# ELECTROCHEMICAL PROPERTIES OF COBALT DOPED GdAlO3

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## ABSTRACT

Nanocrystalline $GdAlO_3$: $Co^{2+}$ is synthesized by combustion process. The XRD study shows that the nano powder is single phase with orthorhombic structure and belongs to the space group Pnma. The DRS spectrum analysis reveals that the material is a wide band gap material with band gap of about 4.4 to 4.9 eV. The electrochemical properties of the $GdAlO_3$: $Co^{2+}$ was measured using cyclic voltammetry (CV) The CV studies clearly indicate that $Co^{2+}$ dopant was successful doping material due to increasing the reversibility by reducing the $E_O$-$E_R$ value of the electrode reaction.

*Keywords*— Combustion method; DRS; cyclic voltammetry; electrochemical impedance spectroscopy

## I. INTRODUCTION

Presently energy is a fundamental worldwide issue for the human society, what we needed energy is provided by the fossil fuels, But it is not renewable and it emits pollutants while burning which degrade the environment and greenhouse gases, which lead to a global warming problem [1-2]. Such frameworks require the advantages of compactness and energy effectiveness while being environmental friendly [3]. The technology and systems of an external thermal interface or that of an external electrical interface embrace by Energy conversion and storage systems [4]. Based on amount of energy and power available for the load they are categorised into groups which includes batteries, fuel cells, capacitors and supercapacitors [5-6].

Nanotechnology is a growing area of research, primarily due to its numerous applications in engineering/science. Therefore, the synthesis of new nanomaterials and improving its properties are of current research interest to many researchers. It has been found that the physical properties of individual nanoparticles can be very different from those of their bulk counterparts [7]. Rare earth compounds have been extensively used in high performance luminescent devices, magnets, catalysts, and other functional materials because of their electronic, optical and chemical characteristics resulting from the 4f shell of their ions [8-10]. These properties depend strongly on the material composition and structure, which are sensitive to the bonding states of rare earth ions.

Compounds having perovskite-type structure as denoted by ABO3 have drawn scientific interest for many decades due to wide range of applications, such as magnetic, optical, ceramics, and catalysis [11]. In this paper the synthesis of nano GdAlO3:CO²⁺ perovskite by the modified combustion method is studied. Its structural characterization, optical properties and cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are also studied.

## II. EXPERIMENTAL

### A. Preparation of sample

GdAlO3:CO²⁺ (1,3&9 mol %) synthesised using the solution combustion method by using stoichiometric quantities of gadolinium nitrate [Gd (NO₃)3], aluminium nitrate (Al (NO3)2, cobalt nitrate CO (NO₃)2, laboratory prepared Oxalyl dihydrazide (ODH:C₆H₆N₄O₂) fuel were dissolved in doubled distilled water. A homogeneous solution obtained after stirring 15min. The resultant solution was placed in a furnace pre heated at400ºC for, until surplus free water evaporated and natural ignition occurred ensuing in a fine powder product obtained after grinding. Finally, the as prepared powders were calcined at 1000ºC for 3 h. The resulting GdAlO₃:CO²⁺powder were cooled down to room temperature and mixed well by using a pestle and mortar [12].

### B. Preparation of the modified electrode

The sample, graphite powder and silicone oil ratio was 15:70:15 % by weight and were mixed in an agate mortar for about 40 min. the carbon paste was packed in to the of the Homemade carbon paste electrode and then smoothened on a tissue paper till the surface become uniform.

## III. RESULTS AND DISCUSSION

### A. PXRD Analysis

The XRD pattern of 1000 ºC calcinated combustion product indicate that fully crystallized single phase GdAlO3:CO²⁺ were obtained as shown in the Fig 1. All the peaks in the XRD pattern are in good agreement with JCPDS File No. 46-0395 [13], demonstrating the formation of GdAlO3 phase with orthorhombic perovskite structure indicates that all the dopants(CO2+) have successfully been incorporated into the host matrix(GdAlO3). The effect of crystallinity on the crystallite size of the samples crystallite size (D) was estimated from the line broadening in X-ray powder using Scherrer's formula [14].

