

Thermal Behavior, Phase Composition, and Surface Chemistry of a Multiphase C_x - NaO_x - La - O - CeO_2 Hybrid Material

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ABSTRACT

This study reports the synthesis and physicochemical characterization of a hybrid material composed of a carbonaceous matrix modified with lanthanum (La), cerium (Ce), and sodium (Na), designated Sample B. Thermoanalytical techniques, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were combined to examine its thermal behavior, phase composition, and surface chemical environments. The study is limited to material characterization and does not evaluate catalytic, chemical-sensing, electrical, or electrochemical performance.

Thermogravimetric (TG-DTG) and differential thermal analysis (DTA) revealed multistep behavior. Moisture and weakly retained species were removed at low temperature, while a broad exothermic event with a maximum at 469.6 °C was attributed predominantly to oxidation of the carbonaceous matrix, with possible overlapping decomposition and reorganization of the inorganic components. DTA alone does not demonstrate crystallization of CeO_2 , La_2O_3 , or another specific phase. XRD supported the coexistence of a low-order carbonaceous matrix with crystalline CeO_2 domains; La_2O_3 and Na_2CO_3 were considered probable, whereas $La(OH)_3$ remained provisional because of reflection overlap.

XPS qualitatively confirmed C, O, Na, La, and Ce at the surface. The corrected C 1s contributions at 284.80, 286.18, and 291.06 eV were compatible with C-C/C=C, overlapping C-O/C-OH/C-O-C environments, and a π - π^* shake-up satellite, respectively. The O 1s contribution at 532.73 eV was treated as an overlapping oxygenated envelope, whereas the component at 537.23 eV remained unresolved and was not assigned to a specific species. Na 1s confirmed sodium in oxygen-containing environments without differentiating NaOH, Na_2CO_3 , Na_2O -like species, or possible interfacial configurations. La 3d was compatible with La^{3+} -O environments, and Ce 3d qualitatively confirmed oxidized cerium; however, the available resolution did not permit reliable differentiation of individual La species, quantification of Ce^{3+}/Ce^{4+} , or determination of oxygen-vacancy concentration.

The combined results support a heterogeneous, multiphase structural model comprising a functionalized low-order carbon matrix, crystalline CeO_2 domains, La-O species, and probably partially carbonated sodium species. These findings establish the material's thermal, structural, and surface-chemical characteristics. Possible catalytic, adsorption, sensing, or electrochemical behavior remains unverified and requires dedicated functional tests, suitable control materials, quantitative composition analysis, and complementary textural, morphological, spectroscopic, and electrical measurements.

Keywords: activated carbon; ceria; lanthanum oxide; sodium species; thermal analysis; X-ray diffraction; XPS; hybrid material.

INTRODUCTION

Activated carbon, obtained from carbon-rich feedstocks such as biomass and lignocellulosic residues, is notable for its high surface area, porosity, and adsorption capacity. Its properties can be tailored by physical or chemical activation using agents such as NaOH, KOH, H_3PO_4 , and $ZnCl_2$, thereby enabling control of pore structure and surface chemistry [1–5].

The incorporation of inorganic species can modify the thermal stability, surface sites, and adsorptive and catalytic properties of carbon. In particular, combining a carbonaceous matrix with Na, La, and Ce species may produce multiphase hybrid materials with potential for CO_2 capture, CO/VOC oxidation, and gas purification [6–10].

In this work, the $C_x-NaO_x-La-O-CeO_2$ hybrid material is examined by TG–DTG/DTA, XRD, and XPS to relate heat treatment to the final phase composition and surface chemistry. The scope is restricted to physicochemical characterization; catalytic, sensing, and electrochemical performance are not evaluated.

Experimental Procedure and Equipment

Materials and Sample Preparation

Activated carbon derived from coconut shell, with an initial specific surface area of approximately 1200–1300 $m^2 g^{-1}$, was used as the support. NaOH, $La(NO_3)_3 \cdot 8H_2O$, and $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ were used as inorganic precursors; all were analytical grade with a stated purity above 99.9% (Aldrich).

The impregnated, dried, and uncalcined material was prepared in two consecutive stages. First, the activated carbon was impregnated with a saturated aqueous NaOH solution, and the resulting suspension was continuously stirred for 8 h to promote the incorporation and distribution of sodium species throughout the porous carbon support. $La(NO_3)_3 \cdot 8H_2O$ and $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ were then added in nominal proportions of 3.5 and 2.0 wt%, respectively. The mixture was continuously stirred for 12 h and dried at room temperature.

The impregnated, dried, and uncalcined material was designated Sample A and was divided into two fractions intended for different treatment and characterization stages.

(i) The first fraction was characterized by TG–DTG/DTA to study desorption of weakly retained species, removal of volatile compounds, decomposition of the inorganic precursors, and oxidation of the impregnated activated-carbon matrix.

(ii) The second fraction underwent a single non-isothermal heat treatment in air at atmospheric pressure. Heating began at room temperature, approximately 25 °C, and was carried out gradually under automatic control. After 300 °C was reached, the temperature continued to rise progressively to 600 °C. The thermal trajectory from 300 to 600 °C lasted a total of 2 h and did not include a constant-temperature holding stage.

At the end of the 2 h trajectory and upon reaching the final temperature of 600 °C, the heating system switched off automatically. The sample remained inside the equipment and cooled naturally to room temperature without forced cooling. The completely cooled solid product was therefore identified as Sample B and was used for XRD and XPS.

Characterization Techniques and Equipment

The initial specific surface area of the activated-carbon support was determined by the BET method using a Micromeritics FlowSorb II 2300. This measurement characterized the support before precursor incorporation and was not used as the final surface area of Sample B.

The thermal behavior of Sample A was investigated by TG–DTG/DTA using a TA Instruments TGA 2050 under air, from 80 to 1000 °C, at a heating rate of 20 °C min^{−1}. Sample B was structurally characterized using a Rigaku XRD-6000 diffractometer with Cu K α radiation over approximately $2\theta = 5\text{--}50^\circ$. Phases were assigned by comparison with JCPDS/ICDD references. Because of the multiphase character and partial overlap of the reflections, assignments were classified by confidence and correlated with XPS and TG–DTG/DTA. The CeO₂ (311) reflection expected near 56.3° was outside the measured range and was not used as evidence.

The elemental composition and surface chemical environments of Sample B were analyzed by XPS using a VSW HA100 analyzer and Al K α radiation (1486.6 eV). Spectra were acquired at a pass energy of 44 eV under ultrahigh vacuum on the order of 10^{−9}–10^{−10} mbar. Instrumental resolution was approximately 1.6 eV, determined from Au 4f_{7/2}. The C 1s, O 1s, Na 1s, La 3d, and Ce 3d regions were examined.

In the general equipment description, the energy scale was referenced to C 1s at 284.5 eV. The detailed charge-correction procedure applied to the reported spectra is specified below.

Charge correction was performed by provisionally setting the C–C/C=C contribution of C 1s to 284.80 eV. Because its maximum was recorded at 286.82 eV, a uniform shift of −2.02 eV was applied:

$$E_{B,\text{corr}} = E_{B,\text{exp}} - 2.02 \text{ eV}$$

This correction preserves relative energy separations within the available spectra. Nevertheless, differential charging between carbonaceous and inorganic domains cannot be fully excluded when interpreting absolute binding energies. Assignments were therefore described as compatible, qualitative, or provisional whenever the evidence did not permit exclusive identification.

