

Article

The La³⁺-, Nd³⁺-, Bi³⁺-Doped Ceria as Mixed Conductor Materials for Conventional and Single-Component Solid Oxide Fuel Cells

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Abstract: Clean energy devices are essential in today's environment to combat climate change and work towards sustainable development. In this paper, the potential materials A₂Ce₂O_{7-δ} (A = La³⁺, Nd³⁺, Bi³⁺) were analyzed for clean energy devices, specifically for conventional and single-component solid oxide fuel cells (SC-SOFCs). The wet chemical route has been followed for the preparation of samples. X-ray diffraction patterns showed that all three samples exhibited a defected fluorite cubic structure. It also revealed the presence of dopants in the ceria, which was confirmed by the fingerprint region of FTIR. The optical behavior, fuel cell performance and electrochemical behavior were studied by UV-vis, fuel cell testing apparatus and EIS, respectively. The SEM results showed that all samples had irregular polygons. In Raman spectra, the F_{2g} mode corresponding to the space group (Fm3m) confirms the fluorite structure. The Raman spectra showed that A₂Ce₂O_{7-δ} (A = La³⁺, Nd³⁺, Bi³⁺) have different trends. The conventional fuel cell performance showed that the maximum power density of Bi₂Ce₂O₇ was 0.65 Wcm⁻² at 600 °C. The performance of A₂Ce₂O_{7-δ} (A = La³⁺, Nd³⁺, Bi³⁺) as a single-component fuel cell revealed that Nd₂Ce₂O_{7-δ} is the best choice with semiconductors conductors ZnO and NCAL. The highest power density (P_{max}) of the Nd₂Ce₂O₇/ZnO was 0.58 Wcm⁻², while the maximum power output (P_{max}) of the Nd₂Ce₂O₇/NCAL was 0.348 Wcm⁻² at 650 °C. All the samples showed good agreement with the ZnO as compared to NCAL for SC-SOFCs.

Keywords: conductor materials; single component; doped ceria nanocomposite; electrolyte application; single-component solid oxide fuel cell (SC-SOFC)



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1. Introduction

Solid oxide fuel cells (SOFCs) contain three components: anodes, electrolytes, and cathodes [1]. In SOFCs, the most significant and basic component is the electrolyte [2]. The electrolyte plays the important role of separating the anode and cathode [3]. It also supports the movement of H⁺ from anode to cathode or O⁻² from cathode to anode as part of the fuel cell function. Typically, SOFC research has been focused on reducing operative temperatures from 1000 °C to, e.g., 600 °C [3,4]. To address this issue, thin-film techniques are being explored to reduce the thickness of the electrolyte from millimeters to micrometers [5] or by using materials that have high ion conductivity and no electron conductivity [6]. However, fuel cell electrolytes need to be dense enough to prevent a cross-over phenomenon where anode gas is mixed with cathode gas. They must also be structurally and chemically stable at high temperatures and in both oxidative and reductive atmospheres [7].

In a recent study, the A₂Ce₂O_{7-δ} structure-type was investigated as a denser material for the fuel cell electrolyte in SOFCs. CeO₂ falls in an n-type semiconductor category and

has the ability to hold its fluorite structure even after the absence of the oxygen atom in its lattice [8]. In addition, it has the potential to absorb oxygen from an environment that contains oxygen and releases oxygen in an environment lacking in it [9].

The ceria-based composition was chosen as it would assure an increase in ion conductivity and high sintering thickness at a temperature of about 1000 °C as compared to the known sintering temperature of about 1400 °C. [10]. The structure $A_2B_2O_{7-\delta}$ was selected as $A_2B_2O_7$ -defected fluorites, like $La_2Zr_2O_7$ and $La_2Ce_2O_7$, showed good proton conduction [11]. Proton conduction has also been demonstrated by $Nd_2Ce_2O_7$ and $Gd_2Ce_2O_7$ [12]; however, $Nd_2Ce_2O_7$ materials have a comparatively reduced sintering activity at densification temperatures up to 1500 °C [13]. If a dense electrolyte film could be produced at a lower temperature, it would reduce the cost and open possibilities for electrode-supported processes. Therefore, it is essential to develop a way for $Nd_2Ce_2O_7$ materials that guarantees the formation of electrolytes at a correspondingly low temperature while having better conductivity.

The dopants used in ceria are La^{+3} , Nd^{+3} and Bi^{+3} , $La_2Ce_2O_7$, $Nd_2Ce_2O_7$, and $Bi_2Ce_2O_7$, respectively. La and Nd are rare earth metals whereas Bi is a post-transition metal. Furthermore, as per our understanding, the bismuth oxide (Bi_2O_3) showed the highest ionic conductivity at comparable temperatures [14]. The ionic conductivity of stabilized Bi_2O_3 makes this material ideal as an electrolyte in SOFCs that function at lower temperatures < 1000 [15]. The objective of this paper is to primarily review the effect of La^{+3} , Nd^{+3} and Bi^{+3} ions in ceria. The secondary objective is to compare dopants used as ceria-based solid electrolytes for conventional as well as single-component SOFCs.

2. Experimental Detail

2.1. Synthesis of $A_2Ce_2O_{7-\delta}$ ($A = La^{+3}$, Nd^{+3} , Bi^{+3}) Nanocomposite

Among wet chemical methods, the sol–gel method was used to fabricate $A_2Ce_2O_{7-\delta}$ ($A = La^{+3}$, Nd^{+3} , Bi^{+3}) nanocomposites. The ceria was doped individually with equal amounts of lanthanum, neodymium and bismuth to study the conduction behavior of nano composites, for single and conventional SOFCs. The $A_2Ce_2O_{7-\delta}$ ($A = La^{+3}$, Nd^{+3} , Bi^{+3}) compositions were prepared through wet chemicals. The precursors used as cerium, lanthanum, neodymium and bismuth sources for powder synthesis were cerium nitrate hexahydrate $Ce(NO_3)_3 \cdot 6H_2O$ (99.9% Sigma Aldrich, China), lanthanum nitrate hexahydrate $La(NO_3)_3 \cdot 6H_2O$ (99.9% Sigma Aldrich), neodymium nitrate $Nd(NO_3)_3 \cdot 6H_2O$ (99.9% Alfa Aesar, China) and bismuth nitrate penta hydrate $Bi(NO_3)_3 \cdot 5H_2O$ (BDH/RDH). Demineralized water was used as the solvent and citric acid (anhydrous) was used as a metal-chelating agent to tightly bind the metal ions [16].

The calculated amount of $Ce(NO_3)_3 \cdot 6H_2O$, $La_2(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ was separately dissolved in deionized water. Three separate solutions were subsequently formed by mixing $Ce(NO_3)_3 \cdot 6H_2O$ and $La_2(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Nd(NO_3)_3 \cdot 6H_2O$, and lastly $Ce(NO_3)_3 \cdot 6H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$. These solutions were heated at 80 °C for half an hour. After the completion of this process, citric acid with the mole ratio of citric acid to cerium 2:1 [17] was added to each respective solution. Ammonia liquor was also pipetted to adjust the pH value of the solutions to 6–7 [18]. To stiffen the mixture, ethylene glycol with the mole ratio of ethylene glycol to cerium of 1:1.8 [19] was also added. Each sol–gel solution was then re-heated at 160 °C in an oven until all the water had evaporated so that the dry solid material could be obtained.

After grinding the solid to powder form, it was placed in a furnace and sintered for 5 h at a temperature of 900 °C. At the end with natural cool and grind, the powder of the nanocomposite was obtained.

2.2. Fabrication of Pellet

The pellets for fuel cell testing are formed in two ways. In the first type, the pellets are fabricated as conventional three-component SOFCs and in the second type, a single layer or single-component SOFCs have been fabricated. For the first method, the traditional SOFC

three-layer structure was formed, where $A_2Ce_2O_{7-\delta}$ ($A = La^{+3}, Nd^{+3}, Bi^{+3}$) was taken as an electrolyte. The $NiCuZnO_x$ (NCZO) was taken as the anode [20] and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSFC) was taken as the cathode [21]. The mass ratios of anodes, electrolytes, and cathodes were 0.3 g, 0.3 g, and 0.4 g, respectively. For the formation of pellets, the anode, electrolyte and cathode powders were successively placed in the stainless-steel die (13 mm). This die was then put in a hydraulic press to co-press in one step under the pressure of approximately 300 MPa. The pellets were then put into a muffle furnace at a temperature of 600 °C for 30 min to sinter. For current collection, the silver paste was used on one side of the cell. Nickel foam was used on the other side for the mechanical strength of the cell. For performance measurement, the pellet was then positioned in the sample fixture, which has four gas supply pipes, two of which are hydrogen supply/exit pipes, and the other two are air supply/exit pipes.

The same procedure was used for the single-component fuel cell, but with fewer steps, as only one coat of powder was employed. Co-pressed ionic and semiconducting material powder weighing over 0.5 g was applied to a porous nickel foam. Here, the ionic conductors were taken as $A_2Ce_2O_{7-\delta}$ ($A = La^{+3}, Nd^{+3}, Bi^{+3}$), while the semiconductors used were NCAL [22] and ZnO [23].

