International Journal of Advanced Chemistry Research
www.chemistryjournals.net
Online ISSN: 2664-679X; Print ISSN: 2664-6781; Impact Factor: RJIF 5.22
Received: 27-06-2020; Accepted: 13-07-2020; Published: 23-07-2020
Volume 2; Issue 2; 2020; Page No. 21-31

Synthesis of doped nano-composite ceramic oxide materials their applications

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DOI: https://doi.org/10.33545/26646781.2020.v2.i2a.24

Abstract
Doped ceria nanocomposite ceramic oxide materials have been successfully developed using economically cheap method, i.e., chemical precipitation method. TGA patterns obtained on the precursor samples revealed the formation of product and the removal of molecules. The conductivity data obtained on all the samples revealed optimum conductivity and the samples proposed in this research work may be suitable for electrolyte application in SOFC systems. Among the six types studied, the sample $Ce_{0.8}Gd_{0.2}O_{2-\delta}$-$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ has shown improved oxide ion conductivity at 600 °C when compared with other samples.

Keywords: nanocomposite, sofc, ceramic oxide, tga, electrolyte

Introduction
Nanocrystalline materials are interesting from the point of view of fundamental research for studying interface characteristics. Nanocrystalline materials are expected to play an important role in developing new materials exhibiting unusual properties [1].

Ceria doped materials as electrolytes
The ceria-based electrolytes for SOFCs have exhibited good performance improvements that have demonstrated a breakthrough in SOFC research. New research activities on the ceria-based materials have shown super ionic and dual or hybrid H^+/O^{2-} conduction with conductivity of 0.1 Scm^{-1} below 600 °C [2]. The ionic conductivity of doped ceria is nearly an order of magnitude greater than that of stabilized zirconia for similar doping conditions.

2 Experimental Method
2.1 Sample preparation
Initially, the precipitating solution (magnesium hydroxide) was mixed with 2 ml of 10% CTAB (as surfactant material). In order to avoid agglomeration this surfactant added to solution. To this mixture, $Ce(NO_3)_3$, $Gd(NO_3)_3$ and $Y(NO_3)_3/Sm(NO_3)_3$ solutions were subsequently added one by one drop wise. They were mixed thoroughly by a magnetic stirring apparatus (1,000 rpm) at room temperature for 2-3 hours. The pH was maintained at greater than 9 during the experiment by the addition of alkali [3, 4]. The resultant yellow-orange colored precipitate (($Ce(OH)_4$ + $Gd(OH)_3$+ $Y(OH)_3$) or ($Ce(OH)_4$ + $Gd(OH)_3$+ $Sm(OH)_3$) with CTAB was filtered and then washed with deionized water and ethanol in the ratio of 9:1 (v/v) five to ten times. The product was dried at 50 °C to 100 °C for 24 h. The resultant material was calcined at 300 °C, 450 °C, 600 °C and 800 °C for 2 h each. During calcination, the surfactant was removed, and phase-pure, yellow-orange colored nanocrystalline material was formed.

3. Results and Discussion
3.1 Thermo Gravimetric Analysis (TGA)
The precursor samples were subjected to thermo gravimetric analysis (TGA) to study the thermal decomposition process. The dried precursor precipitate materials [($Ce(OH)_4$ + $Gd(OH)_3$ + $Y(OH)_3$, $Ce(OH)_4$ + $Gd(OH)_3$ + $Sm(OH)_3$ and $Ce(OH)_4$ + $Gd(OH)_3$) with C-TAB] with an initial mass 8-13 mg was placed in an open platinum crucible. The mass scale of the instrument was calibrated with standard reference materials based on the measurement of curie Points (Tc) of alumel alloy (Tc = 427.35 K) and nickel (Tc = 628.45 K). The TGA patterns obtained with the precursor precipitate materials [($Ce(OH)_4$ + $Gd(OH)_3$ + $Y(OH)_3$, $Ce(OH)_4$ + $Gd(OH)_3$ + $Sm(OH)_3$ and $Ce(OH)_4$ + $Gd(OH)_3$) with C-TAB] are indicated in Figure 1.

