Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 6812–6816

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

New $La_{1-x}Cr_{0.7x}Eu_{0.3x}FeO_3$ nanoparticles: Synthesis via wet chemical route, structural characterization for magnetic and dielectric behavior evaluation

Shokat Nawaz[a], Huma Malik[b], Muhammad Farooq Warsi[a], Muhammad Shahid[a], Imran Shakir[c], Abdul Wadood[a,*], Muhammad Azhar Khan[b,*]

[a]Department of Chemistry, The Islamia University of Bahawalpur, Bahawalpur-63100, Pakistan
[b]Department of Physics, The Islamia University of Bahawalpur, Bahawalpur-63100, Pakistan
[c]Deanship of Scientific Research, College of Engineering, PO Box 800, King Saud University, Riyadh 11421, Saudi Arabia

Received 11 January 2015; accepted 26 January 2015
Available online 3 February 2015

Abstract

$La_{1-x}Cr_{0.7x}Eu_{0.3x}FeO_3$ nanoparticles were fabricated by micro-emulsion route. The value of x was kept in the range of 0.00 to 0.04. The synthesized nanoparticles were then characterized by X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR) and scanning electron microscopy (SEM). The XRD confirmed the orthorhombic phase and estimated the crystallite size in the range of 30–90 nm. The nanoparticles estimated by SEM were in the range 60–100 nm. The XRD data was further supported by FTIR spectrum. The main FTIR bands observed were: Fe–O (418 cm^{-1}), Cr–O (545 cm^{-1}), La–O (570 cm^{-1}) and Eu–O (416 cm^{-1}). After structural elucidation, the $La_{1-x}Cr_{0.7x}Eu_{0.3x}FeO_3$ nanoparticles were subjected to magnetic parameters and dielectric behavior evaluation. The replacement of La^{3+} ions, with Cr^{3+} and rare earth Eu^{3+} exhibited interesting magnetic and dielectric behavior. The $LaFeO_3$ nanoparticles without any dopants showed the paramagnetic behavior. However as the La^{3+} was substituted by Cr^{3+} and Eu^{3+}, the ferromagnetic behavior was observed. Similarly the dielectric parameters were reduced by the replacement of La^{3+} ions with Cr^{3+} and Eu^{3+} metal ions. The maximum magnetic parameters were observed for $La_{0.6}Cr_{0.28}Eu_{0.12}FeO_3$ (Coercivity ~0.04 T, Saturation magnetization ~0.728 $emug^{-1}$ and Retentivity ~0.0.6783 $emug^{-1}$). The maximum dielectric constant (23.52 at 1.5×10^{-2} GHz) was observed for $LaFeO_3$ nanoparticles, while the minimum value of dielectric constant (10.32 at 1.5×10^{-2} GHz) was exhibited by $La_{0.8}Cr_{0.14}Eu_{0.06}FeO_3$ nanoparticles.

Keywords: C. Magnetic properties; D. Perovskites; Nanoparticles; SEM; Dielectric parameters

1. Introduction

Nanoscience and nanotechnology is attracting the attention of the researchers due to their versatile applications that covers approximately all field of life [1]. Its applications ranges from medical diagnosis and therapy [2], catalysis [3], energy storage [4] as well as energy conversion devices [5] etc. Nanoparticles, in most of the cases, behave entirely different from their bulk counter parts. The well known example is the presence of Plasmon resonance band in metal nanoparticles that is normally absent in the bulk metals spectra [2]. Among various nanoparticles, the transition metals nanoparticles have significant importance in various technological devices due to variable oxidation state that is the inherent feature of transition metals and make the metals very rich in chemistry [6]. The combination of transition metals with rare earth metals makes the materials richer and more attractive for researchers and engineers. For example the $LaFeO_3$ has rare earth (La) and transition metal (Fe), is a well known example of perovskite. The applications of $LaFeO_3$ perovskite in numerous technologies are attributed to the structural features of $LaFeO_3$ [7–10].The $LaFeO_3$ has been studied recently for various applications. The main application domain of LaFeO3 and its derivates has been the solid oxide fuel cells. Pecchi et al. [11]] reported that Ca^{2+}

*Corresponding authors. Tel.: +92 3335121491; fax: +92 62 9255474.
E-mail addresses: azhar.khan@iub.edu.pk, azhar_manais@yahoo.com (M.A. Khan).

http://dx.doi.org/10.1016/j.ceramint.2015.01.129
0272-8842/

substitution improved the redox properties of $LaFeO_3$. Kong and Shen [12] observed that Ca^{2+} incorporation into $LaFeO_3$ is an effective way to enhance sensitivity to ethanol. All these recent reports described the effect of transition metals and some other metals effect on various redox and related properties of $LaFeO_3$ perovskite. Rare earth doping in $LaFeO_3$ has also been reported for various applications especially the dielectric parameters. Recently we reported the effect of Eu^{3+} on structural and dielectric behavior of $LaFeO_3$ nanoparticles [13]. However, the combined effect of rare earth metals with transition metals on $LaFeO_3$ is not frequently reported. Here in this article, we plan to explore the combined effect of rare earth (Eu^{3+}) and transition metal (Cr^{3+}) on structural, magnetic and dielectric behavior of $LaFeO_3$ nanoparticles fabricated via cheap micro-emulsion route.

