Synthesis, characterization of Cr-Gd nanocomposites doped with yttrium possessing dielectric properties

Dr. Vinayak Adimule1*, Dr. Debdas Bhowmik2, Miss. Anusha Suryavanshi3

1*Department of Chemistry, Jain College of Engineering and Technology, Sainagar, Unkal, Hubli-580031, Karnataka, India
2High Energy Materials Research Laboratory, Defence Research and Development Organization, Ministry of Defence, Government of India, Sutarwadi, Pune-411021
3Department of Electronics and Communication, Jain College of Engineering and Technology, Sainagar, Unkal, Hubli-580031, Karnataka, India

Abstract.: We report here, a set of perovskite oxide nanomaterials that has been prepared through co precipitation methods. Synthesis of nanocomposite material, chromium-gadolinium doped with various concentrations of yttrium was investigated for their dielectric properties. Nanocompositional hybrid materials were prepared by co precipitation method with composition of Cr0.3 Gd0.3 (Y2O3) x moles. In the present study yttrium is doped with x = 0.1-0.5 moles, the gelated precipitate of hybrid nanomaterials were calcinated at different temperatures and characterized by XRD, FT-IR, UV-Vis, SEM spectroscopic techniques. The doped Y2O3 to chromium and gadolinium multi component nanocomposite with different concentrations (0.1-0.5%). The dielectric constants of the pelletalized samples were examined at 300K and 320K temperature and materials showed variable dielectric polarization with respect to temperature and frequency. The precursor material used for the synthesis is chromium sulphate and gadolinium carbonate which are reduced in presence of triethanol amine (TEA). The aqueous mixture of greenish brown precipitate was filtered, washed with ethanol-water mixture (1:9 volume %) to remove any impurities present with the precipitate, dried at 50-100°C, heat treated at 650-750 °C and obtained pure nanocomposite. Findings: Spectroscopic studies showed that Y2O3 grain size was 12-60 nm in diameter and it’s over layer is 85% optically transparent. XRD pattern demonstrated the formation of hexagonal yttrium and dopant addition moderately affect the crystal structure. Higher dielectric constants were obtained with larger grain size of the nanocomposites.
1. Introduction
A series of pervoskite nanocomposites \([1-3]\) of chromium-gadolinium has been prepared by co-precipitation methods by using triethanol amine as surfactant \([3-5]\). Chromium sulphate is used as precursor and by using sodium hydroxide as gelation agent during the co precipitation high basicity is maintained \([5-7]\). The obtained greenish brown precipitate of chromium and gadolinium powder was calcinated at elevated temperature and doped with further various concentrations of yttrium and studied with their dielectric properties. However literature reports \([7-9]\) showed that Cr-Gd nanocomposites possess nonlinear electrical and electronic properties \([9-11]\). It is envisaged that by doping appropriate amount of yttrium to the Cr-Gd nanocomposite would enhance their dielectric \([11-15]\) properties with respect to the undoped nanocomposites. It is also envisaged that the doped nanocomposites resistivity proportionately increases with respect to polarizibility \([16-17]\) at elevated temperature.

2. Materials and Methods
All the chemical and solvents are purchased from SD-Fine and Spectrochem Ltd, and used without purification, all the synthesized Nanocomposites were characterized by UV-Vis, XRD in PPSIR Bangalore, SEM Images has been recorded in IISc, Bangalore, Karnataka, India

3. Experimental
3.1 Characterization
SEM images were obtained and the experiment was performed using electron field emission in a field microscope at 50 Kilo Volt. The obtained linear peaks were identified by cubic crystalline phase of the image. The perovskite nanocomposites were characterized by using a TGA. The peak determination were achieved using 15 mg of the sample which was initially heated at 850°C, the heating rate was maintained at 10°C/min under standard temperature. The hybrid nanocomposites whose initial conductivity was calculated using probe technique assays. The probes of 10 mm in diameter of 0.3 mm wide. The probes were prepared by compressing the hybrid nano composites at room temperature. A standard electrode cell is used in order to investigate the electro chemical reactions the platinum foil consists of cross sectional are of 0.75cm² and silver and silver chloride used as a secondary reference electrode. The electrolyte used is a 0.1M sulphuric acid. The SEM analysis using scan rate of 50mili volt against Ag/AgCl reference electrode. The reading electrode was a made from graphite or carbon which consists of 5 mg of the coated nanocomposite. Magnetic experimental determination was done at room temperature using a standard magnetometer with maximum applied field \(H_{\text{max}} = 30\text{Kilo electron volt}\). 