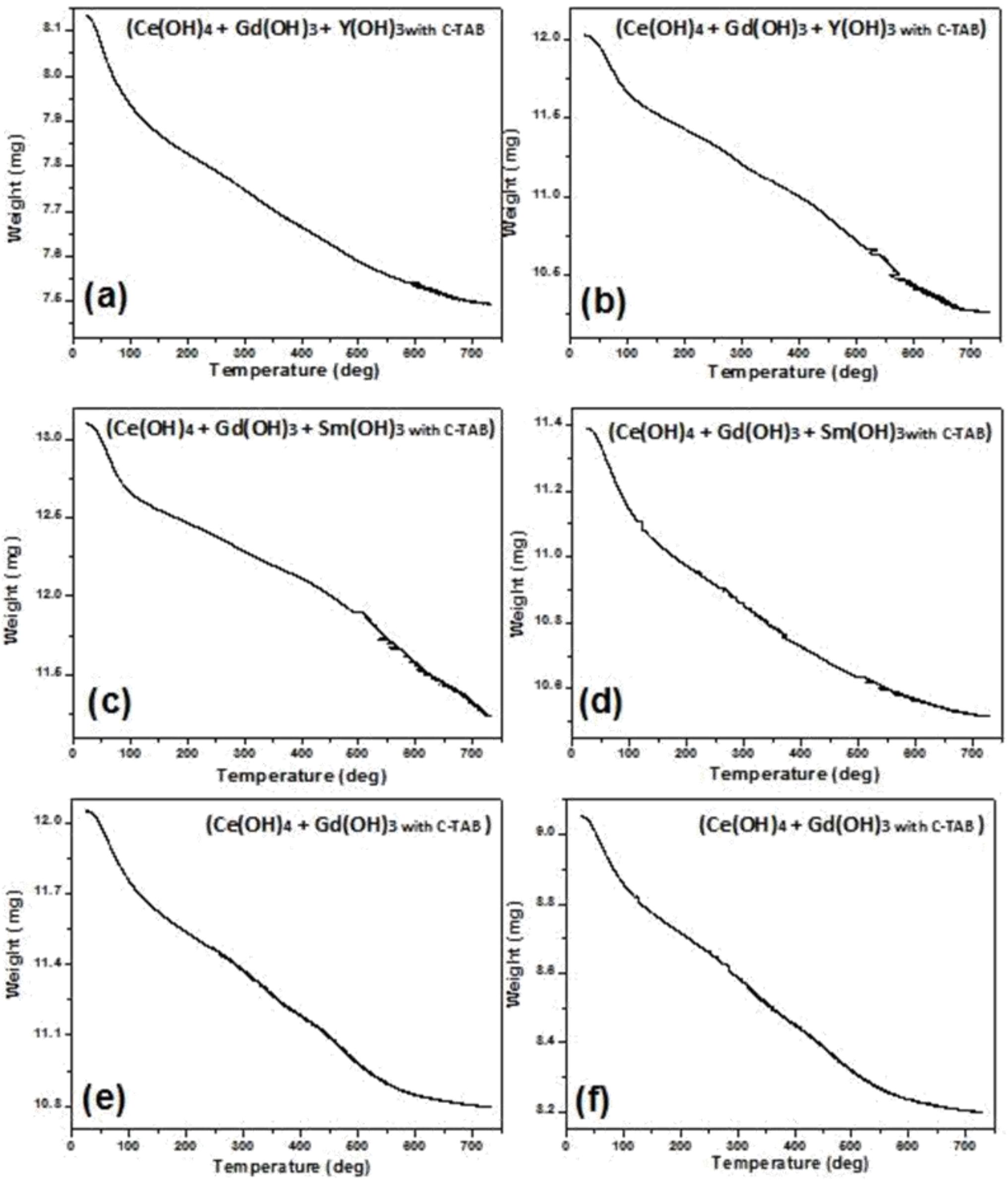

Fig 1: TGA spectra obtained with the doped ceria precursor materials (a) $^{Ce}0.9^{Gd}0.1^{O}2\text{-}\delta\text{-}^{Ce}0.9^{Y}0.1^{O}2\text{-}\delta$, (b) $^{Ce0}.8^{Gd}0.2^{O}2\text{-}\delta\text{-}^{Ce}0.8^{Y}0.2^{O}2\text{-}\delta$, (c) $^{Ce}0.9^{Gd}0.1^{O}2\text{-}\delta\text{-}^{Ce}0.9^{Sm}0.1^{O}2\text{-}\delta$, (d) $^{Ce}0.8^{Gd}0.2^{O}2\text{-}\delta\text{-}^{Ce}0.8^{Sm}0.2^{O}2\text{-}\delta$, (e) $^{Ce}0.9^{Gd}0.1^{O}2\text{-}\delta$ and (f) $^{Ce}0.8^{Gd}0.2^{O}2\text{-}\delta$

The TGA of the doped ceria precursor materials represented the curve of weight loss. From the figures, the total weight loss at the temperatures between of 25 °C to 800 °C was found to be in different percentages for different compositions. From the curves of all the samples, it was understood that the weight loss begins to appear from the initial stage i.e., from 25 °C. From curve the thermal decomposition of the molecule can be split into four separate sections [5]. The first one is related to the evaporation of the absorbed water between 50 and 100 °C, at which most of the water will be evaporated.

In the second section, the residue water will be evaporated at temperature rate.

In third section the structural water, which has band structure with metal and oxygen atoms inside the molecule, will be eliminated before 650 °C. During heat treatments, the compound may lead to form phase pure doped ceria nanocomposite materials. In the last section, the molecule will be stable and the weight of molecule is nearly constant without any change in weight loss. Thermo gravimetric analysis data obtained from the precursor materials is given in Table: 1

Table 1: Thermo gravimetric analysis data obtained from the electrolyte precursor materials

Sample	Initial weight	Final weight	Total	Total
			weight loss	weight loss
	(mg) at 25 °C	(mg) at 800 °C	(mg)	(%)
$^{Ce}0.9^{Gd}0.1^{O}2\text{-}\delta$ -	8.13	7.49	0.64	7%

$Ce_{0.9}Y_{0.1}O_{2-\delta}$				
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ - $Ce_{0.8}Y_{0.2}O_{2-\delta}$	12.02	10.26	1.76	18%
$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ - $Ce_{0.9}Sm_{0.1}O_{2-\delta}$	11.38	10.51	0.87	9%
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ - $Ce_{0.8}Sm_{0.2}O_{2-\delta}$	13.09	11.23	1.86	19%
$Ce_{0.9}Gd_{0.1}O_{2-\delta}$	12.05	10.79	1.26	13%
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	9.05	8.19	0.86	9%

From the Table: 1, it was understood that the weight loss of about 2-3% is found at around 100 °C, which may be due to the removal of water molecule from the samples. Then, the total weight loss is found to be different (1-2 %) for all samples at around 250 °C and which may be attributed to the removal of organics present in the samples.

The further weight loss observed in the sample until 700 °C may be due to the decomposition of remaining carbon/nitrogen-based compounds from the sample.

At around 700 °C, the weight loss is stable, which indicates the formation of phase-pure doped nanocompostie ceramic materials.

Conductivity studies

Doping ceria with certain rare earth oxides can remarkably reduce the enthalpy of association. These rare earth oxides are Gd_2O_3, Sm_2O_3 and Y_2O_3.

When they are properly doped, ceria can have an ionic conductivity one order of magnitude larger than YSZ. At low oxygen partial pressure, ceria exhibits mixed ionic and electronic conductivity [6].

Especially the ionic contribution is high up to a temperature of 800 °C.

That is actually the reason why ceria is considered as an interesting electrolyte material for intermediate temperature SOFCs.

The proposed ceria based nanocomposite ceramic oxide materials were subjected to ionic conductivity measurements as per the details mentioned below.

Preparation of circular compacts

The circular compacts of doped ceria nanocomposite ceramic oxide electrolyte materials (with 2 mm thickness and 10 mm diameter) were prepared using a hydraulic machine by applying a pressure of 1.2 ton.

