INVESTIGATION OF DIELECTRIC AND DC CONDUCTIVITY IMPROVEMENTS IN LANTHANUM FLUORIDE THROUGH RARE EARTH ELEMENT DOPING

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ABSTRACT

This paper deals with the measurement of dc conductivity and the dielectric constants of the $LaF_3:Nd^{3+},Ho^{3+}$ nanoparticles. For this, doped $LaF_3:Nd^{3+},Ho^{3+}$ nanocrystals have been successfully synthesized by microwave assisted technique with co-precipitation method. The X-ray diffraction, SEM, TEM and selected area electron diffraction SAED pattern have been used for identification of crystal structure. Cell parameters are a = b = 7.098AU and c = 7.238AU and confirms with the JCPDS standard card (32-0483) of pure LaF_3 crystals. During dielectric measurements, increase in the applied frequency results in rapid fall in dielectric constant and dielectric loss confirming the normal dielectric behavior attributable to the space charge formation. The ionic conductivity may be due to fluorine ions, as well as the ions on the surface of $LaF_3:Nd^{3+}$, Ho^{3+} due to doping. By doping LaF_3, the ionic conductivity of the sample is seen to be substantially enhanced.

Keywords: Lanthanum fluoride, conductivity, dielectric constant, dielectric loss

INTRODUCTION

In recent years considerable interest has been developed in lanthanide-doped inorganic nanoparticles due to their higher photo-stability and narrow-line luminescence compared to their organic counter-partners (dyes and chelates). Unlike most organic lanthanide complexes, nanoparticles provide a stable and low vibrational energy crystalline environment for the dopant ions, typically resulting in a higher photoluminescence quantum yield [1]. Attempts have been made to study the synthesis, characterisation and applications of LaF_3 nanoparticles doped with various lanthanides. A series of neodymium-doped lanthanum fluoride nanoparticles (NPs) have been synthesized with hydrothermal method, and the effects of several ligands on the luminescence properties of the NPs were investigated [2].

EXPERIMENTAL PROCEDURE

(A)Resistivity And Condutivity Measurement: The LaF_3 have trigonal crystal structure with space group $P\underline{3}c1$. The La^{3+} ions are located in planes which are perpendicular to c axis and are largely immobile [3]. The conductivity in the intrinsic as well as extrinsic LaF_3 crystals are ascribed to formation of fluoride ion vacancies by the Schottky mechanism [4] in the crystal structure and movement of the fluoride ions through these vacancies.

The powder sample of LaF_3 doped Nd^{3+}, Ho^{3+} nanocrystals was kept in pellet form. The

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pellet was annealed for 10 minutes in conventional microwave oven to remove moisture content if any. For proper electrical contact silver paste was applied on both the faces. The pellet was thenplaced in sample holder. The resistance of the pellet at room temperature was measured using 3532-50 Hioki Hitester LCR meter. The conductivity of $LaF_3:Nd^{3+},Ho^{3+}$ nanocrystals was calculated using the relation.

$\sigma_{dc} = t / RA$

Where R is the resistance measured from LCR meter

t is the thickness of the sample

A is the area of the face of pellet in contact with the electrode

Resistivity $\rho = 1 / \sigma_{dc}$

(B) Dielectric Studies: Dielectric constant and loss measurements were carried out on silver coated sample of Nd^{3+} and Ho^{3+} doped LaF_3 nanocrystals prepared in deionized water by using HIOKI 3532-50 make LCR HITESTER in the frequency range 100Hz to 5MHz at room temperature.

The capacitance (C_o) of the sample taken in the form of pellets is obtained by using the formula $C_o = A\varepsilon_0/d$ where A is the cross-section area of the pellet, $\boldsymbol{\varepsilon_0}$ is the permittivity of free space and d is the thickness of the samples.

LCR meter is used to record the capacitance (C_s) of the sample in the frequency range 100Hz to 5MHz. The capacitance values thus obtained were used for calculation of dielectric constant and dielectric loss values given by $\varepsilon' = C_s/C_0$ and $\varepsilon'' = \varepsilon' \times D$ where D is the dissipation factor obtained from the LCR meter, and $\tan\delta = \varepsilon''/\varepsilon'$.

