# Preparation and characterization of perovskite Cu doped LaFeO₃ semiconductor ceramics

**Bandi Vittal Prasad[1], B. Venugopal Rao[1], K. Narsaiah[1], G. Narsinga Rao[2] , J.W.Chen[2] and D.Suresh Babu[1,*]**

[1]Department of Physics, Nizam College (Osmania University), Hyderabad, India.
[2]Department of Physics, National Taiwan University, Taipei, Taiwan, R. O. C.,

[*] Corresponding author E-mail: s_devarasetty1956@yahoo.co.uk

**Abstract**. Orthorhombic structured polycrystalline Cu doped LaFeO₃ perovskite ceramics were prepared by sol-gel route and characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopic (FT-IR) techniques. The complex dielectric properties for these ceramic samples investigated as function of temperature, in the range 80K - 300K, and frequency, in the range 20 Hz -1MHz. These samples exhibiting colossal dielectric constant value of $10^4$ near room temperature at low frequencies. The response is similar to that observed for relaxor ferroelectrics. Impedance spectroscopy (IS) data analysis indicates the ceramics to be electrically heterogeneous semiconductors consisting of semiconducting grains with dielectric constant below 100. We conclude, therefore that grain boundary effects is the primary source for the high effective dielectric constant in Cu doped LaFeO₃ ceramics.

## [1]        Introduction

Materials exhibiting colossal values of the dielectric constant are the subject of intense research today owing to their ability to reduce the size of capacitive components, offering an opportunity to miniaturize electronic systems. In general, high intrinsic dielectric constant $\epsilon'$ ($_n$ ' >10) is exhibited exclusively by ferroelectric and relaxorferroelectrics. In recent years, materials exhibiting a so called giant dielectric constant have been reported [1-8]. One of the giant dielectric constant ($\epsilon'$) materials $CaCu_3Ti_4O12$ (CCTO) has recently attracted much attention. Right from the time this effect was first observed in CCTO, attention has been concentrated on materials with perovskite structure ($ABO_3$), due to the set of specific properties belonged to these materials.

Cu doped LaFeO₃ (LFCO) materials are semi conductive in nature at room temperature and conductive at high temperatures. In this paper we report details concerning the dielectric response of LFCO as a function of frequency and temperature along with the possible underlying mechanisms.

## [2]        Experimental

Polycrystalline powders of Cu doped LaFeO₃ (LFCO) were prepared by the citric acid route. Collected powders were annealed at 700 $^0$C for 2 h. The prepared pellets were sintered at 1000 $^0$C (1200 for LaFeO₃ sample) for 4 h.

### [3]          Results and discussions

The XRD patterns obtained at room temperature of the polycrystalline LFCO synthesized by citric acid method are shown in Figure 1. It is observed that the XRD spectrum is of a single phase LFCO. All the peaks could be indexed to orthorhombic cell associated with space group Pbnm. The lattice parameters were given in the Table1.
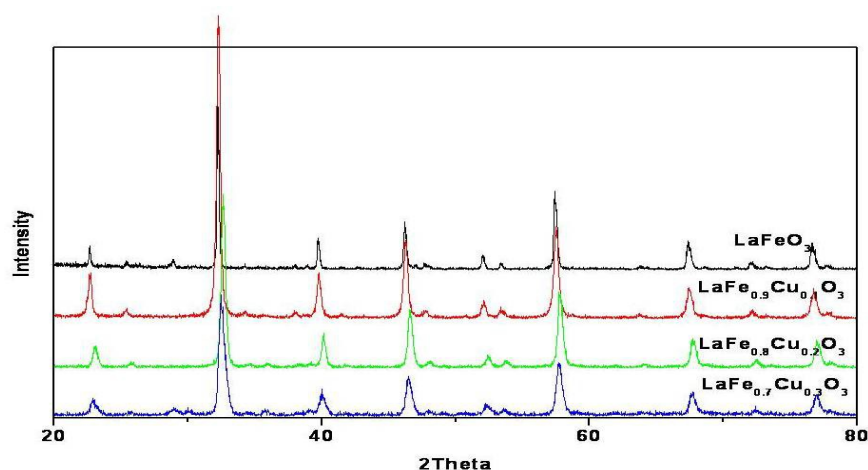


Figure1. The XRD patterns obtained at room temperature of the $LaFe_{1-x}Cu_xO_3$ (x= 0, 0.1, 0.2, 0.3) ceramics

