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ENHANCEMENT OF CONDUCTIVITY OF HYDROTHERMALLY SYNTHESIZED DOPED CERIA FOR FUEL CELL APPLICATIONS

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Abstract
In this work, Rare Earth oxides with ceria are developed as electrolytes for solid oxide fuel cells. This appears to be one of the attractive and efficient renewable energy resources. The main focus of this research work is to enhance the ionic conductivity of ceria based oxides due to decrease in grain size trivalent doping. Recently, these materials have shown great interest due to high potential for power and energy generation in stationary, portable and transport applications.

In the present work, compositions $Ce_{0.75}Gd_{0.25-x}Nd_xO_{2-\delta}$ (x=0.0, 0.17, 0.25) are under consideration for synthesis and characterization. One of wet chemical methods namely composite mediated hydrothermal method (CMHM) is used for its synthesis. Further for nanocrytaline samples, different conditions of CMHM were optimized after synthesis. Different characterization techniques are applied on the samples to have the information of their structural and electrical properties. Microstructural and physical properties of samples were characterized with X-ray diffraction (XRD). For conduction mechanisms, dc and ac conductivities were measured as a function of temperature and frequency. In this work, dielectric constant, dielectric loss tangent, ac conductivity, of the samples are determined as function of frequency (200Hz-1MHz) at different temperatures. The range of temperature is 100˚C to 500˚C. Both ac and dc conductivities increased with the concentration of Nd in the samples.

Keywords: Fuel cell; Electrolyte; conductivity; electrical properties.

1. INTRODUCTION

Basic purpose of this work is the enhancement of ionic conductivity of electrolyte for intermediate temperature solid oxide fuel cells. Determination approach for electrolyte material is very necessary. Materials that show higher ionic conduction, thermal stability and nontoxicity is more facilitating for electrolyte materials [1]. Current study is about Cerium Oxide, Gadolinium Oxide, and Neodymium Oxide. These oxides have been studied broadly in the past few decades for energy utilization and applications specifically as fuel cell material and many researchers have reported Gadolinium doped ceria (GDC) [2 3] and

Neodymium doped ceria (NDC) i.e. their composites and compounds have been reported as electrolyte materials separately but in this work they are used as co-dopant using composition i.e. $Ce_{0.75}Gd_{0.25-x}Nd_xO_{2-\delta}$ x=0.0, 0.17, 0.25 which is synthesized through CMHM Reduction behavior is observed in Ceria i.e. Ce^{+4} to Ce^{+3} because of this reduction phenomenon it exhibits electronic and ionic conductivity both under certain conditions, At intermediate temperature rare earth materials which are ceria based show ionic conduction and behave as electrolyte for SOFCs solid oxide fuel cells [4] and suitable replacement of yttrium-stabilized zirconia. Favorable materials for SOFC are mostly Cerium-oxide and doped-cerium-oxide nanoparticles. It is our requirement to improve the conductivity of these materials to use them as electrolyte so that efficiency of fuel cell increases.

2 EXPERIMENTAL

The materials were synthesized following the protocol as shown in the flow diagram

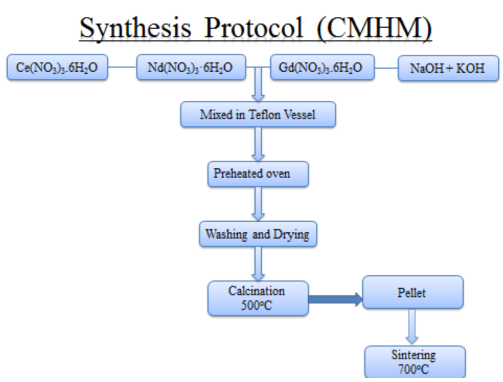

Fig. 1. Schematic diagram of CMHM

The possible chemical reaction is:
$Ce(NO_3)_3.6H_2O + Gd(NO_3)_3.6H_2O$ + $Nd(NO_3)_3.6H_2O$ + NaOH+ KOH → $CeO_2 + Gd_2O_3 + Nd_2O_3 + H_2O$

2. SAMPLE CHARACTERIZATION AND THEIR RESULTS

3.1 X-ray diffraction

To examined structural behavior only one sample is presented here because of limited space. X-ray diffraction of calcined and sintered sample was done. Fig. 2 shows the indexed XRD pattern for x=0.0. Observed structure is cubic fluorite with the lattice constant of 5.4Å [5] calculated by the usual formula given below