Sample identification and applied techniques

Sample	Material state	Preparation treatment or	Main conditions	Techniques	Purpose
Sample A	Impregnated, dried, and uncalcined	NaOH impregnation for 8 h; addition of 3.5 wt% La(NO ₃) ₃ ·8H ₂ O and 2.0 wt% (NH ₄) ₄ Ce(SO ₄) ₄ ·2H ₂ O; 12 h stirring; room-temperature drying	Coconut-shell activated carbon; initial area 1200–1300 m ² g ^{−1} ; precursor purity >99.9%	TG–DTG/DTA	Identify desorption, volatile removal, precursor decomposition, and carbon-matrix oxidation events
Sample B	Solid obtained from the second fraction of Sample A	Single non-isothermal treatment followed by natural cooling in the apparatus	Air; atmospheric pressure; ~25→600 °C; 300–600 °C in 2 h; no isothermal hold or forced cooling	XRD and XPS	Determine crystalline structure/phases and surface elemental composition/chemical states

Sample A → non-isothermal heating in air (25→600 °C; 300–600 °C over 2 h; no isothermal hold) → Sample B → XRD/XPS

Experimental Characterization

Thermal analysis of Sample A by TG–DTG

To investigate the thermochemical evolution of Sample A—the impregnated, dried, and uncalcined material—thermogravimetric, derivative thermogravimetric, and differential thermal analyses (TG–DTG/DTA) were performed in an oxidizing air atmosphere. These techniques delineated the mass-loss intervals associated with removal of adsorbed species, decomposition of the inorganic precursors, and progressive oxidation of the carbonaceous matrix. The TG–DTG curve shown in Figure 1 revealed multistep thermal behavior. The first event, with a DTG maximum at 56.10 °C and an approximate mass loss of 2.10%, was attributed mainly to desorption of physically adsorbed water and partial removal of water associated with the hydrated precursors.

The second stage, characterized by an approximate mass loss of 9.12% and a DTG maximum at 324.12 °C, was related to progressive decomposition of the lanthanum and cerium precursors, accompanied by release of volatile species derived from nitrate, sulfate, and ammonium groups. Transformations of oxygen-containing functional groups on the activated-carbon surface may also have occurred in this interval. The inflection observed near 383.63 °C indicated continuation of these thermal transformations and the onset of more significant oxidation of the carbonaceous matrix. Between 400 and 600 °C, a gradual mass loss was recorded and attributed to superposition of residual-species decomposition and partial oxidation of the carbon support.

Above 600 °C, the most intense mass loss occurred. Events recorded near 741.07 and 850.73 °C, jointly associated with an approximate mass loss of 30.29%, were attributed predominantly to oxidation and combustion of residual carbon in air. In parallel, the more thermally stable inorganic species remained in the solid residue. DTA, shown in Figure 2, complemented the thermogravimetric interpretation. The signal near 92.5 °C was associated mainly with removal of water and other weakly retained species. The principal exothermic event near 469.6 °C was related predominantly to oxidation of the carbonaceous matrix, possibly accompanied by simultaneous transformations of the incorporated inorganic species. Taken together, TG–DTG/DTA delineated the principal thermal-transformation intervals of Sample A during heating in air. Nevertheless, these techniques cannot unequivocally identify specific phases such as La_2O_3 , CeO_2 , and Na_2CO_3 or reliably differentiate other sodium species. The thermochemical interpretation was therefore subsequently contrasted with the XRD and XPS results obtained for Sample B.

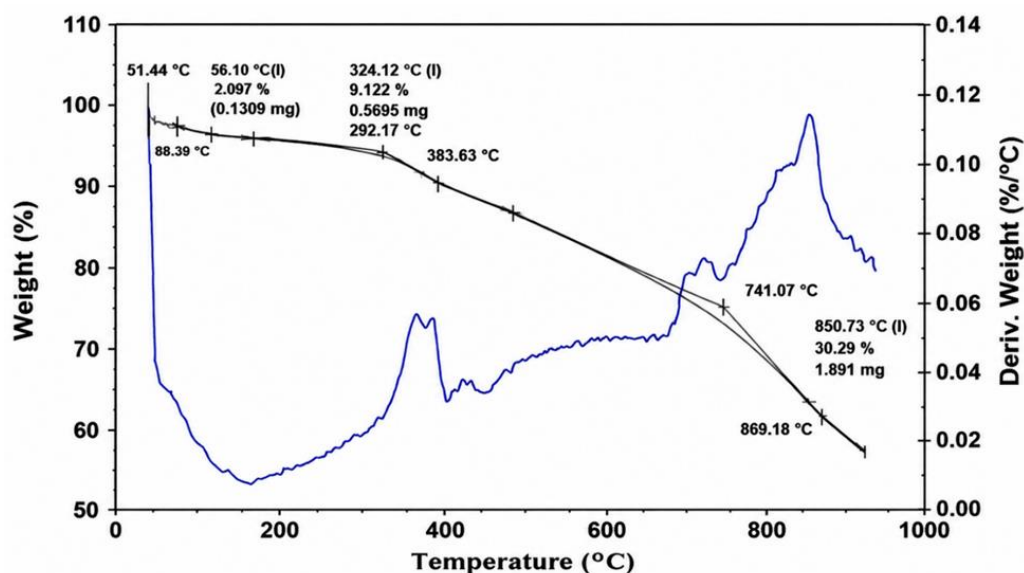


Figure 1. Thermogravimetric and derivative thermogravimetric (TG–DTG) curves of Sample A—the impregnated, dried, and uncalcined material—recorded during heating in oxidizing air. The main mass-loss events

are associated with initial desorption/dehydration, inorganic-precursor decomposition, and progressive oxidation of the carbonaceous matrix.

Thermoenergetic evolution of Sample A by DTA

DTA identified two principal thermoenergetic regions during heating in air (Figure 2). The low-intensity endothermic event near 92.5 °C was attributed mainly to desorption of water and other weakly retained species, consistent with the first TG–DTG mass loss. At higher temperature, a broad exothermic signal with a maximum near 469.6 °C was observed. Under the instrument convention of upward exothermic direction (Exo Up), this feature represents net energy release from simultaneous, partially overlapping processes, including progressive carbon-matrix oxidation, decomposition of residual precursor species, and reorganization of La-, Ce-, and Na-containing components.

The breadth of the event indicates that it does not represent a single reaction. Accordingly, formation of CeO_2 , La_2O_3 , Na_2CO_3 , or specific Na–O–C configurations cannot be established from DTA alone. Likewise, the declining DTA signal above 500 °C does not imply complete thermal stability because TG–DTG shows substantial residual-carbon oxidation at higher temperatures. The approximate 400–500 °C interval is therefore a relevant thermoenergetic region for carbon-matrix transformation and evolution of the inorganic species.

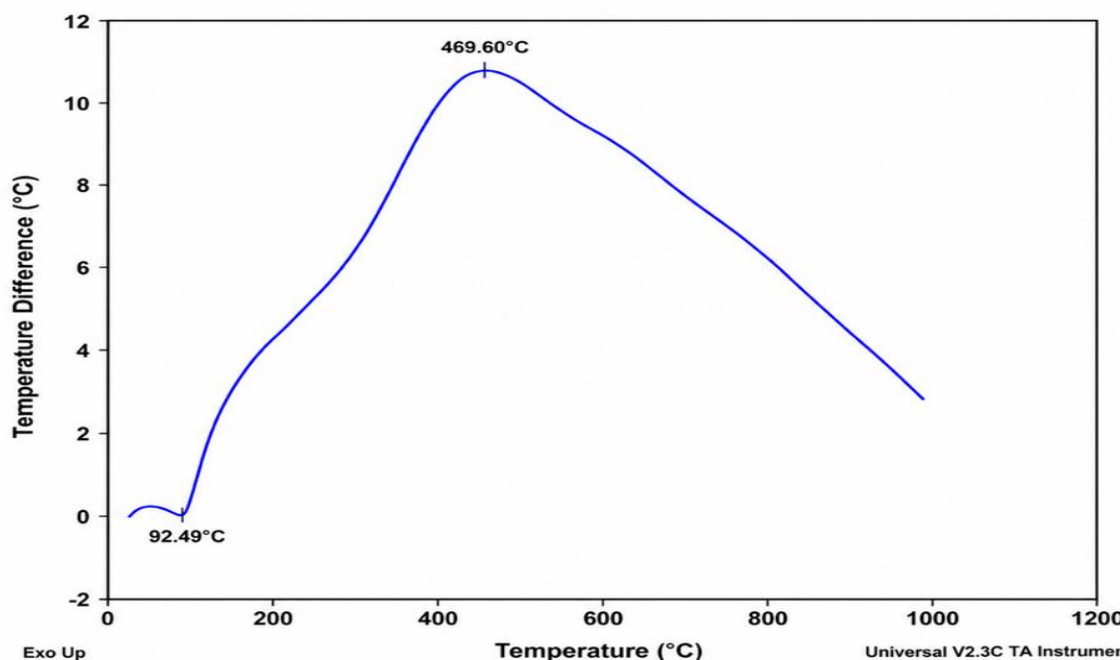


Figure 2. Differential thermal analysis (DTA) curve of Sample A in oxidizing air, showing the low-intensity endothermic event near 92.5 °C and the principal exothermic event with a maximum at 469.6 °C (Exo Up).

