Original Article

Enhancement in dielectric and optical properties of La$_{1-x}$Ce$_x$FeO$_3$ nanoparticles

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**ABSTRACT**

La$_{1-x}$Ce$_x$FeO$_3$; $0 \leq x \leq 0.15$ nanoparticles were prepared in single phase using flash combustion technique. The crystalline structure and morphology of the investigated samples were researched through XRD and HRTEM. As a result, the dielectric constant of LaFeO$_3$ was enhanced by Ce$^{3+}$ ion substitution due to some the Ce$^{3+}$ ions changes its valence to Ce$^{4+}$ ions. The conduction mechanism in La$_{1-x}$Ce$_x$FeO$_3$ samples is the small polaron (SP) tunneling. The type of optical transition is direct allowed transition and the band gap values are in the range of (2.8–1.89 eV). $\varepsilon'$ values of La$_{0.90}$Ce$_{0.10}$FeO$_3$ decreases by increasing the external applied pressure at different frequencies.

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1. Introduction

The general formula of perovskite oxides is ABO$_3$, where A is rare earth, alkaline, or alkaline-earth cations and B transition metal cations. ABO$_3$ have been attracting increasing attention in the last years due to a huge importance and applications [1,2]. The most important feature of ABO$_3$ is the extraordinary structural stability where a wide range of cations can be replaced on the A and/or B sites without destroying the matrix structure. This benefit allows by a great flexibility to tailor their physicochemical properties to better target their applications [3].

There are different preparation methods for perovskite-type oxides, such as the polymerization, thermoelectric conversion, citrate method, sol-gel, flash, heteronuclear complex, precipitation method [4–6]. However, the predominant method for synthesis of perovskites is the solid state reaction between precursor metal oxides and/or carbonates. Additionally, electrospinning plays a role in obtaining nano-materials in fiber form as simple, convenient and low cost technique [7]. A great number of nanomaterials could be prepared using flash combustion technique which give fast results and small size nanoparticles [8].

LaFeO$_3$ crystallized in distorted orthorhombic perovskite structure with centro-symmetric space group and exhibit colossal dielectric constant. It has anti-ferromagnetic char-
La(NO$_3$)$_3$·6H$_2$O + Fe(NO$_3$)$_3$·9H$_2$O + Ce(NO$_3$)$_3$·6H$_2$O

Drop by drop NH$_3$·CH$_2$COOH

Heated on a magnetic stirrer

Fluffy powder of La$_{1-x}$Ce$_x$FeO$_3$ were obtained

Heating at 500 °C for 2h using rate of 4 °C/min

Fig. 1 – Flowchart of the preparation of the La$_{1-x}$Ce$_x$FeO$_3$.

LaFeO$_3$ and their substituted nanoparticles have attracted great attention in studying their characteristics and physical properties. The role of vacancy on A cation was previously studied [16]. We reported an enhancement in the molar magnetic susceptibility, saturation magnetization, exchange bias and ferroelectric properties [16]. On the other hand, the effect of vacancies on Fe cation was investigated resulting in that $\chi_M$ of the sample LaFe$_{0.99}$Ce$_{0.01}$O was increased by 2.5 times than that of LaFeO$_3$ [17]. The ac conductivity for the sample La$_{0.95}$Sr$_{0.05}$FeO$_3$ increases 12.5 times than that of the parent LaFeO$_3$ at $T=553$ K and frequency 1 MHz [18]. For the first time, La$_{0.95}$Sr$_{0.05}$FeO$_3$ is concluded to be a novel single phase multiferroic material. In this work we focus on tuning the electrical and optical properties of LaFeO$_3$ by substitution Ce$^{3+}$ ions at different doping levels.