The circular compacts were sintered at 800 °C for 3h in air before subjecting the same for conductivity studies. A sample sintered circular compact is indicated in Figure 2.

Fig 2: Sintered circular compact prepared from doped nanocomposite ceramic oxide powder

Impedance measurements

The impedance measurements have taken at different temperatures like room temperature, 300 °C, 400 °C, 500 °C and 650 °C using the sintered samples. The standard conditions followed to do the impedance measurements are: voltage-1.3 volts and the frequency range - 42 Hz to 5 KHz. The electrochemical impedance measurements were carried out for all the sintered pellets in air. The impedance curves obtained on the sintered doped ceria nanocomposite ceramic oxide pellets are shown in the Figures 2. Fitting of the measurement data was performed with the ZSimpwin software of version 3.20. The impedance data of the doped ceria nanocomposite ceramic oxide pellets is fitted with the following equivalent circuit as indicated in Figure 2. An equivalent circuit for the fitting can be written as R(C(R(CR))).

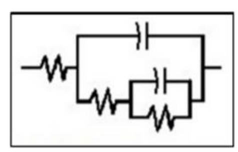

Fig 3: Equivalent circuit, used to fit measurement data obtained on doped ceria nanocomposite ceramic oxide pellets

Where, the symbol ⟶|⟵ referred as capacitor (constant phase element, CPE) and the -⁄\/- referred as resistor. The impedance curves obtained on sintered circular compacts of doped nanocomposite ceramic oxides are indicated in Figures 3. The oxide ion conductivity data calculated for doped ceria nanocomposite ceramic oxide materials is indicated in Tables.

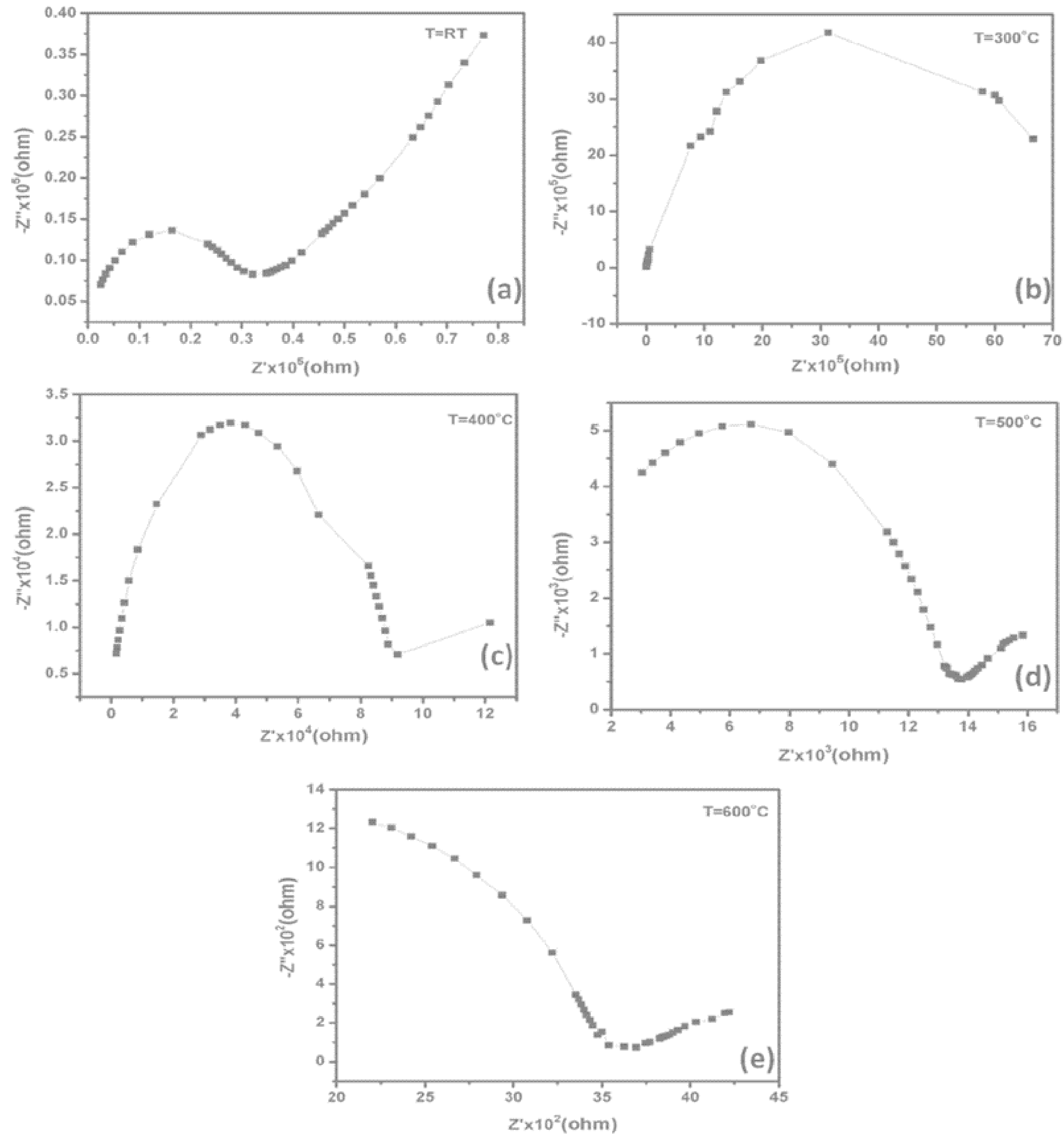

Fig 4: (a-e) Impedance curves obtained on sintered circular compacts of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ -$Ce_{0.9}Y_{0.1}O_{2-\delta}$ at different temperatures.