$$D = K\lambda\beta\cos\theta$$

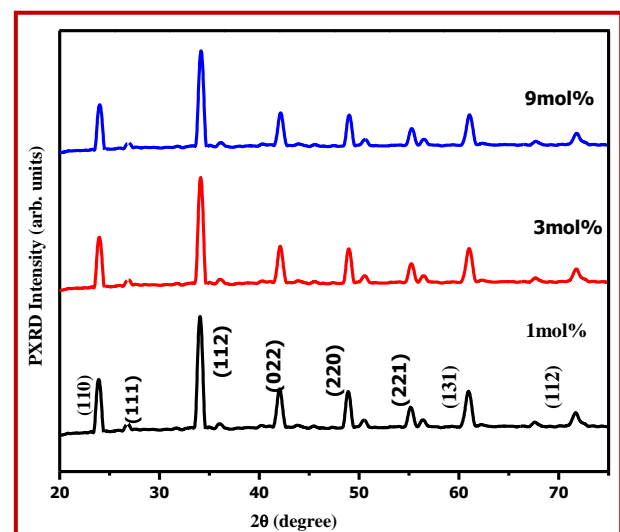Where, 'K'; constant,$\lambda$wavelength of X-rays, and $\theta$; FWHM was found to be in the range 15-25 nm

Fig 1. PXRD patterns of GdAlO3:CO$^{2+}$

## B. Optical studies

In the optical studies, diffuse reflectance spectra were measured and band gap calculated from diffuse reflectance spectra. A sharp band at 280 nm and week absorption band at 215 nm was observed for the samples as shown in Fig. 2. The maximum absorption arises due to transition between valence band to conduction band. The weak absorption in the UV–visible region is expected to arise from transitions involving extrinsic states such as surface traps or defect states or impurities [15]

Band gap is calculated for the GdAlO3:Co$^{2+}$ sample based on Kubelka Munk theory [15-18]. The plot of $(F(R)h\nu)^2$ versus $h\nu$, the value of $E_g$ was obtained by extrapolating the linear fitted regions to $(F(R\infty)h\nu)^2=0$. The curve of Fig. 3 exhibits nonlinear and linear portions, which is the characteristic of direct allowed transition. The nonlinear portion corresponds to a residual absorption involving impurity states and linear portion characterizes the fundamental absorption. The band gap of different mol concentration of Co$^{2+}$doped GdAlO3 is found in the range of 4.4 to 4.9 eV.
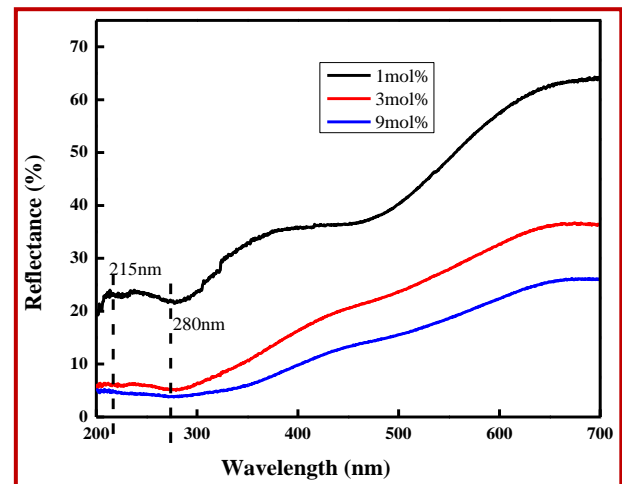


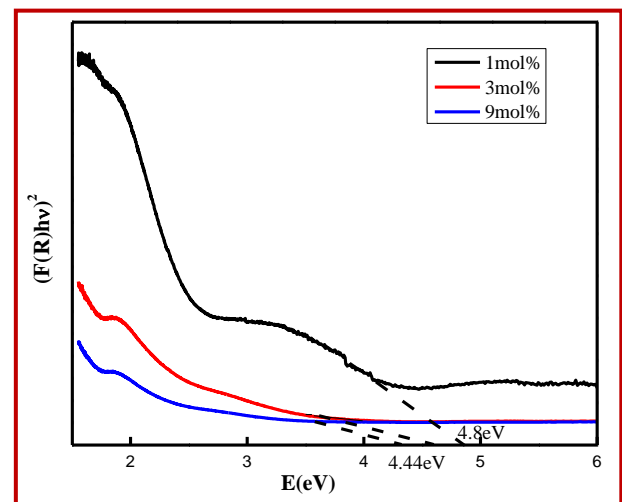Fig.2. Diffuse Reflectance Spectra of Co$^{2+}$ doped GdAlO3.



Fig.3 Band gap values of Co$^{2+}$ doped GdAlO3.

## IV. CYCLIC VOLTAMMETRY

Electrochemical tests, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed, in this study; all of the electrodes were tested in aqueous 1M KOH electrolyte using a three electrode system. Fig.4 exhibits cyclic voltammetry curves obtained at different scan rate (10, 20, 30, 40 & 50 mV s$^{-1}$) in 1M KOH electrolytes.

