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Magnetic properties of lanthanum orthoferrite fine powders prepared by different chemical routes¶

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Abstract. Fine powders of lanthanum iron oxide, $LaFeO_3$, have been prepared by solid state reaction as well as sol–gel synthesis and nebulized spray pyrolysis. Structures, morphologies and magnetic susceptibility measurements of these powders have been examined. The powders prepared by all the three low-temperature routes contain nearly spherical particles with an average diameter of 40 nm. These samples show a lower Neel temperature than the powder prepared by solid state reaction besides showing much lower magnetic susceptibility at low temperatures.

Keywords. Lanthanum iron oxide; nanoparticles; sol–gel synthesis; nebulized spray pyrolysis; magnetization.

1. Introduction

The magnetic properties of ultrafine particles have become of importance in recent years because of their wide range of applications in magnetic recording, catalysis and as ferrofluids, pigments in paints and ceramics.[1–4] Magnetic materials show enormous changes in the values of coercivity,[5] saturation magnetization[6] and ordering temperature[7] when the particle size is of the order of single domain size. In most of the materials, a substantial decrease in the Curie temperature (T_c) is observed with the decreasing particle size. In contrast to this, $MnFe_2O_4$ show increase in T_c due to scaling effects.[8] Antiferromagnetic nanoparticles have recently gained attention because of their magnetization reversal by quantum tunneling.[9,10] The Neel temperature decreases with decreasing particle size and the value is significantly lower compared to the bulk material. Though many methods are available to prepare nano-particles, the synthesis of particles with uniform shape and narrow size distribution poses a real challenge. Vapour condensation, mechanical attrition, spray pyrolysis and sol–gel processing are employed to obtain nanoparticles with a narrow size distribution. Since the magnetic properties are crucially dependent on both the shape and size of particles, choosing the right method of preparation becomes crucial. In recent times, the sol–gel method is widely used as it offers control over the size and shape of the particles.

Rare earth orthoferrites, $RFeO_3$ where R is the rare earth, crystallize in perovskite structure with Fe^{3+} ion surrounded by six oxygen ions giving octahedral coordination. The unit cell consists of four formula units of $RFeO_3$ and the crystal symmetry is

¶Dedicated to Professor C N R Rao on his 70th birthday
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orthorhombic with the space group *Pbnm*.[11] The magnetic structure determined by neutron diffraction indicates the presence of at least four spin configurations. However, with respect to static measurements, the magnetic structure can be visualized as consisting of two Fe^{3+} sublattices with antiferromagnetic interaction.[12] These are weakly ferromagnetic and exhibit unusually high Neel temperature, T_N, due to the canting of Fe sub-lattice spins.[11–13] One of the interesting observations is that T_N depends on the size of the rare earth ion. As La^{3+} is non-magnetic, magnetic interaction between the rare earth ion and Fe^{3+} is absent and is therefore ideal for study of the effect of particle size on T_N. We have studied the properties of $LaFeO_3$ powders prepared by employing four different routes.

2. Experimental

Powders of lanthanum iron oxide were prepared by the high-temperature solid state reaction, sol–gel method as well as by nebulized spray pyrolysis. The high temperature solid state reaction yielded micron-size particles (labelled as SS) and the method involved mixing of high purity oxides La_2O_3 (IRE; 99·9% purity) and Fe_2O_3 (merc; 99·99% purity) thoroughly to ensure homogenization and firing at 1473 K for 20 h. Intermittent grindings were carried out to ensure homogenization. Three different low temperature routes were adopted to prepare $LaFeO_3$ particles of nano-size. To obtain $LaFeO_3$ particles (labelled as LF1), equi-molar amounts of lanthanum nitrate and iron nitrate were dissolved in water and mixed with 60 mole percent of ethylene glycol. The resulting solution was dried in a oven at 350 K and fired at 873 K for 12 h. To obtain $LaFeO_3$ particles (labelled as LF2), lanthanum nitrate and iron acetylacetonate were mixed (1 : 1 molar ratio) and added to 60 mole percent of ethylene glycol. The resulting viscous solution was dried at 350 K and fired at 873 K for 12 h. To obtain $LaFeO_3$ particles (labelled as NSP), nebulized spray pyrolysis method was adopted.[14] Equimolar amounts of lanthanum acetylacetonate and ferric acetylacetonates were dissolved in methanol solvent (0·1% mole). The solution was nebulized and the resulting mist consisting of fine droplets (sub-micron size) of solution was carried to reactor zone which was kept at 673 K, using air as a carrier gas. The metal acetylacetonates decomposed and yielded fine particles of $LaFeO_3$.