2. Experimental techniques

The samples La$_{1-x}$Ce$_x$FeO$_3$; $0 \leq x \leq 0.15$ were prepared in single phase using flash combustion technique. The precursor metal nitrates with purity 99.9% (Sigma-Aldrich) were used without any further purification and then good mixed in stoichiometric ratios using glycine as a fuel. The (glycine/nitrate) ratio is kept constant for all samples and is equal to 1. The mixture was heated on the magnetic stirrer until a highly viscous liquid was formed. Upon further heating, the viscous liquid transferred to a fluffy powder of nanoparticles. The obtained samples were heated at 500 °C for 2 h using heating/cooling rate of 4 °C/min. Fig. 1 shows a flowchart of the preparation of the investigated samples.

The crystalline phases were studied by the X-ray powder diffraction (XRD) using a Proker D8 advance X-ray diffractometer with CuKα radiation ($\lambda=1.5418\,\text{Å}$). The XRD of the investigated samples were indexed according to the International Centre for Diffraction Data (ICDD) card number 74-2203. The high-resolution transmission electron microscope (HRTEM) model (JEOL-2100) was used to analyze the particle shape and distribution.

The powder of the samples was pressed to form pellets and were heated at 500 °C for 2 h by rate 4 °C/min. After that, the two surfaces were coated by silver paste and checked for good conduction. The electrical properties measurements were studied at different frequencies using LCR meter (Hioki model 3532 Japan). Dc conductivity and I–V characteristic data were measured in the temperature range 300–750 K by using Picoammeter Keithley 485. The optical properties were analyzed by transmittance spectra (UV-Visible-NIR spectrometer).

Ac conductivity and dielectric constant were measured for the investigated samples under the effect of external pressure. A homemade holder was connected to the LCR meter (Hioki model 3532 Japan) to study the dependence of $\varepsilon'$ and $\sigma$ on...
Table 1 – The values of the lattice parameters $a$, $b$, $c$, the unit cell volume, the theoretical density ($D_x$), the crystallite size and the tolerance factor ($t$) for the investigated samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$a$(Å)</th>
<th>$b$(Å)</th>
<th>$c$(Å)</th>
<th>$V$(Å$^3$)</th>
<th>$D_x$(g/cm$^3$)</th>
<th>Crystallite size (nm)</th>
<th>Particle size (nm)</th>
<th>Tolerance factor ($t$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFeO$_3$</td>
<td>5.5736</td>
<td>5.4896</td>
<td>7.9863</td>
<td>244.355</td>
<td>6.5977</td>
<td>35</td>
<td>27</td>
<td>0.9549</td>
</tr>
<tr>
<td>La$<em>{0.95}$Ce$</em>{0.05}$FeO$_3$</td>
<td>5.5552</td>
<td>5.5331</td>
<td>7.7992</td>
<td>239.728</td>
<td>6.7267</td>
<td>25</td>
<td>25</td>
<td>0.9546</td>
</tr>
<tr>
<td>La$<em>{0.90}$Ce$</em>{0.10}$FeO$_3$</td>
<td>5.6117</td>
<td>5.4025</td>
<td>8.1735</td>
<td>247.798</td>
<td>6.5093</td>
<td>21</td>
<td>33</td>
<td>0.9542</td>
</tr>
<tr>
<td>La$<em>{0.85}$Ce$</em>{0.15}$FeO$_3$</td>
<td>5.5530</td>
<td>5.5501</td>
<td>7.8225</td>
<td>241.087</td>
<td>6.6921</td>
<td>21</td>
<td>24</td>
<td>0.9538</td>
</tr>
</tbody>
</table>

The applied pressure at constant frequency 10 kHz by the two probe method.

