Facile Soft Chemical Synthesis and Physical Characterization of Aluminum Doped CeO₂ Nanoparticles for Multiple Applications

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In this work, a simple facile preparation of $Ce_{1-x}Al_xO_{2-\delta}$ (where x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles by chemical synthesis route is reported. In the preparation, appropriate quantities of metal nitrate salts were dissolved in water alongwith required amount of sodium hydroxide as precipitant. The resultant precipitate mixture $[Ce(OH)_3 + Al(OH)_3]$ was washed with water, filtered, dried and heat treated to get the phase pure Al doped CeO_2 nanoparticles. The synthesized oxide materials were characterized by XRD, FTIR, particle size analysis, SEM and EDAX to understand their structural, functional and particle properties. The XRD patterns revealed the presence of cubic (FCC) crystalline structure in the samples. The presence of Al-O and Ce-O stretching mode of vibration was confirmed by FTIR analysis. The particle size of the materials was found in the range of 117.23 to 257.06 nm. Presence of nano and micron sized grains was noticed by SEM photographs. EDAX confirmed the presence of appropriate atomic weight percentage of elements in the samples. The results suggested that the prepared Al doped ceria nanoparticles can be useful in several applications.

Keywords: Aluminum, Ceria, Nanoparticles.

INTRODUCTION

Industrial revolution has resulted in the enhancement of manufacturing units, which in turn lead to the generation of waste products, such as harmful gases, effluents and other contaminants [1]. These toxic substances can contaminate the atmosphere further to cause air pollution and the exhaust harmful gases discharged from industries can react with the atmospheric moisture to form toxic acids which again pollute the environment in some way or other [2]. Nanotechnology is an emerging field which can help to reduce environmental pollution in many ways. Nanomaterials because of their large surface area and more surface energy, they can easily absorb greater amount of pollutants, thus retarding the discharge of pollutants [3]. Nanoparticle fuel additives in diesel and biodiesel have resulted in reducing carbon emission characteristics and shown excellent engine performance [4]. Materials at nanosize show a large surface area to volume ratio, which plays a vital role than the materials at macroscale [5]. Nanomaterials are classified into 0D, 1D, 2D and 3D, with the decrease in dimensionality and increase in the surface-to-volume ratio. The smaller dimensional

nanomaterials have high surface area compared to 3D nano-materials [6]. Controllable synthesis and novel design of these materials can enhance their properties further. It was reported that 1D nanomaterials based on metal oxide nanoparticles show unique physical and chemical properties and exhibit potential technological applications [7]. Metal oxide nanoparticles, *viz.* CuO [8], Al_2O_3 [9], AgO [10] and CeO_2 [11] have gained greater interest now-a-days because of their unique properties with respect to their size and shape. Among the metal oxide nanoparticles, CeO_2 nanoparticles pay much attention in recent years due to their excellent physico-chemical characteristics. The oxide of cerium is known as ceria or cerium(IV) oxide [12]. The high surface area to volume ratio in CeO_2 nanoparticles enables them to react effectively [13]. By controlling their size, the specific reactivity of ceria nanoparticles is enhanced compared to bulk ceria [13]. Ceria nanoparticles were prepared by various synthetic routes, such as sol-gel [14], combustion [15], solvothermal [16], solid-state [17], chemical precipitation [18], *etc.*

Ceria materials have used as an electrolyte material for solid oxide fuel cells (SOFCs) due to its relatively high oxygen ion

conductivity at intermediate temperatures of 500-650 ºC with low association enthalpy compared to zirconia based materials [19]. Ceria nanomaterials exhibit wide applications over environmental remediation especially as photocatalysts in the degradation of various organic pollutants present in water [20-22]. Ceria nanoparticles have shown to be a very good at catalyzing the decomposition of unburnt hydrocarbons and other small particle emissions due to their high surface to volume ratio [23]. Metals such as Ni, Co, Fe, Mg, Zn, Sm, *etc*. were doped in CeO_2 to improve their physico-chemical and catalytic behavior [24-26]. In this present study, we report the synthesis and characterization of $Ce_{1-x}Al_xO_{2-\delta}$ (where $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) nanoparticles by chemical synthesis route. The obtained results were discussed in order to use the prepare Al doped CeO_2 in multiple applications.

