Structure and Magnetic Properties of Perovskite LaFeO$_3$ Nanocrystals Synthesized Via Reverse Micelle Technique

Abdullah A. Saad[1*], Wasi Khan[1], Pooja Dhiman[2], A. H. Naqvi[1], M. Singh[2]

[1]Centre of Excellence in Materials Science (Nanomaterials), Department of Applied Physics, Z.H. College of Engg. & Tech., Aligarh Muslim University, Aligarh 202 002, U.P., India

[2] Department of Physics, Himachal Pradesh University, Shimla-171 005, India

* Corresponding author: abdullah_talha2004@yahoo.com

Abstract Orthorhombic structure perovskite LaFeO$_3$ (LFO) nanoparticles (NPs) were prepared by reverse micelles method. The control of particle size was achieved by varying the water to surfactant molar ratio. The dried precipitate was transformed to pure LaFeO$_3$ phase by calcinations at 750 ºC. The average particle size was found to increase with increase in water to surfactant ratio(R). The nanostructure properties were studied by using contact mode of atomic force microscopy (AFM), X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometer (EDS) techniques. These techniques led themselves very well to investigate the structure of NPs and to find out properties and structure on surface of LFO. At room temperature the magnetic properties (M–H) were measured using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 20 kOe.

Keywords Reverse micelle, Nanoparticles, XRD, Magnetization

1. Introduction

Reverse micelles, or water-in-oil microemulsions, incorporate a variety of solutes. The distribution of the solute between the surrounding solvent and the micelles can be described in terms of a partition constant based on a two pseudophases model that can be expanded to three pseudophases in micelles with high water to surfactant mole ratios. In these systems, two partition constants can be defined, one between the external solvent and the micellar interface, and other between the external solvent and the inner water pool [1]. The perovskite structures with general formula ABO$_3$ have been formed by mixed oxides of rare earth elements and d transition metals. Lanthanum ferrite (LaFeO$_3$) has orthorhombic symmetry perovskite structure (a= 8.135 Å, b= 6.040 Å, and c= 8.540 Å) and an antiferromagnetic insulator with Nell temperature T_N = 750K [2]. These materials are interesting for catalytic applications due to the extensive range of elemental compositions that can be prepared as crystalline structures [3]. The molecular structure of the surfactant affects the size of micelle water pools and is it common in some surfactant systems to use a co-surfactant to produce a larger range of micelle sizes, such as CTAB, NP4 and NP7. It has been shown that using this combination also improves solubilization and overall micelle stability when compared to the corresponding single surfactants [4]. By using reverse micelles, we have been able to control the size and partially the shape of metallic copper particles. Recently we observed that the reducing agent plays an important role in the control of particle size and in the final oxidation state at the surface.

2. Experimental

LaFeO$_3$ NPs were prepared using reverse micelle technique. A quaternary system of iso-octane/CTAB/n-buty alcohol/water was selected in this RM process. In this process we used two

kinds of RM solutions namely RM1 and RM2. For first solutionRM1contained (5 wt %) an aqueous solution of an equimolar mixture (0.1M) of ($La(No_3)_3.6H_2O$) and ($Fe(No_3)_3.9H_2O$), CTAB as a surfactant (7.5 wt%), n-buty alcohol as a co-surfactant (7.5 wt%) and iso-octane as oil (30 wt%). The stirring was continued for 30 min resulting in a stable reverse micelle (RM1). While RM2 contained the same constituent as RM1 except that the aqueous solution was NaOH (0.1 M) instead of ($La(No_3)_3.6H_2O$) and ($Fe(No_3)_3.9H_2O$) was prepared under similar conditions. These two reverse micelles were mixed under constant stirring and a brown color solution was obtained. In addition ammonium NH_3 was slowly added to adjust the PH and stirred 24 h on a magnetic stirrer. The resulting precipitate was separated from the surfactant and a polar solvent by centrifugation and washing it one time by ethanol and three times by distilled water. The precipitate was dried in an oven at 80 ºC for 6 h to obtain $LaFeO_3$ powder and heated at 750 ºC for 6 h in air.

The crystal structure was investigated by X-ray diffraction (Rigaku, Japan, Miniflex-II) using Cu-K_α radiation (λ= 1.5418 Å) in 2θ range from 20º to 80º. A scanning electron microscope (JEOL JSM-6510LV) equipped with an energy dispersive spectrometer (EDS) was used to check the morphology and particle size. The atomic force microscopy (Veeco-contact mode) was used to examine the morphology and the surface roughness. Room temperature magnetic measurements (M–H) were measured using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 20 kOe.

