IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 16, Issue 2 Ser. I (February 2023), PP 11-17
www.iosrjournals.org

Influence of Ce on structural and electrical properties on Mg nano chromites synthesized by Citrate Gel Auto Combustion method

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Abstract
A variety of nano spinel chromite with the formula $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0 was synthesised by the citrate auto combustion method. The structural characterization was carried out by XRD, SEM, and FTIR spectroscopy. From the XRD, the crystalline size was calculated and found to be 21.86 to 29.55 nm. Lattice parameter varied 7.81 to 7.87 A^O, indicates obeysVegardslawand SEM images revealed the agglomerated of particles. From FTIR studies, two bands are absorbed at 600 cm^{-1} and 400 cm^{-1}, which are characteristic bands of metal oxygen bands at tetrahedral and octahedral site. A dielectric study was carried out using a LCR metre at room temperature. From this study, dielectric parameters such as AC conductivity,dielectricconstant, dielectric loss and impudence studies were investigated. The AC conductivity measurement showed a linear increment with applied frequency. The dielectric laws and dielectric constant of the synthesised samples decreased with increasing frequency.

Key Words. *Mg-Ce nano chromites, XRD, SEM, FTIR and Dielectric studies.*

Date of Submission: 24-01-2023 Date of Acceptance: 06-02-2023

I. Intraduction

The typical formula for chromite is AB_2O_4, where A is a divalent metal ion, such as Mg^{2+}, Ni^{2+}, or Zn^{2+}, and B is a trivalent metal ion, such as Fe^{3+},Cr^{3+}, and Al^{3+}which are essential for applications in magnetic and electrical fields[1].Nowadays the advanced electromagnetic materials having wide range of applications in different field such has magnetic, electrical, biological and ceramics[2].In recent years soft magnetic materials have been synthesised in different methods and also used in high permittivity and permeability functions of materials due to low eddy current loss and high AC conductivity the nano chromite materials have been used in multi-functional materials[3]. Among the earlier reported materials, the spinal nano chromates posses' wide range of performances in different field. Based on their magnetic parameters such as saturation magnetization, remanence magnetization and dielectric parameters like low dielectric loss and high AC conductivity the chromates are synthesised in different methods especially[4–6]. Various methods were used synthesised the nano spinal chromates such as hydro thermal method,coprecipitation method,citrate-gel auto combustion method micro annulation method,solid state method etc[4,7–11]. Among these sol-gel auto combustion method has more advantage that is low-cost, green method which produced homogeneous crystalline powder.
Presently we discussed about the synthesis of Ce doped Mg nano chromites and their structural properties and dielectric studies.

Experimental methods
Synthesis

The citrate gel auto combustion method was used to synthesize the nano crystalline Ce-doped Mg nano chromites with the formula $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50,and 1.0. This method is considered one of the green ways because it requires less experimental equipment and is inexpensive. Nitrates of magnesium, cerium, chromiumand citric acid individually weighed and dissolved in double-distilled water in stoichiometric ratios. These solutions were mixed together to form a uniform mixture, and then NH_3 was gradually added to the mixture to bring the pH level to 7. The resulting solution mixture is put on a hot plate with a magnetic stirrer and heated to 80°C.When the temperature is raised by 150^OC and the entire volume of the solution is lowered to up to 1/4 of the initial volume, the solution transforms into a viscous gel. The resulting gel self-combusted as a result, producing burnt ash (chromite) that was brown in colour. In an air-muffled furnace, the produced powder was calcined at 500^Oc for four hours[12]. The remaining powder was ground for an hour in an agate mortar and

pestle. Various techniques can also be used to characterise the powder. Step by step of synthesis procedure briefly shown in **Fig 1.**