EXPERIMENTAL

Chemicals such as cerous nitrate hexahydrate (98%, SRL, India), aluminium nitrate nanohydrate (95.0%, Merck, India), sodium hydroxide (97%, Merck, India), ethanol (99.9%, China) were used in this study. The above chemicals were used as procured without any further purification. Double distilled water was used for all the reactions.

Synthesis of Al doped CeO_2 nanoparticles: Appropriate stoichiometric quantities of metal nitrate salts ($M = Ce^{3+}$ and Al^{3+}) were dissolved in known volume of double distilled water and taken in a beaker. Appropriate concentration of NaOH precipitant solution was prepared in double distilled water and taken in a burette. This NaOH solution was added dropwise to the metal nitrate solution and stirred continuously till the completion of precipitation reaction. The pH of the solution was maintained above 9 by adding few NaOH flakes. The entire mixture was stirred with a help of a magnetic stirrer at 800 rpm for about 2 h at room temperature. The precipitate mixture [$Ce(OH)_4$ + $Al(OH)_3$] was filtered using a Bückner funnel. The filtered precipitate was washed thoroughly with ethanol:water mixture. Then, the washed precipitate was dried in a hot air oven to 60 ºC for 2 h and calcination is done in a muffle furnace at varying temperatures of 150, 300,450 and 600 ºC for 2 h each. This will result in the formation of very fine phase pure Al doped CeO_2 ($Ce_{1-x}Al_xO_{2-\delta}$, where $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) nanoparticles. The amount of precursor salts used for the synthesis of CeO_2 and Al doped CeO_2 nanoparticles is shown in Table-1. The main reaction for the preparation of CeO_2 and Al doped CeO_2 is given below:

$$(1-x)\, Ce(NO_3)_3 + x\, Al(NO_3)_3 + 4\, NaOH \longrightarrow$$
$$Ce_{1-x}Al_xO_{2-\delta} + 4\, NaNO_3 + 2\, H_2O \qquad (1)$$
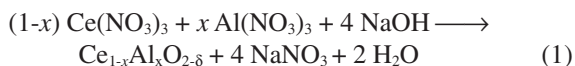
where $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5.

Characterization: The powdered X-ray diffraction (XRD) studies of parent CeO_2 and Al doped CeO_2 nanoparticles were carried out in Shimadzu XRD6000 X-ray diffractometer using CuKα (k = 0.154059 nm) radiation with a nickel filter with a voltage of 40 kV at 30 mA current. The 2θ scanning range was 2º to 80º at a continuous scan mode with a scan speed of 10º/min. The unit cell parameter was measured by DOS computer programming. The average crystallite size for the samples

TABLE-1
AMOUNT OF PRECURSOR SALTS USED FOR THE SYNTHESIS OF CeO_2 AND Al DOPED CeO_2 NANOPARTICLES [VOLUME OF EACH SOLUTION IS 10 mL]

Sample	Weight of $Ce(NO_3)_3$ (g)	Weight of $Al(NO_3)_3$ (g)	Weight of NaOH (g)
CeO_2	4.342	-	1.6
$Ce_{0.90}Al_{0.10}O_{2-\delta}$	3.907	0.375	1.6
$Ce_{0.80}Al_{0.20}O_{2-\delta}$	3.470	0.750	1.6
$Ce_{0.70}Al_{0.30}O_{2-\delta}$	3.030	1.120	1.6
$Ce_{0.60}Al_{0.40}O_{2-\delta}$	2.600	1.500	1.6
$Ce_{0.50}Al_{0.50}O_{2-\delta}$	2.170	1.875	1.6

was determined by Debye-Scherrer's formula. The IR spectral studies of parent CeO_2 and Al doped CeO_2 nanoparticles was measured by Fourier transform infrared spectra, Shimadzu (IR Prestige 21) Spectrophotometer, using KBr pellet technique in the range of 4000 to 400 cm⁻¹.The particle size analysis of the materials were measured using Malvern particle size analyzer. The surface morphology and the elemental composition of parent CeO_2 and Al doped CeO_2 nanoparticles were studied by scanning electron microscope (SEM JEOL JSM-6610) equipped with an energy dispersive X-ray (EDAX) spectrophotometer and operated at 20 kV.