2.3. Characterization Techniques for Material and Fuel Cell Analysis

The Bruker D8 Advance X-ray diffractometer was used to recode the X-ray pattern of synthesized $A_2Ce_2O_7$ ($A = La^{+3}, Nd^{+3}, Bi^{+3}$) nanocomposites at room temperature. The Cu-K α radiation ($\lambda = 0.154$ nm) at 40 KV and 30 mA in a 2θ range of 0°–90° was used. The Scherer's formula was used to calculate the average crystallite size (D_β) [24]:

$$D_\beta = k\lambda / \beta \cos \theta \quad (1)$$

Here, D_β is the measure of crystalline size, k stands for constant having value 0.94, λ is the wavelength, θ is the Bragg angle and β stands for the full width at half maximum (FWHM). The lattice strain (ϵ) was determined by [25]:

$$\epsilon = \frac{\beta}{4 \tan \theta} \quad (2)$$

The UV-2600 spectrometer with the wavelength range of 200–800 nm was used to obtain the UV–visible absorption spectra of synthesized LDC, NDC and BDC. The energy gap was calculated with the following equation [26]:

$$ah\nu = A(h\nu - E_g)^{n/2} \quad (3)$$

Here, A is an empirical value; α stands for absorption coefficient; h represents the proportionality constant, which is called Planck's constant; and E_g is the band gap energy. In the above equation, n represents the transition between energy bands; here, the direct band gap corresponds to $n = 1$, and the indirect band gap corresponds to $n = 4$. The values of the absorption coefficient (α) have been calculated by the following relation:

$$\alpha = 4\pi k / \lambda \quad (4)$$

Here, λ represents the wavelength in nm and k represents the absorption index. The band gap energy was taken by the Tauc plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$).

To study the particle microstructure of prepared nanocomposites, the samples were examined by scanning electron microscopy (JEOL JSM-6480 LV, France). To observe the chemical bonds and functional groups of prepared nanocomposites, Fourier transform infrared spectroscopy (IRTracer-100 FTIR Spectrometer, China) was conducted. The Raman spectrum was analyzed by the InVia Raman Microscope by RENISHAW, UK. Raman spectrometry is an exceptional technique used worldwide to assess oxygen vacancies present in the fluorite structure, the phase present in material, and the quality and purity of

the material. Electrochemical impedance spectroscopy was conducted by an electrochemical workstation (CS350, China) under the range of 0.01 Hz to 1 MHz frequency. Fuel cell performance was carried out by using the fuel cell testing setup at 650 °C with hydrogen as a fuel.

3. Results

3.1. XRD Analysis for $A_2Ce_2O_7$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) Nanocomposite

The X-ray diffraction pattern of prepared $A_2Ce_2O_7$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) nanocomposites are shown in Figure 1. In the graph, the measured peaks of $A_2Ce_2O_7$ depicted that the composite oxide matched with the cubic fluorite structure of pure CeO_2 (Fm3-m, No. 225) with a JCPDS card (01-076-0076). The diffraction pattern showed that the eight prominent diffraction peaks at $2\theta = 28.7^\circ, 33.2^\circ, 47.7^\circ, 56.6^\circ, 59.3^\circ, 69.7^\circ, 77.1^\circ$, and 79.5° correspond to (111), (200), (220), (311), (222), (400), (331), and (420), respectively. These crystal planes indexed to fluorite-type cubic structured $CeO_{2-\delta}$ [27]. A slight right shift was observed among diffraction peaks $La_2Ce_2O_7 < Nd_2Ce_2O_7 < Bi_2Ce_2O_7$. This may be due to the ionic radii of dopants compared to the Ce^{4+} ions. It has also been found that some peaks matched with rhombohedral cerium oxide (Ce_7O_{12}) or ($Ce_{0.698}O_{1.75}$) peaks have a JCPDS card (01-071-0567), which may be referred to the defected fluorite structure of CeO_2 . The reported work showed that Ce_7O_{12} remained stable up to 1072 K, and then transformed into a fluorite-type structure with disordered oxygen vacancies [28]. Among $La_2Ce_2O_7$, $Nd_2Ce_2O_7$ and $Bi_2Ce_2O_7$, it has been observed that $Bi_2Ce_2O_7$ peaks matched well with cubic CeO_2 as compared to the other two.

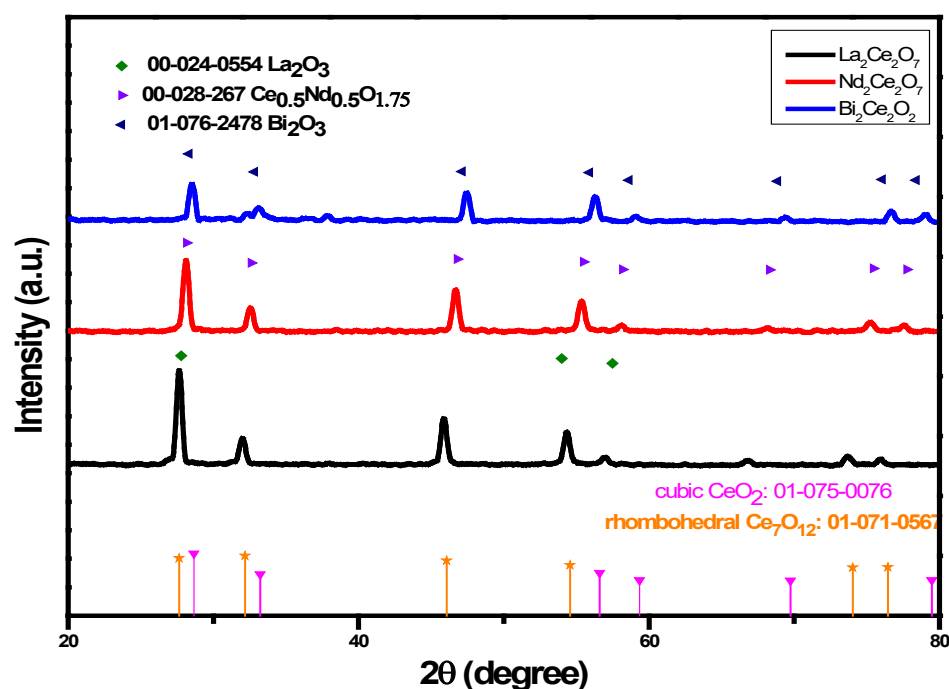


Figure 1. Diffraction pattern for $A_2Ce_2O_7$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) nanocomposites.

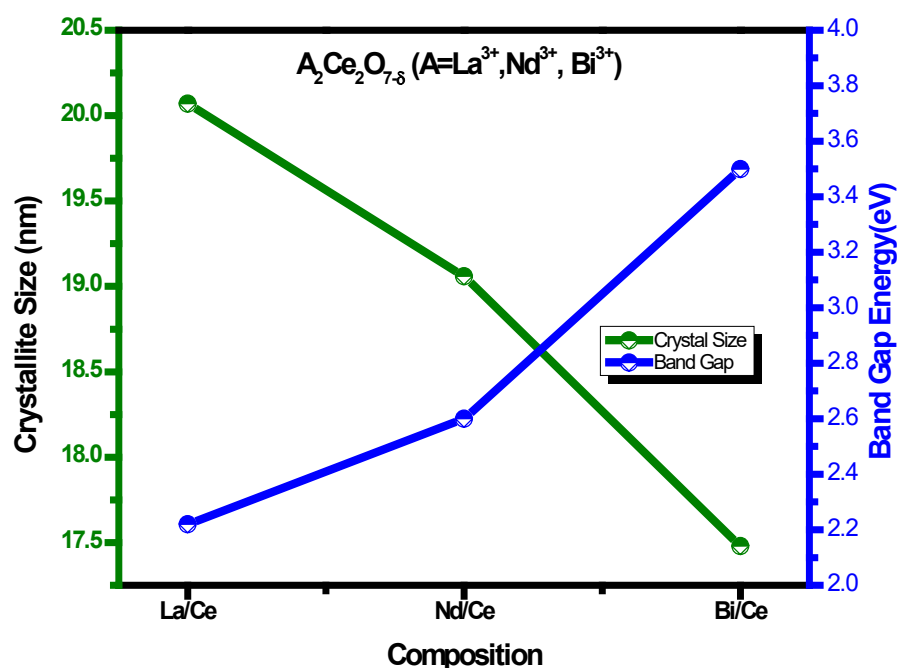
By using the Debye Scherrer relation in Equation (2), the crystallite sizes (D) of $A_2Ce_2O_7$ materials were determined. The lattice strain was measured by using Equation (3) [29]. A steady shift towards higher diffraction angles was observed for $La^{3+} < Nd^{3+} < Bi^{3+}$ doping. Consequently, the lattice parameters were increased. All calculated parameters are given in Table 1. The lattice strain of $La_2Ce_2O_7$ and $Nd_2Ce_2O_7$ was found to be negative, which reflects the compressive nature of strain, whereas $Bi_2Ce_2O_7$ showed the positive value of lattice strain, a sign of tensile strain.

