Materials Chemistry and Physics 202 (2017) 50–55

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Development of multifunctional lutetium ferrite nanoparticles: Structural characterization and properties

Tokeer Ahmad*, Irfan H. Lone

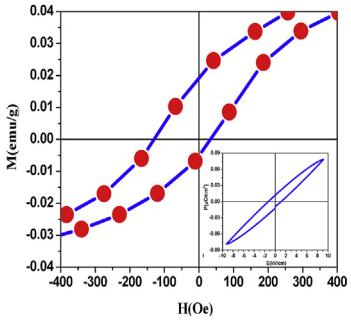
Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi, 110025, India

HIGHLIGHTS

- Monophasic orthorhombic $LuFeO_3$ nanoparticles by citrate precursor route for the first time.
- The average grain size of 90 nm, high surface area of 214 m^2g^{-1} and visible band gap of 2.1 eV was observed.
- Room temperature ferroelectricity along with the ferromagnetic interactions at 5 K with enhanced parameters.

GRAPHICAL ABSTRACT

Graphical abstract:



ARTICLE INFO

Article history:
Received 12 January 2017
Received in revised form
3 August 2017
Accepted 31 August 2017

Keywords:
Nanoparticles
$LuFeO_3$
Surface area
Ferromagnetism
Ferroelectricity
Multiferroics

ABSTRACT

Modified Pechini method has been employed for the synthesis of single phase $LuFeO_3$ nanoparticles. Powder X-ray diffraction technique indicates well crystalline and monophasic $LuFeO_3$ nanoparticles without any secondary phases. Using TEM, SAED, EDAX and BET surface area techniques, the particle size, morphology, chemical composition and surface area of $LuFeO_3$ nanoparticles have been characterized. The TEM analysis suggests that the synthesized nanoparticles are in the uniform manner with an average particle size of 90 nm. It shows that the large value of surface area of 214 m^2g^{-1} and the optical band gap value of 2.1 eV were found for the as-prepared nanoparticles. The electrical characterization indicates that the dielectric constant and dielectric losses varies with temperature and frequency. Furthermore, the butterfly shaped ferromagnetic loop and room temperature ferroelectricity was observed for the multiferroic characteristics in $LuFeO_3$ nanoparticles.

1. Introduction

In past few years, multiferroic materials were adequately taken into consideration because of their ferromagnetic and ferroelectric properties due to which they have been used for a large number of

* Corresponding author.
E-mail address: tahmad3@jmi.ac.in (T. Ahmad).

http://dx.doi.org/10.1016/j.matchemphys.2017.08.068
0254-0584/

device applications [1–11]. These materials are prime candidates for future computer memory concepts, as well as for sensors and also have huge scope of applications in the various fields such as data storage devices, transducers and valves [12]. Nanocrystalline bismuth ferrite was investigated for a ferroelectric memory flipping devices analogous to the other materials that has been reported for showing novel multiferroic properties with less leakage current [13,14]. The magnetic and ferroelectric properties was improved in the pure $BiFeO_3$ compound by the dopant of Dy and Cr ions and the influence of carbon atmosphere also plays a role to reduce the size of nanoparticles [15].

The class of orthoferrite type compounds has many advantages in the case of toxic gas detectors [16], electrochemical materials used in the oxide fuel cells [17], gas separation apparatus [18], and spin valves [19]. The structure of rare-earth ferrites ($RFeO_3$) were analyzed by octahedra (FeO_6) at the corner with three dimensional network resembling with perovskite crystal structure [20,21]. It has been found that the $LuFeO_3$ compound exhibits antiferromagnetism interactions with Neel temperature below 620 K [22,23]. Since the polar structure of $LuFeO_3$ is non-ferroelectric, however, the improper ferroelectricity as reported in $SmFeO_3$ with tiny polarization supports the induced weak ferroelectricity in lutetium ferrite nanoparticles [24]. Rare-earth $LuFeO_3$ gains attention because it consists of lanthanide ion (Lu^{3+}) with smallest ionic radius. The optical, magnetic and other properties of $LuFeO_3$ compound were due to the presence of ferric ion (Fe^{3+}) ion [25]. Wang et al. [26] have reported the optical band gap of 2.0 eV for $LuFeO_3$, however the weakly ferromagnetic interactions in the Fe moments causes to polarize the lutetium based sublattice [27]. It was also reported that orthorhombic $LuFeO_3$ is a strong magnetic material with high values of magnetic parameters. In definite number of methods were reported in literature to produce metal and metal oxide nanoparticles such as reverse micelles [28,29], solvothermal [30,31], hydrothermal [32], sonochemical [33,34] and citrate precursor [5,6,35] methods etc. However, no report is available on the pure phase synthesis of $LuFeO_3$ nanoparticles by the use of citrate precursor method. In the present study, the as-prepared $LuFeO_3$ nanoparticles not only show uniform distribution of nanocrystalline particles but also possess high specific surface area. Ferroic interactions in the electrical and magnetic properties were also studied. We believe that as-prepared high surface area and visible band gap porous multiferroic Lutetium Ferrite nanoparticles may find applications in hydrogen evolution in water splitting and solar energy conversion technologies, including photovoltaic, fuel cells, non-volatile data storage devices, transformers and inductors.