RESULTS AND DISCUSSION

X-Ray diffraction studies: Fig. 1 illustrates the XRD patterns obtained on pure CeO_2 nanoparticles and Al doped CeO_2 nanoparticles synthesized by chemical precipitation method. The XRD patterns are in concurrence with the standard CeO_2 data (JCPDS card no. 65-5923). The samples are indexed to face centred cubic crystalline structure. The diffraction peaks found at 2θ values of 28.81º, 33.33º, 47.76º and 56.61º in parent CeO_2 correspond to (111), (200), (220) and (311) planes, respectively which are in good agreement with the XRD results of CeO_2 [27]. The XRD patterns of Al doped CeO_2 nanoparticles have high intensity diffraction peaks at 2θ values of 28.58º,
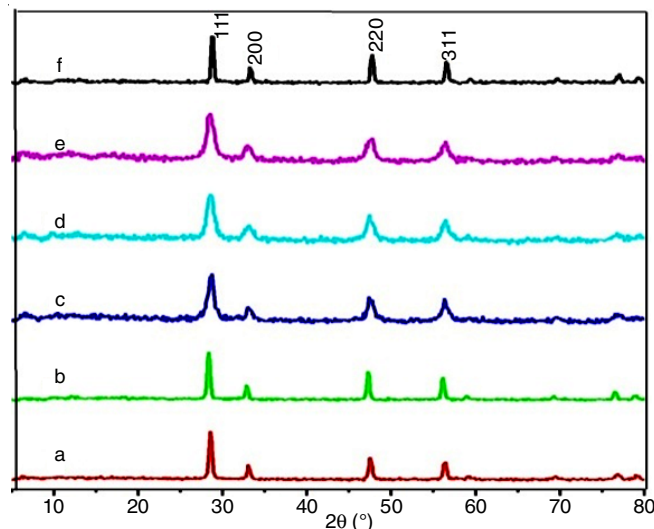

Fig. 1. XRD patterns obtained on CeO_2 based nanoparticles (a) Parent CeO_2, (b) $Ce_{0.90}Al_{0.10}O_{2-\delta}$, (c) $Ce_{0.80}Al_{0.80}O_{2-\delta}$, (d) $Ce_{0.70}Al_{0.30}O_{2-\delta}$, (e) $Ce_{0.60}Al_{0.40}O_{2-\delta}$, (f) $Ce_{0.50}Al_{0.50}O_{2-\delta}$

TABLE-2
CRYSTALLOGRAPHIC PARAMETERS OBTAINED ON PARENT CeO₂ AND Al DOPED CeO₂ NANOPARTICLES

Sample	Crystal structure	Unit cell parameter (Å)	Unit cell volume (Å³)	Crystallite size (nm)	Theoretical density (g cm⁻³)
Parent CeO₂	Cubic (F.C.)	5.39	156.59	20.69	7.3
Ce₀.₉₀Al₀.₁₀O₂₋δ	Cubic (F.C.)	5.41	158.42	17.8	6.74
Ce₀.₈₀Al₀.₂₀O₂₋δ	Cubic (F.C.)	5.42	159.22	19.4	6.23
Ce₀.₇₀Al₀.₃₀O₂₋δ	Cubic (F.C.)	5.41	158.42	9.45	5.79
Ce₀.₆₀Al₀.₄₀O₂₋δ	Cubic (F.C.)	5.42	159.22	8.26	5.29
Ce₀.₅₀Al₀.₅₀O₂₋δ	Cubic (F.C.)	5.41	158.42	7.6	4.84

