Studies on Electrical and Dielectric Properties of LaF₃:Ce,Ho

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Abstract—This paper deals with the measurement of dc conductivity and the dielectric constant of the LaF₃: Ce^{3+} , Ho^{3+} nanoparticles using sophisticated Hioki 3532 LCR Meter. For this, doped LaF₃: Ce^{3+} , Ho^{3+} nanocrystals have been successfully synthesized by microwave assisted technique using deionised water as solvent. The X-ray diffraction, SEM, TEM and selected area electron diffraction SAED pattern have been used for identification of crystal structure. Synthesized nanocrystals are found to belong to hexagonal crystal system with space group P3c1 and lattice parameters $a = b = 7.1260 A^0$ and $c = 7.2550 A^0$. Using Scherrer equation average particle size has been estimated which is found to be 13.72nm. SEM pattern shows dispersed, hexagonal, discs like, assorted particles with traces of some aggregates. SAED pattern indicates formation of strong diffraction rings corresponding to the (110), (111), (202), (113), (220), (221) and (115) reflections which is in agreement with the hexagonal LaF₃ structure. Nanocrystals of hexagonal geometry with particle size 14nm have been traced by TEM analysis which is in agreement with the average crystalline size obtained from XRD studies (13.72nm). The dielectric constant and dielectric loss are seen to be high at low frequency and decay exponentially with increase in frequency up to 5MHz. Plot of log ε'' versus logf of LaF₃: Ce^{3+} , Ho^{3+} shows near straight line with slope (-1.038). The deviation of sample from unity may be due to space charge effects. Variation of Tan\delta versus log of frequency of LaF₃: Ce^{3+} , Ho^{3+} may be attributed to the interface charge relaxation at the grain boundaries. The conductivity of the synthesized sample at room temperature is found to be $1.089 \times 10^{-3}/\Omega cm$. Resistivity at room temperature is found to be 918.27 Ωcm .

1. INTRODUCTION

Significant attention has been paid on rare-earth ions doped nanoparticles to find out the potential applications in optoelectronics, displays, light emitting diodes (LEDs), bio-imaging,etc [1-4]. The electronic f-f transitions of rare-earth ions are localized in atomic orbitals of the ions. Therefore, no size dependent quantization effect occurs due to confinement of the delocalized electrons for these f-f transitions [5]. The spontaneous emission probability of optical transitions (luminescence lifetime) from rare-earth (RE) ions doped in nanoparticles may be significantly different from their bulk counterparts [6]. From the fundamental point of view, the physical understanding of the luminescence properties of rare-earth ions in nanocrystals and the way it changes with crystal phase and local structure is very important. It has already been demonstrated that the luminescence property of the rare-earth doped material depends on the size, shape and crystal phase [7-10].

2. RESISTIVITY AND CONDUCTIVITY MEASUREMENT

The electrical transport in solid is dominated by the movement of ions through voids, or empty crystallographic positions. Both anions and cations can carry the current. In amorphous solids cation motion is found to be most common, along with the motion of anions such as F^- or O^{2^-} . The ionic highest conductivities results for ions like H^+ and Li^+ or very deformable ions like Ag^+ . Ionic conductivities can be as high as above 10^{-2} Scm⁻¹ at room temperature in so called "superionic materials". Owing to high chemical stability and ionic conductivity LaF₃ nanocrystals based chemical sensors shows potential applications in sensing the fluorine, oxygen, carbon monoxide and biosensors with suitable enzymes as auxiliary electrode [11-13].

W.Y. Feng etal [14] reported ionic conductivity for LaF₃ superfine powder using water as solvent. The ionic conductivity (σ) was found to be 3.52 x 10⁻⁷ Scm⁻¹ where t = 1.4 x 10⁻¹cm and cross section area of sample A = 28 x 10⁻² cm². S. G. Gaurkhede [15] synthesized LaF₃: Ce³⁺, Pr³⁺, Sm³⁺ nanocrystals by simple precipitation method and reported conductivity of the samples as 2.5 x 10⁻⁶ (Ω cm)⁻¹ with thickness t = 0.101cm and cross section area of sample A = 1.326 cm².