Table 1. Comparison of crystallite size, lattice constant and lattice strain from the XRD result of $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) nanocomposites for SOFCs.

Samples	Angle	FWHM	Crystallite Size (nm)	Lattice Constant ($\text{\AA}$)	Lattice Strain (ϵ)	Phase
$La_2Ce_2O_7$	27.67	0.4260	20.07	5.5730	−0.15423	Cubic
$Nd_2Ce_2O_7$	28.11	0.449	19.06	5.4890	−0.6769	Cubic
$Bi_2Ce_2O_7$	28.52	0.49	17.48	5.4113	0.488572	Cubic

From Figure 1, it can be observed that the peaks of La^{3+} -, Nd^{3+} - and Bi^{3+} -doped CeO_2 samples matched with the cubic CeO_2 with a slight variation. The diffraction peaks of prepared nanocomposites showed a slight right shift towards greater diffraction angles. This may be due to the ionic radii of dopants compared to the Ce^{4+} ions; consequently, there was an increase in the lattice parameters. The larger La^{3+} cations replaced by smaller Ce^{4+} cations in the fluorite structure [$r(La^{3+}) = 1.06 \text{ \AA}$, $r(Ce^{4+}) = 0.970 \text{ \AA}$] had 8-fold coordination [29], which was further confirmed by Rietveld refinement, and the lattice parameter of LDC ($a = 5.5730 \pm 0.0001 \text{ \AA}$) was increased in comparison with that of undoped CeO_2 ($a = 5.4081 \pm 0.0001 \text{ \AA}$) [30]. The same analogy was observed for Nd^{3+} and Bi^{3+} cation replacement with Ce^{4+} cations having ionic radii $r(Nd^{3+}) = 1.11 \text{ \AA}$ and $r(Bi^{3+}) = 1.03 \text{ \AA}$. The measurements increased the lattice parameter of NDC ($a = 5.4890 \pm 0.0001 \text{ \AA}$) and BDC ($a = 5.4113 \pm 0.0001 \text{ \AA}$) with respect to CeO_2 . This supported the fact that dopants La^{3+} , Nd^{3+} and Bi^{3+} cations were incorporated into the CeO_2 lattice.

The deviation in optical band gap energy and the crystallite size of nanoparticles with different dopants in the ceria lattice is shown in Figure 2. It is inferred that the size of the nanoparticles was reduced while the band gap energy was increased. This means that the lattice parameter and band gap energy increase with decreasing crystallite size. The wide band gap materials show numeral characteristics that make them beneficial as compared to narrower band gap materials. The increase in the energy gap enables the devices to work at higher temperatures. At higher temperatures, band gaps usually shrink, which can cause problems when using conventional semiconductors.

**Figure 2.** Comparison of the crystallite size and band gap of $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) composite materials prepared by the wet chemical method.

3.2. Microstructure Analysis

The SEM was employed to analyze the micro-structure of nanocomposites [31,32]. Figure 3a–c show the SEM images of $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}$, Nd^{3+} , Bi^{3+}) powders of all samples after sintering at a temperature of 1173 K. It can be seen that the particles of all samples have irregular polygon morphology.

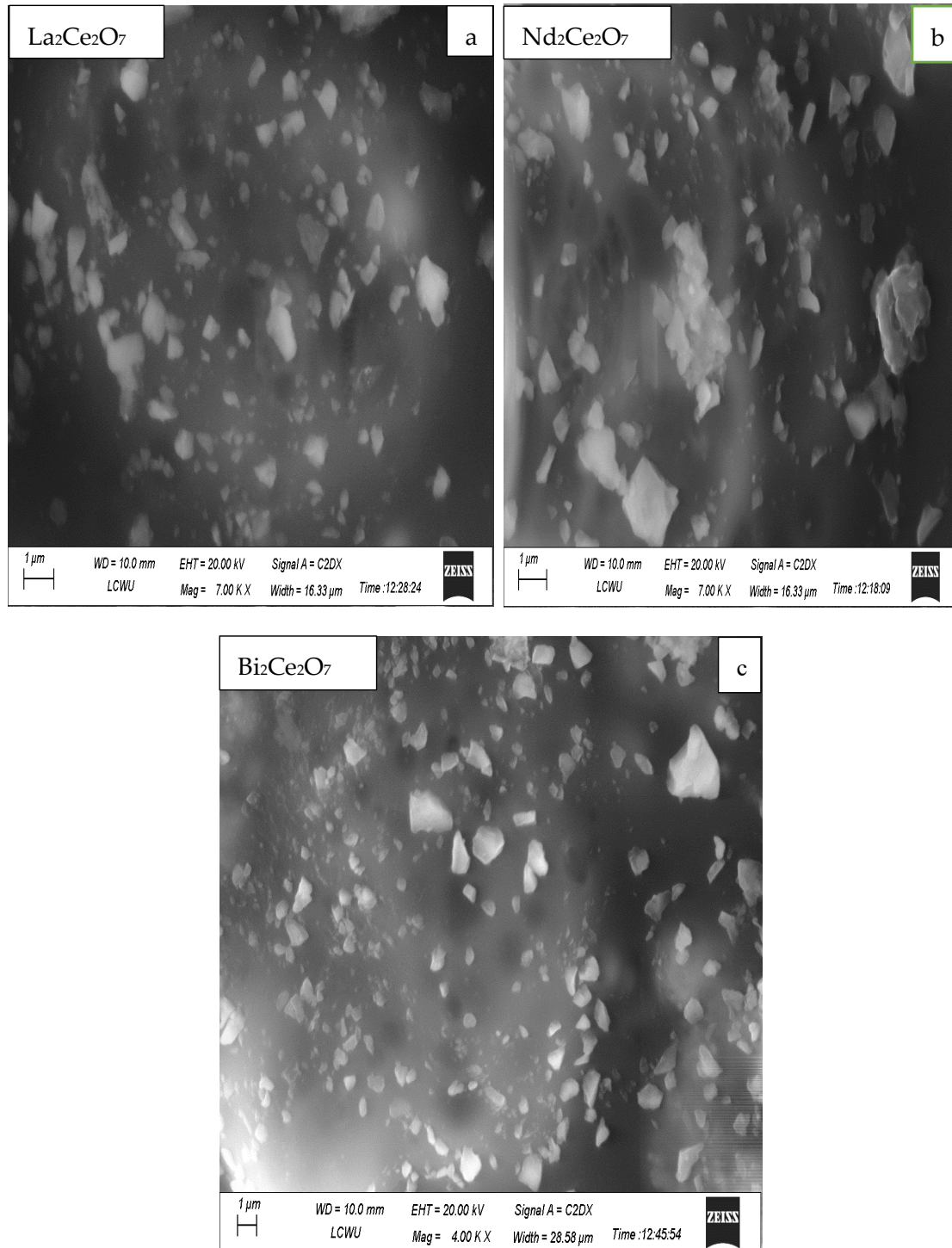


Figure 3. (a–c) SEM micrographs for $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}$, Nd^{3+} and Bi^{3+}) nanocomposite materials prepared by sol–gel and sintered at 1173 K for 5 h.

Figure 4a–d show the EDS spectrum results of the $\text{Nd}_2\text{Ce}_2\text{O}_{7-\delta}$ sample. This spectrum showed the quantity of neodymium, oxygen and cerium elements in the sample. From the EDS quantitative analysis of elements, the neodymium contents on the sample powders were about 34.71 wt% and 9.68 at%, as shown in Table 2, while cerium was detected with as much as 33.15 wt% and 9.52 at%. The EDS spectrum showed that all elements were homogeneously dispersed. Figure 5 represents the EDS spectra.

