectra obtained against that of pure lanthanum oxide. An examination of electron microphotographs of unheated sample shows that it consists of small amorphous particles alongwith some hollow red shaped crystals indicating the morphology characteristic of lanthanum trihydroxide [Fig. 2(a)].

The samples annealed at  $200$ ,  $250$  and  $275\text{ }^{\circ}\text{C}$  (Fig. 2b) exhibit emergence of large monoclinic to oblong shaped crystalline sheets of  $\text{LaOOH}$ . Annealing at  $600\text{ }^{\circ}\text{C}$  results in further dehydroxylation of  $\text{La}(\text{OH})_3$ , through  $\text{LaOOH}$  phase and formation of hexagonal A- $\text{La}_2\text{O}_3$ . Samples annealed to  $900\text{ }^{\circ}\text{C}$  show pronounced growth of hexagonal platelets of A- $\text{La}_2\text{O}_3$  [(Fig. 2 c)].

The calculated  $d$ -values and relative intensities of lines in the powder X-ray diffraction pattern of sample annealed at  $600\text{ }^{\circ}\text{C}$  indicated existence of lanthanum orthoferrite in  $\text{La}_2\text{O}_3$ . In addition, the presence of some hydroxide, bicarbonate and carbonate phases of lanthanum are also discerned from X-ray diffraction.

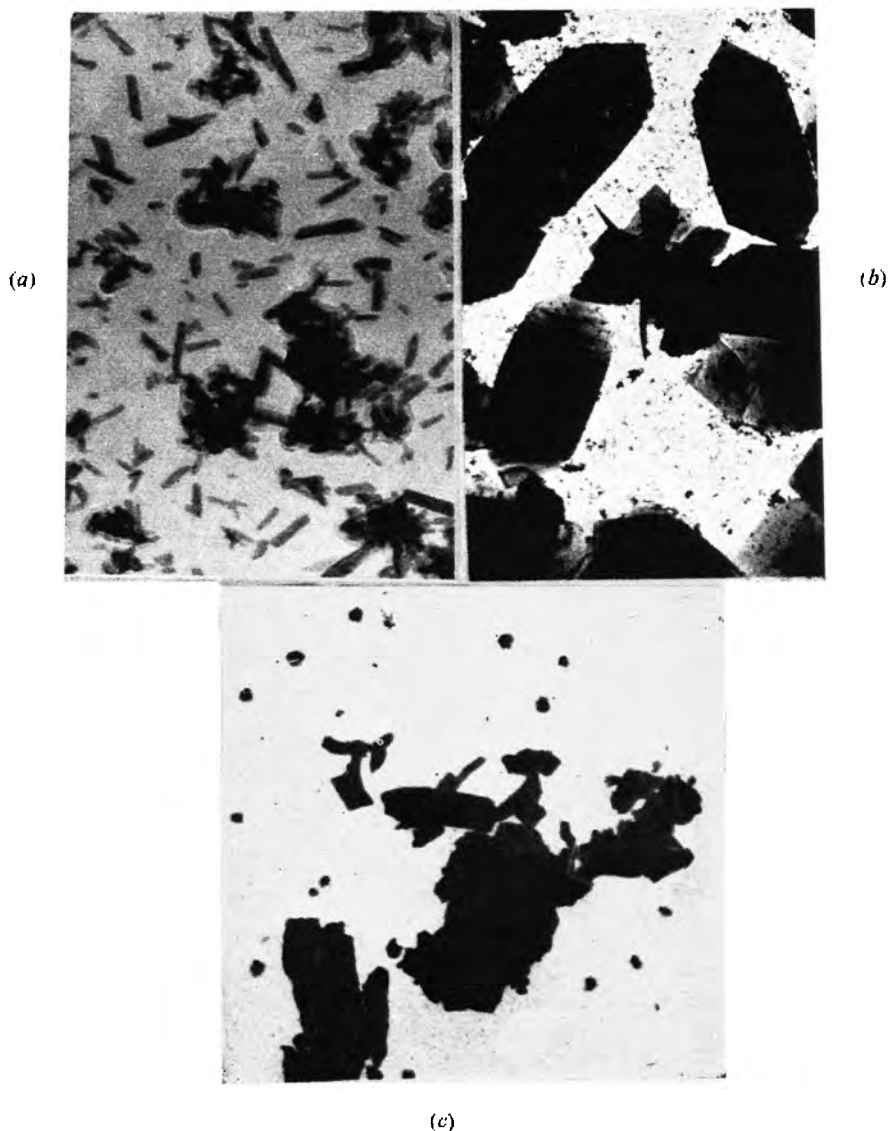


FIG. 2. Crystal morphology and microstructure of coprecipitate, subject to heat treatment: (a) None, (b) Annealed at 275 °C, and (c) at 900 °C for 24 hrs each, at magnifications (a)—( $\times 160000$ ), (b)—( $\times 8700$ ), and (c) at ( $\times 90000$ ).