Cyclic voltammograms (CVs) analysis used for understand the electrochemical performance of Co$^{2+}$

doped GdAlO₃ electrode for super capacitor during charging and discharging processes. In order to understand the effect of various mol concentrations on the electrochemical performance of GdAlO₃: Co²⁺ nanophosphors carbon paste electrodes, the CV experiments were conducted for the electrodes with different mol concentration. [19].

The quantification of charge efficiency, charge-discharge of electrodes and the reversibility of the electrode reaction were carried out using cyclic voltammetry. The reversibility of the electrode reaction was measured by taking into account the difference between the oxidation potential ($E_O$) and the reduction potential ($E_R$) [20] at 10 mV/s scan rate. Smaller the value of $E_O$-$E_R$, more reversible was the electrode reaction. Hence, with the addition of Co²⁺, a phenomenal increase in the reversibility of the electrode reaction was noted at 3 mol % of Co²⁺ and there is no drastic change of reversibility of electrode material due to doping of Eu³⁺, the $E_O$-$E_R$ values of Co²⁺ doped GdAlO₃ are given in the Table 1
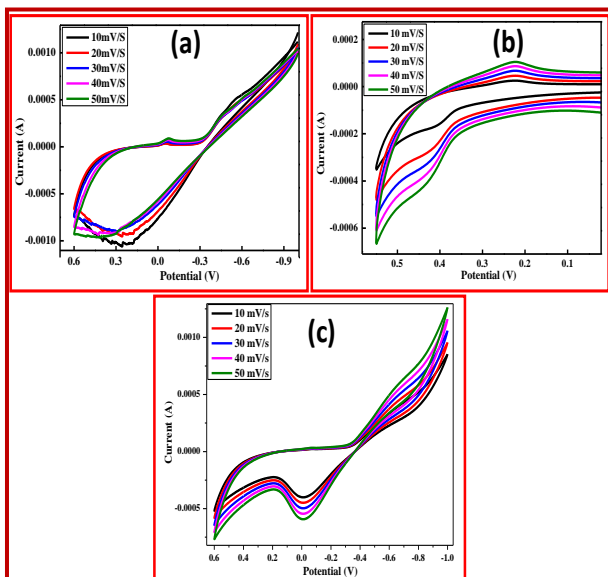
Fig.4 Cyclic voltammogram of Cobalt doped GlAlO₃ in 1M KOH electrolyte. (a) GdAlO₃:Co²⁺ (1 mol %) (b) GdAlO₃:Co²⁺ (3 mol %) (c) GdAlO₃:Co²⁺ (9 mol %).

Table 1 Oxidation potential ($E_O$), reduction potential ($E_R$), the difference between $E_O$ and $E_R$ and diffusion co-efficient of GdAlO₃:Co²⁺ electrodes

| Co²⁺ Concentration mol% | $E_O$(V) | $E_R$(V) | $E_O$-$E_R$(V) | Proton diffusion coefficient (D), cm²S⁻¹ |
|---|---|---|---|---|
| 1 | 0.2332 | -0.0779 | 0.3244 | $1.369 \times 10^{-5}$ |
| 3 | 0.4129 | 0.2237 | 0.1892 | $2.0356 \times 10^{-4}$ |
| 9 | -0.1185 | -0.3739 | 0.2553 | $1.4807 \times 10^{-5}$ |

Further, the peak currents of GdAlO₃:Co²⁺ show that oxidation increase with the increase of scan rates and the peak potentials almost have no change. The anodic peak currents are linearly proportional to the square root of scan rates as observed in Fig. 5 which suggests that the electro catalytic oxidation of GdAlO₃:Co²⁺ on platinum electrode is a diffusion-controlled process. The hydrogen diffusion co-efficient of the samples are shown in Table 6.2 which is calculated using slope of the fitted line. The hydrogen diffusion co-efficient value is high as compared with previous report by E. Shangguan et al. ($6.81 \times 10^{-10}$ cm² s⁻¹), B. Shruthi et al. ($1.44 \times 10^{-12}$ cm² s⁻¹) [21-24].
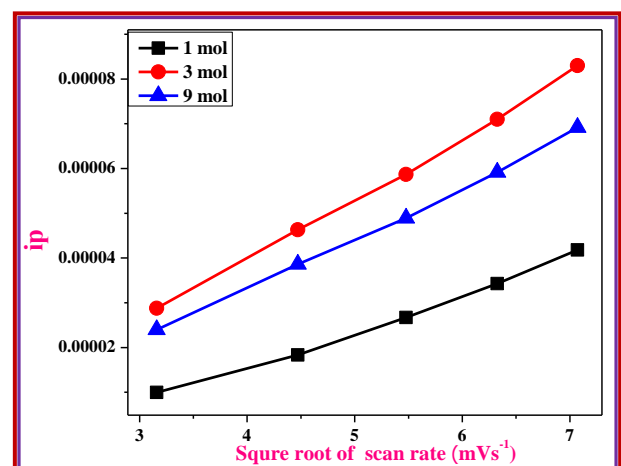
Fig. 5 Relationship between the cathodic peak current (Ip) and the square root of the scan rate for Cobalt doped GlAlO$_3$.