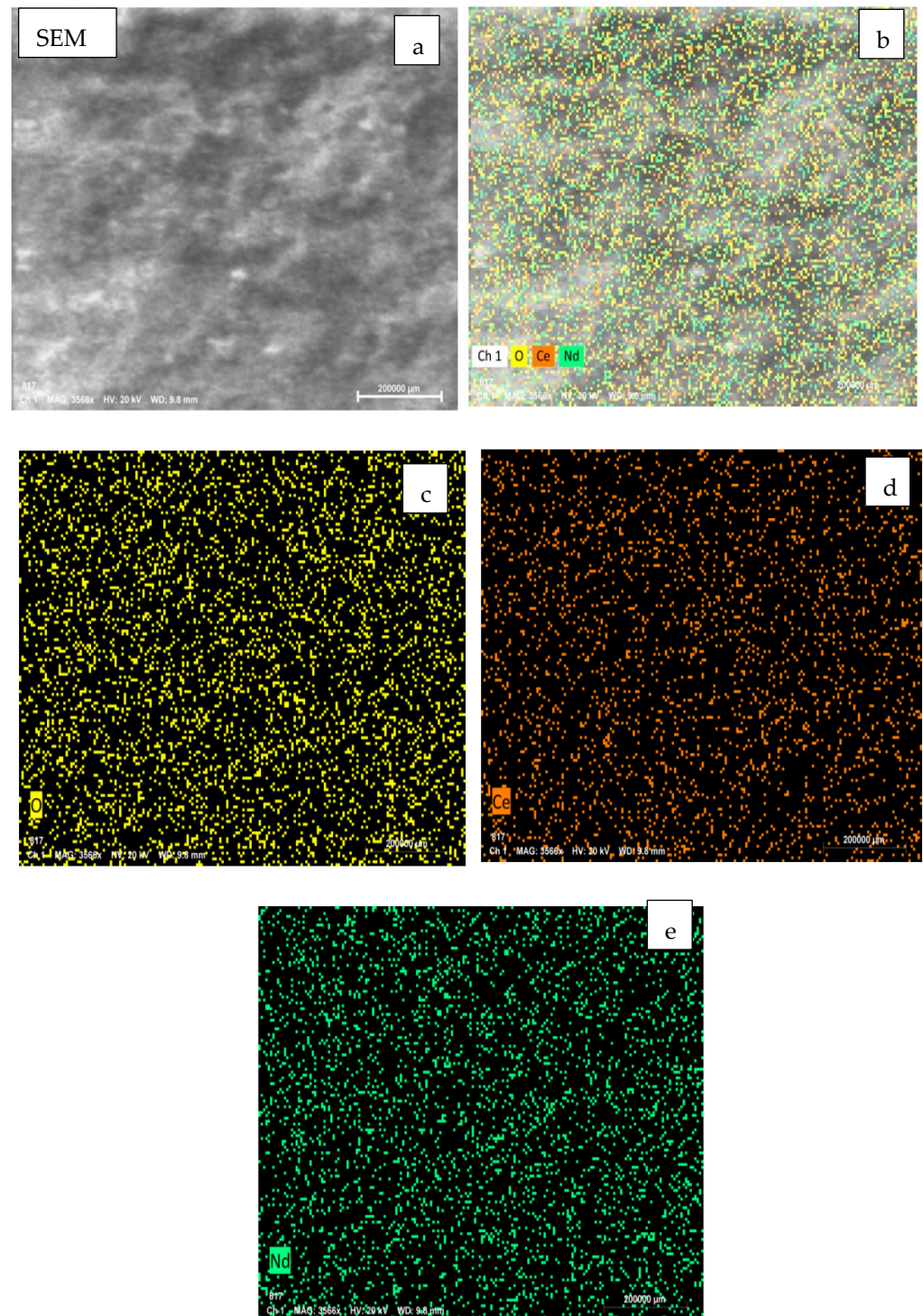
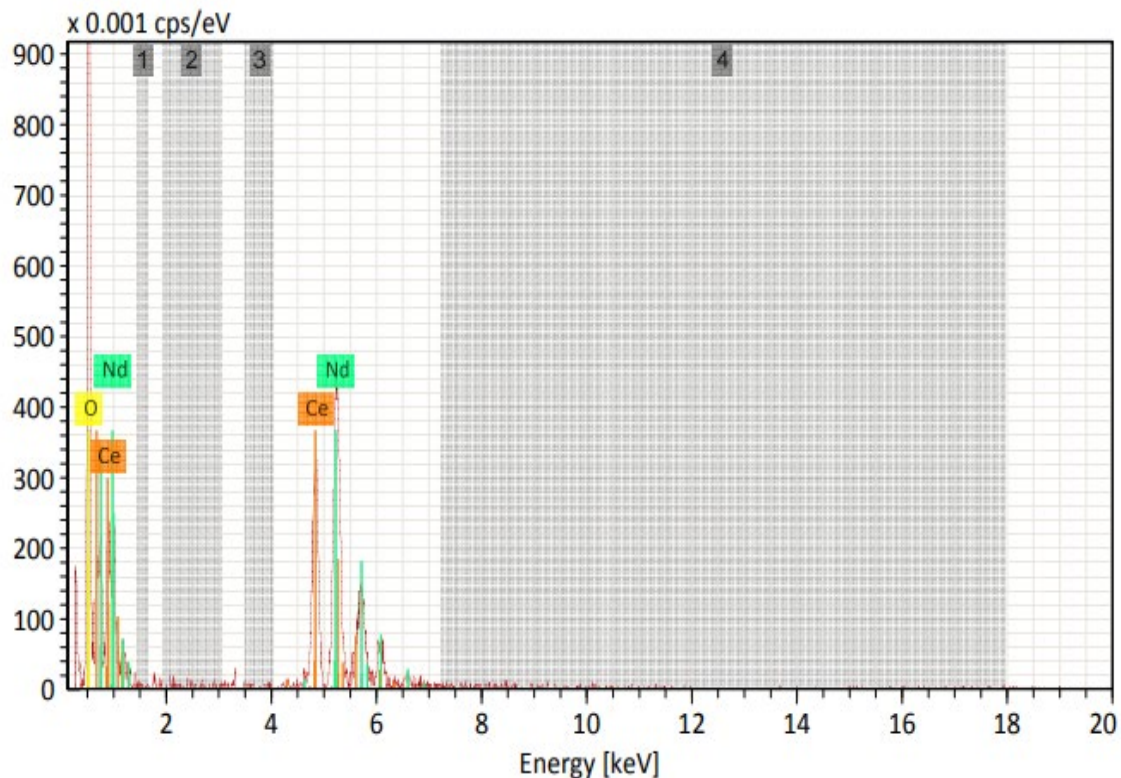


Figure 4. (a–e) Elemental mapping analysis of the $\text{Nd}_2\text{Ce}_2\text{O}_{7-\delta}$ pellet by the sol–gel method after sintering at 1250 °C for 12 h.

Table 2. EDS quantitative analysis of the $\text{Nd}_2\text{Ce}_2\text{O}_{7-\delta}$ pellet.

Element	Weight%	Atomic%
O K	32.14	80.80
Ce L	33.15	9.52
Nd L	34.71	9.68
Total	100	

**Figure 5.** EDS spectrum of the $\text{Nd}_2\text{Ce}_2\text{O}_{7-\delta}$ pellet by the sol–gel method after sintering at 1250 °C for 12 h.

3.3. UV–Visible Analysis (200 to 800 Nanometers)

The UV–visible absorption spectra of $\text{A}_2\text{Ce}_2\text{O}_{7-\delta}$ ($\text{A} = \text{La}^{3+}$, Nd^{3+} and Bi^{3+}) are displayed in Figure 6, ranging between 200 and 800 nm. The trend is the same for all three samples. The previous literature showed that the absorption peak of CeO_2 is found to be at around 349 nm [33]. Currently, the broad absorption peaks for all nanocomposites have started from 340 nm and ended at 370 nm. In the graph, the $\text{La}_2\text{Ce}_2\text{O}_7$ nanoparticles showed very insignificant absorption peaks. In the case of neodymium (Nd) and bismuth (Bi), the absorption peaks became significant.

The Tauc plots are shown in Figure 7. Previously, the direct band gap of pure CeO_2 was found to be 2.69 eV [34]. Moreover, the band gap of $\text{La}_2\text{Ce}_2\text{O}_7$ was found to be 2.22 eV. This means that it shows the red shift with respect to pure ceria. $\text{Nd}_2\text{Ce}_2\text{O}_7$ showed a band gap of 2.6 eV. $\text{Bi}_2\text{Ce}_2\text{O}_7$ showed a band gap of 3.6 eV, of which tilted towards the blue shift. By introducing different dopants in the ceria, the band gap energies of $\text{La}_2\text{Ce}_2\text{O}_7$ and $\text{Nd}_2\text{Ce}_2\text{O}_7$ were decreased as compared to the ceria. This may be due to the creation of oxygen vacancies in the ceria lattice. On the other hand, $\text{Bi}_2\text{Ce}_2\text{O}_7$ showed an increase in band energy with respect to the ceria. This means no significant oxygen vacancies were created.

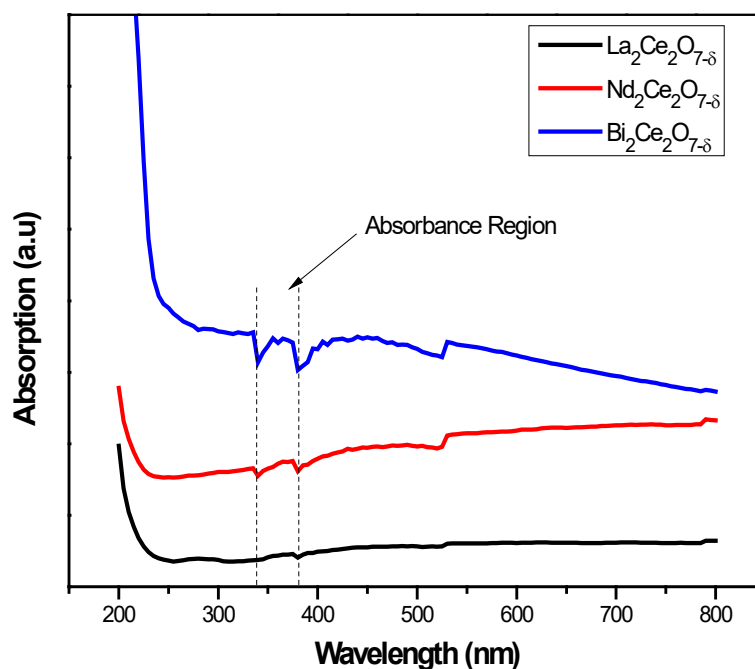


Figure 6. UV-visible spectra for $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}$, Nd^{3+} and Bi^{3+}) nanocomposite materials.