2. Experimental

The preparation of $LuFeO_3$ nanoparticles by the use of modified citrate precursor method, initially the molar content of ethylene glycol: citric acid: ferric nitrate was taken at fixed ratio. The mixture was stirring at room temperature and 25 ml of 0.1 M concentration solution of lutetium nitrate (Alfa Aesar) was added for the time period of 2 h. The contents were stirred till a clear reddish solution was formed. The solution was then warmed to 70 °C until the entire fluid evaporated to leave a reddish brown coloured gel. The excess of solvents were evaporated at 135 °C in oven to get the fine gel precursor. The gel precursor was burned at 300 °C for 2 h in the muffle furnace to remove the excess hydrocarbon and nitrogen-based impurities. The burned sample was lightly ground to a fine powder and then the sample was further calcinated at 900 °C for 12 h in high temperature furnace to obtain reddish-brown $LuFeO_3$ nanoparticles. The flow chart depicting the various steps for the formation of $LuFeO_3$ nanoparticles using citrate precursor route is shown in Fig. 1.

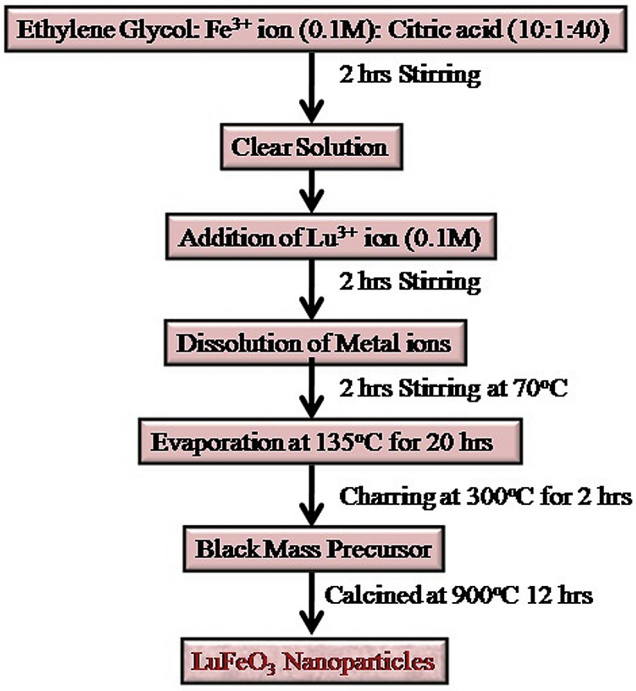


Fig. 1. The flow chart for the synthesis of $LuFeO_3$ nanoparticles by using polymeric citrate precursor method.

X-ray diffraction technique was carried out on Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu-Kα radiations of wavelength (λ) = 1.54056 Å with the step size of 0.05° and step time of 1 s. The crystallite size of $LuFeO_3$ nanoparticles was estimated to be 96 nm by using the Scherrer equation. Microscopic techniques like TEM and SAED studies have been carried out on FEI Tecnai G^2 20 TEM operated at an accelerating voltage of 200 kV which was equipped with the digital imaging device. Energy dispersive analysis of X-rays (EDAX) studies have been carried out on a new versatile series ZEISS EVO 50 operated at 30 kV acceleration voltages. The specimen can be prepared by sticking the powder on the carbon tape and pressed to get uniform film.

The surface area of the sample was determined at liquid nitrogen temperature (77 K) using B.E.T. surface area analyser (Nova 2000e, Quantachrome Instruments Limited, USA), by using 'Multipoint BET Method'. The band gap was determined by using Perkin-Elmer double-beam Lamda-35 spectrophotometer in reflection mode. For the study of dielectric properties pellet was prepared and colloidal silver paint (Ted Pella, Inc.) was applied to both faces. Using high frequency LCR meter (6505 P, Wayne Kerr electronics, UK) in the frequency range of 100 kHz-2 MHz over a temperature range of 50–450 °C, the dielectric measurements was made. The P-E loop studies were carried out by using the P-E loop tracer (M/s Radiant Instruments, USA). The magnetic data was collected by the use of (MPMS) SQUID magnetometer.

3. Results and discussion

The monophasic nature, purity and structure of $LuFeO_3$ nanoparticles prepared by citrate precursor method were examined by powder X-ray diffraction studies. All the reflections in the PXRD pattern have been matched with the orthorhombic $LuFeO_3$ (JCPDS. 47-0071). The Rietveld fit of the room temperature powder X-ray diffraction data for the polycrystalline orthorhombic $LuFeO_3$ (space group *Pbnm*) nanoparticles was also carried out as shown in Fig. 2a. A close fit of experimental and calculated pattern confirms the