Table 2. Thermal transformation intervals and proposed thermochemical assignments for Sample A

Temperature range	Experimental evidence	Thermochemical interpretation	Possible species	Predominant process
≈25–200 °C	DTG maximum 56.10 °C; 2.097% (0.1309 mg) loss; minor changes near 51.44 and 88.39 °C	Removal of surface moisture and part of the precursor hydration water	Adsorbed H_2O ; hydration water; weakly retained volatiles	Initial desorption and dehydration

≈200–292 °C	Slow progressive loss; no clearly defined DTG maximum	Advanced dehydration and onset of precursor/surface-group transformation	Residual water; oxygen groups; La, Ce, and Na precursor species	Advanced dehydration and initial decomposition
≈292–384 °C	Onset ≈292.17 °C; DTG maximum 324.12 °C; 9.122% (0.5695 mg) loss; inflection 383.63 °C	Overlapping decomposition of La/Ce precursors and evolution of carbon functionalities	Precursors and derivatives; NO _x , NH ₃ , H ₂ O, sulfur species; C–O/C=O groups	Main inorganic-precursor decomposition
≈384–600 °C	Continuous mass decrease and overlapping DTG signals	Residual decomposition and increasingly significant carbon oxidation; consolidation of stable inorganic species may occur	Reactive carbon; nitrate/sulfate/ammonium residues; oxidized La/Ce and Na species	Residual decomposition and partial carbon oxidation
≈600–741 °C	Accelerating mass loss; slope change near 741.07 °C	Intensified carbon oxidation with overlapping inorganic transformations	C _x , oxygen groups, supported inorganic species	Onset of intense residual-carbon oxidation
≈741–869 °C	Main loss stage; event near 850.73 °C; 30.29% (1.891 mg) loss; end near 869.18 °C	Predominant oxidation/combustion of residual carbon and relative enrichment of stable inorganic residue	Residual carbon and stable La, Ce, and Na species	Carbon-support combustion and inorganic-residue formation

Note. Species listed are thermochemically compatible assignments based on the initial composition and TG–DTG behavior. Thermal analysis alone does not confirm formation of specific CeO₂, La₂O₃, or Na₂CO₃ phases. In this work, NaO_x collectively denotes NaOH, Na₂CO₃, possible Na₂O-like species, and potential Na–O–C/Na–O–La/Na–O–Ce interfacial configurations. The techniques used do not directly demonstrate specific interfacial bonds. In this study, the expression NaO_x is used as a collective designation for the different sodium species that may be present or evolve during impregnation and thermal treatment, including NaOH, Na₂CO₃, and possible Na₂O-like species. Potential interfacial configurations, such as Na–O–C, Na–O–La, and Na–O–Ce, may also be considered. However, the techniques employed do not provide direct evidence of specific interfacial bonds.

Structural Characterization of Sample B by X-ray Diffraction

The XRD pattern of Sample B displayed numerous defined reflections between $2\theta \approx 9$ and 48° , superimposed on a broad, variable background (Figure 3). This behavior indicates crystalline inorganic domains dispersed within a low-order carbonaceous matrix and confirms the structurally heterogeneous, multiphase nature of the material. Phase assignments were based on comparison with JCPDS/ICDD patterns and literature data. Because CeO₂, La₂O₃, Na₂CO₃, and La(OH)₃ reflections overlap substantially, confidence was based on the joint agreement of several signals rather than on isolated maxima.

The positions, proposed planes, and corresponding correlations are presented in Table 3. The assignments were expressed at different confidence levels because several candidate phases contribute in the same angular regions.

The highest-confidence assignment was cubic fluorite CeO₂, supported by signals near 28.5 – 29.0° , 32.5 – 33.1° , and 47.5 – 48.3° , compatible with the (111), (200), and (220) reflections. Regions near 25.8 – 26.2° , 30.0 – 30.5° , 39.5 – 40.0° , and 47.5 – 48.3° were compatible with hexagonal La₂O₃ but overlapped other phases; La₂O₃ was therefore regarded as probable with moderate confidence. Na₂CO₃ formation was chemically plausible because NaOH could react with atmospheric or process-generated CO₂. Signals near 30.0 – 30.5° , 36.8 – 37.2° , and 38.2 – 38.5° supported a probable carbonate contribution, but no isolated peak was exclusive to Na₂CO₃. La(OH)₃ remained provisional, mainly because its possible reflections near 39.5 and 48.0° overlapped La₂O₃ and CeO₂.

Although the CeO_2 regions contain contributions from other phases, the joint agreement of all three characteristic reflections provides reasonable evidence for formation of crystalline CeO_2 domains.

The signals near $25.8\text{--}26.2^\circ$, $30.0\text{--}30.5^\circ$, $39.5\text{--}40.0^\circ$, and $47.5\text{--}48.3^\circ$ are compatible with hexagonal La_2O_3 . However, these reflections overlap CeO_2 and possible carbonated or hydroxylated species. The presence of La_2O_3 was consequently considered probable, with moderate confidence, rather than unequivocally identified.

Previous incorporation of NaOH and its possible reaction with CO_2 during drying, heat treatment, or subsequent air exposure make formation of Na_2CO_3 chemically plausible. Signals at approximately $30.0\text{--}30.5^\circ$, $34.0\text{--}35.0^\circ$, $36.8\text{--}37.2^\circ$, $38.2\text{--}38.5^\circ$, and $44.2\text{--}44.8^\circ$ are compatible with this phase. In particular, the intense reflections near $34\text{--}35^\circ$ and $44\text{--}45^\circ$ indicate that crystalline sodium species must be considered, although overlap prevents their exclusive attribution to Na_2CO_3 .

The possible presence of $\text{La}(\text{OH})_3$ was retained as a provisional assignment, mainly from coincidences near 39.5 and 48.0° . Because these signals may also contain La_2O_3 and CeO_2 contributions, the diffractogram does not conclusively distinguish oxidized and hydroxylated lanthanum species.

Low-angle features near 9.3° , 18.2° , and 22.3° were not treated individually as conclusive evidence of carbon. The low-order carbon contribution was recognized chiefly through diffuse background and broad intensity in the approximate $20\text{--}30^\circ$ region. Narrower low-angle maxima may include unresolved inorganic or partially ordered structures.

Overall, the XRD pattern demonstrates that Sample B has a multiphase architecture comprising a low-order carbonaceous matrix and several crystalline inorganic domains. CeO_2 has the highest-confidence assignment, whereas La_2O_3 and Na_2CO_3 are considered probable phases and $\text{La}(\text{OH})_3$ a provisional contribution. Because the reflections overlap, these assignments were contrasted with the composition and surface chemical states determined by XPS.

