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Studies on electrical and dielectric properties of LaFeO₃

S. M. Khetre^{a*}, H. V. Jadhav^b, P. N. Jagadale^b, S. R. Kulal^b and S. R. Bamane^b

^aDahiwadi College Dahiwadi, Tal. Man, Dist. Satara(M.S.), India ^bMetal Oxide Research Laboratory, Dr. Patangrao Kadam College Sangli (M.S.), India

ABSTRACT

X-ray diffraction pattern of LaFeO₃ synthesized by the combustion method reveals the pervoskite type of the material. Synthesized material has crystallite size of 28-63 nm. Characterization techniques such as X-Ray diffraction studies, scanning electron microscopy, etc., were employed to study morphology and the average particle size, phase and composition of the material. The effect of constituent phase variation on the dielectric, resistivity and impedance properties was examined. The dielectric dispersion with frequency has been explained on the basis of an electron-hole hopping mechanism which is responsible for conduction and polarization. From the ac conductivity study, it is confirmed that the conduction in the present material is of small polaron type. Such materials may be useful to fabricate the interconnecting materials for the solar cell, gas sensors, gas transducers, optoelectronic devices, etc.

Keywords: Nanocrystalline LaFeO₃; XRD; SEM; TEM; Dielectric properties.

INTRODUCTION

Rare earth orthochromatic RCrO₃ (R~Y or lanthanide) and RFeO₃ orthoferrites constitute a family of Dzyaloshinsky interaction antiferromagnets which exhibit an unusual variety of magnetic properties and structural changes [1-3]. LaFeO₃ is chemically stable in both reducing as well as oxidizing atmosphere. The doped LaFeO₃ shows high electrical conductivity, outstanding thermal stability, high dielectric constant, low dielectric loss, moderate permittivity, susceptibility, polarizability, ferroelectricity, piezoelectricity therefore used as separator material in solid oxide fuel cell (SOFC) [4-6]. It is also used as hot electrode for magneto hydrodynamic [MHD] power generation [7] .Doped LaFeO₃ shows oxygen ion conductivity and has been studied for its applications in oxygen permeable membrane [8-10] catalytic activity in the complex oxidation of hydrocarbons and catalytic combustion of methane [11], as well as being used as sensors, utilized in microwave dielectrics and as solid electrolytes [12-14].

In the present work, efforts are made to develop the dielectric materials for their potentials in the field of advanced communication technology and in various fields.

MATERIALS AND METHODS

2.1. Materials synthesis

Polycrystalline LaFeO₃ was synthesized by the combustion synthesis method using glycine as fuel (organic fuel). All chemical reagents were analytical grade and used without further purification. Stoichiometric quantity of solid mixture of one mole reagents i.e. Lanthanum nitrate La $(NO_3)_3.6H_2O$, Fe $(NO_3)_3.9H_2O$ and two mole of glycine were mixed together in a flat Pyrex disc. The solid were stirred for five minutes (clear solution was obtained). Solution formed was evaporated on hot plate in temperature range $80-90^{\circ}C$ gives thick gel. The gel was kept on a hot plate for auto combustion and heated in the temperature range of $160 - 180^{\circ}C$. The polycrystalline LaFeO₃ powder was formed within few minutes. The mixed powders were uniaxially pressed into pellets using a hydraulic press. The pelletized samples were then finally sintered at $1000^{\circ}C$ for 8 h and then used for various characterizations.

2.2. Characterizations

X-ray diffraction (CuK_{α}, Bruker D 8 Advance) was used for confirming the phase and structural study. The surface morphological features were observed by using scanning electron microscopy (JSM-6360A).Transmission electron microscopy was used for confirmation of particle size. The dc resistivity was measured by the two probe method as a function of temperature (~ Room temperature to 550°C.) The room temperature dielectric constant was measured by using a precision LCR meter bridge (model HP 4284 A) with frequency range from 20 Hz to 1 MHz, at room temperature. The ac conductivity was calculated from the dielectric data and using the following relation [15].