3.2 Morphology
The SEM (Scanning electron microscopic) images of the pure hybrid nanocomposites were obtained and consists of nano sized semi-spherical structures the different grain sized nanocomposites. Figure 2 shows that were observed as the grey line consists of the yttrium doped nanocomposite having 20nm nanoparticles. In the SEM image grain interaction between doped and undoped materials were observed. The interaction between different polymeric grain planes were explained in terms of the continuous surface activity of the different surfactants. The surfactants get adsorbed to the hybrid composites, which develops the crystalline inter phase of the hybrid nano material which intern reduces reaggumentation of the composite matrix. Figure 3 shows magnetic interaction of the hybrid nano composites of yttrium particles. Average particle size was 17.7 nm. Considering the standard deviation the 68% of the hybrid nanoparticles are close to the surface and the particle size was 22.5 nm.
3.3 Synthesis

3.3.1 Synthesis of Chromium-Gadolinium Nanocomposites
Chromium sulphate (0.3 moles) and Gadolinium carbonate (0.3 moles) is added with TEA (triethanol amine) in presence urea acetate (2 moles), ammonium chloride (2-3 times) and refluxed for 3h in an acid mixture of Conc. HNO$_3$ and HCl. The reduced chromium was precipitated by adding NaOH solution drop wise after the formation of gelation in 36h the entire mass was concentrated and dried, calcinated at 650$^\circ$C and obtained Cr-Gd nanocomposite.

3.3.2 Purification and Isolation of Cr-Gd Nanocomposites
The obtained chromium nanocomposite was taken in a 25 ml round bottom flask added with 10% ethanol water mixture and warmed in a water bath and filtered, the filtered solid was further given with THF or 1, 4-dioxan solvent washed and calcinated at 600$^\circ$C to get the pure chromium-gadolinium nanocomposite.

3.3.3 Doping of Yttrium to the Chromium-Gadolinium Nanocomposites
In a flask A Y$_2$O$_3$ powder was added with concentrated HCl in presence of urea and TEA and refluxed for 3h. The reaction mixture was cooled and added with ammonium hydroxide and the precipitate was dried, the yttrium was doped with 1-5 % to the mixture of Cr-Gd dissolved in TEA and processed to obtain the desired doped nanocomposites (S1 to S5).

Table 1. Dielectric constant parameters of the Cr-Gd Nanocomposites with dopant yttrium

| Sample       | W g(1*10$^4$ radius/s) (PF) | Cgb  | Temperature | R gb (K ohm) | µ (10$^{-6}$) *g(*10$^6$) |
|--------------|-------------------------------|------|-------------|--------------|--------------------------|
| S1           | 1.23                          | 0.09 | 300K        | 1232.00      | 0.09                     |
| S2           | 2.34                          | 2.45 | 300K        | 985.00       | 1.87                     |
| S3           | 3.45                          | 4.56 | 300K        | 640.00       | 2.67                     |
| S4           | 0.97                          | 0.08 | 300K        | 76.00        | 0.87                     |
| S5           | 2.45                          | 2.10 | 300K        | 198.00       | 5.67                     |
| Undoped Cr-Gd| 1.22                          | 8.87 | 300K        | 789.00       | 0.98                     |

Table 2. Dielectric constant parameters of the Cr-Gd Nanocomposites with dopant yttrium