Table 1. Lattice parameters of $LaFe_{1-x}Cu_xO_3$ (x= 0, 0.1, 0.2, 0.3)

|  | $a$ ($A^0$) | $b$ ($A^0$) | $c$ ($A^0$) |
|---|---|---|---|
| $LaFeO_3$ | 5.576(3) | 7.857(3) | 5.550(2) |
| $LaFe_{0.9}Cu_{0.1}O_3$ | 5.554(4) | 7.854(4) | 5.554(2) |
| $LaFe_{0.8}Cu_{0.2}O_3$ | 5.567(3) | 7.869(3) | 5.563(2) |
| $LaFe_{0.7}Cu_{0.3}O_3$ | 5.571(4) | 7.862(4) | 5.560(2) |



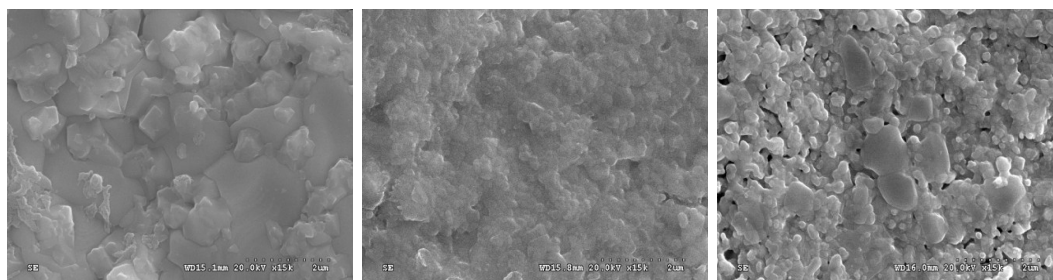Figure 2. SEM micrograph of the $LaFe_{1-x}Cu_xO_3$ (x= 0, 0.1, 0.2, 0.3) ceramics pellets

SEM micrograph of the sintered LFCO pellets in air shown in Figure 2. The micrograph reveals that the pellet consists of small grains with considerable porosity.

The deferential thermal analysis has been performed for all the dried gel. The DTA curves for LFCO compounds are shown in Figure 3(a). Strong exothermic peaks on DTA curves are observed, which are due to vigorous combustion reactions of the organic compounds, where maximum weight loss ( 70%) seen in TG. Weight loss is also observed between 600 $^0$C and 700 $^0$C which corresponds to the exothermic peaks in DTA curves it corresponds to the decomposition of an amorphous Oxyhydroxycarbonate. Beyond this temperature range, the curves tend to be very flat, showing no intense decomposition.
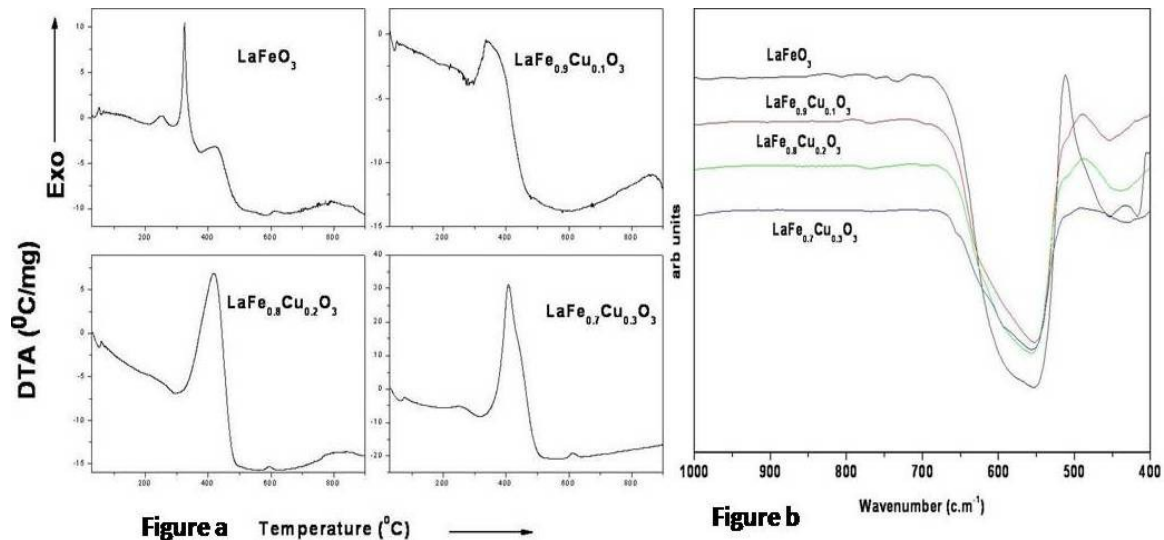


