

بسم الله الرحمن الرحيم

## **The Effect Of Ternary Additives On The Electrical Properties of Nano-Sized BaTiO<sub>3</sub>**

**Dr. Fadhil Abd Rasin**

*College of science, Babylon University*

Fadhil\_rasin@yahoo.com

**Dr. Atheel Mohamed Jasim**

*Al-Nahrain University*

*College of Science*

**Dr. Ahmed Kamal Ahmed**

*Al-Nahrain University*

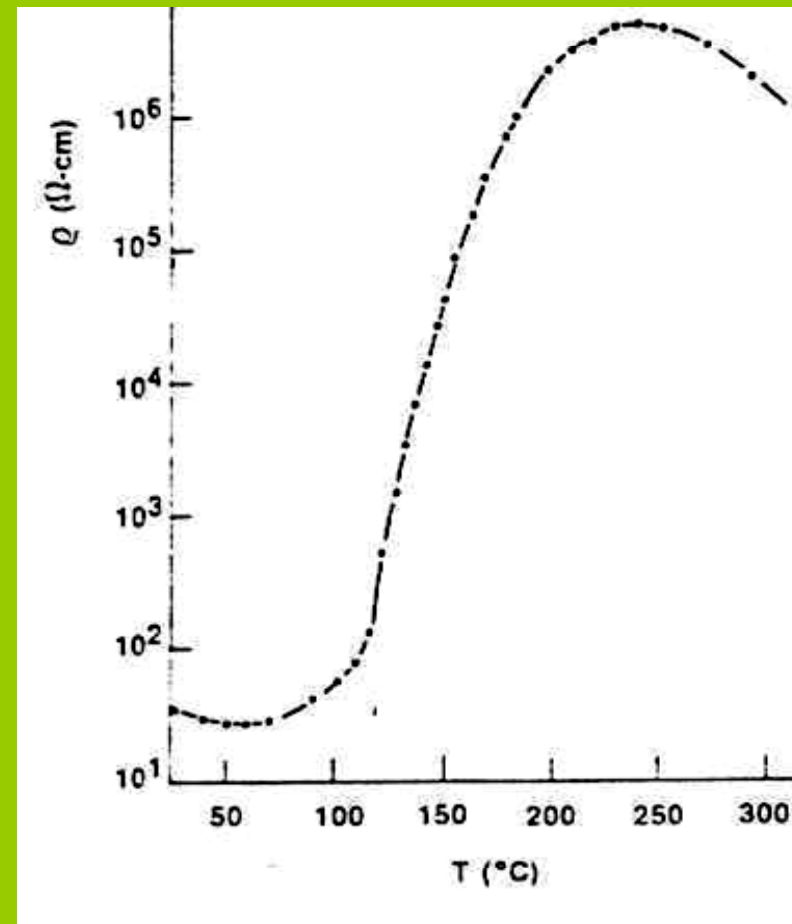
*College of Science*

# Why Barium Titanate?

- Barium Titanate ( $\text{BaTiO}_3$ ), the first commercial piezoelectric ceramic, was independently discovered by researchers in USA, Japan, and Russia in the early 1940s. Today, it is used in manufacturing electronic components for many applications including thermistors, actuators, sensors, and transducers.  $\text{BaTiO}_3$  is popular not only because of its attractive dielectric, ferroelectric, piezoelectric properties, but also because it is mechanically and chemically stable. Even more interesting is the flexibility of the structure to different compositional changes which is useful in tailoring electrical properties of the ceramic.