$\sigma_{\rm ac} = 2\pi\varepsilon_0\varepsilon_r f \tan\delta$

Where σ_{ac} is ac conductivity of the sample, ε_0 is the permittivity of air, ε_r is the real part of dielectric constant of the sample, *f* is the frequency of the applied field, tan δ is the loss factor. To improve the better ME signal, the samples have been poled electrically and magnetically. For electrical poling, the samples were heated to approximately 50 °C above the ferroelectric Curie temperature and then allowed to cool slowly in the presence of an electric field of about 2 kV cm⁻¹. A magnetic field of 4 kOe was applied across the sample in the direction of the electric field. The voltage developed on the surface of the samples, i.e. ME output was measured at room temperature by varying the applied dc magnetic field with the help of a Keithley electrometer (Model-6514).

RESULTS AND DISCUSSION

When reactants were heated at 180° C the reaction proceeded by the mechanism indicated in equation number 1 and 2 give the final product LaFeO₃.

$$2C_2NH_5O_2 + (9/2) O_2 \rightarrow N_2 + 4CO_2 \uparrow + 5H_2O \uparrow$$
(1)
$$La(NO_3)_3 + Fe(NO_3)_3 + 4 C_2H_5NO_2 \rightarrow LaFeO_3 + 8CO_2 \uparrow + 10H_2O\uparrow + 5 N_2 \uparrow$$
(2)

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X-ray diffraction XRD measurements were performed on Philips Analytic X-ray B.V. (PW-3710 Based Model) Advanced X-ray diffraction using Cu K α 1.54056 radiation. The XRD pattern shows that the product is pure perovskite oxide LaFeO₃ with an orthorhombic structure [Figure1]. The diffraction data is good agreement with JCPD card of LaFeO₃ (JCPDS No.37-1493). The average crystalline size of LaFeO₃ perovskite powder is determine with the help of Scherrer's equation $t=0.9\lambda/\beta cos\theta$, where t is the average size of the particles, λ is wavelength of X-ray radiation, β the full width at half maximum of the diffracted peak and θ is the angle of diffraction [16-18]. The average crystalline size obtained for nanocrystalline LaFeO₃ calcinated at 1000^oC is found to be 28-63 nm. LaFeO₃ nanocrystals are more attractive in the field of catalytic application. The BET surface area is measured on a Benchman coulter SA 3100 plus instrument using nitrogen adsorption at 200^oC. The surface area of the synthesized powder is 15.5 m²/g.



Fig. 1 X-ray diffraction patterns of $LaFeO_3$ powder heated at $1000^{\circ}C$

The SEM technique was employed for finding morphology of LaFeO₃ as synthesized powder and heated at 1000° C. One can notice the presence of macro-agglomerations of very fine particles having size less than 1µm. The particle shapes are not well defined. Many large and small pores are present in the whole material. We assumed that the pores are mainly intergranular because intragranular pores are not seen on the SEM photograph.

The TEM specimens were prepared by placing microdrops of colloid solutions on a carbon film supported by a copper grid. The TEM images of the nanocrystalline LaFeO₃ calcinated at 1000° C in air for 5 h are shown in [Figure3 (a)] it indicates the presence of LaFeO₃ nanoparticles with 28-63 nm size which form spherical type of oriental aggregation, agglomeration and polymeric linkage throughout the region. The HRTEM image [Figure 3 (b-c)] shows the porous nature of the material.



Figure 3 Transmission electron microscopy image of LaFeO₃ calcinated at 1000⁰C (a): high resolution transmission electron microscopy image of nanocrystalline LaFeO₃ (b-c): selected area electron diffraction pattern (d).

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The pores are well developed spherical shape with diameter from 9-13 nm size. The results are correlated with the XRD. The selected area diffraction (SAED) pattern [Fig 4 (d)] shows the spot type pattern which is indicative of single crystalline particles. No evidence was found for more than one pattern, suggesting the single phase nature of the material.

3.1. Thermoelectric power measurements

The n-type semiconductivity of thick films of $LaFeO_3$ was confirmed by measuring thermoelectromotive force of the thick film samples. The $LaFeO_3$ was observed to be n-type material.

3.2. I-V characteristics

Fig.4 depicts the I-V characteristics of the LaFeO₃ films. It is clear from the symmetrical I-V characteristics that the silver contacts on the film were ohmic in nature.



Fig. 4 I-V characteristic of nanocrystalline LaFeO₃.