Figure 3. The DTA(Figure a.) and FTIR(Figure b.) curves of the LaFe$_{1-x}$Cu$_x$O$_3$ (x = 0, 0.1, 0.2, 0.3) ceremics

The Crystal structure of the rare earth ferrites is known to be of the distorted GdFeO$_3$ – type structure The two infrared-active vibrations are shown in the Figure 3(b). The bands around 556 cm$^{-1}$ and 435 cm$^{-1}$ corresponds to stretching mode v$_s$, which involves the internal motion of the Fe-O bond and the bending mode v$_b$, which is sensitive to a change in the Fe-O-Fe bond angle

The temperature dependence of the dielectric constant ($\epsilon'$) and dielectric loss (tan $\delta$) for LaFe$_{1-x}$Cu$_x$O$_3$ (x = 0, 0.2, 0.3) samples are shown in Figure 4. The room temperature dielectric constant attains a value ~ $10^4$ at 1 kHz. Two $\epsilon'$ plateaus at higher and low temperature are clearly seen Figure 4. Between two plateaus the dielectric constant ($\epsilon'$) increases sharply by a factor of ~100, accompanied by a peak in the dielectric loss (tan $\delta$) at the temperature T$_P$. The peak positions (value of T$_P$) shifted to high temperatures with increase in Cu composition, and with increase in measuring frequency. It can also be seen that there is an exponential like increasing background in tan $\delta$ curve.
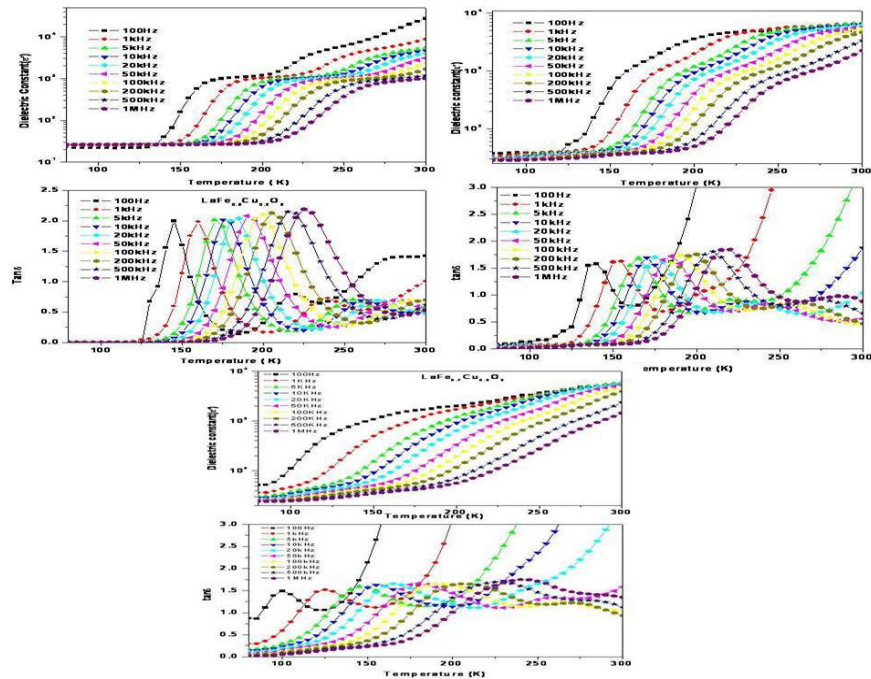
Figure 4. Plots between dielectric constant ( $\varepsilon'$) and tan$\delta$ versus temperature for
LaFe$_{1-x}$Cu$_x$O$_3$ (for x= 0, 0.2, 0.3)
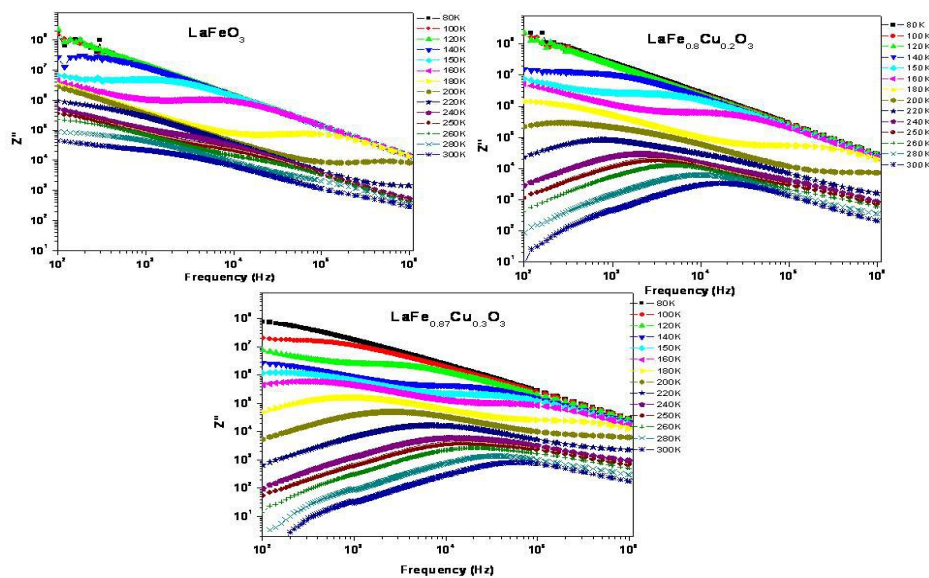