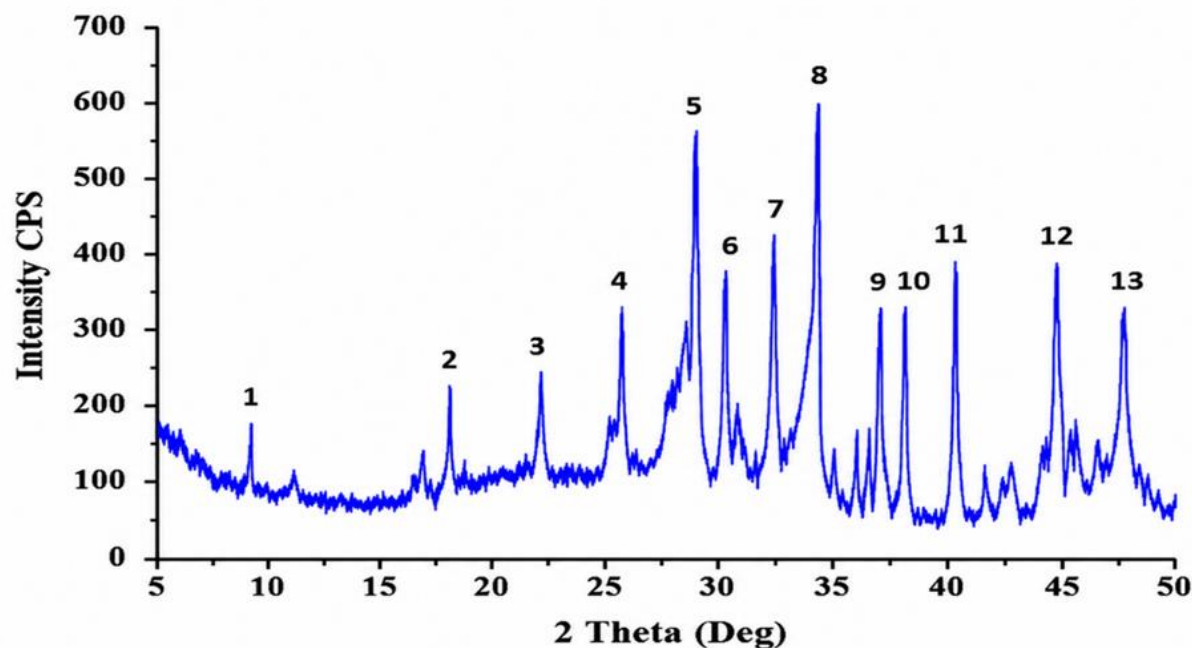


Figure 3. X-ray diffraction pattern of Sample B, with the main signals numbered and regions compatible with contributions from the low-order carbonaceous matrix and possible CeO_2 , La_2O_3 , Na_2CO_3 , and $\text{La}(\text{OH})_3$ phases. Individual assignments have different confidence levels because of reflection overlap.

Table 3. Crystallographic assignments and thermostructural correlation of Sample B reflections

Obs .	2 θ (°)	Proposed assignment	Plane/structure	JCPD S/ICD D	Relation to thermal behavior	Structural interpretation	Confidence	Ref.
1	≈9.3	C _x or secondary contribution	Undetermined	—	Partial preservation of the carbon matrix after treatment	Non-diagnostic low-angle signal; may contain unresolved secondary contributions	Low	[11]
2	≈18.2	C _x or secondary phase	Undetermined	—	Possible reorganization of carbon or incorporated species	Must not be assigned exclusively to carbon or Na ₂ CO ₃ without complementary evidence	Low	—
3	≈22.3	C _x with possible secondary contribution	Low-order carbon	—	Persistence of the carbon fraction after treatment	Compatible with diffuse disordered carbon, but not independently diagnostic	Low–medium	[11]
4	≈25.8–26.2	La ₂ O ₃ + possible C _x	Hexagonal La ₂ O ₃ , near (100); disordered carbon	05-0602	Compatible with thermal transformation of the La precursor	Possible La ₂ O ₃ reflection overlapping the carbon-matrix contribution	Medium	[11, 12]
5	≈28.5–29.0	CeO ₂ + possible La ₂ O ₃	CeO ₂ (111), cubic fluorite; nearby La ₂ O ₃ reflection	34-0394/05-0602	Compatible with Ce-precursor transformation and evolution of La species	First characteristic CeO ₂ reflection, with possible partial overlap	High for CeO ₂	[12, 13]
6	≈30.0–30.5	La ₂ O ₃ + possible Na ₂ CO ₃	La ₂ O ₃ (101)/Na ₂ CO ₃	05-0602/37-0451	Compatible with precursor transformation and evolution of sodium species	Overlap region to which La ₂ O ₃ and Na ₂ CO ₃ may both contribute	Medium/overlapped	[12, 14]
7	≈32.5–33.1	CeO ₂	CeO ₂ (200), cubic fluorite	34-0394	Compatible with formation of a stable oxidized Ce phase	Second characteristic CeO ₂ reflection; assignment to La(OH) ₃ is less probable	High	[13, 15]
8	≈34.0–35.0	Possible sodium carbonate or secondary phase	Not unequivocally determined	—	Possible thermal evolution of sodium species	An isolated coincidence does not permit unequivocal Na ₂ CO ₃	Low	[14]

						assignment		
9	≈36.8–37.2	Possible Na ₂ CO ₃ or secondary phase	Sodium carbonate/secondary structure	37-0451, possible	Compatible with carbonated species after treatment	Compatible with Na ₂ CO ₃ but not independently diagnostic	Low–medium	[14]
10	≈38.2–38.5	Na ₂ CO ₃ + possible secondary contribution	Sodium carbonate	37-0451	Compatible with thermal evolution of sodium species	Consistent with a Na ₂ CO ₃ reflection, although overlap may occur	Medium	[14]
11	≈39.5–40.0	La ₂ O ₃ + possible La(OH) ₃	La ₂ O ₃ (102) + La(OH) ₃ (201)	05-0602/3 6-1481	Compatible with transformation and reorganization of La species	XRD cannot conclusively separate La ₂ O ₃ and La(OH) ₃ contributions	Medium/overlapped	[12, 15]
12	≈44.2–44.6	Unresolved secondary phase	Undetermined	—	Possible minor inorganic phase after treatment	No specific assignment is recommended without refinement or complementary evidence	Low	—
13	≈47.5–48.3	CeO ₂ + La ₂ O ₃ + possible La(OH) ₃	CeO ₂ (220) + possible La-phase contributions	34-0394/0 5-0602/3 6-1481	Compatible with crystalline inorganic phases remaining after treatment	Strong overlap; agreement with CeO ₂ (111) and (200) reinforces CeO ₂ identification	High for CeO ₂ ; moderate/provisional for La phases	[12, 13, 15]

Note. CeO₂ has the highest-confidence assignment; La₂O₃ and Na₂CO₃ are probable, whereas La(OH)₃ remains provisional. Signals 1, 2, and 12 do not identify a specific phase unequivocally. Because XRD was performed only on Sample B and no *in situ* or temperature-resolved series was acquired, the data do not directly establish progressive structural evolution during heating.

Taken together, the XRD analysis indicates that **Sample B** exhibits a multiphase structure consisting of a low-order C_x carbonaceous matrix and crystalline inorganic domains. Fluorite-type CeO₂ represents the assignment with the highest level of confidence; the presence of La₂O₃ is considered probable, with moderate confidence because of the overlap of its reflections; carbonated sodium species, particularly Na₂CO₃, are also considered probable; and La(OH)₃ remains a provisional assignment.

Correlation with the TG–DTG/DTA results makes it possible to associate these phases with the general temperature ranges of precursor decomposition and thermal transformation. However, because XRD analysis was performed only on **Sample B**, and no *in situ* measurements or measurements at different temperatures were conducted, the results do not directly demonstrate progressive structural evolution during heating. The chemical nature of the species present at the surface is subsequently examined by XPS

Structural Contribution of the C_x Carbonaceous Matrix

The signals observed near $2\theta \approx 9.3^\circ$ and 18.2° , together with the broadened contribution near 22.3° , were cautiously associated with a structurally low-order C_x carbonaceous matrix. This behavior is compatible with limited local organization and the absence of long-range crystallographic periodicity. Likewise, the narrow and intense reflections characteristic of a highly ordered graphitic structure were not observed.