Consistent with these observations of IR, electron microscopy and XRD studies, it follows from thermal analysis that decomposition of Fe (III) coprecipitated lanthanum trihydroxide begins at 140 °C and through an intermediate phase  $\text{LaOOH}$ , crystallization of  $\text{La}_2\text{O}_3$  occur around 450 °C. However, the initially absorbed carbon dioxide was retained throughout subsequent dehydroxylation and was later evolved in the range 650–800 °C as indicated by an endothermic effect in this region in DTA-curve.

*Mössbauer Resonance Studies*

Mössbauer spectra of original coprecipitate and of samples annealed at different temperatures are set out in Fig. 3 and parameters from the spectra are summarised in Table I.

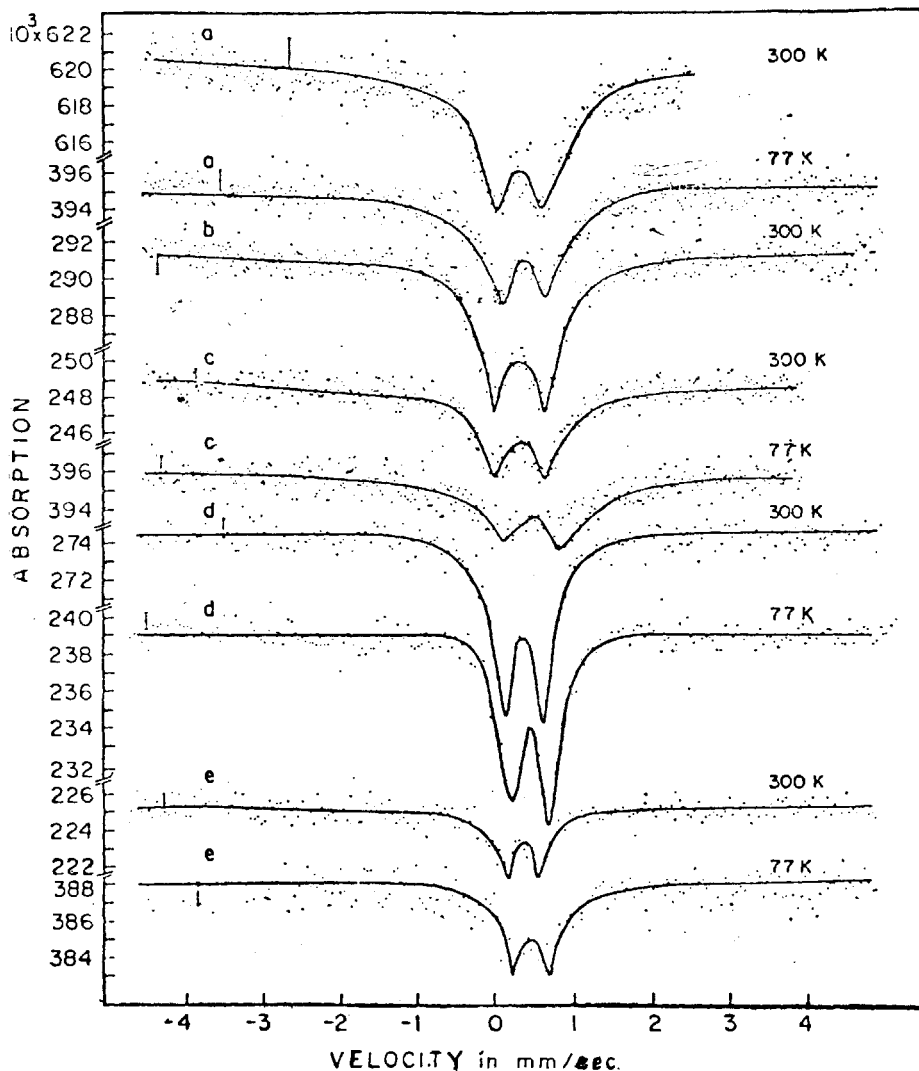


FIG. 3. Mössbauer spectra at 300 and 77 K of Fe(III) 5 weight per cent coprecipitated with lanthanum hydroxide, and annealed at different temperatures—Thermal treatment: (a) None (b) Annealed at 100 (c) 350 (d) 600 and (e) at 725 °C each for 24 hours.