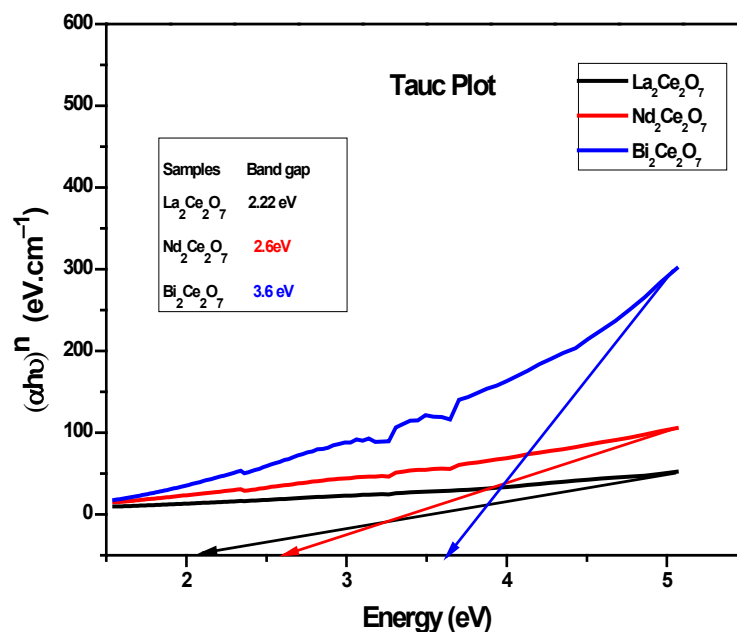


Figure 7. Comparison of Tauc plots using UV-visible spectra for $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}$, Nd^{3+} and Bi^{3+}) nanocomposite materials.

3.4. FTIR Spectra of $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}$, Nd^{3+} , Bi^{3+})

The FTIR spectroscopy of $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}$, Nd^{3+} , Bi^{3+}) nanoparticles was carried out in the range of $4000\text{--}400\text{ cm}^{-1}$, as shown in Figure 8. Chemical bonds as well as functional groups were confirmed by a FTIR spectrum. In these results, most of the peaks exist in the region, $2500\text{--}2000\text{ cm}^{-1}$, which is attributed to triple bond region. Almost all of the peaks are broad, which implies the presence of intermolecular hydrogen bonding [35]. The medium peak was found at 2345 cm^{-1} , which may be ascribed to N-H stretching. In previous studies, peaks between 2000 and 2300 cm^{-1} occur due to a conjugated effect, like carbon-di-amide, rather than pure nitriles $C\equiv N$, $N\equiv C$, $C\equiv O$, etc. [36]. Absorption peaks found at 2162 cm^{-1} and 2017 cm^{-1} are due to azide ($N\equiv N\equiv N$) and

ketenimine ($C=C=N$), respectively. In prior studies, a peak at 1516 cm^{-1} has been labelled as an unidentified nitrate vibration [37]. Therefore, the absorption peak around 1532 cm^{-1} may also be due to unidentified nitrate vibrations.

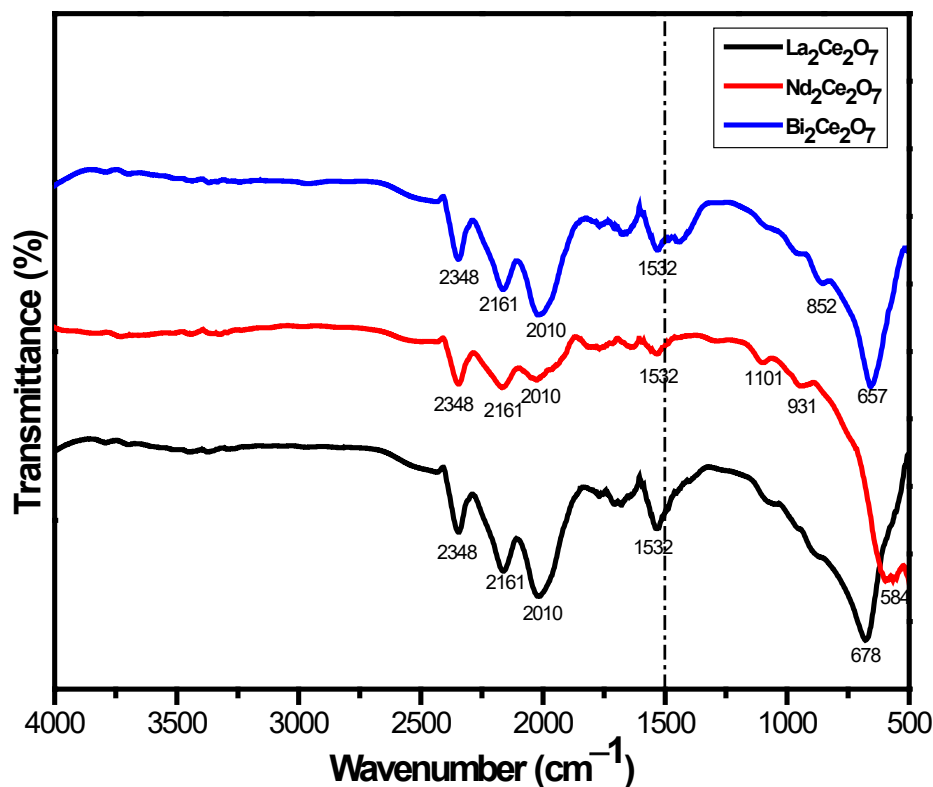


Figure 8. FTIR spectra of $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) composite material for energy devices.

In FTIR, the finger print region (400 cm^{-1} and 1500 cm^{-1}) is called fundamental infrared because most inorganic substances absorb IR in this region [38]. The peak at 653 cm^{-1} corresponds to the La–O stretching vibrations in reported work [39]. For $La_2Ce_2O_7$, the absorption peak in the fingerprint region found at 678 cm^{-1} may be caused by La–O stretching. The peaks at 411 [40] and 533 cm^{-1} [41] correspond to the characteristic Nd–O vibrations of Nd_2O_3 particles. The $Na_2Ce_2O_7$ band in the fingerprint region was found at 584 cm^{-1} , near the literature value. For $Bi_2Ce_2O_7$, the fingerprint peak was found at 852 and 657 cm^{-1} , which may be due to Bi–O stretching, as the Bi–O band has been found at 844 cm^{-1} previously [42]. Overall, the FTIR results showed the presence of nitriles and carbenes (triple bonds) and some peaks for double bonds. The fingerprint values showed the presence of Ce, La, Nd and Bi oxides in the compositions.

3.5. Analysis of Crystal Structure and Oxygen Vacancies by Raman Spectroscopy

The changes in crystal lattices and oxygen vacancies caused by the dopants in each $A_2Ce_2O_{7-\delta}$ powder were studied by Raman spectroscopy. Figure 9 clearly shows the Raman spectra of $La_2Ce_2O_7$, $Nd_2Ce_2O_7$ and $Bi_2Ce_2O_7$ nanocomposites. Samples $La_2Ce_2O_7$ and $Nd_2Ce_2O_7$ exhibited the two characteristic peaks, whereas $Bi_2Ce_2O_7$ showed only one peak. As previously reported [43], a well-crystallized CeO_2 with an ideal cubic fluorite structure possesses only one Raman-active F_{2g} mode at $\sim 460\text{ cm}^{-1}$, matching the Ce–O bond vibration. Therefore, the existence of a peak near $\sim 460\text{ cm}^{-1}$ confirms the fluorite structure of all prepared samples.