Table 2: Oxide ion conductivity values calculated for sintered circular compacts of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ -$Ce_{0.9}Y_{0.1}O_{2-\delta}$ at different temperatures

Temperature (°C)	Conductivity (S/cm)
Room temperature	4.3665×10^{-06}
300	1.9519×10^{-08}
400	2.0160×10^{-06}
500	1.1915×10^{-05}
600	4.5799×10^{-05}

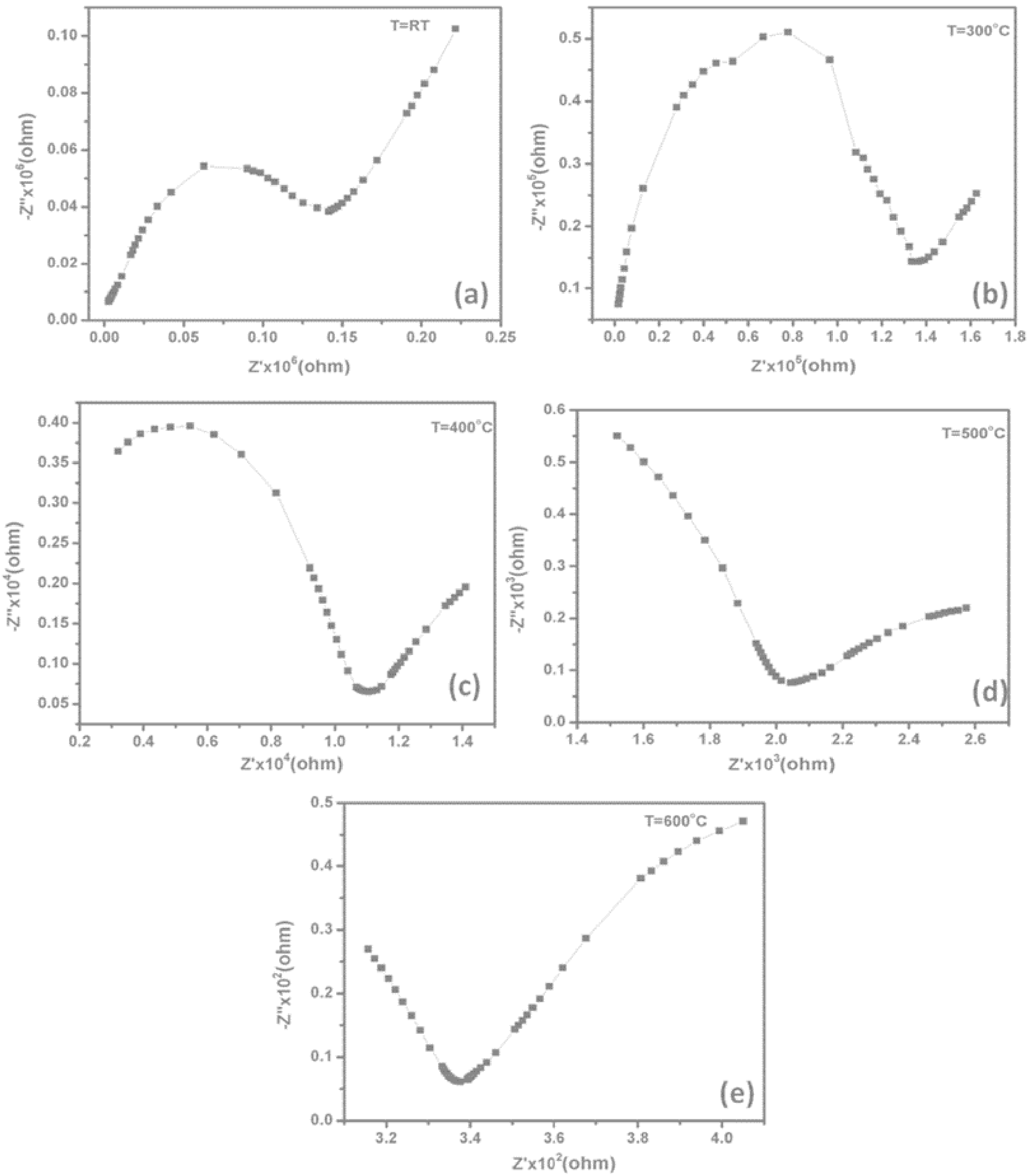

Fig 5: (a-e) Impedance curves obtained on sintered circular compacts of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ –$Ce_{0.8}Y_{0.2}O_{2-\delta}$ at different temperatures

Table 3: Oxide ion conductivity values calculated for sintered circular compacts of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ –$Ce_{0.8}Y_{0.2}O_{2-\delta}$ at different temperatures

Temperature(°C)	**Conductivity (S/cm)**
Room temperature	1.1152×10^{-06}
300	1.3098×10^{-06}
400	1.7814×10^{-05}
500	9.4639×10^{-05}
600	5.6563×10^{-04}