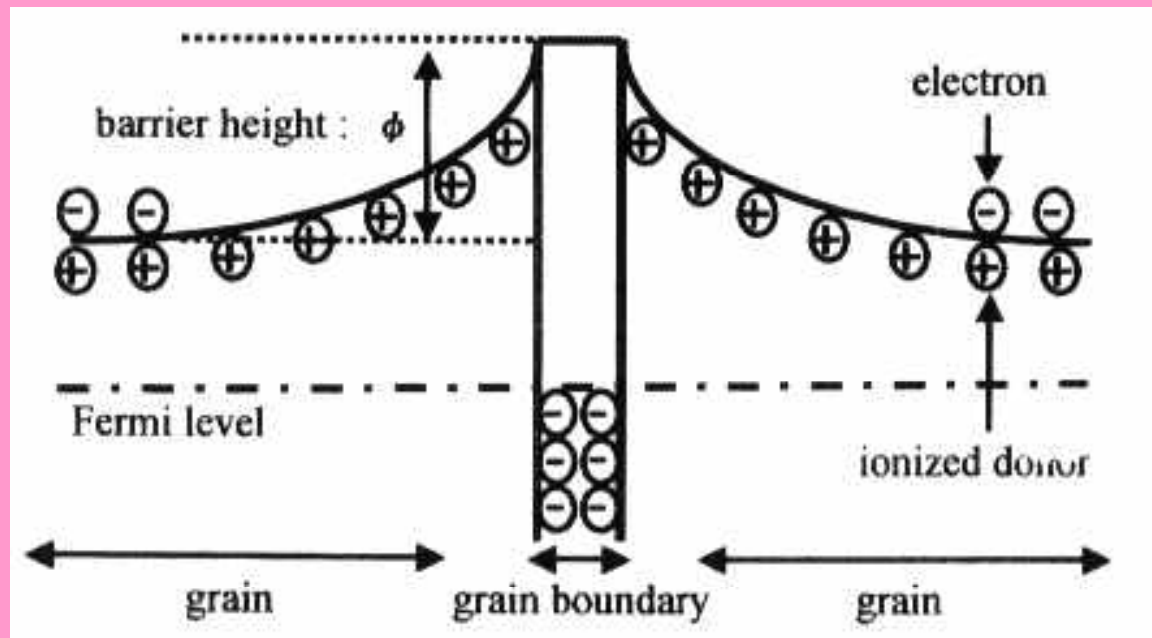
# Doping of Barium Titanate by donor ions ( $\text{Ce}^{3+}$ , $\text{La}^{3+}$ , $\text{Mn}^{5+}$ ) leads to Positive Temperature Coefficient of Resistivity PTCR

$\text{BaTiO}_3:\text{Y}$  system.  
Yttrium amount is  
0.25% molar. Therefore,  
it is used as mainly as  
thermister. Donor  
doping of Barium  
Titanate changes the  
material from dielectric  
to N-type  
semiconductor



# Heywang Model Explained the PTCR characteristics

- The double Schottky-type potential barrier, which controls the electrical resistivity, is formed by capturing electrons at the grain-to-grain interface in its band gap



# Aim of this study

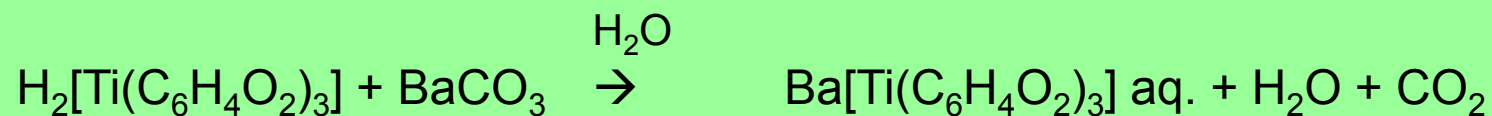
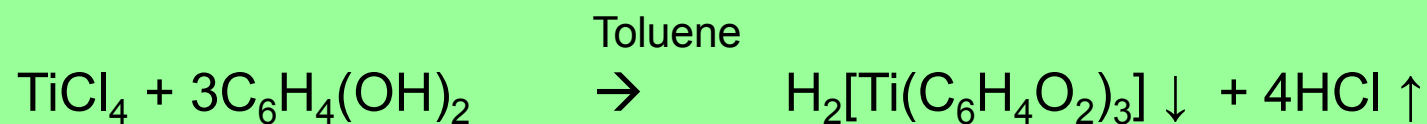
- Synthesize the Barium Titanate fine powder by three methods (Thermal, catecholate-freeze-drying, Chloride-Hydroxide) and study the resulting Barium Titanate powder by XRD, FTIR and Scherrer formula.
- Selecting one out of the three methods for doping. The decision depend on purity, time consumed, amounts of chemicals used, number of sub-processes used.
- Dope the synthesized Barium Titanate fine powder by (Ce, Y, La) separately and study the effect on resistivity and permittivity.
- Co-dope the synthesized Barium fine powder by (La, Sr) and (La, Mn). A study of the effect is to done.
- Dope the Barium Titanate by Ternary additives (La, Sr, Mn) to study the change on resistivity and perittivity.