The contribution near 22.3° may be related to disordered carbonaceous domains that retain a certain degree of local organization, but it does not constitute unequivocal evidence of graphitization. The low-angle signals near 9.3° and 18.2° may also include contributions from intercalated species, partially ordered structures, or unresolved secondary phases. Therefore, their individual assignment to C_x is maintained at a low confidence level.

The persistence of these contributions in the diffractogram of **Sample B** indicates that a fraction of the carbonaceous matrix was preserved after heat treatment in air. This interpretation is consistent with the TG–DTG/DTA results obtained for **Sample A**, which revealed transformation of the inorganic precursors and progressive, but not immediate, oxidation of the carbonaceous support.

From a structural perspective, defects, edges, cavities, and oxygen-containing functional groups in the matrix may act as anchoring sites for Na, La, and Ce species and may partially restrict the growth of the inorganic domains. However, conventional XRD does not directly demonstrate their spatial dispersion, their location within the porous structure, or the formation of specific chemical bonds with carbon.

Consequently, C_x is described as a predominantly disordered carbonaceous matrix that was partially preserved after heat treatment and acts as a structural support for the inorganic domains present in Sample B.

Identification of CeO_2 : Crystalline Phase with the Highest Confidence

The identification of CeO_2 constitutes the most robust crystallographic assignment for Sample B. The reflections located at $2\theta \approx 28.5\text{--}29.0^\circ$, $32.5\text{--}33.1^\circ$, and $47.5\text{--}48.3^\circ$ are compatible with the (111), (200), and (220) planes, respectively, of the cubic fluorite-type CeO_2 structure, according to JCPDS/ICDD pattern 34-0394 (Table 3). The agreement of this sequence of reflections permits the phase to be assigned with a high level of confidence, although the regions corresponding to the (111) and (220) planes may contain partial contributions from lanthanum phases.

The fluorite-type structure can accommodate defects associated with oxygen vacancies and different surface chemical environments of cerium. However, XRD primarily confirms the presence and crystalline symmetry of CeO_2 , whereas determination of the oxygen-vacancy concentration and quantification of the Ce^{3+}/Ce^{4+} ratio require complementary spectroscopic techniques and higher-resolution data.

The presence of CeO_2 is consistent with the general thermal transformation of the cerium precursor observed by TG–DTG/DTA. Nevertheless, the event near 324°C corresponds to a global transformation of Sample A and therefore must not be attributed directly to the nucleation or crystallization of CeO_2 . Determining the sequence and temperature of formation of this phase would require *in situ* XRD measurements or a series of diffractograms obtained at different temperatures.

Crystallite size was not estimated using the Scherrer equation because such an estimation requires determination of the full width at half maximum of the reflections, correction for instrumental broadening, and rigorous separation of the overlapping signals. Consequently, the results support, with high confidence, the presence of crystalline CeO_2 domains with a cubic fluorite-type structure in Sample B. Detailed determination of their microstructural parameters and formation sequence during heat treatment represents a complementary stage for future studies.

Identification of La_2O_3 and Evolution of Lanthanum Species

The regions located at $2\theta \approx 25.8\text{--}26.2^\circ$, $28.5\text{--}29.0^\circ$, $30.0\text{--}30.5^\circ$, $39.5\text{--}40.0^\circ$, and $47.5\text{--}48.3^\circ$ are compatible with different reflections of hexagonal La_2O_3 , according to JCPDS/ICDD pattern 05-0602 (Table 3). The first region may include a contribution from the La_2O_3 (100) plane superimposed on the signal from the carbonaceous matrix;

the second partially coincides with the CeO_2 (111) reflection; the third may contain contributions from Na_2CO_3 ; and the final two regions overlap CeO_2 and possible hydroxylated lanthanum species.

Because of these overlaps, the presence of La_2O_3 is considered probable, with a moderate level of confidence. The joint agreement of several regions with the crystallographic pattern supports this assignment, although the individual contributions cannot be completely separated by direct inspection of the diffractogram.

The presence of oxidized lanthanum species is consistent with dehydration, removal of nitrate groups, and thermal transformation of the $\text{La}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ precursor. However, the event near 324°C corresponds to a global transformation of Sample A and must not be interpreted as the specific nucleation or crystallization temperature of La_2O_3 .

Furthermore, the affinity of lanthanum species for atmospheric H_2O and CO_2 may promote hydration or carbonation processes during cooling, handling, or storage. This reactivity must be considered when interpreting the possible contributions of $\text{La}(\text{OH})_3$ and other surface lanthanum species.

Taken together, the results support the probable presence of hexagonal La_2O_3 domains in Sample B, with moderate confidence conditioned by the overlap of their reflections with contributions from the carbonaceous matrix, CeO_2 , and other secondary species in the system.

Possible Contribution of $\text{La}(\text{OH})_3$

The regions near $2\theta \approx 39.5\text{--}40.0^\circ$ and $47.5\text{--}48.3^\circ$ may contain contributions associated with the (201) and (300) reflections of $\text{La}(\text{OH})_3$, according to JCPDS/ICDD pattern 36-1481. However, these signals overlap extensively with the La_2O_3 and CeO_2 reflections; therefore, the diffractogram does not permit unequivocal identification of a crystalline $\text{La}(\text{OH})_3$ phase. The possible presence of this species could be related to the partial hydration of reactive lanthanum species during cooling, handling, or exposure of Sample B to atmospheric moisture. This interpretation constitutes a chemically plausible hypothesis rather than direct demonstration of the phase.

XPS analysis of the La 3d and O 1s regions may provide complementary information about La–O environments and hydroxylated species. Nevertheless, because of the overlap among the oxygen contributions and the spectral complexity of La 3d, this technique also cannot independently confirm a specific crystalline $\text{La}(\text{OH})_3$ phase. Consequently, $\text{La}(\text{OH})_3$ is retained as a provisional and possibly minor assignment. Its confirmation would require additional well-resolved reflections, suitable structural refinement, or complementary techniques sensitive to hydroxyl groups and the local coordination environment of lanthanum.

Identification of Carbonated Sodium Species

The signals located at $2\theta \approx 30.0\text{--}30.5^\circ$, $36.8\text{--}37.2^\circ$, and $38.2\text{--}38.5^\circ$ are compatible with possible Na_2CO_3 contributions, according to JCPDS/ICDD pattern 37-0451 (Table 3). The region near 30° may contain simultaneous contributions from Na_2CO_3 and La_2O_3 , whereas the other signals may also include contributions from unresolved secondary phases. Therefore, none of these reflections individually permits unequivocal identification of a Na_2CO_3 phase. The formation of carbonated species is consistent with the preparation route. The incorporated NaOH may react with atmospheric CO_2 , with CO_2 generated during partial carbon oxidation, or with surface species undergoing transformation. This carbonation process may also continue during cooling and subsequent exposure of **Sample B** to air.

XPS provides complementary evidence of surface sodium through the Na 1s signal and reveals, through O 1s, the presence of different oxygen-containing environments. However, these signals alone do not permit identification of a specific carbonated species. Furthermore, the available C 1s spectrum does not unequivocally resolve an independent contribution attributable to CO_3^{2-} . Consequently, the presence of Na_2CO_3 is considered probable

mainly on the basis of XRD and its consistency with the preparation route. The combined XRD and XPS results do not permit determination of the relative proportion or spatial distribution of the carbonated fraction, nor do they allow quantitative differentiation among the contributions of NaOH, Na₂CO₃, possible Na₂O-type species, and interfacial configurations. For this reason, the collective designation **NaO_x** is retained to represent the set of sodium species present in the material.