Figure 5. Imaginary part of impedance versus frequency at different temperatures for the
LaFe$_{1-x}$Cu$_x$O$_3$ (for x= 0, 0.2, 0.3) ceramic samples

To clarify reason for the high dielectric constant we performed impedance analysis. Figure 5. shows Z'' vs frequency for different temperatures. The higher values of Z'' at lower frequencies and at lower temperatures and the merging of Z'' curves at higher frequency end indicate the presence of space charge polarization in these samples. we can observe a weak peak at low frequencies and the peak are shifted to higher frequencies as temperature increases and the peak are moved out of measuring window as temperature is more then 200K. As temperature increases further a strong peak is observed at lower frequencies for LC02 and LC03 samples which is moving to higher frequencies as temperature increases with decrease in intensity, indicating the both electric responses are thermally activated. The broadness of the peak indicates presence of multiple relaxations in the material [9-10]. Peak width at half maxima of Z'' curves is more than a decade (> 1.14 decades) indicating non-Debye relaxation behavior.

## 1.  **Conclusions**

LaFeO$_3$ samples with Cu doping are prepared through chemical route and single-phase formation is confirmed by XRD. SEM micrographs pour size and number of pours increases with Cu and grain size decreases. The temperature dependent dielectric constant for LaFe$_{1-x}$Cu$_x$O3 (x = 0, 0.2, 0.3) resembles to that of CaCu3Ti4O12, widely studied in recent year. The observed temperature and frequency dependent high dielectric constant in semiconducting LaFe$_{1-x}$Cu$_x$O3 (x = 0, 0.2, 0.3) ceramics showing non Debye relaxation and is dominated by grain boundary response.

**References**
[4]    M.A.Subramanian, D.Li,N.Duan, B.A.Reisner, and A. W. Sleight, 2000 *J.Solid State Chem*. **151** 323.
[5]    T. B. Adams, D. C. Sinclair, and A. R. West, 2002 *Adv. Mater.* (Weinheim, Ger.) **14**, 1321.
[6]    D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West 2002, *Appl. Phys. Lett.* **80**, 2153.
[7]    M. Li, A. Feteira, and D. C. Sinclair 2005, *J. Appl. Phys*. **98**, 084101.
[8]    A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, and S. M. Shapiro, 2000 *Solid State Commun*. **115**, 217.
[9]    Bandi Vittal Prasad, G. Narsinga Rao, J. W. Chen, D.Suresh Babu, 2011 *Mater. Chem. Phy.* **126**, 918.
[10]   Bandi Vittal Prasad, G. Narsinga Rao, J. W. Chen, D.Suresh Babu,2011 *Mater. Res. Bull.* **46**, 1670.
[11]   Bandi Vittal Prasad, G. Narsinga Rao, J. W. Chen, D.Suresh Babu,2012 *solid state sci.* **14**, 225.
[12]   A. K. Jonscher, 1983 *Dielectric Relaxation in Solids*, (Chelsea Dielectrics London).
[13]   J. R. Macdonald 1987 *Impendance Spectroscopy* (Wiley  New York)