2. Materials and methods

Following chemicals were used as received without any further purification for synthesis of Cr^{3+} and Eu^{3+} doped $LaFeO_3$ nanoparticles ($La_{1-x}Cr_{0.7x}Eu_{0.3x}FeO_3$): $EuCl_3 \cdot 6H_2O$ (Sigma-Aldrich, 99.9%), $Fe(NO_3)3 \cdot 9H_2O$ (Merck, 98%),$Cr(NO_3)_3 \cdot 9H_2O$ (sigma-Aldrich, 99.9%) and NH_3(BDH, 35%). Wet chemical route i.e. micro-emulsion route [6] was followed for the synthesis of required $La_{1-x}Cr_{0.7x}Eu_{0.3x}FeO_3$ nanoparticles. This route involved the preparation of aqueous solutions with required accurate concentrations of all the metal salts used in the synthesis. The aqueous solutions were then mixed at room temperature. The temperature was elevated to ~50 °C. At this elevated temperature the aqueous solution of surfactant cetyltrimethylammoniumbromide (CTAB). Aqueous ammonia was used to raise the pH to ~10. The stirring was done for ~4 h. Washing with deionized water was carried out to remove all the water soluble impurities and for neutralization purpose. The drying, grinding and annealing was carried out to get the final powdered $La_{1-x}Cr_{0.7x}Eu_{0.3x}FeO_3$ nanoparticles.

3. Results and discussion

3.1. XRD analysis

X-ray diffraction analysis for $La_{1-x}Cr_{0.7x}Eu_{0.3x}FeO_3$ nanoparticles was carried out at Philips X' Pert PRO 3040/60 diffractometer using Cu Kα as radiation source. The XRD patterns for all samples of $La_{1-x}Cr_{0.7x}Eu_{0.3x}FeO_3$ are shown in Fig. 1. The major reflections were observed at two theta values 23.00° [002], 25.28° [111], 32.70° [112], 33.96° [021], 40.27° [022], 46.91° [002], 52.73° [131], 58.11° [230] and 68.35° [040]. This data was found compatible with standard diffraction patterns of JCPDS (ICSD-01–074-2203). From XRD data the lattice parameters (*a*, *b* and *c*), cell volume, bulk density and crystallite size was also determined (Table 1). All the lattice parameters were decreased as the La^{3+} was substituted with Cr^{3+} and Eu^{3+} ions. This decrease is attributed to the larger ionic radius of La^{3+} (~1.03 Å), whereas both Cr^{3+} (0.64 Å) and Eu^{3+} (0.947 Å) have ionic radii less than 1.00 Å. The cell volume therefore was also found to decrease. The

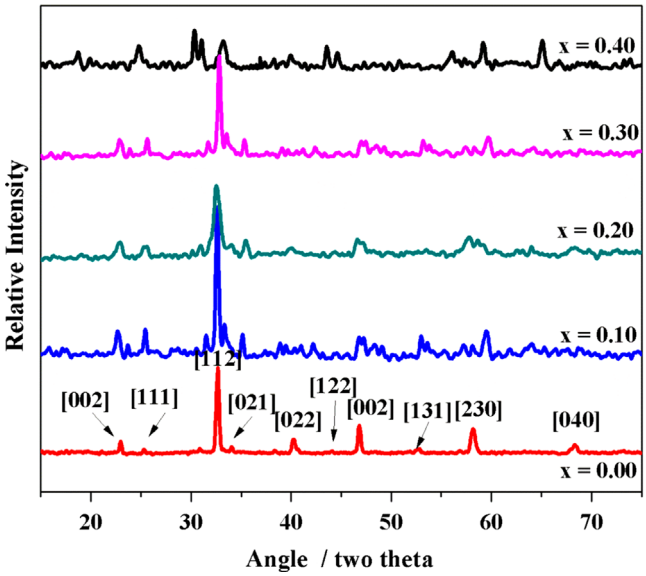

Fig. 1. XRD patterns of "La_{1-x} $Cr_{0.7x}$ $Eu_{0.3x}FeO_3$" nanoparticles.

Table 1
Various lattice parameters and physical parameters for La_{1-x} $Cr_{0.7x}$ $Eu_{0.3x}FeO_3$ nanoparticles.

***x* (mole)**	**0.0**	**0.01**	**0.02**	**0.03**	**0.04**
Cr (mole)	0.0	0.07	0.14	0.21	0.28
Eu (mole)	0.0	0.03	0.06	0.09	0.12
Lattice constant *a* (Å)	5.5545	5.5303	5.5109	5.4843	5.4798
Lattice constant *b* (Å)	5.5703	5.5567	5.5364	5.5164	5.4890
Lattice constant *c*(Å)	7.8647	7.8456	7.8345	7.8123	7.7987
Cell volume $(Å)^3$	243.3356	241.0969	239.0348	236.3501	234.5741
Bulk density (g/cm^3)	1.14	1.17	1.23	1.25	1.29
Crystalline size (nm)	56.76	41.98335	46.39727	33.56	89.56

crystallite size was determined by Sherrer formula and was found in the range of 30–90 nm. This range is compatible with the particles size determined by SEM images. The bulk density also followed a regular trend as the La^{3+} was substituted with Cr^{3+} and Eu^{3+} ions. Similar trend has been already reported in our previous reports for the similar compounds of nanosized [14–16].

3.2. FTIR analysis

FTIR spectrum of $La_{0.6}Cr_{0.28}Eu_{0.12}FeO_3$ nanoparticles was recorded on Nexus 470 spectrometer at room temperature (Fig. 2). The IR bands of Fe–O, Eu–O, La–O, Cr–O and were observed at 418 cm^{-1}, 416 cm^{-1}, 570 cm^{-1} and 545 cm^{-1}, respectively. These IR band positions are compatible with already reported values of corresponding metal–oxygen IR bands [17,18].

3.3. SEM images

SEM analysis for the $La_{1-x}Cr_{0.7x}Eu_{0.3x}FeO_3$ nanoparticles was recorded on Jeol JSM-6490A electron microscope. Typically the SEM image of $La_{1-x}Cr_{0.7x}Eu_{0.3x}FeO_3$ nanoparticles