3.2. Electrical properties

Linear decrease in resistivity with increase in temperature reflects the semiconductor behavior of the samples. The decrease in resistivity with increase in temperature is due to increase in the thermally activated drift mobility of charge carriers according to the hopping conduction mechanism [19]. The temperature dependence of dc resistivity is shown in Fig. 5 (a) and Fig. 5 (b). The electric resistivity of the material is reduced significantly because of the low resistivity of the material phase [20] as well as to the parallel connectivity between the material and ferroelectric grains in the composites [21].

The LaFeO₃ is a good dielectric material. It was observed that the dielectric constant decreases steeply at lower frequencies and remains constant at higher frequencies indicating the usual dielectric dispersion. Fig. 6 shows the frequency dependence of the dielectric constant of constituent phases. This may be attributed to the dipoles resulting from changes in valence states of cations and space charge polarization. At higher frequencies, the dielectric constant remains

independent of frequency due to inability of electric dipoles to follow the alternating applied electric field [22]. These frequency independent values are known as static values of the dielectric constant.



Figure 5 (b)Variation of Resistivity with temperature for LaFeO₃.

The higher dielectric constant at lower frequencies is associated with heterogeneous conduction in composites [23], but sometimes the polaron hopping mechanism results in electronic polarization contributing to low frequency dispersion. This is also attributed to Maxwell–Wagner [24] and [25] type interfacial polarization in agreement with the Koop's theory [26]. The dielectric behavior in the material can also be explained on the basis of polarization mechanism, which is similar to the conduction process because conduction in composites beyond phase

percolation limits is due to the ferrite phase [27]. The existence of Fe^{3+}/Fe^{2+} ions has rendered ferrite materials dipolar. Since in ferrite, the rotation of $Fe^{2+} \leftrightarrow Fe^{3+}$ dipoles results in orientational polarization that may be visualized as an exchange of electrons between the ions, the dipoles align themselves with the alternating field. The constant values of *r* at higher frequencies may be attributed to the fact that beyond a certain fixed frequency, the electron exchange between $Fe^{2+} \leftrightarrow Fe^{3+}$ does not follow the alternating field. In the present material , the presence of $La^{3+} \leftrightarrow La^{4+}$ ions give rise to p-type carriers and their displacement in an external electric field direction contributes to the net polarization in additional n-type carriers. However, the p-type carrier contribution is smaller than that from the electronic exchange between ions and opposite in sign [28]. The electrical conductivity and dielectric dispersion of material is mainly due to the exchange mechanism of charge carriers among the ions situated at crystallographically equivalent sites [29]. The dielectric constant is roughly inversely proportional to the square root of resistivity and same behavior is observed in the present study.



Variation of dielectric constant with frequency at room temperature

Fig. 6. Variation of dielectric constant with frequency for LaFeO3 at room temperature.

3.3. Ac conductivity

It is well known that in large polaron hopping the ac conductivity decreases with frequency and in small polaron hopping conductivity increases with frequency [30], and [31]. In order to understand the conduction mechanism and the type of polarons responsible for conduction ac conductivity measurements were carried out at room temperature in the frequency range from 20Hz to 1 MHz. Fig. 7 shows the frequency-dependent ac conductivity plot. From this figure, the conductivity is increase with an increase in frequency for the material. The results are similar to the one observed by other workers [32] and [33]. Variation of ac conductivity indicates that the conduction occurs by the hopping of charge carriers between localized states. For the present composites plots are linear confirming small polaron type of conduction. It has been shown that for ionic solids the concept of small polaron is valid [34]. The frequency dependent conduction may be attributed to small polarons, as reported by Alder and Fienleib [35]. Hence the present

results indicate that the conduction is due to small polarons in the material which is responsible for the good dielectric response.



Fig. 7 shows the frequency-dependent ac conductivity plot

CONCLUSION

The material containing LaFeO₃ was successfully prepared by combustion method, orthorhombic perovskite structure and phase formation was confirmed by X-ray diffraction. The temperaturedependent resistivity reflects the semiconducting behavior of the material. The dielectric dispersion with frequency has been explained on the basis of an electron–hole hopping mechanism which is responsible for conduction and polarization. The measurements of dielectric constant and ac conductivity with frequency suggest that the conduction in material is similar to the conduction in ferrites and occurs due to polaron hopping. Material may be useful to fabricate the interconnecting materials for the solar cell, gas sensors and applicable for catalytic purposes.

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