# Synthesizing BaTiO<sub>3</sub> by thermal solid state method

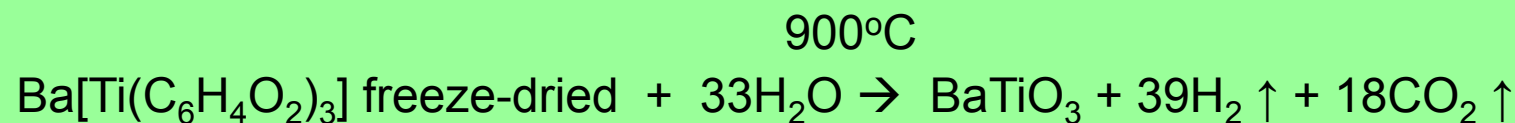
1000°C, 4 hours



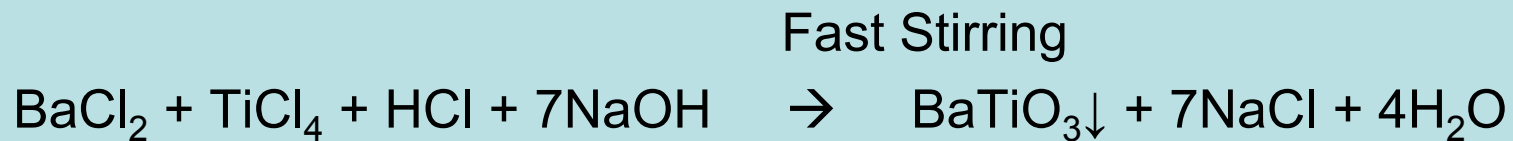
# Synthesizing BaTiO<sub>3</sub> by Catecholate-Freeze-Drying method



Ba[Ti(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>3</sub>] aq. is freeze-dried to get nano-powder

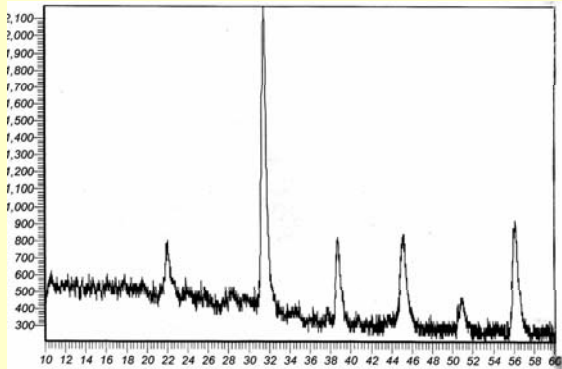


# Synthesizing BaTiO<sub>3</sub> by Chloride-Hydroxide method

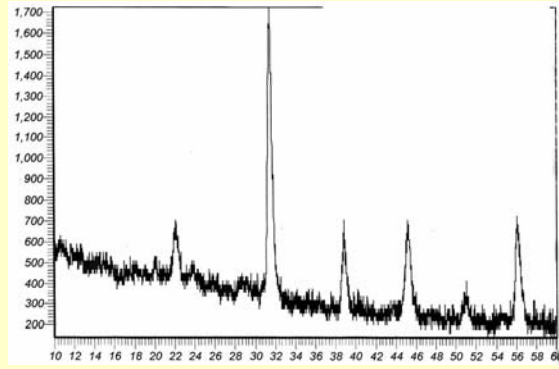


((No use of furnace in this method))