Thermostructural Correlation and Multiphase Nature of Sample B

Integration of the TG–DTG/DTA and XRD results makes it possible to relate the thermal behavior of **Sample A** to the structure observed in **Sample B** after treatment. In the initial temperature range, the removal of water and weakly retained species predominated. Between **200 and 400 °C**, including the event near **324 °C**, decomposition of the La and Ce precursors, transformation of the sodium species, and evolution of the surface functional groups of the carbonaceous matrix occurred. The broad exothermic signal, with a maximum near **469.6 °C**, reflects the superposition of carbon-oxidation processes and reorganization of the inorganic components. The progressive mass loss at higher temperatures indicates the continuation of support oxidation in air. However, the contributions attributed to C_x in the XRD pattern of **Sample B** indicate that a fraction of the carbonaceous matrix remained after treatment and coexisted with the crystalline inorganic domains.

The principal structural result does not correspond to the formation of a homogeneous La–Ce–Na phase, but rather to a multiphase carbon–oxide–carbonate architecture. Within this architecture, fluorite-type CeO₂ constitutes the phase identified with the highest confidence; La₂O₃ has a moderate-confidence assignment because of the overlap of its reflections; carbonated sodium species, particularly Na₂CO₃, are considered probable mainly on the basis of XRD and their consistency with the preparation route; and La(OH)₃ remains a possible minor and provisional contribution. The thermostructural correlation must be interpreted by considering that TG–DTG/DTA records global mass and energy changes in **Sample A**, whereas XRD identifies the crystalline phases present in **Sample B** after treatment. Consequently, the event near **324 °C** represents a relevant region of precursor transformation, but not a specific temperature for the nucleation or crystallization of CeO₂ or La₂O₃.

The coexistence of C_x, CeO₂, La species, and NaO_x makes it possible to propose potential C_x/oxide, CeO₂/La–O, and NaO_x/oxide contact regions. However, their spatial arrangement, electron transfer, oxygen-vacancy concentration, and the formation of specific Na–O–C, Na–O–La, or Na–O–Ce bonds cannot be established directly by XRD and therefore remain hypotheses for future studies. Taken together, the results support a structural model in which a low-order C_x carbonaceous matrix supports crystalline CeO₂ and probably La₂O₃ domains, accompanied by possibly carbonated sodium species and a provisional La(OH)₃ contribution. This multiphase description provides the structural framework for the subsequent XPS analysis of the composition and chemical environments present at the surface of **Sample B**.

Surface Chemical Characterization by XPS

The elemental composition and chemical environments present at the surface of **Sample B** were analyzed by XPS in the C 1s, O 1s, Na 1s, La 3d, and Ce 3d regions. The purpose of the analysis was to correlate the surface chemistry of the heat-treated material with the phases identified by XRD and with the general transformations observed by TG–DTG/DTA.

Because of the multiphase and partially insulating nature of the material, the spectra may exhibit apparent shifts in binding energy as a consequence of electrostatic charge accumulation. The main C 1s component was experimentally recorded at **286.82 eV** and referenced to the conventional value of **284.80 eV**, assigned to C–C/C=C bonds. Accordingly, a uniform shift of **–2.02 eV** was applied to the experimental binding energies:

$$E_{B,corr} = E_{B,exp} - 2.02 \text{ eV}$$

This correction provides a common energy scale and enables coherent comparison among the different spectral regions. Nevertheless, because of the chemical and structural heterogeneity of the sample, a uniform shift does not completely exclude the possible occurrence of differential charging between the carbonaceous and inorganic domains. Therefore, the assignments were made by considering the corrected binding energies, signal shapes, possible spectral overlaps, and their agreement with the XRD results and the preparation route.

C 1s region: carbon matrix and oxygen functionalities

After binding-energy correction, the C 1s spectrum of Sample B showed contributions at 284.80, 286.18, and 291.06 eV (Figure 4). These signals are compatible with persistence of a partially functionalized carbonaceous matrix after heat treatment. Component C1 at 284.80 eV was attributed to C–C/C=C bonds in aromatic or conjugated domains. This assignment agrees with the diffuse XRD contribution in the approximate 20–30° region, associated with a low-order carbon matrix. The presence of local aromatic carbon, however, does not imply a graphitic structure with long-range order.

Component C2 at 286.18 eV is compatible with carbon bound to oxygen in C–O, C–OH, and C–O–C environments. Because the instrumental resolution is approximately 1.6 eV, these functionalities cannot be separated individually. The signal therefore qualitatively demonstrates persistence of oxygen-containing surface groups but does not determine their relative distribution. The contribution at 291.06 eV was assigned to a π – π^* shake-up satellite. Its separation of approximately 6.26 eV from C1 is compatible with transitions associated with conjugated aromatic domains. This signal does not represent an independent functional group and does not demonstrate long-range graphitization.

The maximum observed near 287.00 eV on the experimental scale before correction was not considered an additional component because its separation of approximately 0.18 eV from C1 is substantially below the instrumental resolution. Independent contributions attributable to C=O, O–C=O, or CO_3^{2-} could likewise not be resolved. Consequently, C 1s does not by itself confirm carbonate; the probable Na_2CO_3 assignment is supported mainly by XRD and consistency with the preparation route. Overall, C 1s confirms persistence of a low-order aromatic carbonaceous matrix with oxygen-containing surface functionalities in Sample B, in agreement with XRD. The available data do not, however, permit quantification of the proportion of the original carbon retained after heat treatment.

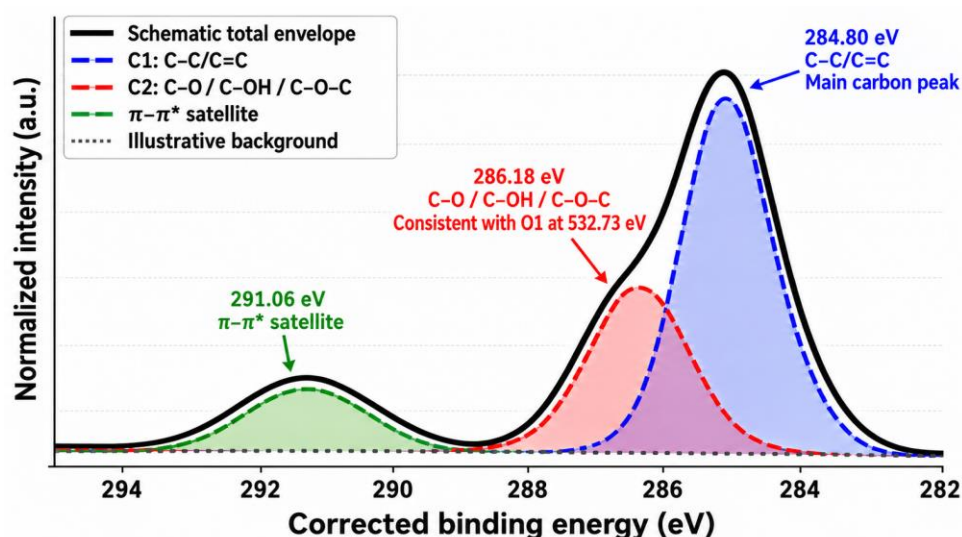


Figure 4. Schematic representation of the corrected C 1s region of Sample B: C–C/C=C (284.80 eV), C–O/C–OH/C–O–C (286.18 eV), and the π – π^* shake-up satellite (291.06 eV). Intensities, widths, and the total envelope are illustrative and do not replace fitting of the experimental spectrum.