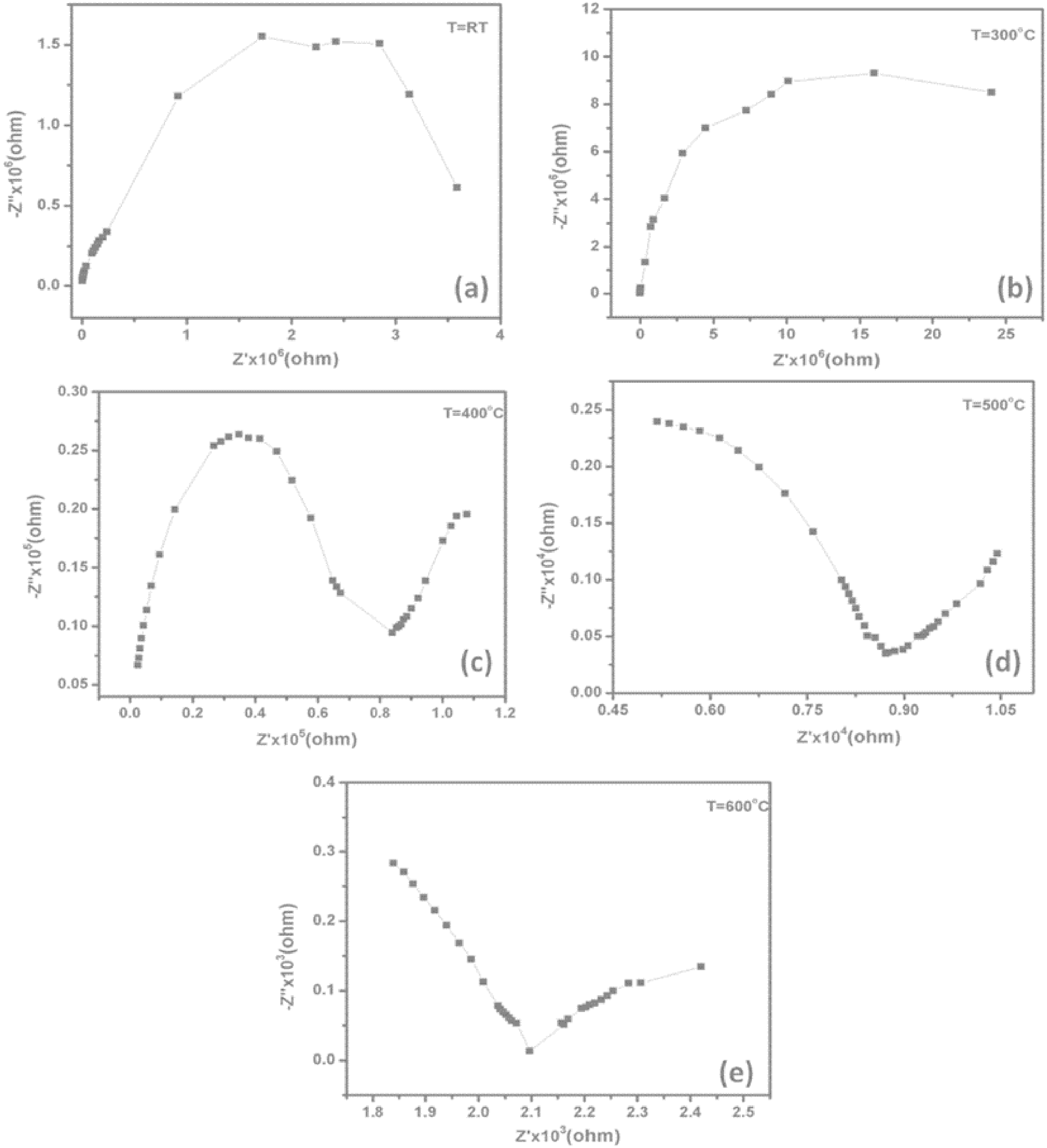

Fig 6: (a-e) Impedance curves obtained on sintered circular compacts of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ -$Ce_{0.9}Sm_{0.1}O_{2-\delta}$ at different temperatures

Table 4: Oxide ion conductivity values calculated for sintered circular compacts of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ -$Ce_{0.9}Sm_{0.1}O_{2-\delta}$ at different temperatures

Temperature (°C)	Conductivity (S/cm)
Room temperature	3.7487×10^{-08}
300	6.4253×10^{-09}
400	1.5581×10^{-06}
500	1.3405×10^{-05}
600	5.4315×10^{-05}

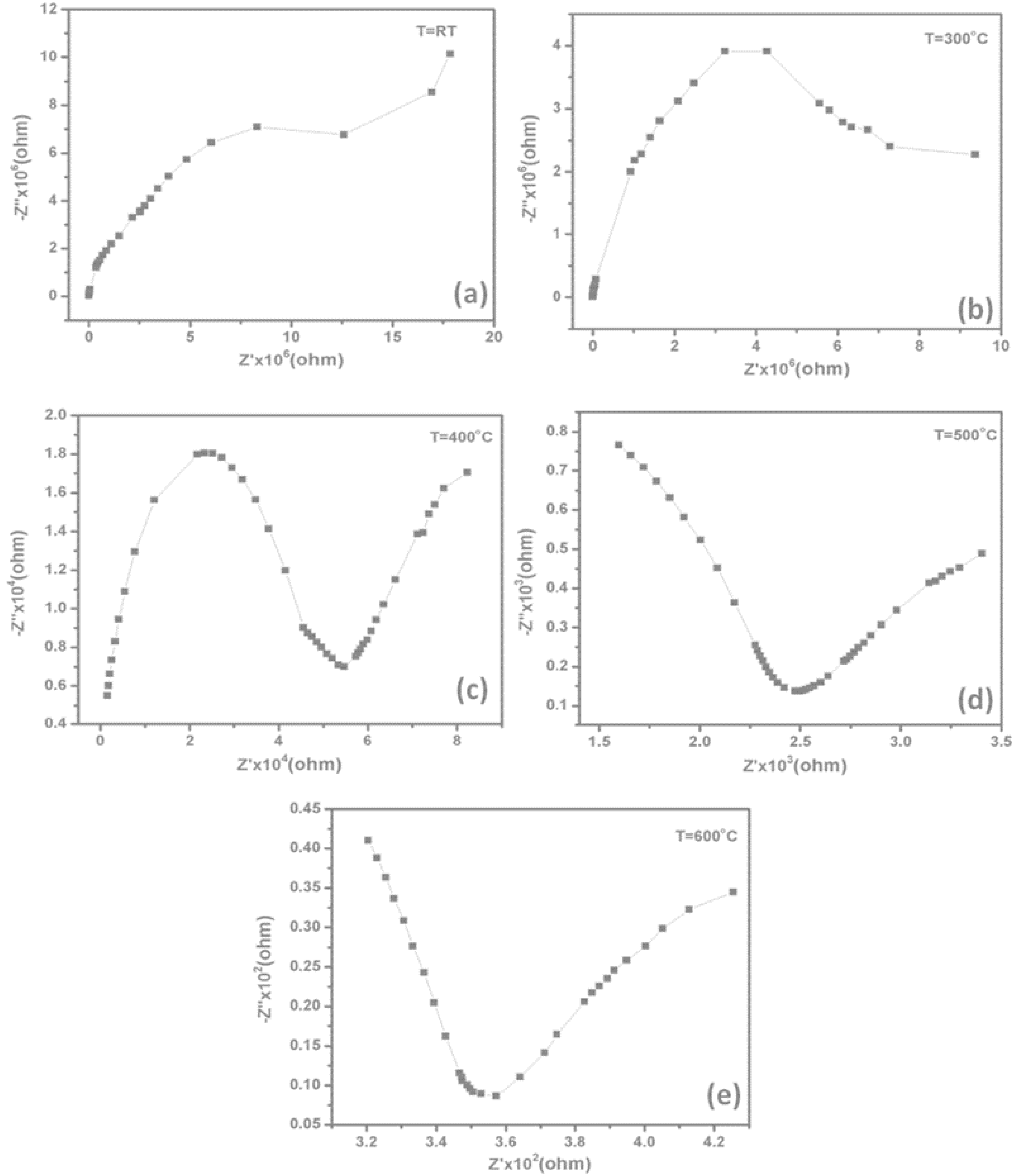

Fig 7: (a-e) Impedance curves obtained on sintered circular compacts of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ -$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ at different temperatures

