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Conductivity dependence on synthesis parameters in hydrothermally synthesized ceria nanoparticles

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ABSTRACT

Nanoparticles of cerium oxide were synthesized by Composite Mediated Hydrothermal Approach (CMHA). The synthesis conditions were optimized to enhance the conduction properties and for narrow range of nanocrystallites. The synthesis parameters like hydrothermal treatment temperature (at 180 °C and 220 °C) and time (for 45 min, 70 min and 90 min) were optimized. The structural properties of the prepared ceria were examined by X-ray diffraction (XRD) data. Scherrer's formula was used to calculate the crystallite sizes of average and most intense peak. Temperature dependent dc conductivity was measured in temperature range 200–700 °C and found to be increasing with the increase in measuring temperature and controlling the other synthesis conditions. The frequency dependent ac conductivity and dielectric properties were measured in frequency range 20 Hz–3 MHz at different temperatures. The ac conductivity increased (from 0.00091 to 2.661 S cm^{-1}) with the increase in temperature (from 200 to 700 °C). Raman spectrum was observed for the different bands of cerium oxide and oxygen vacancies at 514 nm excitation laser line.

1. Introduction

The nanocrystalline rare earth ceria based materials are very good ionic conductors at intermediate temperatures, and these materials are to be found the alternate of the yttria-stabilized zirconia as the electrolyte materials in solid oxide fuel cells (SOFC). The reduction of Ce^{4+} to Ce^{3+} under certain reducing conditions at higher temperatures is the major problem now days, which contributes to the high electronic conductivity [1–4]. However, for the lower temperatures below 700 °C this reduction can be neglected. So it is very much need to increase the ionic conductivity of these materials below 700 °C to increase the efficiency and to decrease the working temperature [5,6].

Cerium oxide (CeO_2) is one of the most significant rare-earth oxides. Potential applications of nanocrystalline ceria, such as UV absorbents and filters, electronic ceramic, ultra-precise polishing, gas sensor, catalysts and electrolyte in the fuel cell technology (SOFC) [4], catalytic wet oxidation, engine exhaust catalysts and photocatalytic oxidation of water. However, the material performances in practical uses are strongly influenced by the properties of constituent CeO_2 particles. Doped-cerium oxide nanoparticles are promising electrolyte materials for SOFC [3,7]. The capacity of the modern automotive exhaust treatment catalysts containing CeO_2 is much more effective than that of the predecessors due to its high "oxygen storage capacity". Therefore, the extensive synthesis of CeO_2 becomes an urgent task for further research and applications [8,9].

Various solid state and wet-chemical synthesis techniques have been proposed to synthesize nanoceria particles, such as hydrothermal method, co-precipitation and sol–gel method. Among these methods, due to various advantageous like economical, environment friendly and phase purity hydrothermal method is regarded as effective technique [10,11]. Grain size-dependent electrical conductivity was also observed in electrical application. The effect of temperature on electrical conductivity was also observed in this work and Raman spectrum was studied for 514 nm excitation laser line [12].

2. Experimental procedure

2.1. Preparation and materials

Cerium nitrate hydrated ($Ce(NO_3)_3.6H_2O$) was used as precursor for the synthesis of ceria nanoparticles. The Potassium Hydroxide (KOH) and Sodium Hydroxide (NaOH) were used as composite hydroxides/reactants as well as precipitating agents. The corresponding nomenclature for samples was H14, H17, H19, H24, H27 and H29 as given in Table 1.

The CMH approach was preferred due to the simplicity of procedure, easy to control the synthesis conditions, fewer impurities (practically zero) and environmental friendly. The NaOH and KOH have melting temperatures 323 °C and 406 °C respectively but the NaOH–KOH system at the weight percent ratio 51.5% and 48.5% have eutectic point at 170 °C [13,14]. No water is required for this technique.

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Table 1
The nomenclature designed for the samples at different optimized parameters.

Sample name	H14	H17	H19	H24	H27	H29
Temperature (°C)	180	180	180	220	220	220
Time (min)	45	70	90	45	70	90

All chemicals in powder form were mixed in autoclave, sealed and were shifted into the pre-heated oven at 180 °C and 220 °C for 45 min, 70 min and 90 min. At this temperature, the autoclave achieves a certain pressure which causes the reaction to occur for nucleation of ceria nanoparticles. Then the autoclave is allowed to cool at room temperature. The final product was washed with de-ionized water several times to remove the by-products and then dried in oven at 105 °C for overnight. The calcination of the prepared powder was done at 500 °C for 2 h. Then pellets of 13 mm diameter were made at a pressure of 6 MPa with the help of hydraulic press and were then sintered at 750 °C for 5 h.

X-ray diffraction (XRD) analysis was done to study the phase purity, crystallite size and lattice constants of the samples. Temperature dependent dc conductivity (from 200 to 700 °C) and frequency dependent ac conductivity was done by using LCR meter in frequency range from 20 Hz to 3 MHz at 200 °C, 300 °C, 400 °C, 500 °C, 600 °C and 700 °C.