3. Results and discussions
The X-ray diffraction (XRD) pattern of $LaFeO_3$ nanopowders calcined at 750 ºC is shown in Fig. 1.
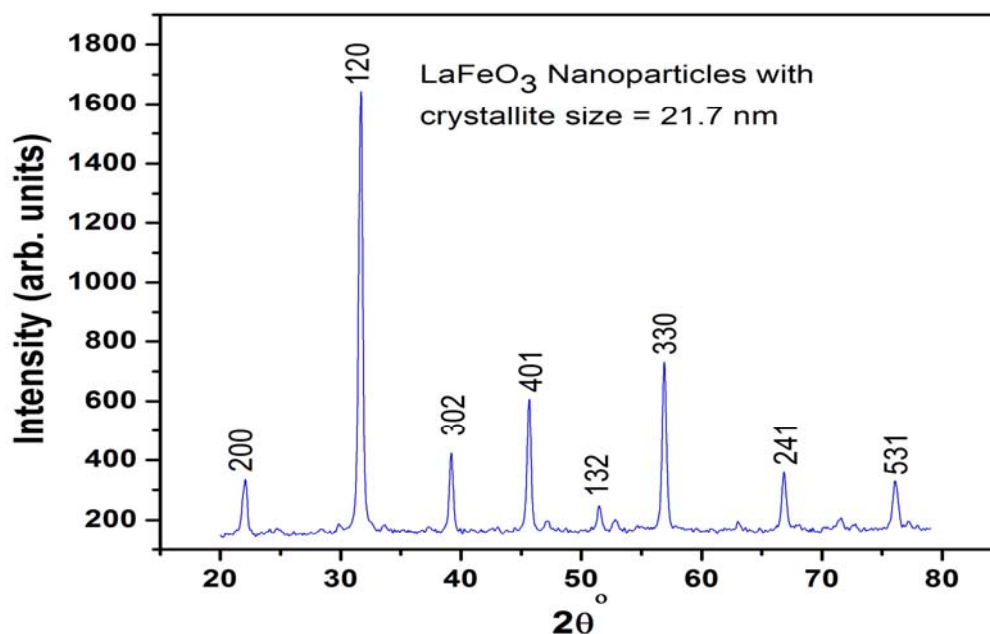

Figure 1. XRD pattern of the LFO NPs.

The position of the all peaks confirmed the high crystallinity and perovskite structure of the NPs and no other impurity peaks were detected in the XRD patterns. Furthermore, the products of the

three samples were observed in orthorhombic perovskite structure with space group Pbnm, which is well consistent with the standard JCPDS card of perovskite $LaFeO_3$ (JCPDS88-0641) [5] and lattice parameters were found a= 8.135 Å, b= 6.040 Å, and c= 8.540 Å. The average of crystallite size using the most intense peak (120) at angle $2\theta \sim 33°$ was estimated from the XRD pattern by using Debye–Scherer's formula.

The AFM images of $LaFeO_3$ standard roughness, two and three dimensions have shown in Fig. 2. The Fig. 2a, 2b and 2c are displayed the standard roughness of $LaFeO_3$ NPs, where R_a is the roughness average, R_p is the maximum height of the profile above the mean line, R_t is the maximum peak to valley height the profile and R_{pm}, R_{tm} are the mean values more representative of the entire profile. Fig. 2d and 2e are shown the uniform grains of $LaFeO_3$ NPs surface morphology. Actually, a homogeneous surface was formed and the grains were observed in different area. The AFM images for two and three dimensions reveal grains with size of few tens nanometers, that is meaning that the micron sized grains consisted of an agglomeration of small grains.
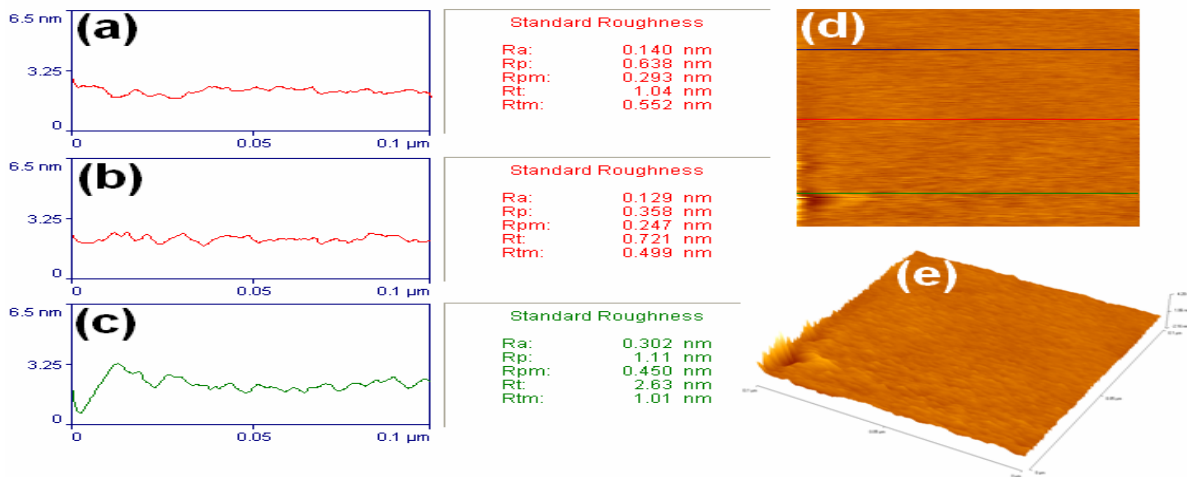