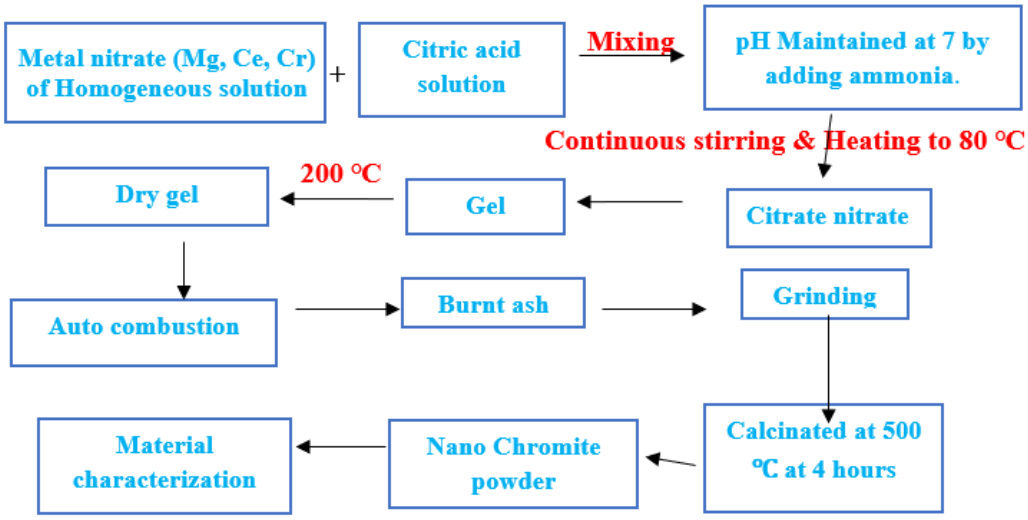


Fig 1. Flow chart for synthesis $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

XRD

Synthesised sample Phase and crystalline nature conformed by x-ray diffraction analysis. **Fig 2** illustrates the XRD pattern of the prepared$MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0. of the spinal nano chromates. Synthesised samples contain single Phase cubic spinal structure, without any other impurity peaks. In XRD pattern one broad and high intensity peak appeared between 34^O to 36^O which indicates the FD_3M space group[13]. structural parameters like average crystalline size, lattice parameter, volume of unit cell, x– ray density.

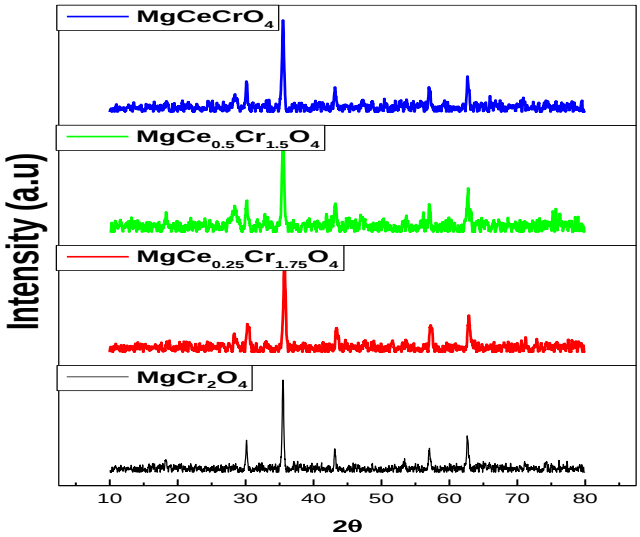


Fig 2. XRD pattern of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

Average crystalline size of the prepared samples were calculated by following Debye- Scherrer formula[14].

$$Average\ crystalline\ size\ (l) = \frac{0.94\lambda}{\beta COS\theta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1).$$

Where λ = Wave length

β = Full width half maxima

Θ = Braggs angle

Fig 3. Indicates the variation of crystalline size and lattice parameter of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0. Average crystalline size of the sample found to be 21.86 to 29.55 nm. The crystalline size of the

samples decreases with increasing dopant concentration. Lowest crystalline size found to be 21.86 for $MgCe_{0.25}Cr_{1.75}O_4$. The lattice parameter of the samples were calculated by given equation.

$$Lattice\ parameter\ a = d\sqrt{h^2+k^2+l^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

Where h, k, l are miller indices.

Lattice parameter variation varied from 7.81 to 7.87 A^O. Variation of lattice parameter indicates the obeys the Vegards law.