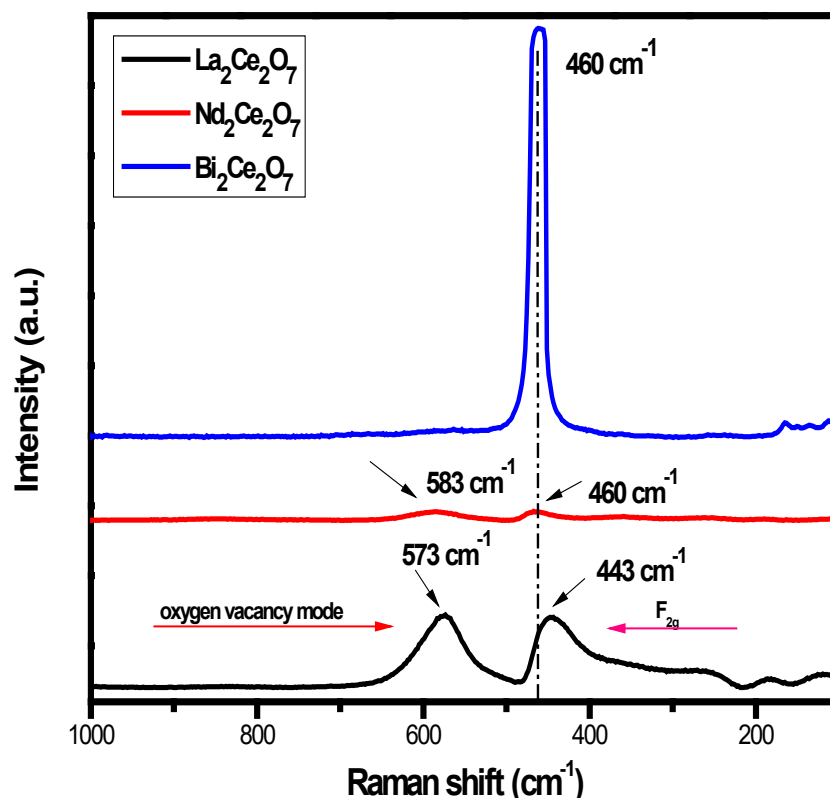


Figure 9. Raman spectra of the $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) composite material for SC-SOFCs.

In these results, the F_{2g} peak of $La_2Ce_2O_7$ was moved to a lower wave number. This may be due to the doping of La^{3+} into the CeO_2 lattice, of which has also been reported previously [44]. Another paper also confirmed that F_{2g} mode peaks in cerium oxide migrated to the lower area (by 2 cm^{-1} to 14 cm^{-1}) [45]. Due to this, the Raman peak of the $La_2Ce_2O_7$ sample at $\sim 443\text{ cm}^{-1}$ may be attributed to the F_{2g} mode of the defective cubic fluorite phase, and the peak at $\sim 574\text{ cm}^{-1}$ can be attributed to surface oxygen vacancies that were created by the integration of La^{3+} into the CeO_2 lattice. Junwei Xu also found two Raman peaks of the $La_2Ce_2O_7$ -based samples at $\sim 445\text{ cm}^{-1}$ and $\sim 575\text{ cm}^{-1}$, which are quite near to the present results [46]. Previous studies explain that the shift in F_{2g} mode is due to structural expansion when La^{3+} fuses into the fluorite structure. $Nd_2Ce_2O_7$ showed almost the same behavior with blunter peaks. The peak at $\sim 460\text{ cm}^{-1}$ is assigned to the F_{2g} mode, and the bluntness of the peak is assigned to the expansion of the structure due to Nd^{3+} ions' incorporation in the fluorite structure. The case of $Bi_2Ce_2O_7$ is different from $La_2Ce_2O_7$ and $Nd_2Ce_2O_7$. The peak for $Bi_2Ce_2O_7$ found at $\sim 460\text{ cm}^{-1}$ is well-matched with the fluorite structure. This may show the full fusion of Bi^{3+} ions in the ceria lattice. No additional modes were observed. Accumulatively, no significant oxygen vacancy is created in case of $Bi_2Ce_2O_7$. This also supports the band gap result of $Bi_2Ce_2O_7$.

Due to oxygen vacancies, additional peaks were seen in spectra that had been doped with rare earth metals [47]. As charge compensation defects caused by the introduction of other metal cations into the crystal lattice of CeO_2 . To maintain the charge neutrality, Ce^{4+} ions replaced by La^{3+} and Nd^{3+} ions, which create extrinsic vacancies. The peak positions at 573 cm^{-1} and 583 cm^{-1} correspond to oxygen vacancies.

3.6. Electrochemical Impedance Spectroscopy (EIS)

Figure 10a shows the electrochemical properties of energy devices using $A_2Ce_2O_{7-\delta}$ as an electrolyte for conventional fuel cells. The conventional device used $LiNiCuZnO_x$ (LNCZ) as an anode and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSFC) as a cathode. The EIS spectra for conventional

cells with the following combinations LNCZ/La₂Ce₂O₇/LSFC, LNCZ/Nd₂Ce₂O₂/LSFC and LNCZ/Bi₂Ce₂O₇/LSFC have been recorded. The entire Nyquist plot for conventional SOFCs demonstrates two components: a depressed small semicircle at the high-frequency region and another complete arc at a low-frequency range. It is noticeable that Bi₂Ce₂O₇ showed the lowest value of Ro among the other candidates.

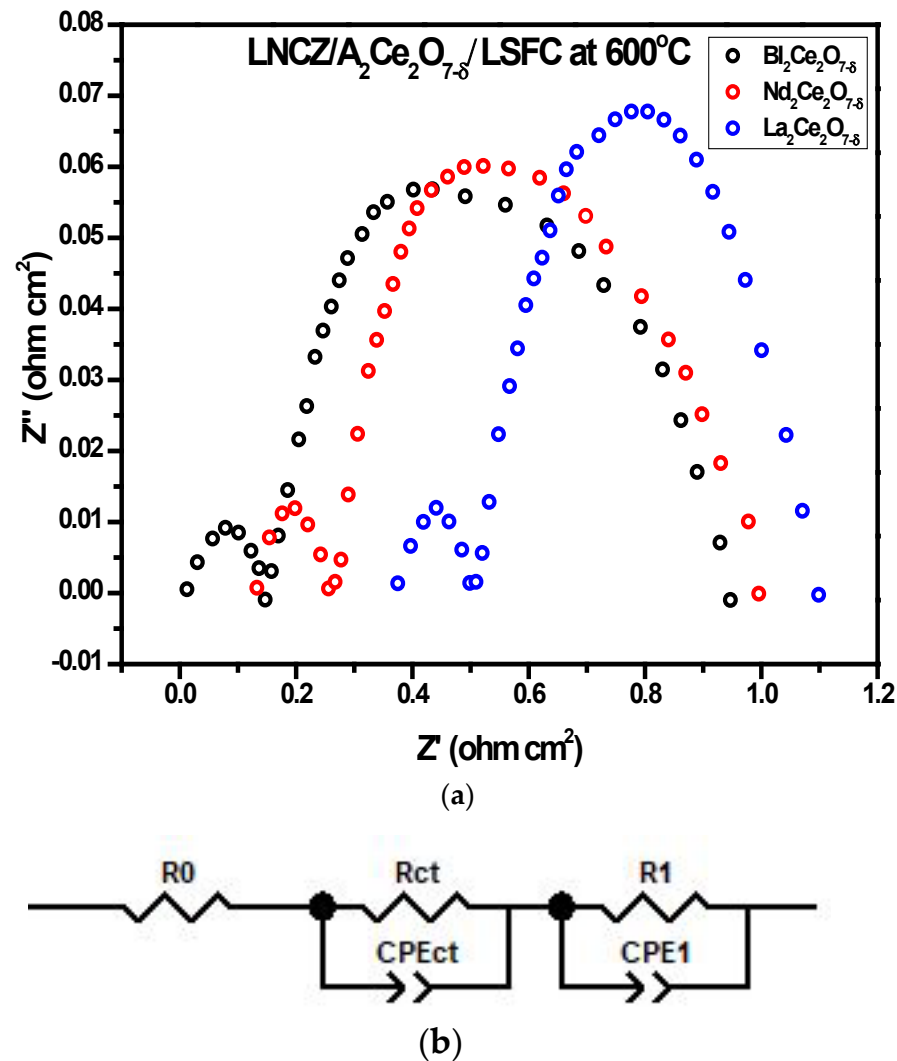


Figure 10. (a) EIS spectra of A₂Ce₂O₇ (A = La³⁺, Nd³⁺, Bi³⁺) as an electrolyte for conventional SOFCs at 600 °C. (b) The equivalent circuit with model Ro(RctCEPct)(R1CEP1).

Furthermore, the EIS data were simulated with Z-View software using the equivalent circuit model of Ro(RctCEPct)(R1CEP1), as shown in Figure 10b. Where R represents a resistance and CEP is the constant phase element representing a non-ideal capacitor! where ohmic resistance (R₀), charge transfer (R_{ct}), mass transfer (R₁), according to the simulated Ro + R_{ct}, the total conductivity (σ), as presented in the Supplementary Materials.

The A₂Ce₂O₇/NCAL and A₂Ce₂O₇/ZnO composite materials were used for a single-component solid oxide fuel cell (SC-SOFC) with a weight ratio of 5:5, measured at a temperature of 600 °C. The composite mixtures to be analyzed were La₂Ce₂O₇/NCAL, Nd₂Ce₂O₂/NCAL, Bi₂Ce₂O₇/NCAL La₂Ce₂O₇/ZnO, Nd₂Ce₂O₂/ZnO, and Bi₂Ce₂O₇/ZnO. In Figure 11, it was noticed that A₂Ce₂O₇/NCAL nanocomposite materials were represented by the two semicircles on the Nyquist plot. The first semicircle was completed, whereas the second was incomplete. In Figure 12, the mixture of A₂Ce₂O₇/ZnO show clear small semicircles for high frequencies, and for lower frequencies, curve lines are noticed.