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \dots \quad (1)$$

Crystallite sizes were determined using Scherrer Formula as

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \dots\dots \quad (2)$$

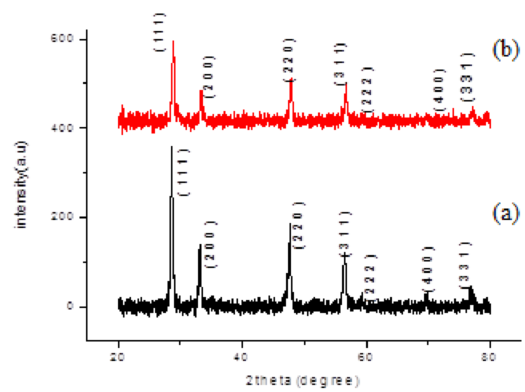

Fig. 2. X-Ray Diffraction pattern (a) calcined and (b) sintered

Sample	Crystallite size	a (Å)	Volume	porosity
Sintered x=0.0	57nm	5.402 Å	157.639	66%

3.2 Electrical characterization

Ac and Dc measurements were done using **Wayne** Kerr LCR meter 6440B, dielectric constant (Ɛ`), loss factor (tanδ) and ac conductivity (σ_{ac}) relations are shown in eq(3) (4).The dc conductivity (σ_{dc}) was measured as function of temperature and composition according to eq(5)

$$\varepsilon' = \frac{cd}{A\varepsilon_o} \dots \quad (3)$$

$$\sigma_{ac} = \omega_o\, \varepsilon'\, \varepsilon_o \tan\delta \; (Scm^{-1}) \dots \quad (4)$$

and

$$\sigma_{dc} = \frac{L}{RA}\,(Scm^{-1}) \dots \quad (5)$$

Where c is the capacitance, d is the thickness and A is the cross-sectional area of the pellet and ε_o is the permittivity of the free space ($8.85 \times 10^{-12}\ F/m$) and R is the resistance obtained from LCR meter at fixed frequency of 1kHz.

In Fig. 3 the σ_{dc} as a function of temperature ranging from 100˚C to 500 ˚C is given. With increase in temperature and dopant concentration conductivity also increased due to the presence of oxygen ions

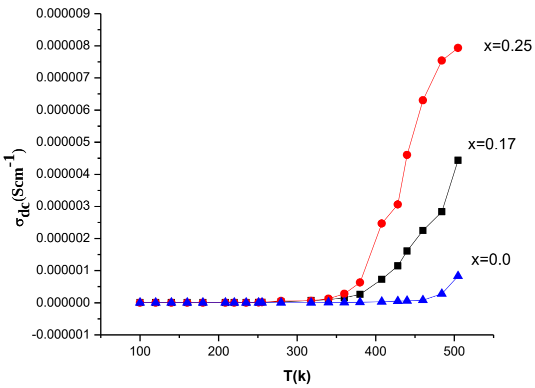

Fig.3. The σ_{dc} as a function of temperature and compositions

In Fig. 4 the σ_{ac} as a function of frequency at 300˚C is shown, it is evident that σ_{ac} increases with the increase in frequency. This phenomenon is explained by jump relaxation model [6].

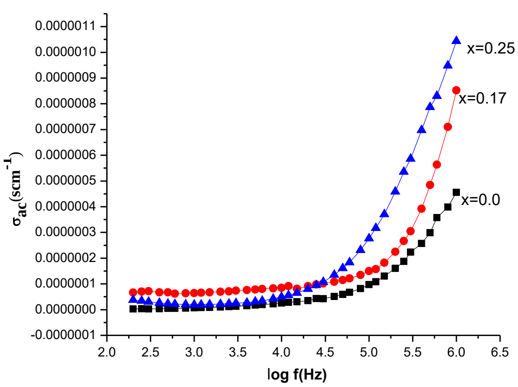

Fig. 4. The σ_{ac} as a function of frequency and composition.

3. CONCLUSIONS

Compositions $Ce_{0.75}Gd_{0.25-x}Nd_xO_{2-\delta}$ (x=0.0, 0.17, 0.25) were synthesized by CMHM. X-ray diffraction confirmed the phase and structure of the given samples. Conductivities of the samples increased with the increase in dopant concentration [7] and temperature. So it is confirmed that these materials can be employed as electrolyte for fuel cell applications.

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