33.11°, 47.54°, 56.39° corresponding to (111), (200), (220) and (311) planes, respectively whose *hkl* values were concurrent with the reported data [27]. The results revealed that all the samples had sharp peaks which show their crystalline behaviour. The crystallite size (D_x) was calculated by using Debye-Scherrer formula:

$$D_x = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where, β is the full width at half maximum (FWHM) of a diffraction peak, K is the shape factor approx. 0.91, λ is the wavelength of the X-ray source that equals 1.54 Å and θ is the Bragg's angle. The calculated crystallite size values of pure CeO₂ and Al doped CeO₂ are shown in Table-2. The crystallalite size of the samples varied between ranges from 7 to 20.69 nm, which is in line with the reported data *i.e.* 9.4 to 12.8 nm [28]. The theoretical density (D_p) was calculated by using eqn. 3:

$$D_p = \frac{Z*M}{N \times V}(g\ cm^{-3}) \quad (3)$$

where, Z = number of chemical species in the unit cell, M = molecular mass of the sample (g/mol), N = Avogadro's number (6.023×10^{23}); V = unit cell volume equals to a³ which is the lattice constant in cm. The theoretical density of the samples was in the range of 4.84 to 7.3 g/cc. The crystallographic parameters derived on parent CeO₂ and Al doped CeO₂ nanoparticles are presented in Table-2.

FTIR studies: Fig. 2 indicates the FTIR spectra obtained on CeO₂ and Al doped CeO₂ nanoparticles prepared by chemical precipitation method. The spectrum shows the absorption peak at 3432 cm⁻¹ attributed the O-H stretching vibration due to adsorbed water on the surface of CeO₂ nanoparticles. The peak corresponds to bending vibration of H-O-H was observed in the range of 1632 cm⁻¹. The absorption band at 452 and 1020 cm⁻¹ in the spectrum shows the presence of Al-O and Ce-O stretching mode of vibration which is in accordance with the reported data [29].

Particle size analysis: The particle size distribution curves of CeO₂ and Al doped CeO₂ nanoparticles are given in Fig. 3. The samples were sonicated in water for about 10 min and subjected for the particle size analysis. It was found that the samples are present in the range of 117.23 to 257.06 nm. The particles were present uniformly in the samples. The higher range of particles *i.e.* > 200 nm may be due to calcination process.

SEM studies: SEM images of parent CeO₂ and Al doped CeO₂ nanoparticles are shown in Fig. 4. It was found that the samples have both nano and micron sized grains. The presence
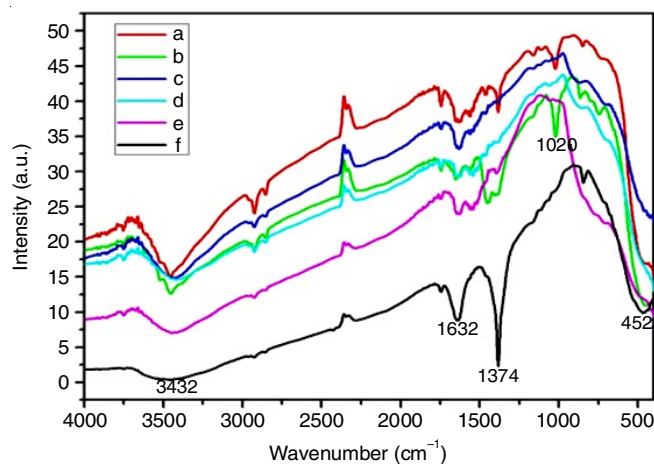

Fig. 2. FTIR spectra obtained on CeO₂ based nanoparticles (a) Parent CeO₂, (b) Ce₀.₉₀Al₀.₁₀O₂₋δ, (c) Ce₀.₈₀Al₀.₂₀O₂₋δ, (d) Ce₀.₇₀Al₀.₃₀O₂₋δ, (e) Ce₀.₆₀Al₀.₄₀O₂₋δ, (f) Ce₀.₅₀Al₀.₅₀O₂₋δ

of bigger sized grains in the sample may be due to the agglomeration effect because of calcination process. By adopting suitable heating rate during the calcination process, the grain structure of the materials may be controlled as reported [30].

EDAX studies: The elemental composition of CeO₂ and Al doped CeO₂ nanoparticles nanoparticles was derived from EDAX spectral analysis (Fig. 5). The occurrence of Ce, Al and O was confirmed in the samples by EDAX data. Further, the presence of appropriate quantities of elements was also confirmed through this analysis. The elemental composition data of the sample is shown in Table-3.