Tabla 4. Componentes C 1s de la Muestra B y correlación con O 1s, XRD y TG–DTG/DTA

Component	Experimental energy (eV)	Corrected energy (eV)	Compatible assignment	Correlation with other techniques	Interpretation	Confidence	Ref.
C1	286.82	284.80	C–C/C=C	Consistent with the diffuse XRD contribution at approximately 20–30°, associated with low-order C _x	Low-order carbon matrix with aromatic or conjugated domains; does not demonstrate long-range graphitization	Medium–high	[16–18]
C2	288.20	286.18	C–O, C–OH, and C–O–C	Compatible with O 1s at 532.73 eV and with the transformation of surface functionalities observed by TG–DTG/DTA	Persistence of oxygen-containing surface groups; instrumental resolution prevents individual differentiation	Medium	[16,17]
Satellite	293.08	291.06	π – π^* shake-up	Energy separation of approximately 6.26 eV from C1, compatible with conjugated aromatic domains	Evidence of local electronic conjugation; not an independent functional group and not proof of long-range graphitization	Medium	[16,17,19]

Note. Binding energies were corrected using $E_{B,corr} = E_{B,exp} - 2.02$ eV. The shift was established by setting the C–C/C=C contribution of C 1s to 284.80 eV and was applied uniformly to all analyzed spectral regions. Assignments represent compatible chemical environments rather than exclusive identifications. The approximate instrumental resolution of 1.6 eV does not permit unequivocal differentiation of individual C=O, O–C=O, and CO₃^{2–} contributions. Therefore, C 1s does not independently identify a carbonate species; probable Na₂CO₃ is supported mainly by XRD and the preparation route.

O 1s region: chemical heterogeneity of surface oxygen

The O 1s region of Sample B may contain contributions from oxygen functionalities of the carbonaceous matrix, inorganic domains, hydroxyl groups, carbonated species, and adsorbed molecules. Experimentally, two contributions were observed at 534.75 and 539.25 eV; after application of the uniform –2.02 eV shift, they were located at 532.73 and 537.23 eV, respectively (Figure 5).

Component O1, corrected to 532.73 eV, is compatible mainly with an overlapping envelope of C–O, C–OH, and C–O–C functionalities. This interpretation agrees with component C2 of the C 1s region at 286.18 eV and supports persistence of oxygen-containing groups on the carbonaceous matrix after heat treatment: C–O / C–OH / C–O–C (C 1s, 286.18 eV) ↔ O 1s (532.73 eV).

Because of the characteristic overlap in O 1s and the available instrumental resolution, O1 may also contain unresolved contributions from M–OH groups, CO_3^{2-} , and adsorbed molecular species. These alternative environments therefore cannot be individually identified or quantified from the available spectrum.

Lattice O^{2-} associated with Ce–O and La–O bonds is expected approximately in the 529.0–530.5 eV interval. However, no independent experimental component is clearly resolved in this region. The presence of CeO_2 and oxidized lanthanum species is therefore supported mainly by XRD and analysis of Ce 3d and La 3d, rather than by isolated identification of an O 1s contribution.

Component O2, corrected to 537.23 eV, lies outside the ranges usually associated with conventional surface-oxygen chemical states. It may be related to differential charging among material domains, energy-loss phenomena, or background and spectral-processing effects. Because the available data do not distinguish these possibilities, O2 remains an unresolved secondary contribution with no specific chemical assignment.

Overall, O 1s demonstrates a chemically heterogeneous surface and primarily supports oxygen functionalities associated with the C_x matrix. Possible contributions from hydroxyl groups, carbonates, and lattice oxygen require correlation with XRD and the C 1s, Na 1s, La 3d, and Ce 3d regions.

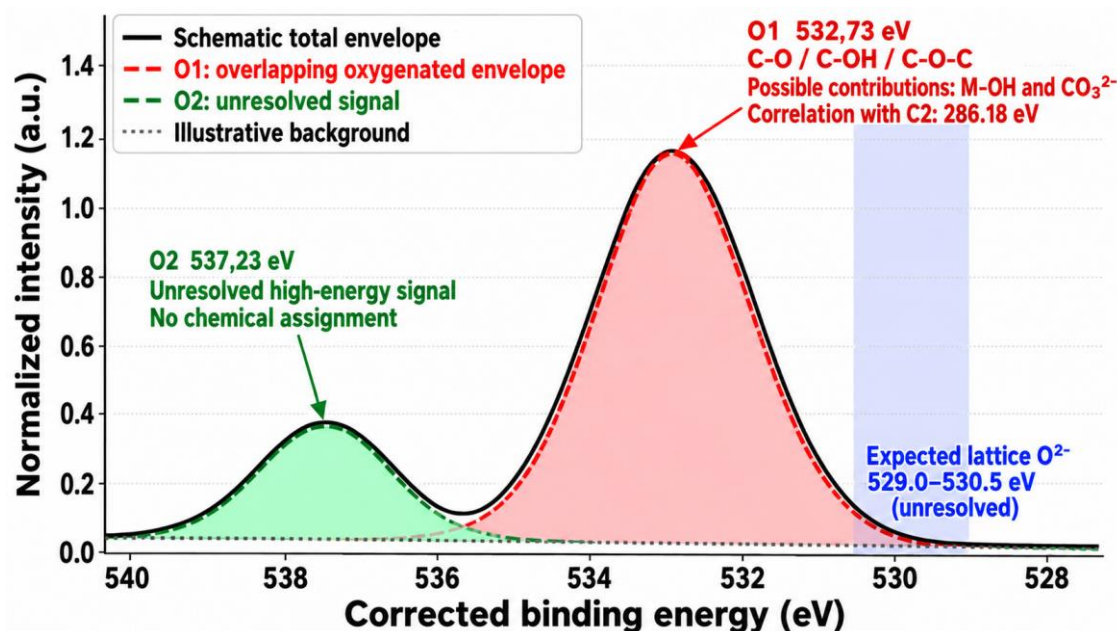


Figure 5. Schematic representation of the corrected O 1s region of Sample B. O1 at 532.73 eV is an overlapping oxygenated envelope, whereas O2 at 537.23 eV remains unresolved and has no specific chemical assignment. The 529.0–530.5 eV interval indicates the expected position of lattice O^{2-} , without identification of an independent experimental component. Intensities and widths are illustrative and do not replace experimental fitting.

The R1 interval in Table 5 (≈ 529.0 –530.5 eV) corresponds to literature values characteristic of lattice O^{2-} in Ce–O and La–O environments. Although the O 1s spectrum of Sample B does not show a clearly resolved independent component in this region, this interval is chemically consistent with the presence of CeO_2 and La–O species, supported mainly by XRD and by the Ce 3d and La 3d regions. Therefore, R1 is used solely as a reference for chemical and structural consistency and not as a direct assignment of an experimental O 1s signal. The R1–R5 intervals are indicative literature ranges and not components derived from spectral fitting.

Tabla 5. Componentes experimentales e intervalos de referencia de O 1s y su correlación con C 1s, XRD y TG–DTG/DTA

Region	Information type	Experimental energy (eV)	Corrected energy/range (eV)	Compatible environment	Correlation and interpretation	Assignment status	Ref.
O1	Experimental component	534.75	532.73	Mainly C–O, C–OH, and C–O–C; possible overlapping M–OH, CO ₃ ^{2–} , and adsorbates	Agrees with C2 of C 1s at 286.18 eV and is the principal evidence for oxygen functionalities associated with C _x	Medium confidence for C–O; provisional for M–OH and CO ₃ ^{2–}	[20,24]
O2	Experimental component	539.25	537.23	Unresolved high-energy contribution	May relate to differential charging, energy losses, background, or processing effects; does not support a particular species	No specific chemical assignment	—
R1	Literature interval	—	≈529.0–530.5	Lattice O ^{2–} in Ce–O and La–O	Expected for CeO ₂ and oxidized La species; no independent experimental component was clearly resolved	Orientative reference; no direct O 1s identification	[21,23, 24]
R2	Literature interval	—	≈530.5–532.0	M–OH, defective surface oxygen, and possible C=O environments	Broadly overlapping region; no independent experimental component was identified	Orientative reference	[24,25]
R3	Literature interval	—	≈531.0–532.5	CO ₃ ^{2–} and M–OH	Compatible with possible carbonated/hydroxylated species indicated by XRD, but not independent confirmation	Possible assignment, not experimentally differentiated	[21,24, 25]
R4	Literature interval	—	≈532.0–533.5	C–O, C–OH, and C–O–C	Shows the closest correspondence with O1 at 532.73 eV and C2 at 286.18 eV	Medium confidence	[20,24]
R5	Literature interval	—	≈533.5–535.5	H ₂ O and other molecular adsorbates	Desorption in TG–DTG of Sample A provides context but does not confirm presence on Sample B	Low; orientative reference	[22,25, 26]

Note. O1 and O2 energies were corrected using $E_{B,corr} = E_{B,exp} - 2.02 \text{ eV}$. R1–R5 are exclusively literature reference intervals and are not components obtained by fitting the experimental spectrum. Because these intervals overlap and the instrumental resolution is approximately 1.6 eV, they must not be interpreted as exclusive chemical identifications. O2 remains without a specific chemical assignment.