(a) GdAlO$_3$:Co$^{2+}$ (1 mol %) (b) GdAlO$_3$:Co$^{2+}$ (3 mol %) (c) GdAlO$_3$:Co$^{2+}$ (9 mol %).

## V. CONCLUSION

The structure were analyzed by PXRD CV studies clearly indicate that Co$^{2+}$ dopant was successful doping material increasing the reversibility by reducing the E$_O$-E$_R$ value of the electrode reaction. . The hydrogen diffusion co-efficient value is high as compared with previous report. The electrode reaction has a larger exchange current density and thus during charge discharge process the active material of electrode reaction will be fully used and exhibit higher utilization of active material and larger discharge capacity.

## VI. REFERENCE

[1] J. B. Goodenough,Y. Kim, Chem.Mater. 22 (2010) 587.

[2] H. Li, Z. Wang, L. Chen, X. Huang, Adv. Mater. 21 (2009) 4593.

[3] L. Dong, R. R. S. Gari, Z. Li, M. M. Craig, S. Hou, Carbon 48 (2010) 781.

[4] J. Baker, Energy Policy. 36 (2008) 4368.

[5] T. Christen, M. W. Carlen, J. Power Sources. 91 (2000) 210.

[6] G. Wang, L. Zhang, J. Zhang, Chem. Soc. Rev. 41 (2012) 797.

[7] L.V. Interrante, M.J. Hampden-Smith, Chemistry of Advanced Materials: An

[8] Overview, Wiley VCH, New York, 1998.

[9] X. Qu, J. Dai, J. Tian, X. Huang, Z. Liu, Z. Shen, P. Wang, J. Alloys Compd. 469 (2009) 332–335.

[10] L. Qian, Y. Gui, S. Guo, Q. Gong, X. Qian, J. Phys. Chem. Solids 70 (2009) 688–693.

[11] R. Bazzi, M.A. Flores-Gonzalez, C. Louis, K. Lebbou, C. Dujardin, A. Brenier, W.

[12] Zhang, O. Tillement, E. Bernstein, J. Lumin. 445 (2003) 102–103

[13] X. Duan, M. Pan, F. Yu, D. Yuan, J. Alloys Compd. 509 (2011) 1079.

[14] S.C. Prashantha, B.N. Lakshminarasappa, Fouran Singh. Curr. Appl. Phys. 11 (2011) 1273–1277.

[15] P. Wang , Shanghai inst. of Ceramics, Chinese Academy of science, Shanghai, china, ICCD grant-in-Aid. (1994).

[16] P. Klug, L. E., Wiley, New York. 1954

[17] H. Q. Cao, X. Q. Qiu, B. Luo, Y. Liang, Y. H. Zhang, R. Q. Tan, M. J. Zhao, Q. M. Zhu, Adv. Funct. Mater. 14 (2004) 243.

[18] J. H. Ryu, B. G. Choi, J. W. Yoon, K. B. Shim, K. Machi, K. Hamada, J. Lumin. 124 (2007) 67.

[19] A. E. Morales, E. S. Mora, U. Pal, Rev. Mex. Fis. S53 (2007) 18.

[20] P. Baraldi, G. Davolio, Mater. Chem. Phys. 21 (1989) 143

[21] X. Cao, J. Wei, Y. Luo, Z. Zhou, Y. Zhang, Int. J. Hydrogen Energy. 25 (2000) 643.

[22] I. Krejci, P. Vanysek, J. Power Sources. 47 (1994) 79.

[23] E. Shangguan, Z. Chang, H. Tang, X. Z. Yuan, H. Wang, Int. J. Hydrogen Energy. 35 (2010) 9716.

[24] B. Shruthi, V. Bheema Raju, B. J. Madhu, Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. 135 (2015) 683.

[25] K. Watanabe, M. Koseki, N. Kumagai, J. Power Sources. 58 (1996) 23.

[26] M. G. Ortiz, E. B. Castro, S. G. Y. Real, Int. J. Hydrogen Energy. 37 (2012) 10365.