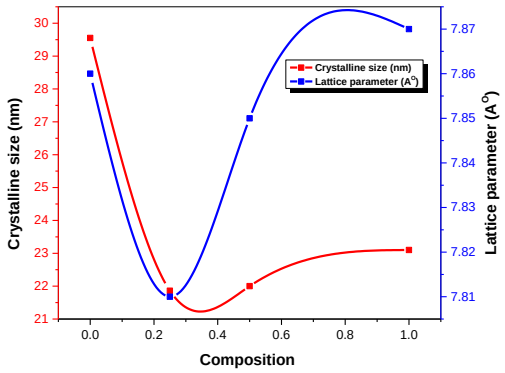


Fig 3. Variation of crystalline size and lattice parameter of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

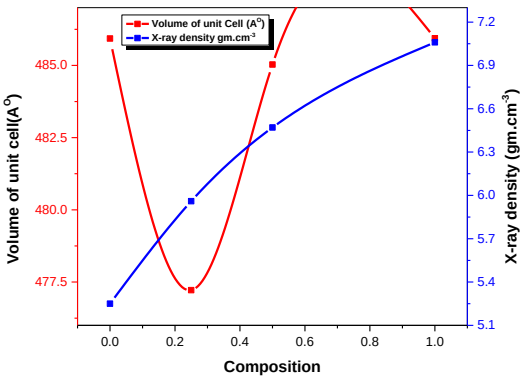


Fig 4. Variation of volume of unit cell and x-ray density of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

The lattice parameter of the sample depends on ionic size of the metal (M) cations.The prepared sample volume of unit cell (v) calculated by given formula

$$Volume\ of\ unit\ cell\ V = a^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

Volume of unit cell found to be between 477.22 to 485.94 A^O volume of unit cell increases with increasing the dopant concentration. X-ray density of the prepared samples observed by following equation.**Fig 4.** illustrates variation of volume of unit cell and x-ray density of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

$$x - ray\ density\ d_x = \frac{ZM}{Na^3} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

Where Z= No. of molecules per unit cell. For the samples it is 8

M= Molecular weight of samples.

a= Lattice parameter

X ray density was increased with increasing the dopant concentration, highest x-ray density found to be7.06 for $MgCeCrO_4$. X-ray density depends on method of synthesis, sinteringtemperature, sintering time, molecule wight of the sample and nature of metals.

Table 1: Crystalline size, lattice parameter, volume of the unit cell and x-ray density for various compositions of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, 0.75, and 1.0.

S.No	Composition	Crystalline Size(nm)	Lattice Constant (A°)	Volume of unit cell (A°)	X-ray Density gm/cc
1	$MgCr_2O_4$	29.55	7.86	485.93	5.25
2	$MgCe_{0.25}Cr_{1.75}O_4$	21.86	7.81	477.22	5.96
3	$MgCe_{0.50}Cr_{1.50}O_4$	22.00	7.85	485.03	6.47
4	$MgCeCrO_4$	23.10	7.87	485.94	7.06

SEM Analysis Mg-Cr nano chromites

The synthesized Mg-Ce nano chromites of surface morphology carried out by scanning electron microscope.**Fig 5** shows the SEM images of synthesized $MgCe_xCr_{2-x}O_4$ where x=0.0, 0.25, 0.50,and 1.0 nano chromites. SEM images reveals the agglomeratedwith small inhomogeneousdistribution observed in all the synthesized materials. As increasing Ce content samples surface area was increased and materials grain size was

decreased. Remarkable changes were observed with dopant content of Ce metal on Mg nanochromites. SEM images also revealed synthesized samples are in spherical shape with crystalline shape[15]. The average particle size of the samples less than 100 nm region, which is predicted by XRD. The prepared samples agglomeration due to magnetic interaction between the particles.