Mössbauer spectra of unheated sample consist of a well-resolved quadrupole split doublet both at 300 and 77 K with slight asymmetry in intensity of the doublet components. Iron ions exist in high spin ferric form with distorted octahedral

TABLE I

*Mössbauer parameters of iron (III) (5 weight per cent) coprecipitated with lanthanum hydroxide heated for 24 hours at different temperatures*

Heat treatment (°C)	Room temperature			Liquid nitrogen temperature		
	I. S.	Q. S.	FWHM	I. S.	Q. S.	FWHM
	$\delta$ (mm/s)	$E_Q$ (mm/s)	(mm/s)	$\delta$ (mm/s)	$E_Q$ (mm/s)	(mm/s)
None	0.32	0.58	0.59	0.37	0.56	0.65
100	0.31	0.65	0.65			
350	0.31	0.65	0.66	0.48	0.70	0.80
600	0.41	0.44	0.51	0.49	0.48	0.58
725	0.39	0.39	0.29	0.49	0.48	0.52

I. S. are with respect to iron metal. Error in  $\delta$  and  $E_Q$  is  $\pm 0.03$  mm/s.

coordination as is evident from I. S. and Q. S. values (see Table I). These values are quite close to those reported for ferric oxide hydrate gel particles (Vajpei, 1978; and Saraswat *et al.* 1977a, 1980). Asymmetry observed in doublet component emerges from the involvement of surface effects. As for iron ions dispersed at highly asymmetric surface sites, vibrational amplitudes would not be the same in all directions. Thus the anisotropy of recoil free fraction i.e., Goldanskii-Karyagin effect leads to an asymmetry observed in intensity of quadrupole split doublet. Besides, the texture and spin lattice relaxation effects may manifest themselves to different extents depending on the varying degrees of iron ions dispersion in the host lattice. These effects again result in asymmetry in intensities of doublet components. Mössbauer spectrum at 77 K compared to that of 300 K for unheated sample shows increase in line broadening and second order Doppler variations. Effects of freezing and differential agglomeration at 77 K (Saraswat *et al.*, 1977b; and Vajpei, 1978) also seem to affect the features observed in Mössbauer spectra of Fe (III) ions coprecipitated with lanthanum trihydroxide.

Samples annealed at 100 °C show an increase in quadrupole splitting and broadening of resonance lines. These features indicate distortions in symmetry around iron ions as a result of partial removal of water from the coprecipitate and are reminiscent to the variations observed earlier for ferric oxide hydrate gels (Vajpei, 1978; and Saraswat *et al.*, 1977a, 1980). Increase in the resonance effect magnitude observed in samples annealed at 100 °C indicate that iron ions are more rigidly held in the absorber lattice which becomes more compact.

In samples annealed at 350 °C, a pronounced dehydroxylation of samples occur resulting in increase of surface area and defects in the lattice. Structural inhomogeneities of environment in the form of vacancies and lattice strains result in broadening of lines and a substantial decrease in the resonance effect magnitude, which thereby indicate loosening of iron ions in octahedral sites during dehydroxylation. Mössbauer parameters of the samples annealed at 100 and 350 °C are much the same indicating persistence of iron oxide hydrate species till this stage. It seems

that lanthanum hydroxide inhibits conversion of finely dispersed ferric oxide hydrate gel like species into  $\alpha\text{-Fe}_2\text{O}_3$ .

A distinct lowering in the quadrupole splitting from 0.65 mm/s to 0.44 mm/s; and an increase in isomer shift  $\delta/\text{Fe}$  from 0.31 mm/s to 0.41 mm/s has been observed in samples annealed at 600 °C for 24 hours against the samples annealed at 350 °C. Powder X-ray diffraction analysis of the same has already shown reflections characteristic of the formation of lanthanum orthoferrite. Observed broadening and lack of sharpness of X-ray reflections indicated that orthoferrite phase exists in highly dispersed form with lattice imperfections.