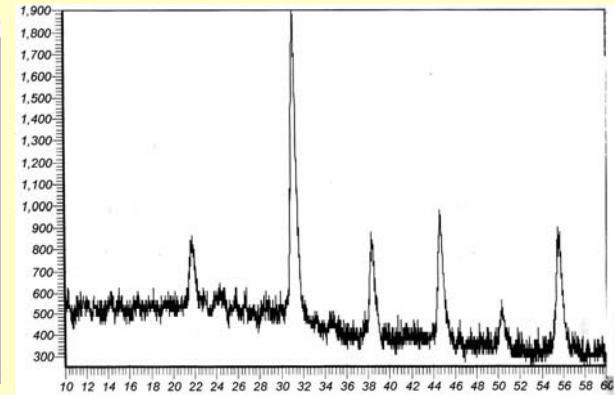
# XRD test of the produced powders



Thermal  
Solid State method



Catecholate  
Freeze-Drying method

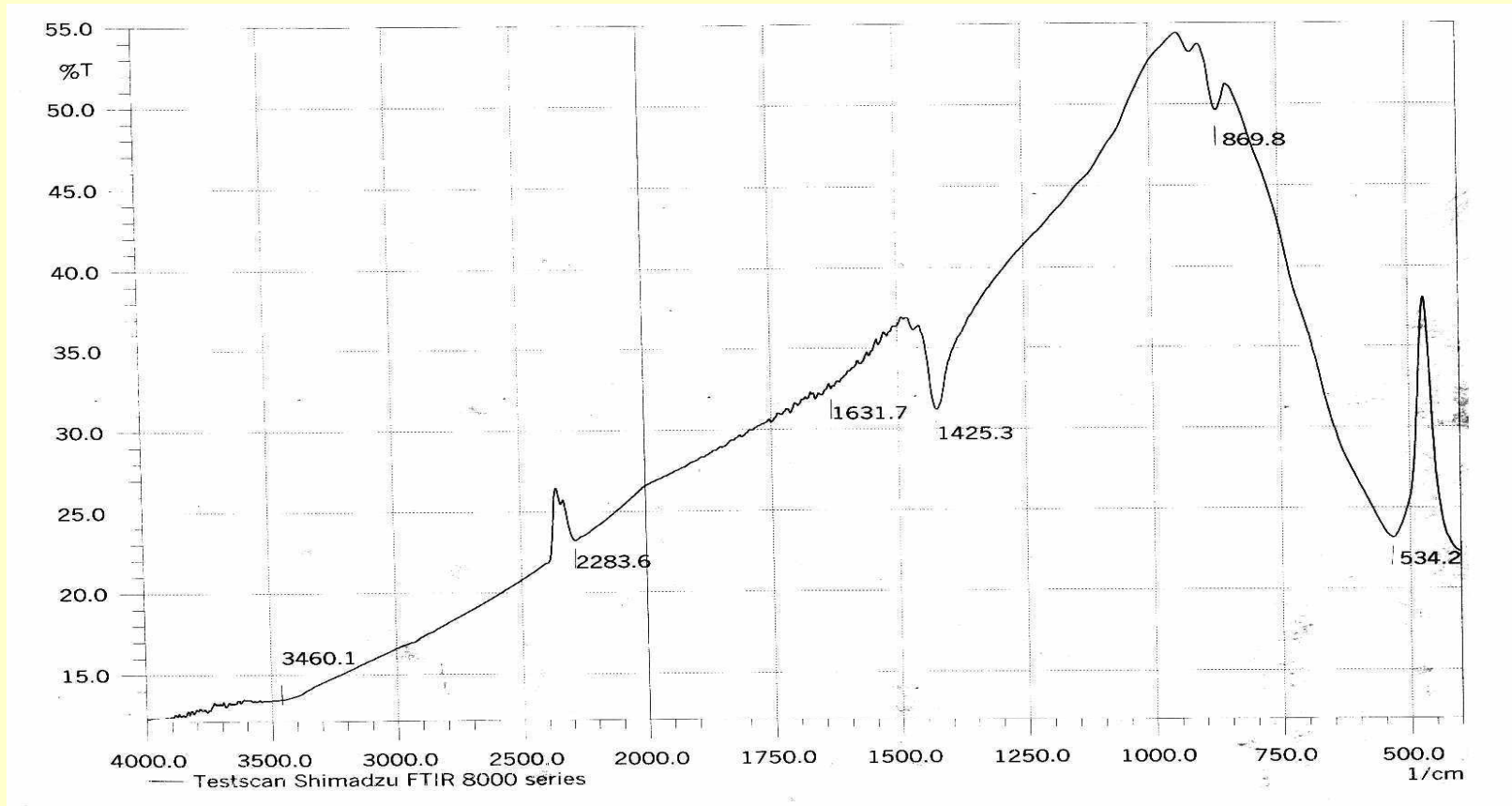


Chloride-Hydroxide  
method

# Scherrer Formula test

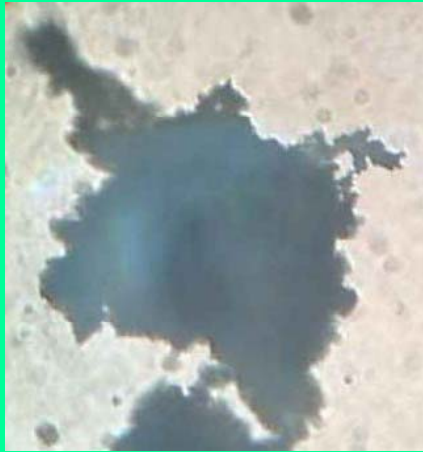
- $D = k \lambda / (B * \cos(\theta_B))$
- D is the thickness of the crystal (Å); K= 0.9 is a constant related to the crystallite shape;  $\lambda$  is the X-ray wavelength (1.54051Å for Cu alpha);  $\theta_B$  is the Bragg angle (between incident and diffracted beam); and B is the line broadening, measured from the peak width at half the peak height (radians) or called Full Width at Half Maximum FWHM in  $\theta_B$  scale. B value is calculated in radians.
- The result was 43nm for the thermal solid state method, 47nm for the catecholate freeze drying method and 38nm for the Chloride-Hydroxide method.

# FTIR test

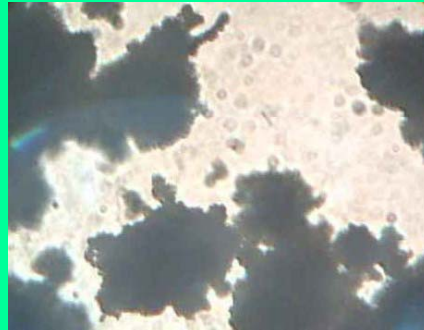


FTIR (500-4000 $\text{cm}^{-1}$ ) result for the Catecholate freeze drying method