OBSERVATIONS

Table 1: Resistivity and Conductivity of $LaF_3:Nd^{3+}, Ho^{3+}$ at room temperature

Sample	ickness t (cm)	Area A(cm^2)	Resistance Ω	Conductivity σ (/Ωcm)	Resistivity ρ (Ωcm)
$LaF3:Nd^{3+},Ho^{3+}$	0.113	1.326	144.9	0.588×10^{-3}	1700.68

Table 2: Dielectric measurements of $LaF_3:Nd^{3+}, Ho^{3+}$

$C_0 = 103.898 \times 10^{-12}$F

f Hz	logf	Cs	Dielectricconstant ε'= Cs/C0	electricLoss ε"= ε'x D	Tanδ=ε"/ ε'	log ε"
100	2	148.6µF	1.430×10^6	13.670×10^6	9.560	7.1357
1k	3	16.99µF	0.163×10^6	1.628×10^6	9.990	6.2116
10k	4	918nF	8.835×10^3	88.261×10^3	9.990	4.9457
100k	5	33.62nF	0.323×10^3	2.086×10^3	6.460	3.3193
1M	6	2.00nF	0.019×10^3	0.044×10^3	2.315	1.6434
5M	6.69	765pF	7.362	17.528	2.381	1.2437

Figure 1 and Figure 2 shows the graph of dielectric constant ε' as a function of logf and the graph of dielectric loss ε" as a function of logf for deionized water. It is observed that both ε' and ε" shows similar variations with frequency. Both dielectric constant and the dielectric loss are found to be inversely proportional to frequency. This is normal dielectric behavior where ε' and ε" decay exponentially with applied frequency [5]. Further the low dielectric loss value observed in $LaF_3:Nd^{3+}$, Ho^{3+} nanocrystals at high frequencies indicate its suitability for electronic applications.

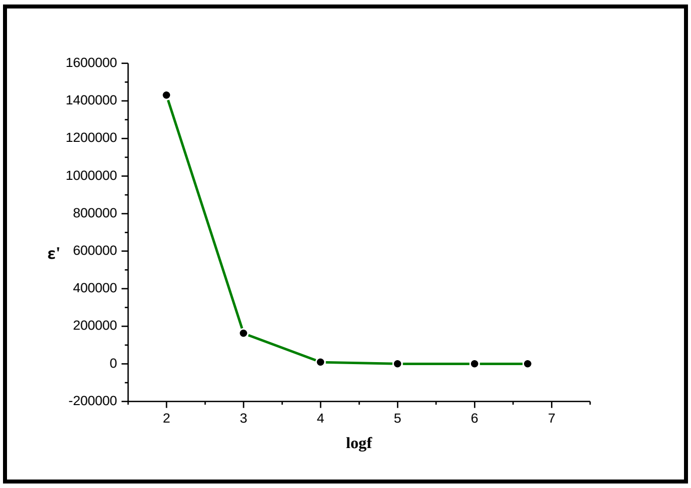

Figure 1: Variation of dielectric constant (ε') with log frequency of $LaF_3:Nd^{3+},Ho^{3+}$

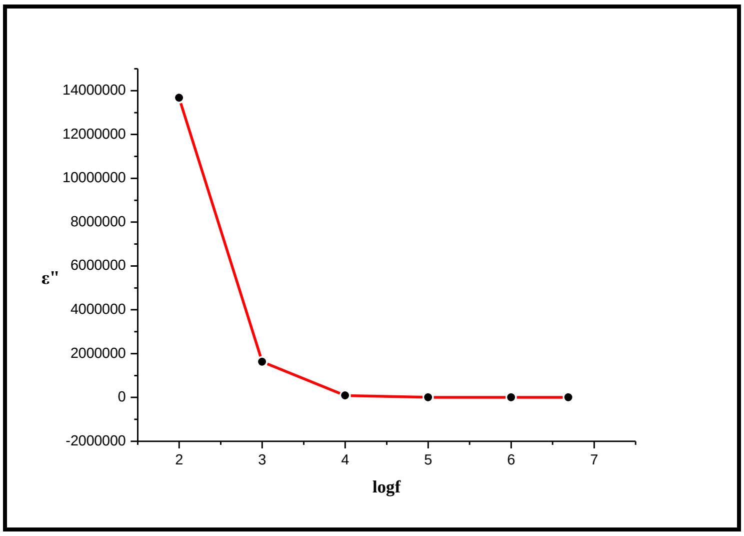

Figure 2: Variation of dielectric loss (ε") with log frequency of $LaF_3:Nd^{3+},Ho^{3+}$

Plot of log dielectric loss (ε") with log frequency (Figure 3) of $LaF_3:Nd^{3+}$, Ho^{3+} shows linear nature with slope = -1.446. Graph of Tanδ versus log of frequency (Figure 4) shows relaxation peak at a frequency of 10 KHz.