In the present case, the powder sample was put in the form of pellet. It was annealed for 10minutes in microwave oven at low power to remove moisture content if any. Quick drying silver paste was applied on opposite faces of the pellet to form electrical

contact. The sample was then placed in sample holder and the resistance of the pellet was recorded by using the Hioki LCR meter. The dc electrical conductivity (σ_{dc}) of the pellet 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 $\rho = 1 / \sigma_{dc}$

Table 1	Resistivity	and Conduct	ivity of the	sample at roo	m temnerature
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Sample	Thickness	Area	R	σ	ρ
	t (cm)	(cm ²)	Ω	(/Ωcm)	(Ωcm)
LaF ₃ :Ce ³⁺ ,Ho ³⁺	0.109	1.326	75.46	1.089 x 10 ⁻³	918.27

The conductivity of the synthesized sample at room temperature is found to be of the order of $10^{-3}/\Omega$ cm. Resistivity at room temperature is 918.27 Ω cm.

3. DIELECTRIC STUDIES

Dielectric measurement was carried out for LaF₃ doped Ce³⁺, Ho³⁺ nanocrystals. The sample was silver coated and then placed inside a sample holder in the frequency range 100Hz to 5MHz using HIOKI3532-50 LCR Hitester. Care has been taken to avoid stray capacitance. Figure 1 shows variation of dielectric constant (ϵ') versus log of frequency and Figure 2 shows dielectric loss (ϵ'') versus log of frequency for LaF₃:Ce³⁺, Ho³⁺. It was found that both ϵ' and ϵ'' decay exponentially with applied frequency [16].Thus both dielectric constant (ϵ') exhibit normal dielectric behavior.

Figure 3 shows the plot of log dielectric loss (ϵ ") with log frequency of LaF₃:Ce³⁺,Ho³⁺. The plot shows near straight line with slope (-1.038).

Figure 4 indicate variation of Tan δ versus log of frequency of LaF₃:Ce³⁺, Ho³⁺. Maximum value of Tan δ is 10 till f = 1MHz beyond which it decreases and gives the value of 7.52 at about 5MHz. The nature is typical of polar dielectric consisting of dipole and migration polarization.



Figure 1: Variation of dielectric constant (ɛ') with log frequency of LaF₃:Ce³⁺,Ho³⁺



Figure 2: Variation of dielectric loss(ϵ ") with log frequency of LaF₃:Ce³⁺,Ho³⁺



Figure 3: Variation of log dielectric loss(ϵ ") with log frequency of LaF₃:Ce³⁺,Ho³⁺



Figure 4: Variation of Tano versus log of frequency of LaF₃:Ce³⁺,Ho³⁺

4. CONCLUSION

From dielectric studies, dielectric constant and dielectric loss are seen to be high at low frequency and decay exponentially with increase in frequency up to 5MHz. Plot of log ε " versus logf of LaF₃:Ce³⁺,Ho³⁺ shows near straight line with slope (-1.038). The deviation of sample from unity may be due to space charge effects. Variation of Tan δ versus log of frequency of LaF₃:Ce³⁺, Ho³⁺ may be attributed to the interface charge relaxation at the grain boundaries. The ionic conductivity of single crystal LaF₃ is of the order of 10⁻⁶/Ωcm. The conductivity of the synthesized sample at room temperature is found to be of the order of 10⁻³/Ωcm. Thus by doping LaF₃ the ionic conductivity of the sample is observed to be enhanced. Resistivity at room temperature is found to be 918.27Ωcm.

5. FUTURE SCOPE

The dielectric studies of the synthesized nanocrystals can be studied by varying the temperature and the corresponding conductivity and resistivity. Doped LaF₃ nanocrystals can be use as dielectric medium. Also there are reports on the use of LaF₃ as thin film oxygen detectors [17]. This part can be extended for development of LaF₃ sensors in future.

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