However, for bulk  $\text{LaFeO}_3$  Eibschutz *et al.* (1967) have reported isomer shift  $\delta/\text{Fe} = 0.358$  mm/s and  $\delta/\text{Fe} = 0.428$  mm/s at 296 and 85 °K respectively. Considering finely dispersed state of iron microphases in our samples, observed shift values at 300 and 77 K are in good agreement with those for bulk  $\text{LaFeO}_3$ . A sizable quadrupole splitting observed for iron ions is attributable to the large lattice contribution from the asymmetric surfaces of  $\text{La}_2\text{O}_3$  to the EFG on the iron ions. Low concentration and dispersion of  $\text{LaFeO}_3$  accounts for complete absence of magnetic hyperfine structure at 300 and 77 K.

In the form of  $\text{LaFeO}_2$  species in  $\text{La}_2\text{O}_3$ , iron ions may exist on the surface of  $\text{La}_2\text{O}_3$  grains as isolated  $\text{Fe}^{+3}$ -species, or as pairs or large groups. The above is indeed shown by the large line width of the doublet of the Mössbauer spectra of these samples at 300 and 77 K. The EPR signal at  $g = 4.3$  and  $g = 2$  values observed by us for these samples confirm the existence of  $\text{LaFeO}_3$  in the above two forms. The signal at  $g = 4.3$  has been attributed (Vajpei, 1978; and Saraswat *et al.*, 1979) to iron ions as isolated  $\text{LaFeO}_3$  centres on the surfaces of  $\text{La}_2\text{O}_3$  grains and these are the ions with negligible exchange coupling. Vacancies and species like  $\text{OH}^-$  groups absorbed on the surfaces appear to prevent the access of the paramagnetic species to form large clusters. The high field absorption with a distinct tendency for hyperfine splitting observed by us around  $g = 2$  characterizes  $\text{LaFeO}_3$  species in the form of pairs or large groups forming ultrafine lanthanum orthoferrite particles. The spins deep inside these microphases are anticipated to remain locally aligned in anti-ferromagnetic sense characteristic of  $\text{LaFeO}_3$  phase (Eibschutz *et al.*, 1967).

In samples annealed at 725 °C and above, inhomogeneous distribution of iron ions giving isolated as well as clusters of  $\text{LaFeO}_3$  species is finally destroyed to such an extent that narrow linewidth in the Mössbauer spectra are observed indicating uniformity in the structure and distribution of  $\text{LaFeO}_3$  microphases formed in  $\text{La}_2\text{O}_3$  lattice.

Further, according to thermal and IR analyses, removal of sorbed carbon dioxide from lanthanum sesquioxide takes place which result in creation of macropore structure and surface irregularities on the lattice. An enlargement in the size of  $\text{LaFeO}_3$  particles as a result of annealing at a higher temperature and its more uniform distribution is implied by narrower lines of the doublet. That iron microphases are loosely held in the host lattice is again reflected by a decrease in resonance effect.

At a higher temperature of annealing e.g., at 875 °C transition to well crystallized  $\text{La}_2\text{O}_3$  is complete and an increase in resonance effect is observed as a conse-

quence of local densification of host lattice and an increase in the strength of binding of iron ions on to  $\text{La}_2\text{O}_3$  grains.

It is interesting to note here that Clifford's (1967) investigation on iron doped  $\text{La}_2\text{O}_3$  is qualitatively similar to the work presented here in that no magnetic ordering was discerned for iron ions. However, the Mössbauer parameters reported by Clifford are different. In fact, large value of quadrupole splitting in Clifford's sample indicates for a more severe distortion of iron ions due to the presence of internal compressions and differential stresses in the interior of  $\text{La}_2\text{O}_3$ . Summary studies presented in this work indicate that iron ions in  $\text{La}_2\text{O}_3$  A-hexagonal form, exist in the form of  $\text{LaFeO}_3$  species in highly dispersed state showing no spin ordering down to 77 K in their Mössbauer spectra. Involvement of host lattice surface is ascribed to cause distortions in the site symmetry and disruption of magnetic ordering of iron ions.  $\text{LaFeO}_3$  species are formed directly from coprecipitated hydroxide without prior formation of any intermediate phase. Variations observed in distribution of iron ions are identifiable with the differences in microstructure evolved in the lattice obtained at different stages of annealing and show the formation of isolated as well as clustered  $\text{LaFeO}_3$  species in samples annealed at 600 °C.

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