Table 5: Oxide ion conductivity values calculated for sintered circular compacts of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ -$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ at different temperatures

Temperature (°C)	Conductivity (S/cm)
Room temperature	7.0156×10^{-09}
300	1.7361×10^{-08}
400	2.7550×10^{-06}
500	5.7031×10^{-05}
600	3.9771×10^{-04}

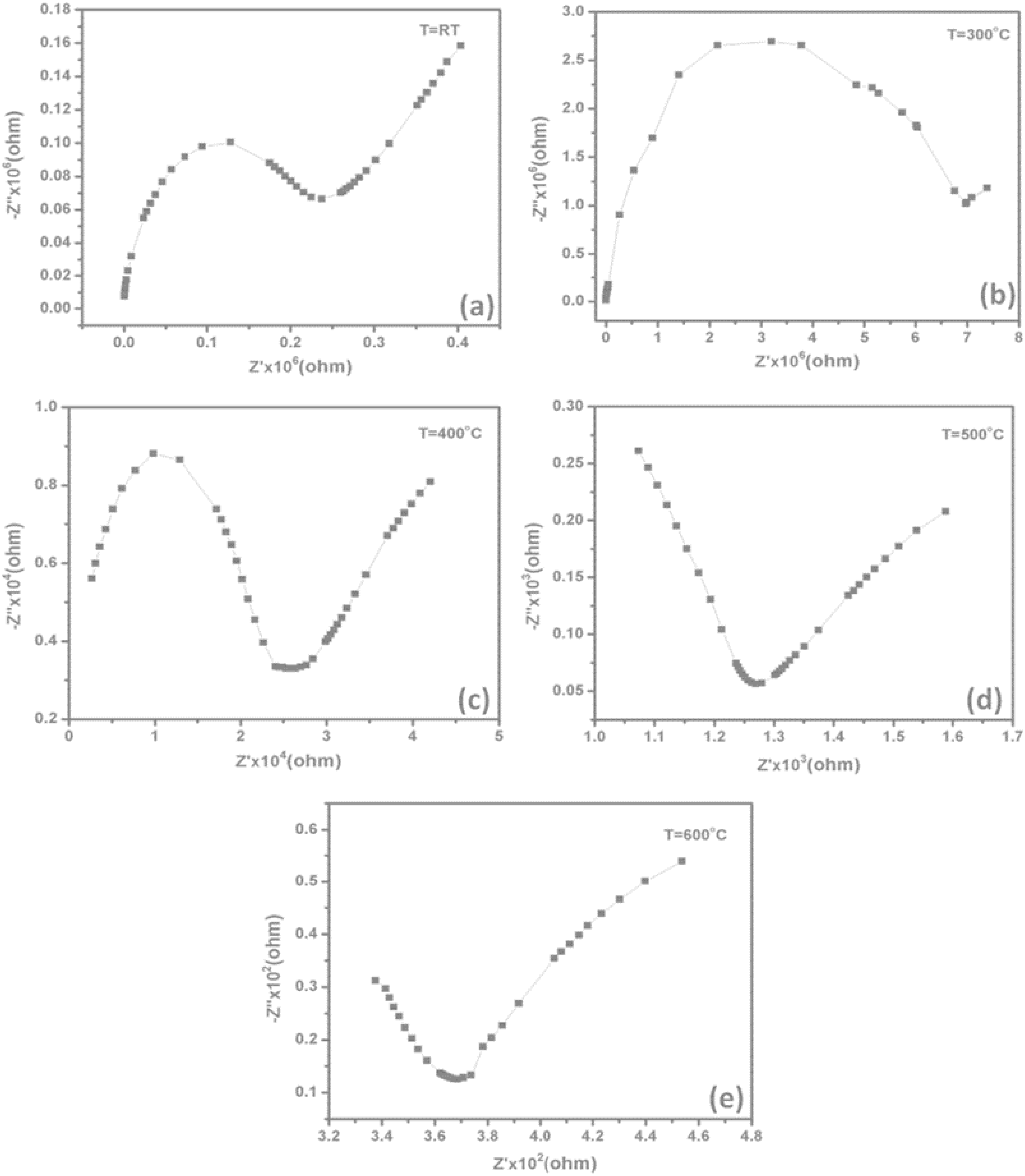

Fig 8: (a-e) Impedance curves obtained on sintered circular compacts of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ at different temperatures

Table 6: Oxide ion conductivity values calculated for sintered circular compacts of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ at different temperatures

Temperature (°C)	**Conductivity (S/cm)**
Room temperature	6.1413×10^{-07}
300	3.1579×10^{-08}
400	6.4479×10^{-06}
500	1.2797×10^{-04}
600	4.4255×10^{-04}