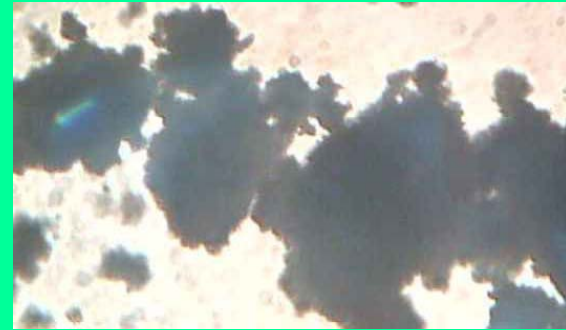
# Optical Microscope test



Thermal  
Solid State method



Catecholate  
Freeze-Drying method



Chloride-Hydroxide  
method

# Why Chloride-Hydroxide method was selected for the *next* doping process ?

- Due to limitations of time, effort and funding one method of the synthesis methods was used for the next doping procedure. The Hydroxide-Chloride method was selected for the following reasons:
  - It has fast, direct procedure.
  - It does not include the necessity for furnace at all.
  - It has low particle size necessary for good mixture with dopants.
  - It has an adequate level of purity. The impurity is introduced by the reaction of the atmosphere  $\text{CO}_2$  with the mixture of  $\text{BaCl}$  and  $\text{HCl}$  to produce  $\text{BaCO}_3$ .

# Why additives are used?

- Additives change Barium Titanate characteristics (Electric, grain size, Curie Temperature shift, Improve PTCR curve).
- Therefore, doped Barium Titanate is of industrial interest.