TABLE-3
ELEMENTAL COMPOSITION DATA OBTAINED ON
PARENT CeO₂ AND Al DOPED CeO₂ NANOPARTICLES

Sample	Atomic weight % of the elements		
	Ce	Al	O
Parent CeO₂	26.23	-	73.77
Ce₀.₉₀Al₀.₁₀O₂₋δ	25.70	3.03	71.27
Ce₀.₈₀Al₀.₂₀O₂₋δ	23.28	4.07	72.64
Ce₀.₇₀Al₀.₃₀O₂₋δ	22.53	7.42	70.05
Ce₀.₆₀Al₀.₄₀O₂₋δ	21.84	7.24	70.94
Ce₀.₅₀Al₀.₅₀O₂₋δ	16.84	20.48	62.68

Conclusion

Phase pure CeO₂ and Al doped CeO₂ (Ce₁₋ₓAlₓO₂₋δ, where x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles were prepared by simple facile chemical precipitation method. The XRD patterns
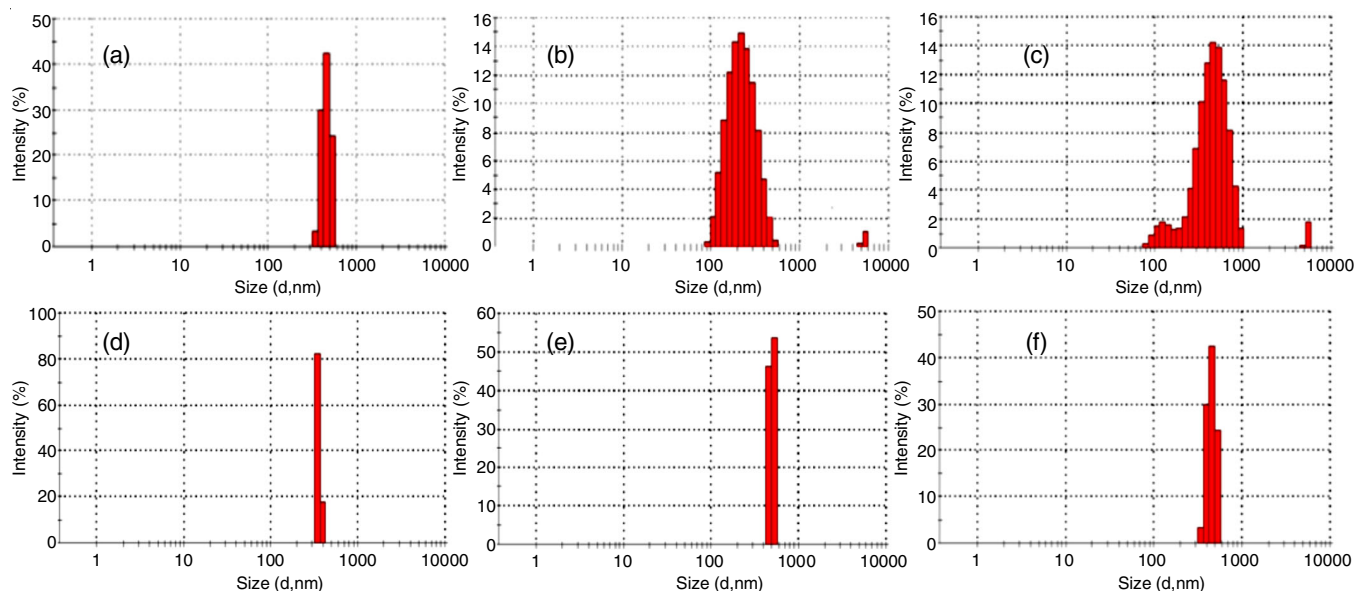
Fig. 3. Particle size analysis patterns obtained on CeO_2 based nanoparticles (a) Parent CeO_2, (b) $Ce_{0.90}Al_{0.10}O_{2-\delta}$, (c) $Ce_{0.80}Al_{0.80}O_{2-\delta}$, (d) $Ce_{0.70}Al_{0.30}O_{2-\delta}$, (e) $Ce_{0.60}Al_{0.40}O_{2-\delta}$, (f) $Ce_{0.50}Al_{0.50}O_{2-\delta}$
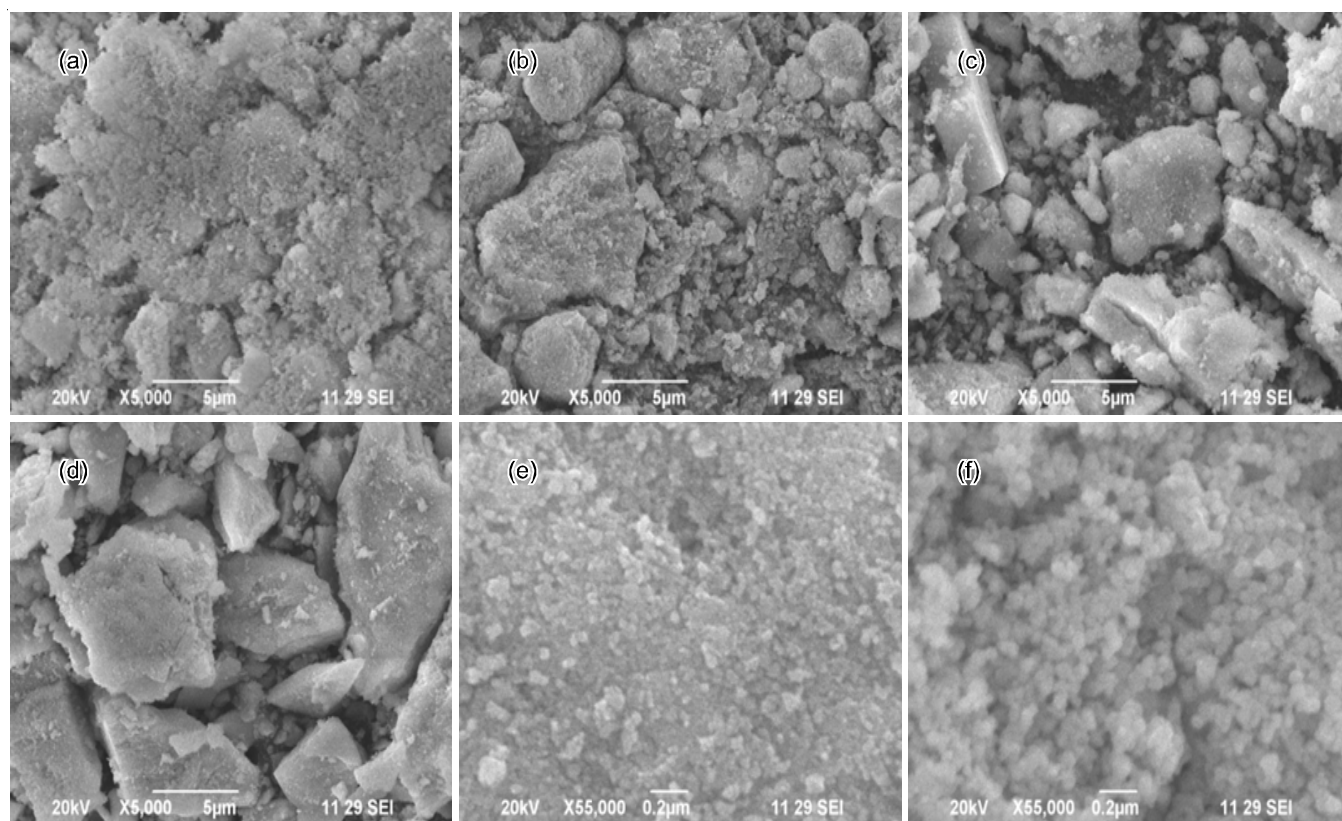