Powder X-ray diffraction patterns were recorded using an XDL 3000 powder X-ray diffractometer to check the phase formation and purity. Lattice parameters were calculated using high angle reflections of XRD. The full width at half maximum (FWHM) of X-ray reflections were used to calculated particle size by using Debye Scherrer formula. A Leica 440I scanning electron microscope (SEM) was used to study the morphology of the powders. An Oxford EDX analyser attached with SEM was used for the compositional analysis. Magnetic susceptibility measurements were carried out using a Faraday balance by field cooling the sample from 900 K in a field of 4000 Oe.

3. Results and discussion

3.1 *Structure and morphology*

X-ray diffraction patterns of powders prepared by four different routes are shown in figure 1. All the reflections observed were indexed based on the orthorhombic unit cell of space group *Pbnm*. No extra peaks were observed, indicating that the powders prepared were single phasic in nature. The refined unit cell parameters for the powders SS, LF1,

LF2 and NSP are listed in table 1. The cell parameters for the powders obtained from solid state reaction matched with the values reported in the literature and the other three samples showed a little deviation in the cell parameters. The cell parameters for all the samples studied are presented in table 1. XRD reflections of SS are very sharp indicating the presence of micron-size particles. Whereas, particles obtained by other methods (LF1, LF2 and NSP) showed broad reflections indicting the presence of fine particles. The particle size is calculated by the Debye–Sherrer formula:

$$t = 0{\cdot}9\,\lambda/B\cos\theta_B,$$

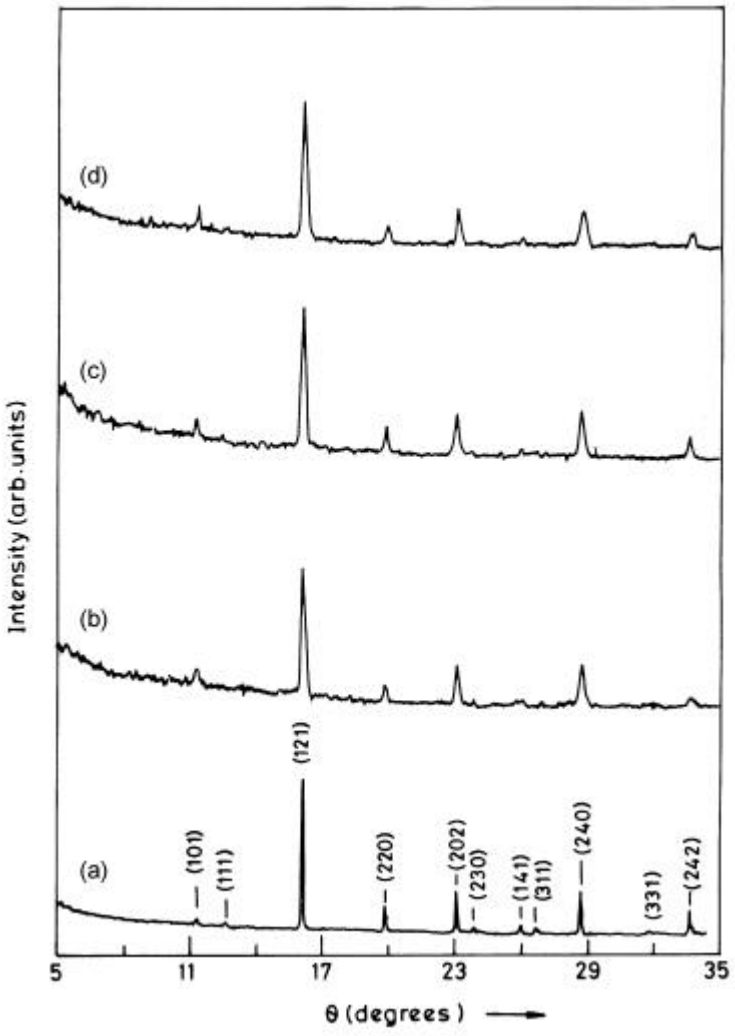

Figure 1. X-ray diffraction patterns of $LaFeO_3$ powders prepared by (a) solid state reaction (SS), (b) sol–gel synthesis (LF1), (c) sol–gel synthesis (LF2) and (d) nebulized spray pyrolysis (NSP).