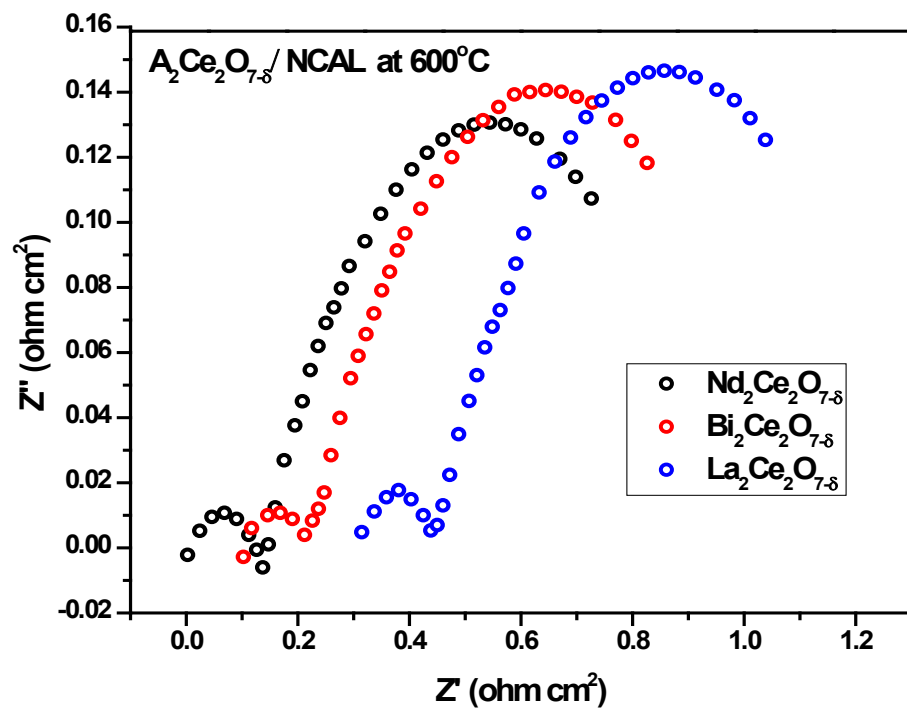


Figure 11. EIS spectra of $A_2Ce_2O_7$ ($A = La^{+3}, Nd^{+3}, Bi^{+3}$)/NCAL as a single-component fuel cell at 600 °C.

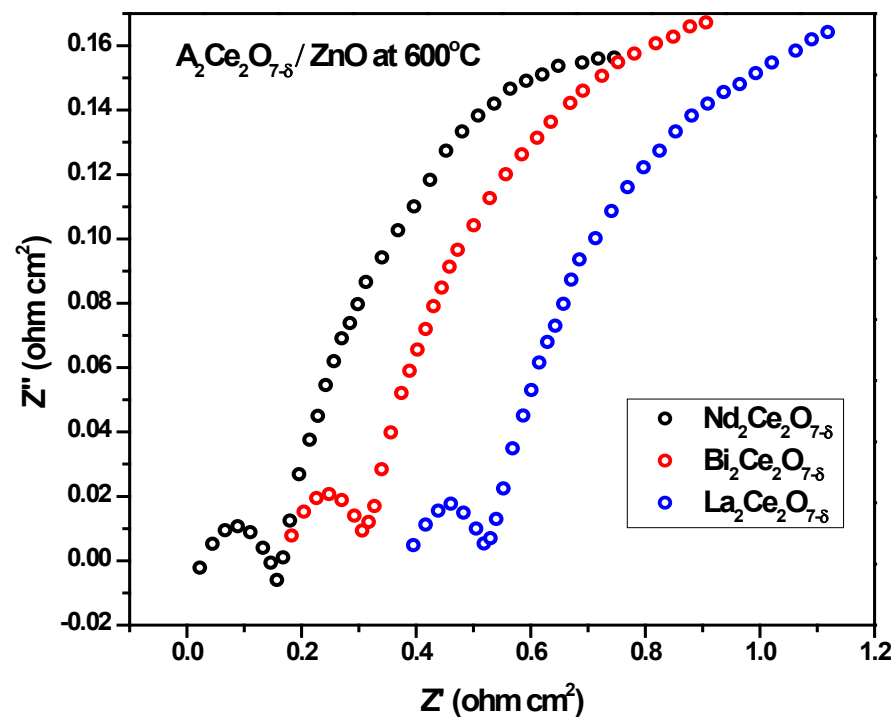


Figure 12. EIS spectra of $A_2Ce_2O_7$ ($A = La^{+3}, Nd^{+3}, Bi^{+3}$)/ZnO as a single-component fuel cell at 600 °C.

For all nanocomposites, SC-SOFC were represented by the two semicircles on the Nyquist plot. The first semicircle depicts the inside of the grain, and the second one stands for the electrodes. At higher frequencies, the intercept on the real axis (Z') corresponds to R_o . This is generally because of ionic and electronic resistances in the cell, and it varies

with dopants. It was observed that $\text{Nd}_2\text{Ce}_2\text{O}_{7-\delta}$ showed the lowest value of R_o than $\text{La}_2\text{Ce}_2\text{O}_{7-\delta}$ and $\text{Bi}_2\text{Ce}_2\text{O}_{7-\delta}$ for both combinations.

3.7. The Cell Performance with Hydrogen Fuel Using Conventional Fuel Cells

The fuel cell performance was investigated using various compositions in two ways:

- $\text{A}_2\text{Ce}_2\text{O}_{7-\delta}$ ($A = \text{La}^{3+}, \text{Nd}^{3+}, \text{Bi}^{3+}$) were used as an electrolyte in conventional SOFCs with LNCZ as an anode and LSFC as a cathode.
- For a single-component solid oxide fuel cell (SC-SOFC), a mixture of ionic- and semiconductors was used as a single layer. The performance was tested with the mixtures $\text{A}_2\text{Ce}_2\text{O}_{7-\delta}/\text{NCAL}$ and then $\text{A}_2\text{Ce}_2\text{O}_{7-\delta}/\text{ZnO}$.

The obtained fuel cell power for conventional devices is shown in Figure 13. The IV measurements of three devices NCZO/ $\text{La}_2\text{Ce}_2\text{O}_7$ /LSFC, NCZO/ $\text{Nd}_2\text{Ce}_2\text{O}_7$ /LSFC, and NCZO/ $\text{Bi}_2\text{Ce}_2\text{O}_7$ /LSFC were recorded. In Figure 13, it can be seen that the open circuit voltage (OCV) has values ~ 0.95 V, 0.97 V and 1.05 V for $\text{La}_2\text{Ce}_2\text{O}_7$, $\text{Nd}_2\text{Ce}_2\text{O}_7$ and $\text{Bi}_2\text{Ce}_2\text{O}_7$ electrolytes, respectively. Among them, NCZO/ $\text{Bi}_2\text{Ce}_2\text{O}_7$ /LSFC showed a maximum power density of $0.65788 \text{ W cm}^{-2}$ measured at 650°C . This indicates that the $\text{A}_2\text{Ce}_2\text{O}_7$ material can serve as a good electrolyte candidate.

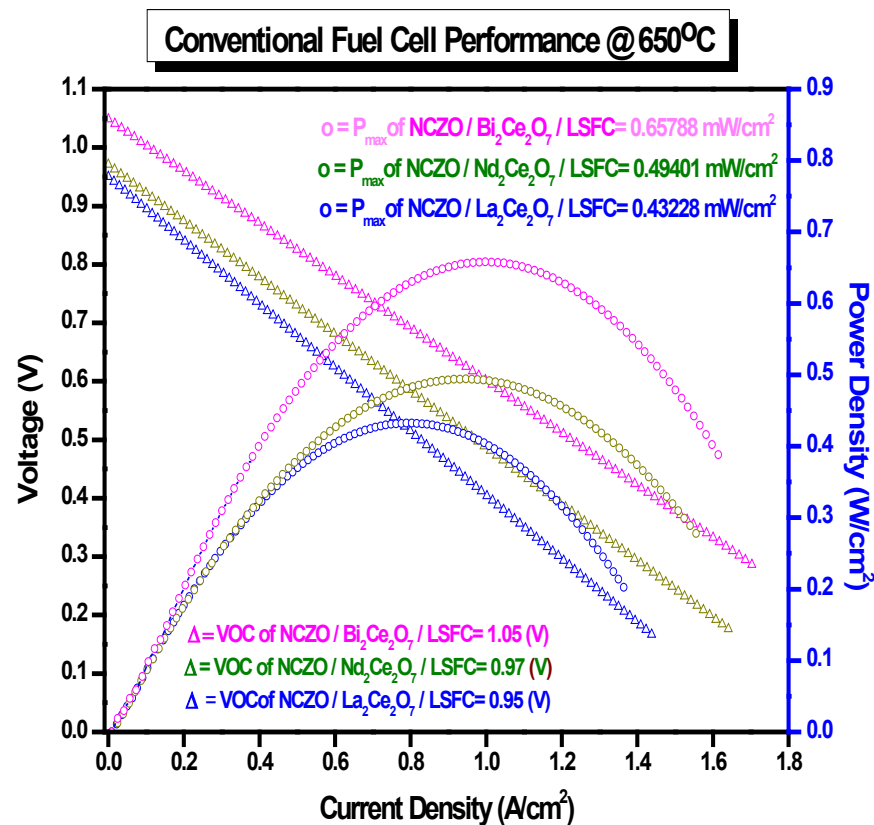


Figure 13. Conventional fuel cell performance with $\text{La}_2\text{Ce}_2\text{O}_7$, $\text{Nd}_2\text{Ce}_2\text{O}_7$ and $\text{Bi}_2\text{Ce}_2\text{O}_7$ as electrolyte materials using H_2 fuel at 650°C .