Fig. 4. SEM photographs obtained on CeO_2 based nanoparticles (A) Parent CeO_2, (b) $Ce_{0.90}Al_{0.10}O_{2-\delta}$, (c) $Ce_{0.80}Al_{0.80}O_{2-\delta}$, (d) $Ce_{0.70}Al_{0.30}O_{2-\delta}$, (e) $Ce_{0.60}Al_{0.40}O_{2-\delta}$, (f) $Ce_{0.50}Al_{0.50}O_{2-\delta}$

of the samples were indexed to cubic (FCC) structure as per the standard JCPDS data for CeO_2. The presence of Ce-O and Al-O stretching mode of vibration in the samples was confirmed by FTIR analysis. The particle size data confirmed presence of samples in the range of 117 to 257 nm. Presence of larger sized grains in the samples was revealed by SEM data. The grain structure of the samples may be controlled by choosing proper heating rate during the calcination process. Occurrence of Ce, Al and O in appropriate levels was confirmed by EDAX analysis. Based on the results, it was suggested that the facile synthesized Al doped CeO_2 based nanoparticles can be used in several applications.
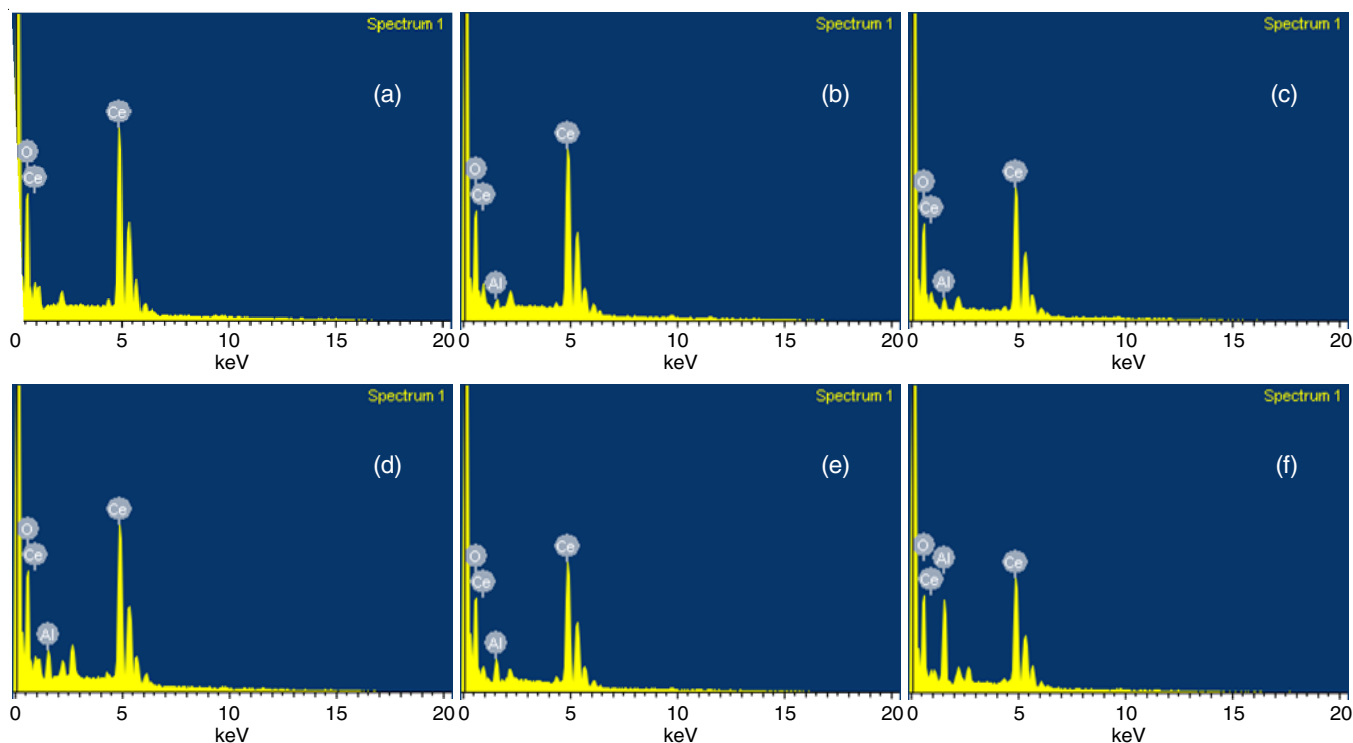
Fig. 5. EDAX spectra obtained on CeO$_2$ based nanoparticles (a) Parent CeO$_2$, (b) Ce$_{0.90}$Al$_{0.10}$O$_{2-\delta}$, (c) Ce$_{0.80}$Al$_{0.80}$O$_{2-\delta}$, (d) Ce$_{0.70}$Al$_{0.30}$O$_{2-\delta}$, (e) Ce$_{0.60}$Al$_{0.40}$O$_{2-\delta}$, (f) Ce$_{0.50}$Al$_{0.50}$O$_{2-\delta}$

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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