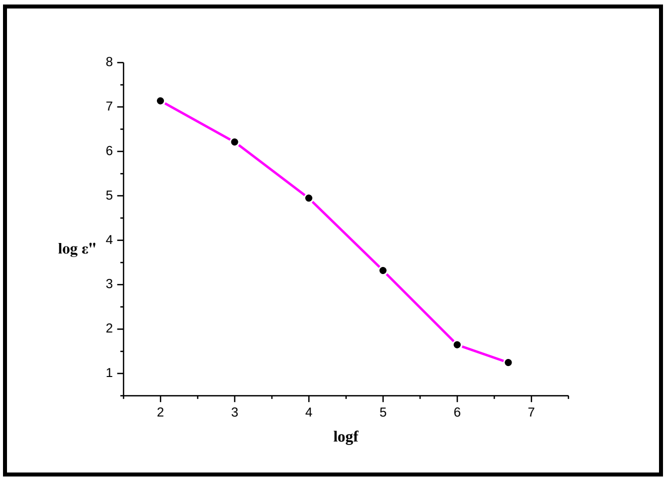

Figure 3: Variation of log dielectric loss (ε") with log frequency of LaF_3:Nd^{3+},Ho^{3+}

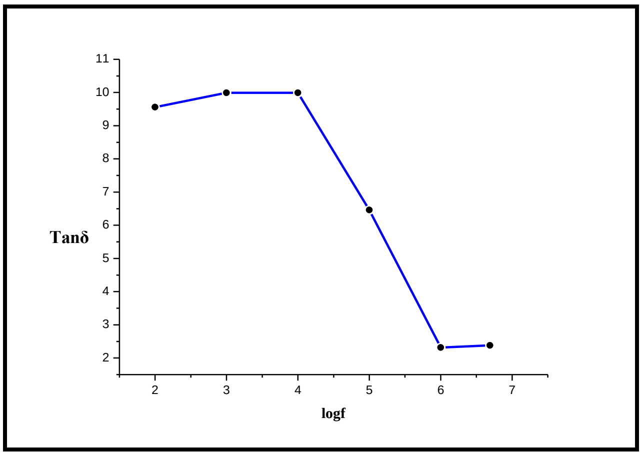

Figure 4: Variation of Tanδ versus log of frequency of LaF_3:Nd^{3+},Ho^{3+}

CONCLUSION

The dielectric properties of the synthesized samples were studied by plotting the graphs(i) dielectric constant versus log of frequency(ii) dielectric loss versus log of frequency (iii) log of dielectric loss versus log of frequency and iv) Tanδ versus log of frequency. It has been observed from the graphs of dielectric constant versus log of frequency and dielectric loss versus log of frequency that there is an exponential decrease in both the parameters with the increase in the frequency which is the normal behavior of dielectric materials as the dipoles lag behind in orientation as proposed by Debye [5-6]. The plot of log dielectric loss (ε") with log frequency exhibits near linear behavior using linear fit with slope equal - 0.9198. The value of the slope near unity indicates that dc conduction is dominant due to space charge effect in the synthesized sample [7]. Room temperature resistivity of the synthesized sample was 1700.680 Ωcm. The ionic conductivity of single crystal LaF_3 is of the order of 10^{-6}/Ωcm [8, 9]. The conductivity of the synthesized LaF_3: Nd^{3+}, Ho^{3+} sample at room temperature is found to be of the order of 10^{-3}/ Ωcm. Thus by doping LaF_3 the ionic conductivity of the sample is observed to be enhanced. The irradiation by microwave during the synthesis process leads to granularity of the nanoparticles[10]. The increase in the ionic conductivity may be attributed to granularity of the synthesized nanoparticles[11].

FUTURE SCOPE

The dielectric studies of the synthesized nanocrystals can be studied by varying the temperature and the corresponding conductivity and resistivity. Doped LaF_3 nanocrystals can be used as dielectric medium. Also there are reports on the use of LaF_3 as thin film oxygen detectors [12-13]. This part can be extended to development of LaF_3 sensors in future.

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