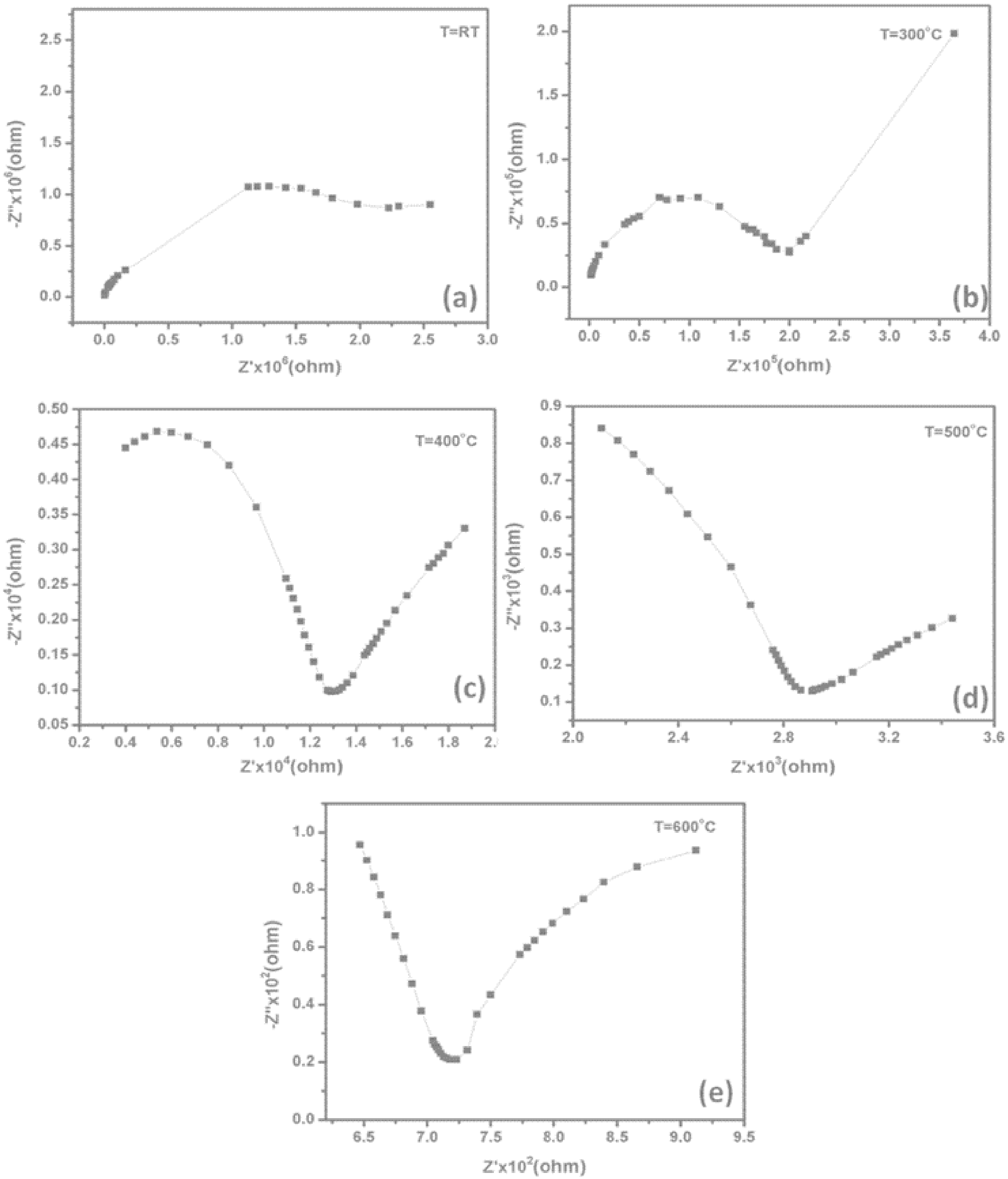

Fig 9: (a-e) Impedance curves obtained on sintered circular compacts of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ at different temperatures

Table 7: Oxide ion conductivity values calculated for sintered circular compacts of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ nanocrystalline powder at different temperatures

Temperature (°C)	Conductivity (S/cm)
Room temperature	5.4545×10^{-08}
300	7.3433×10^{-07}
400	9.9489×10^{-06}
500	4.5740×10^{-05}
600	1.8134×10^{-04}

From the obtained oxide ion conductivity values, a graph has been drawn to compare the oxide ion conductivity values of different compositions of doped ceria nanocomposite ceramic oxide materials at 600 °C which is shown in Figure 10. The comparative table showing the oxide ion conductivity values of doped ceria based electrolyte materials is shown in Table 8.

Table 8: Oxide ion conductivity values obtained on sintered circular compacts of doped ceria nanocomposite ceramic oxide based electrolyte materials

S.No.	Sample	Conductivity (S/cm)
1	$^{Ce}0.9^{Gd}0.1^{O}2\text{-}\delta\ ^{-Ce}0.9^{Y}0.1^{O}2\text{-}\delta$	4.5799×10^{-05}
2	$^{Ce}0.8^{Gd}0.2^{O}2\text{-}\delta\ ^{-Ce}0.8^{Y}0.2^{O}2\text{-}\delta$	5.6563×10^{-04}
3	$^{Ce}0.9^{Gd}0.1^{O}2\text{-}\delta\ ^{-Ce}0.9^{Sm}0.1^{O}2\text{-}\delta$	5.4315×10^{-05}
4	$^{Ce}0.8^{Gd}0.2^{O}2\text{-}\delta\ ^{-Ce}0.8^{Sm}0.2^{O}2\text{-}\delta$	3.9771×10^{-04}
5	$^{Ce}0.9^{Gd}0.1^{O}2\text{-}\delta$	4.4255×10^{-04}
6	$^{Ce}0.8^{Gd}0.2^{O}2\text{-}\delta$	1.8134×10^{-04}

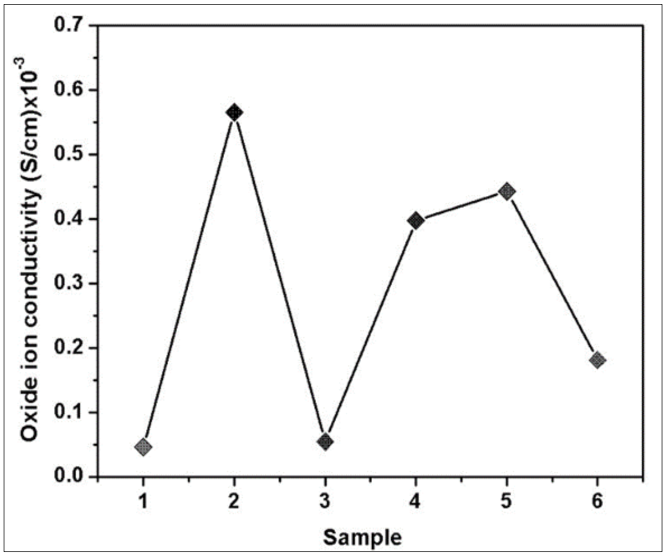

Fig 10: Curve obtained from conductivity values at 600 °C for different Compositions of nanocrystalline electrolyte powders

From the Table 8 and Figure 10, it was understood that the sample $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ -$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ has shown better oxide ion conductivity when compared with other samples.