Figure 2. (a, b and c) the standard roughness area of $LaFeO_3$ NPs, (d) two dimensions AFM image for $LaFeO_3$ and (e) three dimensions AFM image for the same.

SEM image of $LaFeO_3$ NPs is displayed in Fig. 3a. The surface morphology of NPs reveals the uniform grains, which displays that the complete incorporation of 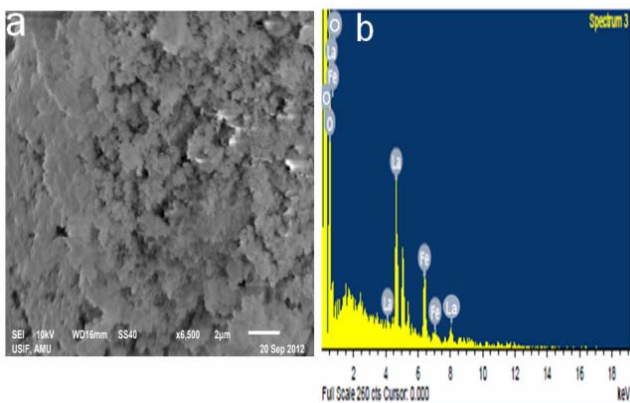$LaFeO_3$ as supported by XRD analysis. In addition the EDS analysis also confirms the presence of La, Fe and O elements in good stoichiometric as displayed in the Fig. 3b.

The magnetization hysteresis (M-H) loops measured at room temperature of $LaFeO_3$ with maximum applied field of 20 kOe as displayed in Fig. 4. We can see that the magnetization of $LaFeO_3$ NPs is 0.136(emu/gm). The plot of the magnetization indicting that the ferromagnetic behavior was observed on the $LaFeO_3$ NPs.
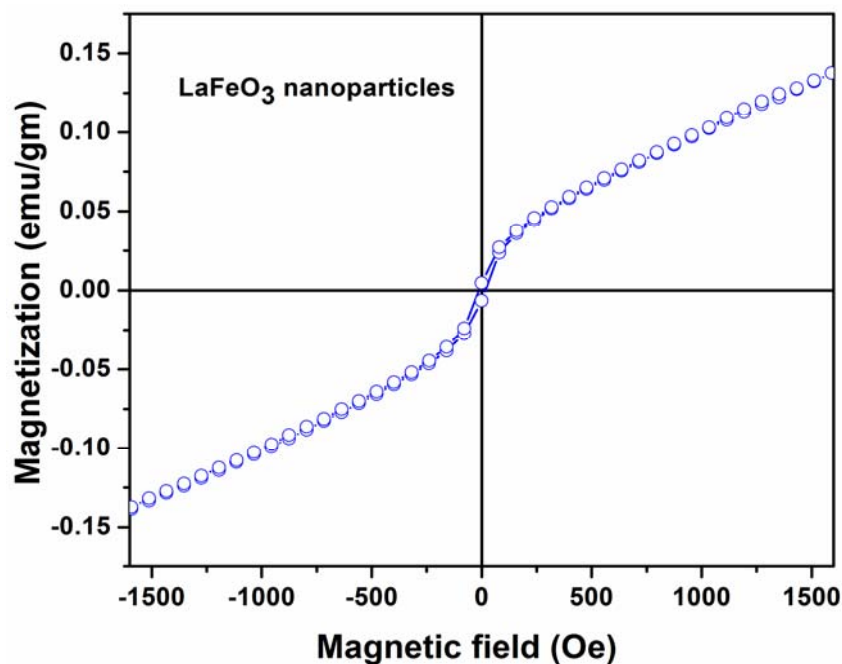

Figure 3. a) SEM image of the LFO NPs b) EDS microstructure of LFO NPs spectrum for the same.

Figure 4. Magnetization versus field for LaFeO$_3$ NPs.

In summary, the LaFeO$_3$ NPs were successfully prepared by reverse micelle method, orthorhombic perovskite structure and phase conformation was confirmed by X-ray diffraction. Ferromagnetic behavior was observed in the LaFeO$_3$ NPs.

Acknowledgements

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