3. Results and discussion

3.1. Structure and microstructure

Fig. 2 shows the XRD pattern of the samples La$_{1-x}$Ce$_x$FeO$_3$ where 0.0 $\leq x \leq$ 0.15. The observed peaks are compared and indexed with ICDD card number 74-2203. The XRD pattern confirmed that the samples were obtained in single phase without any impurity peaks. The XRD pattern demonstrates that the investigated sample possesses the orthorhombic structure with Pnma space group. The lattice parameter values were calculated using Debye-Scherrer formula reported in Eq. (1) [19]

$$L = (0.9\lambda)/(\beta\cos\theta)$$

(1)

Where $L$ is the average crystallite size, $\lambda$ is the wave length of the x-ray radiation, $\theta$ is the Bragg angle and $\beta$ is the corrected full width in radians subtended by the corrected half maximum intensity of the powder pattern peak. Table 1 represented the values of lattice parameters, unit cell volume and crystallite size. The values in Table 1 indicate that the samples were prepared in nano scale. The crystallite size decreases by
increasing Ce$^{3+}$ ions as a result of replacing La$^{3+}$ large ionic radius (1.216 Å) ion by the smaller Ce$^{3+}$ one (1.196 Å).

The tolerance factor (t) was calculated from the following Goldsmith formula [20]:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_{Fe} + r_O)}$$ (2)

where $r_A$, $r_{Fe}$ and $r_O$ are the ionic radii of the A, iron cations and the oxygen anion respectively. The ionic radius of A site cation ($r_A$) was calculated according to the relation $r_A = (1-x)\ r_{La} + x \ r_{Ce}$ where $x = 0.00, 0.05, 0.10$ and 0.15. The values of (t) reported in the Table 1 are in the range 0.9549 < t < 0.9538. They assure that the investigated samples have orthorhombic structure and confirm the results obtained from XRD. By increasing the Ce content, the tolerance factor decreases which leads to increasing the distortion in the crystal structure thereby, decreasing the angle between Fe–O–Fe and increasing the tilting of $<\text{FeO}_6>$ octahedron.

The HRTEM was used to photograph the investigated samples La$_{1-x}$Ce$_x$FeO$_3$. The particle sizes (L) of the samples were measured from HRTEM images and reported in Table 1. The values of (L) illustrate that the samples were prepared in nano size scale and agree with the results obtained from XRD. The particles seemed to have geometric platelet shape with slight agglomeration due to the absence of capping agent. The size is found to depend on the Ce content. The inset in the Fig. 3 is selected area electron diffraction (SAED) pattern for the samples La$_{1-x}$Ce$_x$FeO$_3$. The SAED is seen as clear diffraction concentric rings indicating that all samples are formed in the polycrystalline form with excellent crystallinity despite the reduced size of the crystallites.
3.2. Dielectric constant and loss factor

Fig. 4 shows the relation between dielectric constant with the temperature at different frequencies for the sample La$_{0.90}$Ce$_{0.10}$FeO$_3$. The values of $\varepsilon'$ in the first temperature region (300–650 K) are nearly frequency independent. While the former increases with rising temperature where the thermal energy causes a transition at about 750 K. In the second temperature range (750–870 K), by increasing the temperature the electric dipoles are aligned in the direction of applied field leads to enhancement of the polarization and increasing the values of $\varepsilon'$. The investigated samples are characterized by large values of dielectric constant and can be used in many applications such that multilayer capacitor, memory devices, resonators, low magnetic field sensors [21].

The dependence of the dielectric loss factor ($\varepsilon''$) on the temperature as a function of frequencies for the sample La$_{0.90}$Ce$_{0.10}$FeO$_3$ is shown in Fig. 5. The trend of $\varepsilon''$ is the same as of $\varepsilon'$ as the general trend of dielectrics.

The large values of dielectric constant ($\varepsilon'$) in the low frequency region are instigated from grain boundaries, interfacial polarization and oxygen vacancies. While at higher frequencies, the values of $\varepsilon''$ nearly remain constant, this was in fact due to that the dipoles do not have enough time to follow up the applied ac electric field variations. Agreeing with the well-known Maxwell-Wagner model [22], the dielectric material structure is regarded as well conducting grains separated by non-conducting thin grain boundaries. As a consequence, the space charge polarization is built at the grain boundaries.