Activation energy measurements

In this research work, the samples were sintered at 800 °C for 3 hours. By using the sintering temperature, the oxide ion conductivity can be improved. The Arrhenius plots obtained on doped nanocomposite ceramic oxide materials are shown in Figure 11.

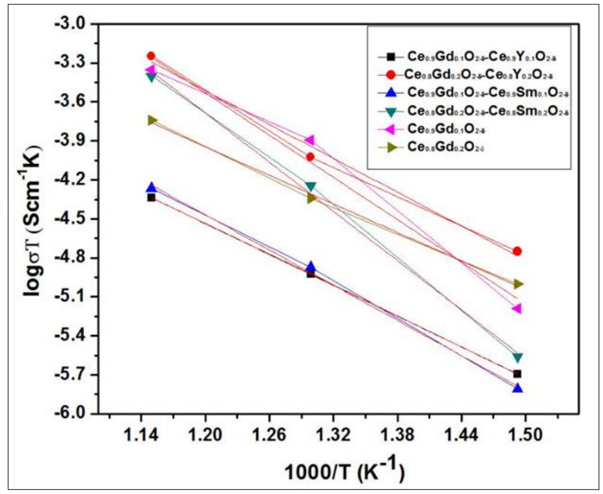

Fig 11: Arrhenius linear relationship plot obtained on nanocrystalline ceramic composite oxide pellets.

From the Arrhenius plots, it was understood that the ionic conductivity of doped ceria electrolytes is influenced not only by the concentration and the distribution of oxygen vacancy levels, but also by the lattice strain.From the results, it was found that partial substitution of Gd with Y and Sm in ceria might cause two reverse effects. First one is the suppression of ordering of the oxygen vacancy levels and which may lead to the decrease in the activation energy of conductivity and increase in the ionic conductivity. Second one is the deviation of the lattice parameter from pure CeO_2 and which may lead to the increase in the activation energy of conduction and the decrease in ionic conductivity. Therefore, the electrolyte with the higher ionic conductivity and lower activation energy must be with an appropriate dopant concentration.The activation energies calculated for doped nanocomposite ceramic oxide materials are indicated in Table. 9 From the observation, it was found that the activation energy increases with the decrease in oxide ion conductivity values.

Table 9: Activation energies calculated from Arrhenius linear fit relationship for doped nanocomposite ceramic oxide materials

Sample	Temperature (°C)	1000/T	logσT ($Scm^{-1}K$)	slope	Activation energy (eV)
$^{Ce}0.9^{Gd}0.1^{O}2\text{-}\delta$ –	400	1.492	-5.695	-3.954	0.341
$^{Ce}0.9^{Y}0.1^{O}2\text{-}\delta$	500	1.298	-4.923		
	600	1.149	-4.339		
$^{Ce}0.8^{Gd}0.2^{O}2\text{-}\delta$ –	400	1.492	-4.749	-4.345	0.375
$^{Ce}0.8^{Y}0.2^{O}2\text{-}\delta$	500	1.298	-4.023		
	600	1.149	-3.247		
$^{Ce}0.9^{Gd}0.1^{O}2\text{-}\delta$ –	400	1.492	-4.749	-4.510	0.389
$^{Ce}0.9^{Sm}0.1^{O}2\text{-}\delta$	500	1.298	-4.023		
	600	1.149	-3.247		
$^{Ce}0.8^{Gd}0.2^{O}2\text{-}\delta$ –	400	1.492	-5.807		0.544
$^{Ce}0.8^{Sm}0.2^{O}2\text{-}\delta$	500	1.298	-4.872	-6.317	
	600	1.149	-4.265		

$Ce_{0.9}Gd_{0.1}O_{2-\delta}$	400	1.492	-5.190		0.471
	500	1.298	-3.892	-5.417	
	600	1.149	-3.354		
	400	1.492	-5.002		
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	500	1.298	-4.339	-3.661	0.316
	600	1.149	-3.741		

Conclusion

In this work, a set of nanocrystalline electrolyte materials ($Ce_{0.9}Gd_{0.1}O_{2-\delta}$- $Ce_{0.9}Y_{0.1}O_{2-\delta}$, $Ce_{0.8}Gd_{0.2}O_{2-\delta}$-$Ce_{0.8}Y_{0.2}O_{2-\delta}$, $Ce_{0.9}Gd_{0.1}O_{2-\delta}$-$Ce_{0.9}Sm_{0.1}O_{2-\delta}$, $Ce_{0.8}Gd_{0.2}O_{2-\delta}$-$Ce_{0.8}Sm_{0.2}O_{2-\delta}$, $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$) for SOFC was developed. The following conclusions are drawn from the results achieved from this research activity. Doped ceria nanocomposite ceramic oxide materials have been successfully developed using economically cheap method, i.e., chemical precipitation method. TGA patterns obtained on the precursor samples revealed the formation of product and the removal of molecules. The conductivity data obtained on all the samples revealed optimum conductivity and the samples proposed in this research work may be suitable for electrolyte application in SOFC systems. Among the six types studied, the sample $Ce_{0.8}Gd_{0.2}O_{2-\delta}$-$Ce_{0.8}Sm_{0.2}O_{2-\delta}$ has shown improved oxide ion conductivity at 600 °C when compared with other samples.

Acknowledgement

Author wants to thanks the Dean, Faculty of Science, Motherhood University, Roorkee for the kind support and help.

Conflict of Interest

Author shows no conflict of interest

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