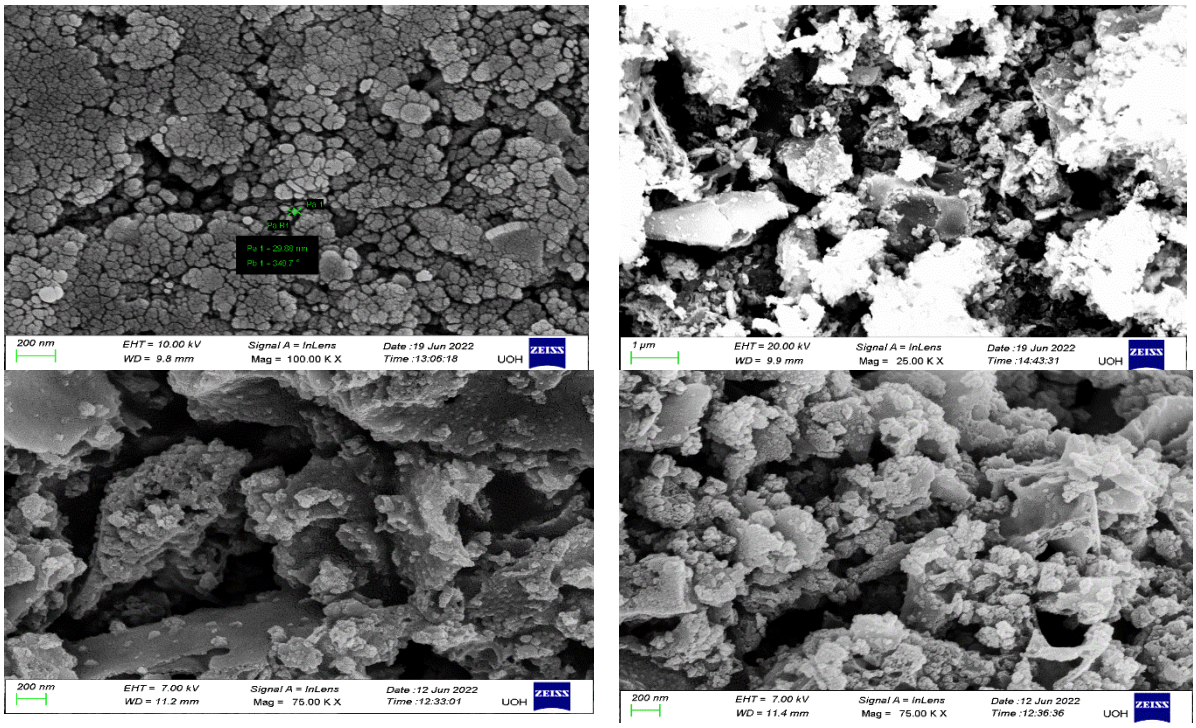
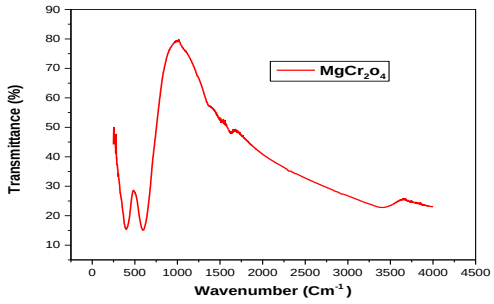
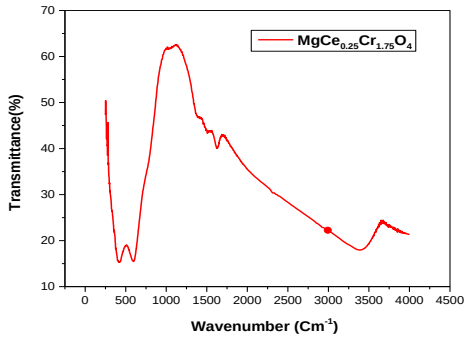


Fig 5. SEM images of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

FTIR spectrum of Mg-Cr nano chromites

Synthesized samples structural elucidation and chemical species identification confirmed by Fourier Transform infrared spectroscopy. Metal ions oscillation of the nano chromites investigated by FTIR absorption spectra. **Fig 6** illustrates the FTIR spectra of the prepared spinel chromites of $MgCe_xCr_{2-x}O_4$ where x=0.0, 0.25, 0.50,and 1.0. in FTIR spectrum two absorption peaks were appeared below 1000 cm^{-1} wavenumber region. One band appeared at 400 cm-1 attributes octahedral metal oxygen stretching frequency and another band appeared 600 cm-1 illustrates the stretching frequency of tetrahedral wides[16]. As doping Ce content FTIR band positions varied, due to may crystalline size difference of the samples. Spectral peak positions were tabulated in Table 2.