By applying an external voltage on the sample, it drops on grain boundaries. Conferring Koop’s [22] model, at low frequencies the influence of grain boundaries is leading where higher dielectric constant is owing to ultra-thin layer of grain boundaries. Hence at low frequencies, the space charges trail the frequency of the applied electric field while at high frequencies there is no sufficient time to build up.

The dielectric constant is using the complex function as: $\varepsilon''(\omega) = \varepsilon' (\omega) - i\varepsilon'' (\omega)$. The real part of dielectric constant $\varepsilon'$ $(\omega)$ represents the elastic reaction of the material to an external applied ac electric field. While the imaginary part $\varepsilon''(\omega)$ is related to the conductivity according to the relation $\sigma(\omega) = \varepsilon''(\omega)/\varepsilon_0\omega\varepsilon''(\tan\delta)$ [23].

The imaginary part of dielectric constant $\varepsilon''(\omega)$ increases slowly with increasing the temperature and then rapidly from 700 K due to the improvement in the conductivity [23].

Fig. 6 represents the temperature dependence of $\varepsilon'$ at 100 kHz for the investigated samples. By doping the LaFeO$_3$, $\varepsilon'$ is growing to be greater than that of the parent sample. The enhancement in the values of dielectric constant $\varepsilon'$ is a result of the valence exchange of Ce$^{3+}$ ions into Ce$^{4+}$. This in turns increases the polarization in the perovskite orthorhombic lattice. We could not also neglect the change of Fe$^{3+}$ ions to Fe$^{2+}$ ions to allow charge neutrality in the investigated samples. Further increasing Ce$^{3+}$, $\varepsilon'$ decreases.

3.3. AC and dc conductivity measurements

Fig. 7 correlates $\ln\sigma$ (σ: conductivity) with the reciprocal of absolute temperature (1000/T) at frequency 10 kHz for the sample LaFeO$_3$. The conductivity increased with increasing the temperature exhibiting a semiconducting like behavior. The data were found to follow the known Arrhenius relation [24]:

$$\sigma = \sigma_0 \exp(-E/kT)$$

(3)

where $E$ is the activation energy, $T$ is the absolute temperature and $k$ is the Boltzmann's constant. The activation energies values were calculated and reported in Table 2. The activation energy $E_{\text{fit}}$ at high temperature region is greater than that.
where the electric current intensity increases as the potential difference increases. From this plot, we considered 100 V as constant value during dc conductivity-temperature measurement.

Fig. 11 shows the relation between dc conductivity and absolute temperature for the investigated samples. The values of $\sigma_{dc}$ are nearly constant in the first temperature region up to 500 K and then increases rapidly. The inset of Fig. 11 elucidates the values of $\sigma_{dc}$ up to T = 500 K. There is a peak for the sample La$_{0.95}$Ce$_{0.05}$FeO$_3$. At high temperature region, the thermal energy increases the distance between the molecules and makes the molecules and ions more flexible to be aligned in the direction of applied field.

3.4. Optical band gap studies

The determination of energy gap ($E_g$) can be carried out using different methods but in our work, we focused on Kubelka-Munk (K-M or F (R)) method [26]. The equation of K-M method is:

$$F(R) = \frac{(1 - R)^2}{2R}$$

(4)

Where F (R) is proportional to the extinction coefficient ($\alpha$) and R is the reflectance. This method is applied to a materials characterized by high light scattering and absorbing particles in a matrix.