Table 1. Refined unit cell parameters, FWHM values and particle size from X-ray diffraction as well as from SEM measurements for SS, LF1, LF2 and NSP powders.

$LaFeO_3$	Unit cell parameters (nm)	FWH (dq)	Particle size from XRD (nm)	Particle size from SEM (nm)
SS	0·5552 0·7856 0·5558	0·1055	–	1000
LF1	0·5548 0·7839 0·5541	0·2346	41·4	60
LF2	0·5538 0·7853 0·5554	0·2297	42·5	65
NSP	0·5557 0·7830 0·5531	0·2449	37·6	55

where t is the size of the grain, λ is the wavelength of X-ray used (CuK_a = 1·5421 Å) and θ_B is Bragg's angle. FWHM measured for (202) reflection was used to calculate the value of B from the following equation:

$$B = (B_m^2 - B_s^2)^{1/2},$$

where B_m is the FWHM of the sample and B_s is the FWHM of any standard particle of size greater than 200 nm and is used to correct instrumental broadening. In the present case, the FWHM of SS particles was used to obtain values of B_s. Particle sizes obtained by X-ray line broadening measurements for LF1, LF2 and NSP are 60, 65 and 55 nm respectively and are presented in table 1.

EDX analysis shows that La and Fe are in 1 : 1 ratio indicating the uniform stoichiometry of the compounds. No segregated minority phases were seen when particles of different routes were subjected to EDX analysis. In figure 2 we show the SEM micrographs of all the powders prepared. Nearly spherical particles with clear grain boundary are observed for powder obtained by SS method (figure 2a). The size of the particles is in the range 1 μm. Figure 2b–d show the size and the shape of the particles obtained by LF1, LF2 and NSP respectively. The particle size of all these powders is small compared to that of SS and in the nanometre range. Nearly spherical particles with narrow size distribution is seen in all the cases. The particle size obtained from XRD line broadening corroborates well with the particle size seen on the SEM pictures (table 1). The average particle size is around 80 nm.

3.2 *Magnetic susceptibility measurements*

Magnetic susceptibility (χ) versus temperature (T) plots are presented in figure 3. Particles obtained by SS route show substantial increase in χ below 750 K indicating the onset of magnetic ordering and this value saturated at lower temperatures. For the particles prepared by other methods, the ordering temperature T_N is 700 K which is substantially low compared to that of the SS particles. The suppression of T_N can be