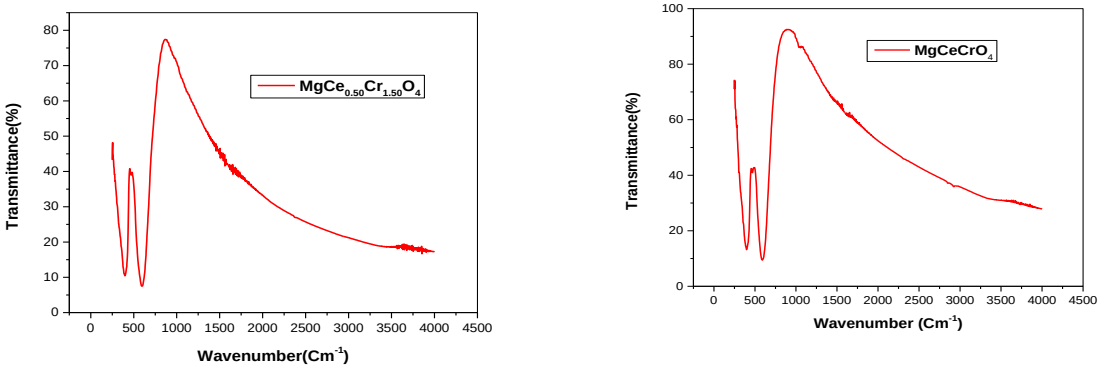


Fig 6. FTIR spectrum of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

Table 2. FTIR band positions $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

S.No	Composition	υ_1	υ_2
1	$MgCr_2O_4$	590.03	397.96
2	$MgCe_{0.25}Cr_{1.75}O_4$	596.36	418.01
3	$MgCe_{0.5}Cr_{1.5}O_4$	602.69	391.63
4	$MgCeCrO_4$	583.70	397.96

Dielectric Studies

AC Conductivity of Mg-Ce nano chromites

Fig 7 illustrates the AC conductivity variationof $MgCe_xCr_{2-x}O_4$ where x=0.0, 0.25, 0.50,and 1.0 nano chromites.AC conductivity of the prepared samples increased as increasing frequency, due to hopping of carrier increases[17]. The AC conductivity variation also explained by Koop's theory of mechanism[18]. According to this theory at low frequency region grain boundaries active, whereas at high frequencygrains are active.So, grains and grain boundaries playa key role in conduction mechanism. AC conductivity of the samples may also be influenced by small polarons in conduction mechanism. The nature of polarization in spinel chromites is related to that of hopping conduction.

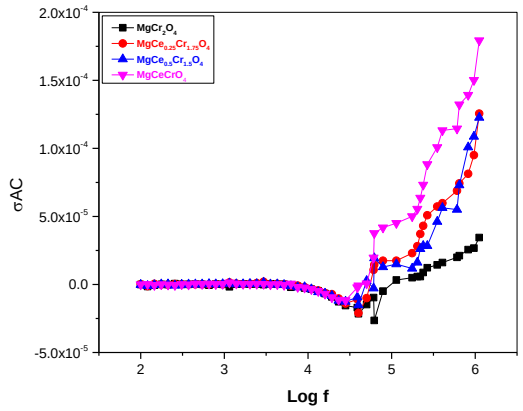


Fig 7. Sigma AC variation of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

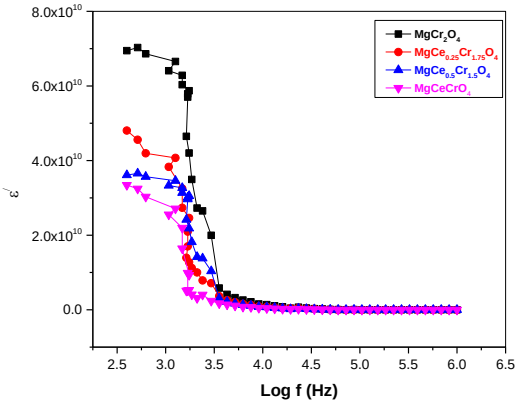


Fig 8. Variation of dielectric constant of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