Equation (5) represent a modified Kubelka-Munk function obtained by multiplying F (R) function by the energy of photon ($h\nu$), using the coefficient (n) which is related to an electronic transition.

$$(F(R) \times h\nu)^n$$

(5)

For the $E_g$ calculation and determination the type of transition in the investigated samples, the following well-known Tauc’s equation [27] was used:

$$\alpha(h\nu) \approx B(h\nu-E_g)^n$$

(6)

where ($\alpha$) is the extinction coefficient, which is proportional to F(R), $h$ is the Planck’s constant (J.s), $\nu$ is the light frequency (s$^{-1}$), B is the absorption constant, $E_g$ is the band gap (eV). The value of n for the specific transition can be experimentally determined from the best linear fit as the following: $n = \frac{1}{2}$ for direct allowed transition, $n = \frac{3}{2}$ for a direct forbidden transition, $n = 2$ for an indirect allowed transition and $n = 3$ for an indirect forbidden transition.

Fig. 12 shows the Tauc plot for the investigated samples. The optical band gap of the samples La$_{1-x}$Ce$_x$FeO$_3$ was estimated from the extrapolation of F(R) $h\nu = 0$. The type of transition is direct allowed transition where $n = \frac{1}{2}$. The values of band gap were reported in Table 3.

It is clear that the values of $E_g$ decreases from 2.54 eV for the parent sample LaFeO$_3$ to 1.89 eV for the sample La$_{0.85}$Ce$_{0.15}$FeO$_3$. The reasons for the enhancement of optical properties are:
The release of excess charge from transferring some Ce$^{3+}$ to Ce$^{4+}$ cations which counter by replacing Fe$^{3+}$ ions to Fe$^{2+}$ ions to keep a balanced columbic interaction.

2 Ce$^{3+}$ ions dopant form a donor level at a lower potential than the top of the valence band composed of O 2p orbitals. Thus, the band-gap energy became narrowed by replacing Ce$^{3+}$ ions on the Fe$^{3+}$ site [28].

The decrease in the optical band gap of the investigated samples by Ce$^{3+}$ doping increases the ability of exploiting these samples in gas sensing and photo catalytic activity as it is compared to the improved TiO$_2$ [29].

### 3.5 Effect of pressure on electrical properties

Fig. 13 shows the relation between dielectric constant ($\varepsilon'$) and the external pressure as a function of frequencies at room temperature for the sample La$_{0.90}$Ce$_{0.10}$FeO$_3$ as an example. It is clear that the values of $\varepsilon'$ at low frequencies are greater than that at high frequencies due to the electric dipoles need more time to follow the applied electric field. $\varepsilon'$ values decreases by...
increasing the external applied pressure at different frequencies.

Fig. 14 illustrates the relation between \( \varepsilon' \) and external pressure at frequency 10 kHz for the Ce\(^{3+} \) doped samples. \( \varepsilon' \) increases in the samples containing Ce\(^{3+} \) ions as a result of releasing more ions and charge carriers due to converting Ce\(^{3+} \) ions to Ce\(^{4+} \) ions and some Fe\(^{3+} \) ions converting to Fe\(^{2+} \) ions. The change in valences of the Ce\(^{3+} \) and Fe\(^{3+} \) ions lead to increasing the polarization, dielectric constant as well as the ac conductivity. The enhancement in the ac conductivity with Ce\(^{3+} \) ion doped is illustrated in Fig. 15.

4. Conclusion

1. XRD confirmed that the samples were prepared in single phase orthorhombic structure.

2. HRTEM shows that the particle size of the samples are in the range of (24–33) nm.

3. The dielectric constant and conductivity of LaFeO\(_3\) were increased by Ce\(^{3+} \) ions doping.

4. The conduction mechanism in La\(_{1-x}\)Ce\(_x\)FeO\(_3\) samples is the small polaron (SP) tunneling.

5. La\(_{1-x}\)Ce\(_x\)FeO\(_3\) samples obey optical direct allowed transition and \( E_g \) decreases by increasing Ce\(^{3+} \) ions.

6. \( \varepsilon' \) values of La\(_{0.90}\)Ce\(_0.10\)FeO\(_3\) decreases by increasing the external applied force at different frequencies.

7. We recommend the use of the samples of low optical band gap in gas sensing and improved magnetic photocatalysis.

References


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