3. Results and discussion

3.1. Structural properties

The indexed XRD patterns of the prepared cerium oxide samples are shown in Fig. 1, which indicate that the samples were of single phase. The crystal structure was found to be cubic with lattice constants varying between 5.40 Å and 5.43 Å. The crystallite sizes of as prepared and annealed samples were calculated by using Scherrer formula [15].

$$D = \frac{0.9\lambda}{\beta \cos\theta_B} \quad (1)$$

where D is the crystallite size, λ is the wave length of the incident X-rays, β is the full width at half maximum (FWHM) and θ_B is the diffraction angle and having values in radians. The crystallite sizes

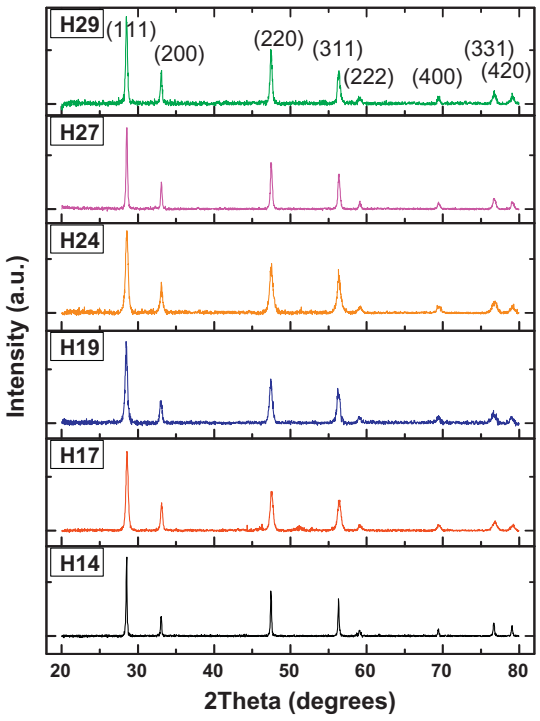

Fig. 1. X-ray diffraction patterns of CeO_2 samples prepared at different optimized parameters.

Table 2
The crystallite size corresponding to the most intense peaks ($D_{(111)}$), average crystallite size, lattice constants (a) of the prepared samples.

Samples	Crystallite size $D_{(111)}$ (nm)	Crystallite size average (nm)	Lattice constants (a) (Å)
H14	67	60	5.41
H17	37	31	5.41
H19	41	39	5.40
H24	48	64	5.40
H27	27	44	5.42
H29	37	38	5.43

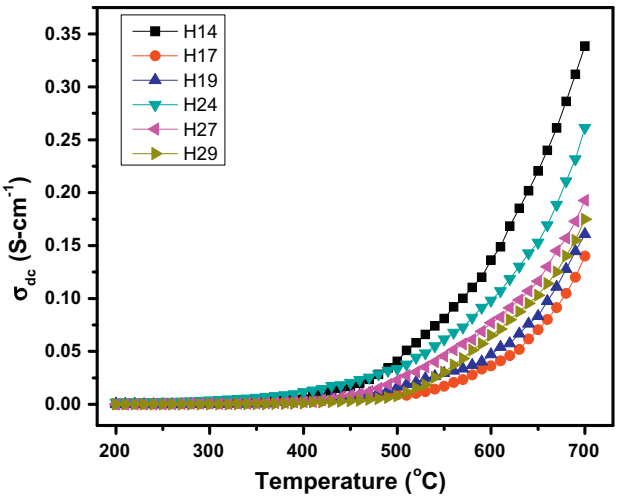

Fig. 2. DC conductivity plots of the prepared samples as a function of temperature.

Table 3
DC conductivity (σ_{dc}) (at 300 °C, 500 °C, 600 °C and 700 °C) of the prepared samples.

Sample	Density (g/cm^3)	DC conductivity σ_{dc} (S cm^{-1}) at			
		300 (°C)	500 (°C)	600 (°C)	700 (°C)
H14	3.721	0.0013	0.0406	0.1364	0.3386
H17	3.296	0.0034	0.0089	0.0364	0.1402
H19	3.457	0.00015	0.0167	0.0471	0.1609
H24	3.656	0.0039	0.0334	0.0982	0.2613
H27	3.387	0.00094	0.0228	0.0771	0.1927
H29	3.252	0.00057	0.0078	0.0651	0.1752

corresponding to the most intense peak, average crystallite size obtained from all peaks and lattice constants of the samples are given in Table 2. The lattice constants are calculated by the formula given,

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

where 'a' is the lattice constant and 'd' is the d-spacing. The indexed XRD pattern is shown in Fig. 1 for all the samples.

Narrow range of crystallite size of ceria was obtained due to optimization of synthesis conditions and annealing temperature.

3.2. Electrical properties

3.2.1. DC electrical properties

In dc electrical properties, the resistance of the samples was measured as a function of temperature. The resistance in the temperature range 200–700 °C was measured by using the Wayne-Kerr LCR meter 6440B at 1 V applied voltage. The resistivity was measured by using the formula,