Dielectric constant

Room temperature dielectric constant of the prepared $MgCe_xCr_{2-x}O_4$ where x=0.0, 0.25, 0.50, and 1.0 nano chromites shown in Fig 6. Dielectric constant of the material decreased with increasing the applied frequency. It reveals the at low frequency region dielectric constant high, whereas at increasing frequency it is slowly decreases and saturated at high frequency region. Dielectric constant variation of the samples was explained by Maxwell-Wagner theory of homogeneous structure[19].As per this theory the dielectric materials are composed by two layers, in which one layer is highly conducting layer and another layer is poor conducting medium. Highly conducting medium with grains and poor conducting medium with grain boundaries. The grain boundaries found at lower frequency region and grains found at high frequency region[20]. For the prepared nano chromites shows normal dielectric behaviour and indicates ferrimagnetic nature.

Dielectric loss

Prepared samples $MgCe_xCr_{2-x}O_4$ where x=0.0, 0.25, 0.50,and 1.0 nano chromitesroom temperature dielectric loss shown in **Fig9**. Dielectric loss of the samples decreases while increasing the frequency. Dielectric loss for the prepared samples found high at low frequency region, then slowly decreases with increasing the frequency finally it was saturated. Low dielectric loss observed for all the samples[21,22]. Dielectric loss gives the loss of energy from the field into the samples.Since domain wall motion is prevented at higher frequencies and magnetization is forced to shift rotation, the losses are shown to be minimal.

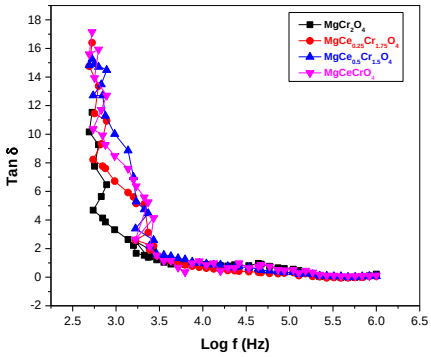


Fig 9. Variation of Tan D of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

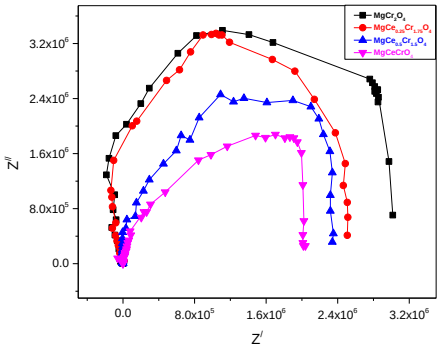


Fig 10. Impedance spectra of $MgCe_xCr_{2-x}O_4$ where x = 0.0, 0.25, 0.50, and 1.0

Impedance spectrum

At room temperature, impedance measurements were carried out in the 50 Hz to 5 MHz frequency range. Fig 8 shows the impedance spectra of the prepared samples $MgCe_xCr_{2-x}O_4$ where x=0.0, 0.25, 0.50,and 1.0 nano chromites. Impedance spectra plotted plotbetween real part of impedance and imaginary part of impedance. Semicircle behaviour observed for all the prepared samples. With increasing dopant concentration semicircle arc decreasing, which indicates the enhancing conduction nature of the samples[23]. The diameter of the semicirclesare representative of the resistance of the relaxation effects involved.The semicircle displays the conducting behaviour of thematerial.

II. Conclusions

- From citrate gel auto combustion method$MgCe_xCr_{2-x}O_4$ where x=0.0, 0.25, 0.50, and 1.0 nano chromites.
- Synthesized samples phase and crystalline size confirmed by XRD
- Lattice parameter varied from 7.14 to 8.15 A^O.
- Surface morphology of the samples revealed by SEM
- Two FTIR bands presence, indicates tetrahedral and octahedral site
- AC conductivity increases with increasing the applied frequency.

Acknowledgement

The authors are very much thankful to Head, Department of chemistry, O.U. Hyderabad for provided necessary facilities to carry out the research work.

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