For a single-component device, the mixture of ionic- and semiconductors was taken with ratio $5\text{A}_2\text{Ce}_2\text{O}_7$ - 5NCAL . Figure 14 shows the fuel cell performance of $\text{La}_2\text{Ce}_2\text{O}_7/\text{NCAL}$, $\text{Nd}_2\text{Ce}_2\text{O}_7/\text{NCAL}$ and $\text{Bi}_2\text{Ce}_2\text{O}_7/\text{NCAL}$. Among them, $\text{Nd}_2\text{Ce}_2\text{O}_7/\text{NCAL}$ showed the maximum power output ($P_{\max}$), reaching 0.348 W cm^{-2} at 650°C , and the OCV reached as high as 0.966 V.

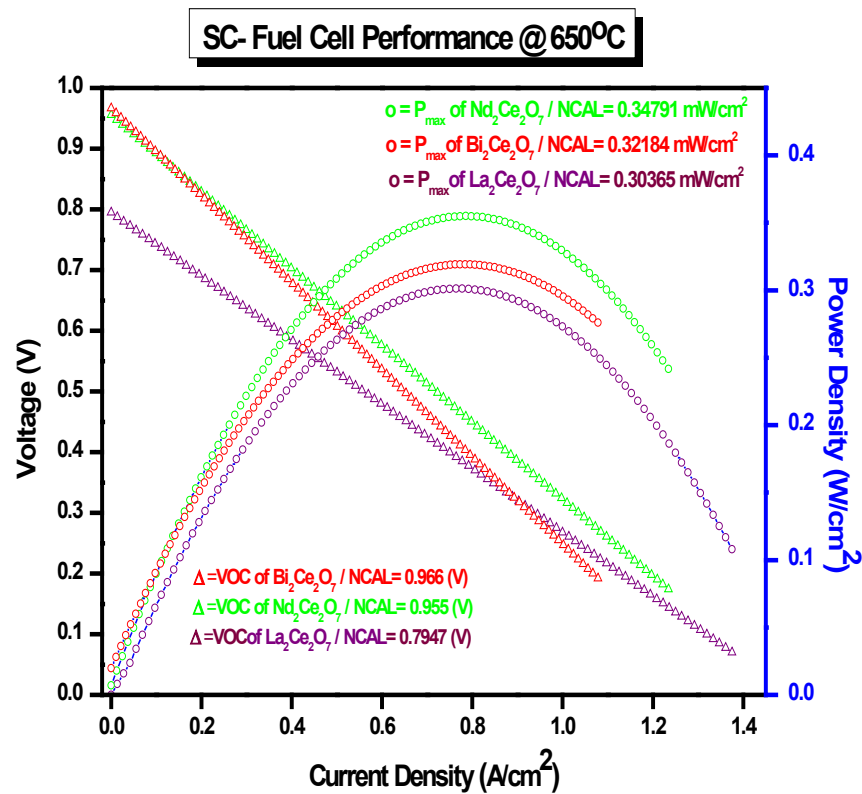


Figure 14. Fuel cell performance of $\text{La}_2\text{Ce}_2\text{O}_7/\text{NCAL}$, $\text{Nd}_2\text{Ce}_2\text{O}_7/\text{NCAL}$ and $\text{Bi}_2\text{Ce}_2\text{O}_7/\text{NCAL}$ nanocomposite materials for SC-SOFCs operated with H_2 fuel at 650°C .

Figure 15 shows the fuel cell performance of $\text{La}_2\text{Ce}_2\text{O}_7/\text{ZnO}$, $\text{Nd}_2\text{Ce}_2\text{O}_7/\text{ZnO}$, and $\text{Bi}_2\text{Ce}_2\text{O}_7/\text{ZnO}$. Among them, $\text{Nd}_2\text{Ce}_2\text{O}_7/\text{ZnO}$ showed the best performance as SC-SOFCs. It exhibited the maximum power output ($P_{\max}$), reaching 0.5899 W cm^{-2} at 650°C , and the OCV reached as high as 1.01 V .

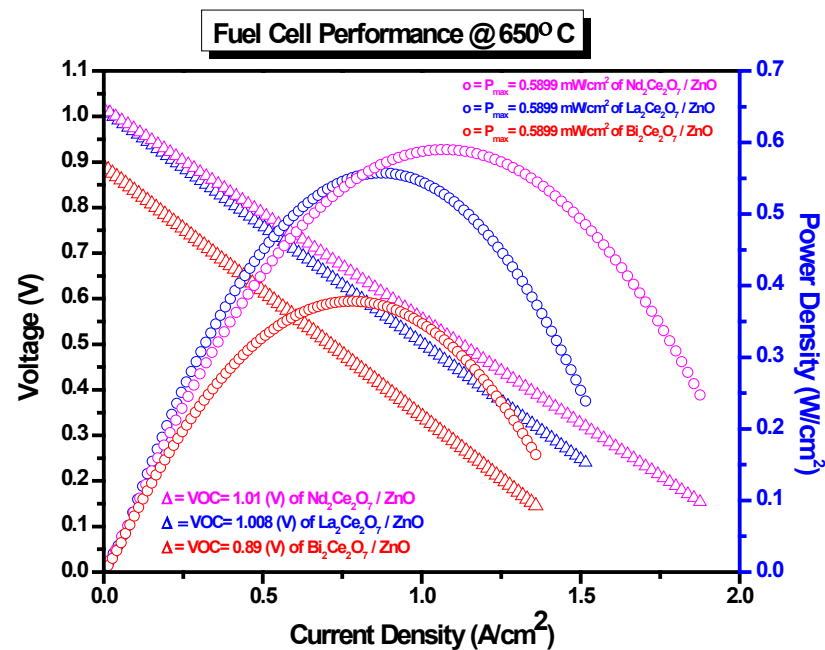


Figure 15. Fuel cell performance of $\text{La}_2\text{Ce}_2\text{O}_7/\text{ZnO}$, $\text{Nd}_2\text{Ce}_2\text{O}_7/\text{ZnO}$ and $\text{Bi}_2\text{Ce}_2\text{O}_7/\text{ZnO}$ nanocomposite materials for SC-SOFCs operated with H_2 fuel at 650°C .

The performance results show that the $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) are good candidates for conventional as well as for single-component SOFCs. Among them, $Bi_2Ce_2O_7$ showed the best performance as an electrolyte for conventional SOFCs, whereas $Nd_2Ce_2O_7$ showed the best performance as SC-SOFCs for both combinations.

4. Conclusions

The nanocomposite materials $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) were efficiently fabricated using the wet chemical method. The prepared composite materials were evaluated for conventional as well as for single-component SOFCs. The crystalline structure of $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) verified the defective cubic fluorite structure. The FTIR spectra confirmed that dopants were well settled in the ceria by their associated bands. The particles of all samples had irregular polygon morphology. The Tauc plot demonstrated an increase in band gap energy with a decrease in crystalline size, which might be due to the generation of oxygen vacancies (O_v). The Raman results confirmed the defective cubic fluorite structure. The EIS and fuel cell performance of conventional fuel cells showed that $Bi_2Ce_2O_7$ produced the best result with a maximum power density of 0.65788 W/cm^2 at 650°C . The EIS and fuel cell performance of $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) with NCAL as ionic and semiconductor composites showed the best performance of $Nd_2Ce_2O_7$, with a power density of 0.34 W/cm^2 . The fuel cell performance of $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) with ZnO as ionic and semiconductor composites again showed $Nd_2Ce_2O_7/\text{ZnO}$ as the best candidate for SC-SOFCs with a power density of 0.58 W cm^{-2} . The $Nd_2Ce_2O_7$ showed good agreement with ZnO as compared to NCAL for SC-SOFCs. Overall, $A_2Ce_2O_{7-\delta}$ ($A = La^{3+}, Nd^{3+}, Bi^{3+}$) proved to be worthy candidates for conventional as well as for single-component SOFCs.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en16145308/s1>.

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