| Sample       | W g(1*10$^4$ radius/s) (PF) | Cgb  | Temperature | R gb (K ohm) | µ (10$^{-6}$) *g(*10$^6$) |
|--------------|-------------------------------|------|-------------|--------------|--------------------------|
| S1           | 2.23                          | 2.10 | 320K        | 1232.00      | 1.09                     |
| S2           | 3.34                          | 1.45 | 320K        | 985.00       | 3.87                     |
| S3           | 0.45                          | 2.96 | 320K        | 640.00       | 0.67                     |
| S4           | 2.70                          | 1.88 | 320K        | 76.00        | 3.87                     |
| S5           | 3.45                          | 2.33 | 320K        | 198.00       | 5.07                     |
| Undoped Cr-Gd| 2.30                          | 6.87 | 320K        | 789.00       | 0.09                     |
Figure 1. Scanning electron microscope image of chromium-gadolinium oxide 2 % doped with yttrium nanocomposite. The particle size distribution in the 2 % doped yttrium nanocomposite is almost 70-80 nm in the SEM image. ; Figure 2: second picture. Scanning electron microscope image of chromium-Gadolinium oxide 3 % doped with yttrium nanocomposite. In the 3 % doped nanocomposite shows particle distribution is uniform and in the range of 40-60 nm and the nanocomposite of this category exhibits wide range of electrical and electronic properties. ; Figure 3: third picture. Scanning electron microscope image of chromium-Gadolinium oxide 5 % doped with yttrium nanocomposite. In the 5 % doped nanocomposite shows particle distribution is uniform and in the range of 80-100 nm and the nanocomposite of this category exhibits nonlinear optical and electrical properties. Figure 4: Forth picture. Depicts the fine grain size of the nanocomposites

4. Dielectric Properties

The electrical conductivity of the different grain sized particles were examined and found to be much (µ) higher than that of nanoparticles present in grain boundaries. For S1 to S5 the numerical values of µg at room temperature was found to be 2.09 multiples of 10⁶ Ω/cm. Which is about 20 times higher than µgb (0.09*10⁻⁶ Ω/cm). The dielectric constants µg & µgb were found to increase with increase in temperature. The dielectric properties of the hybrid nanomaterials were examined in the frequency range from 10⁻¹ to 10⁶ Hz at 300 and 320K temperature. The each sample having the error in the measurements is maintained within 3%. Impedance Spectroscopy (IS) is used to determine the total current gain of the hybrid nanomaterials and also employed to calculate the total electric behaviour of the hybrid nanomaterials. Impedence spectra and the correlation diagrams were directly related to the grain boundary structure of the nanoparticles and can affect the total conductivity of the doped nanomaterials. The grain of the nanocomposite contribution to the complex impedance was higher than that of the grain boundary. In this research dielectric conductivity was described at two different temperatures.

Figure 5: Variation of conductivity of the hybrid nanocomposite material of Cr-Gd doped with Yttrium with respect to temperature.
5. Electrical Properties

The Electrical conductivity of the yttrium doped and chromium and gadolinium undoped hybrid nanocomposites were found to be 6.67 and 0.08 multiples of \(10^{-8}\) respectively. The literature reports the common behavior of the reduction of electrical conductivity at elevated magnetite content of the hybrid nanocomposite. This behavior has been related to the charge transport mechanism. Figure 4 shows the grain size of the doped hybrid nanocomposite was 15 nm. As expected, magnetite loadings of the different ratio of the composite showed no electrochemical response. Furthermore, the total current gain was maximum for the yttrium doped with 0.4% to the undoped Cr-Gd nanocomposite.

![Figure 6: XRD summery picture of the Cr-Gd nanocomposites doped with yttrium in various concentrations](image)

6. Results and Discussion

In this research work we have synthesized chromium-gadolinium nanocomposites doped with different concentrations of yttrium and studied for their diversified dielectric properties. The hybrid nanocomposites were synthesized by co precipitation methods by using suitable surfactant, isolated, purified and obtained the SEM images of doped assembly of Cr-Gd nanocomposites. Further the composites are characterized by XRD and it shows peak purity of (112) in case of yttrium doped with 0.5%. FRET absorption studies also carried out for the doped nanocomposite VR characteristic studies shows non linear relationship with observed resistance across voltage ration. In the present investigation, observed with variable conductivity as compared with the impedance or resistivity of the different hybrid nanocomposites that were examined at two different temperatures. Impedance of the hybrid nanocomposite mixture was found to be higher than the particles in the grain boundary which is having smaller fraction of the 20 nm nanoparticles present in its volume. The presence of grain boundary nanoparticles are very important in detemining the electrical and electronic properties of the materials. The complex impedance of the yttrium doped with Cr-Gd nanomaterials may be co related to the partial or completely resisting the passage of the charge carriers in it’s over relay. The blockage of the charge carrier is due to the presence of the defects in the nanomaterials solid structure in the matrix of the nanocomposite. Impendence spectra containing the grain boundary of the doped structure as well as undoped structure ids directly correlated to the overall charge carriers present in the hybrid nanocompositional matrix.

Conflicts of Interest

All the authors and Coauthors hereby declare that they do not have any conflicts of interest in any part of the published manuscript.
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