# What additives to use?

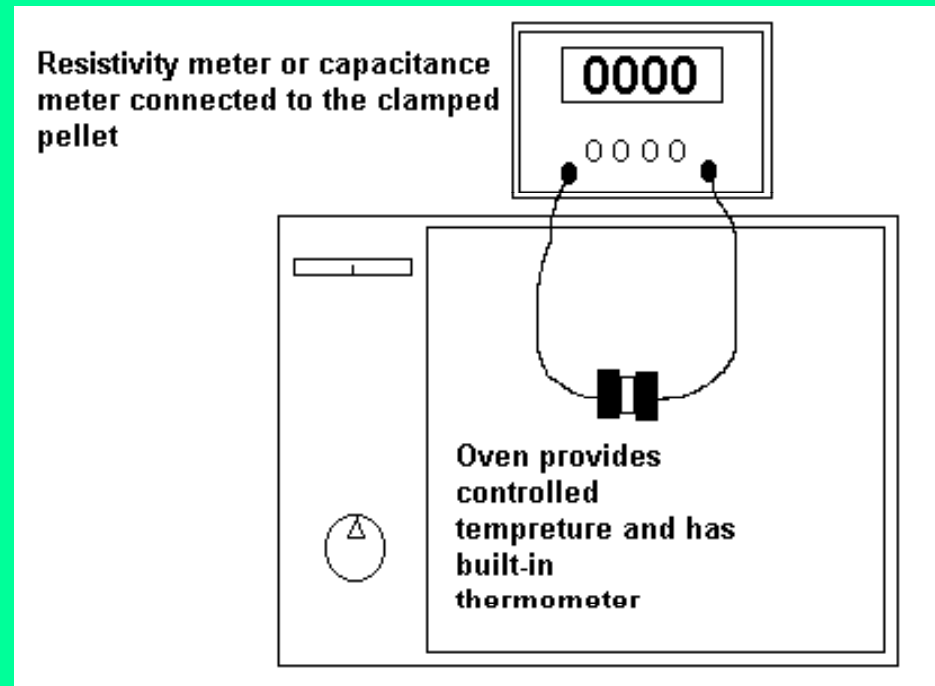
- This study is focused on making Barium Titanate N-type semiconductor with improved PTCR characteristics.
- Therefore, the elements Ce, Y, La were selected as donors ions.
- Mn is added to improve PTCR characteristics.
- Sr is added to shift Curie Temperature to lower range.
- The elements (La,Sr,Mn) were used as ternary system to tailor the product to better results.

# How much and how to add the additives?

- Wet mixing (Ethylene Alcohol) was used.
- 0.1-0.3% molar of Ce, La, Y is effective with maximum effect around 0.2% molar.
- 0.1% molar of Mn is effective to make the improvement of PTCR.
- 5-20% molar of Sr is effective to produce the shift in Curie temperature.

# How to test the product?

- 3g amount of each sample is pressed with binder (Polyvinyl).
- Pellets were sintered at 1400°C for one hour.
- Copper contacts were used to connect the pellets to resistivity and permittivity meters.



# Mono-doping of Barium Titanate

- Mono-doping by Ce shows that the minimum Curie Temperature and best PTCR characteristics is reached with 0.2% molar. The permittivity with 0.2% molar was stable over temperature.
- Mono-doping by Y shows that the minimum Curie Temperature and best PTCR characteristics is reached with 0.4% molar. Permittivity is decreased with increasing the Y dopant content.
- Mono-doping by La shows that the minimum Curie Temperature and best PTCR characteristics is reached with 0.4% molar. Permittivity is decreased with increasing the La dopant content.
- Mono-doping by Ce 0.2% molar gave higher linearity in the PTCR characteristics than mono-doping with Y or La. Mono-doping with Ce 0.2% molar gave higher stability over temperature than doping with Y or La.

# Co-doping of Barium Titanate

- Co-doping by La and Mn shows that increasing the Mn doping gave higher linearity to PTCR characteristics, higher resistance values and drop in Curie Temperature. Co-doping with La and Mn decreased the permittivity.
- Co-doping by La and Sr shows that doping by Sr 10% molar and La 0.2% molar gave higher linearity to PTCR characteristics than the other values. Also, increasing the Sr content decreases the Curie Temperature. Co-doping with La and Sr increased the permittivity.

# Ternary doping of Barium Titanate

Ternary-doping by La, Mn and Sr shows that doping by (Sr 20% molar, Mn 0.1% molar and La 0.2% molar) gave higher linearity, higher resistivity values than the other values. The same system is higher in Curie temp than co-doping (Mn 0.3% molar, La 0.2% molar), and higher in resistance values than the system of (Sr 10% molar, La 0.2% molar).

Therefore, ternary doping helped further increasing the resistivity and linearity with little decrease in Curie temperature.

Ternary doping with Sr 20% molar, Mn 0.1% molar and La 0.2% molar gave higher stability over temperature than other ratios. Clearly, the Sr content (try to increase the permittivity) is compensated by the Mn and La content (which tries to decrease the permittivity). Therefore, ternary doping of (La, Mn, Sr) helped improve the stability over temperature as compared to the classical commercial ceramic capacitor.

**Thanks for your attention.**