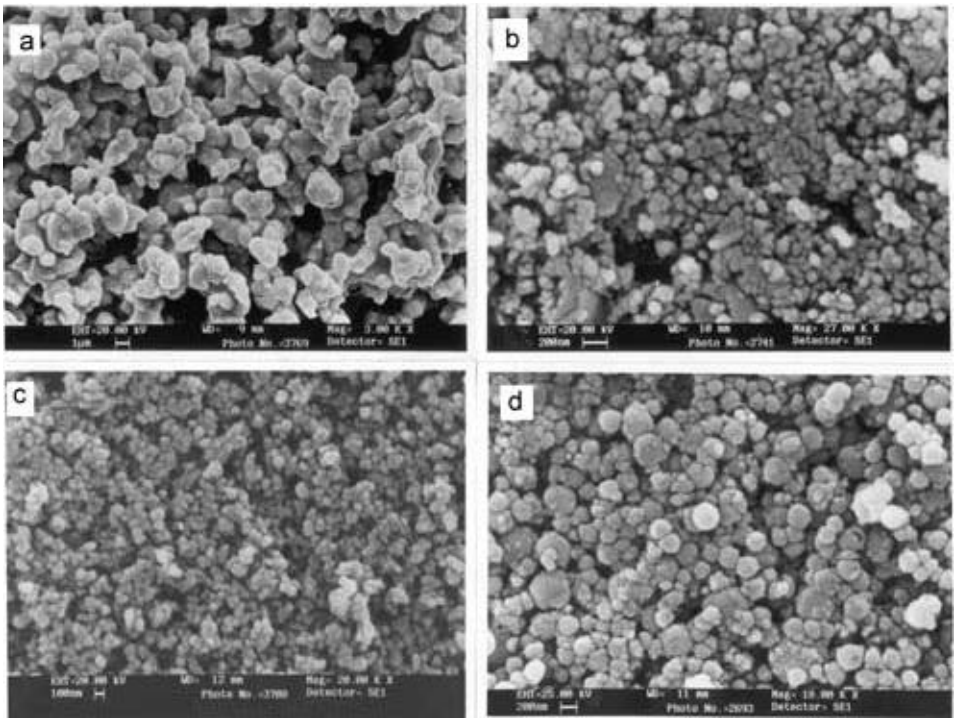

Figure 2. Scanning electron micrographs of $LaFeO_3$ powders prepared by (**a**) solid state reaction (SS), (**b**) sol–gel synthesis (LF1), (**c**) sol–gel synthesis (LF2) and (**d**) nebulized spray pyrolysis (NSP).

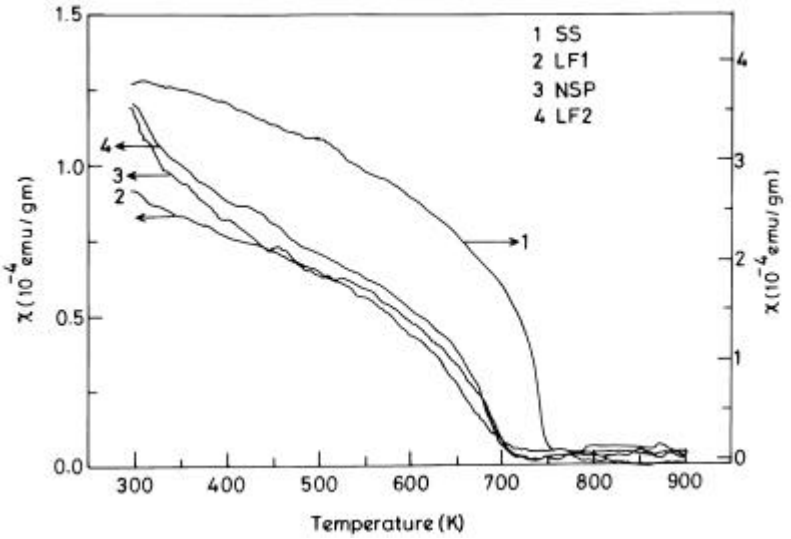

Figure 3. Temperature variation of susceptibility of $LaFeO_3$ powders prepared by (**a**) solid state reaction (SS), (**b**) sol–gel synthesis (LF1), (**c**) sol–gel synthesis (LF2) and (**d**) nebulized spray pyrolysis (NSP).

explained by using finite size scaling theory.[15] According to this theory, the shift in the transition temperature depends on the size of the particle. Well below the ordering temperature the susceptibility value saturates. It is to be noted that the magnetic susceptibility of particles prepared by low temperature routes is substantially lower than that of the SS particles. The difference may be either due to presence of non-magnetic oxide layer around the grain boundary or high degree of canting of the magnetic moments in the oxide layer coating the particles.

4. Conclusions

In summary, $LaFeO_3$ particles prepared by low temperature routes yielded nano-sized particles of around 40 nm with narrow size distribution. The particles are spherical in nature with narrow size distribution. The EDX analysis shows that all the powders prepared have stoichiometric compositions. The magnetic measurements shows that the ordering temperature T_N, for these nanoparticles is substantially lower than that of the SS particles. The decrease in T_N may be due to finite size scaling effect. Below ordering temperature, the c values of nanoparticles are lower compared to that of the bulk.

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