La 3d and Ce 3d regions

The spectrum recorded over approximately 820–940 eV contains contributions from the La 3d and Ce 3d regions, qualitatively confirming the presence of both elements at the surface of Sample B after heat treatment (Figure 6).

Interpretation of this spectral interval is complex because of partial overlap of La and Ce signals, spin–orbit splitting, multiplet structure, and satellites associated with charge-transfer processes. The analysis was therefore directed toward establishing the general chemical states of both elements and their consistency with XRD and TG–DTG/DTA, without detailed quantification of individual contributions.

Experimental signals near 838.7 and 859.0 eV were located at 836.68 and 856.98 eV, respectively, after application of the uniform -2.02 eV shift. These positions must be interpreted while recognizing that the global C 1s-based reference provides a common energy scale but may not completely compensate differences in charging between the carbonaceous matrix and inorganic domains.

Consequently, assignments in the La 3d and Ce 3d regions were based on the combined spectral characteristics and correlation with XRD, rather than solely on the positions of individual signals.

Surface characterization of lanthanum by La 3d

The La 3d region is compatible with surface lanthanum predominantly in the La^{3+} state and coordinated to oxygen. This interpretation agrees with the nature of the $\text{La}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ precursor and with XRD reflections probably assigned to hexagonal La_2O_3 domains.

TG–DTG/DTA results show that dehydration, nitrate-group removal, and progressive transformation of the lanthanum precursor occur between approximately 200 and 400 °C. However, the event near 324 °C represents a global transformation of Sample A and must not be attributed exclusively to La_2O_3 nucleation or crystallization.

Interpretation of La 3d is conditioned by spin–orbit splitting, multiplet structure, satellites, and charge-transfer processes characteristic of La^{3+} . Moreover, the affinity of lanthanum species for H_2O and CO_2 may favor hydration or carbonation during cooling, handling, and storage.

The available spectrum therefore cannot unequivocally distinguish La_2O_3 , $\text{La}(\text{OH})_3$, oxycarbonates, lanthanum carbonates, or other La^{3+} –O environments. The most robust conclusion is that lanthanum remains at the surface of Sample B predominantly as La^{3+} in oxygen-containing environments. Probable La_2O_3 domains are supported through correlation with XRD but are not established as the only surface lanthanum species.

Surface characterization of cerium by Ce 3d

The Ce 3d region qualitatively confirms surface cerium in oxidized environments. This evidence agrees with the XRD reflections assigned to the (111), (200), and (220) planes of cubic fluorite CeO_2 . Among the proposed inorganic phases, CeO_2 shows the strongest structural correlation because several crystallographic reflections coincide and cerium is detected at the surface by XPS.

The presence of CeO_2 is also consistent with the general thermal transformation of $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$. Removal of water and volatile species, accompanied by reorganization of Ce–O environments, may favor

formation of ceria domains during treatment. Nevertheless, TG–DTG/DTA records global, overlapping processes and cannot establish a specific temperature for CeO_2 formation.

Ce 3d has a complex multiplet structure originating from spin–orbit splitting and different final-state configurations. Reliable separation of Ce^{3+} and Ce^{4+} requires spectra of higher resolution and adequate signal-to-noise ratio, together with rigorous energy correction and physically constrained deconvolution.

Accordingly, the available data do not permit quantitative determination of $\text{Ce}^{3+}/\text{Ce}^{4+}$, oxygen-vacancy concentration, defect density, or possible electron transfer at interfaces. This limitation does not affect crystallographic identification of CeO_2 but advises against specific deductions concerning redox or catalytic mechanisms.

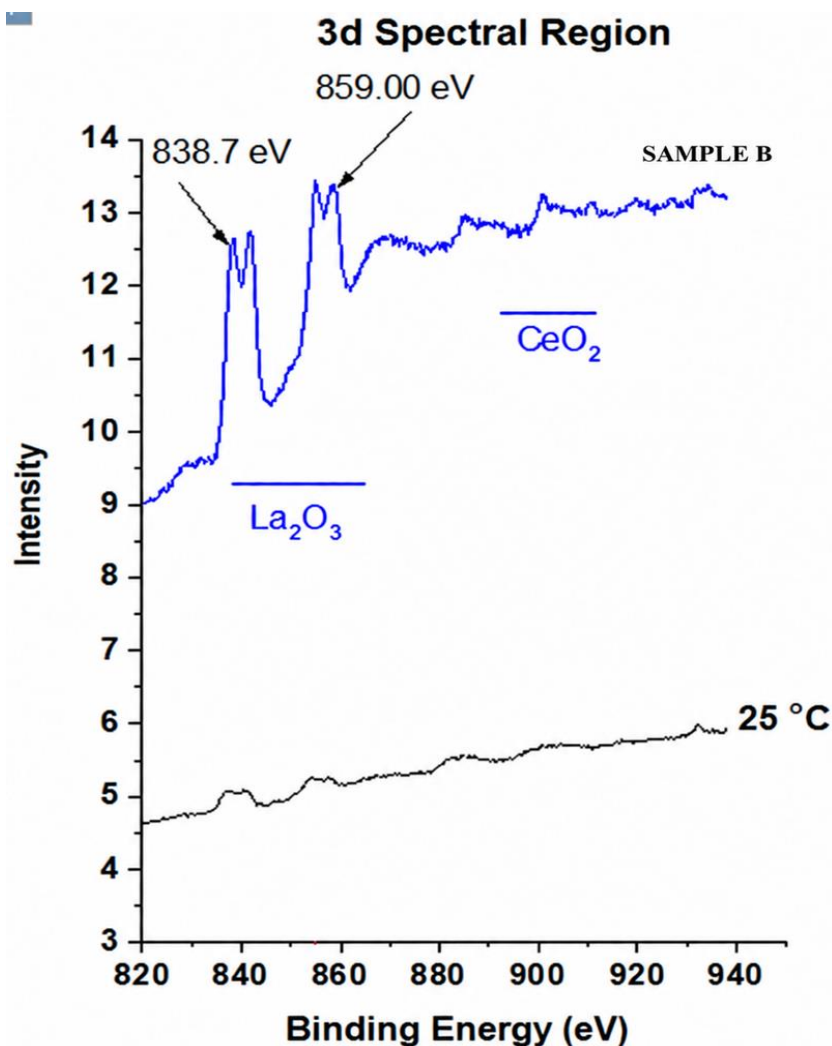


Figure 6. XPS spectra of the La 3d and Ce 3d regions of Sample B and unheated Sample A. The signals qualitatively confirm surface La and Ce in environments compatible with oxidized species. The available spectra do not unequivocally differentiate individual $\text{La}^{3+}\text{--O}$ species or permit quantification of the $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio.

Na 1s region: surface sodium species

The Na 1s spectrum of Sample B displayed an experimental maximum at 1074.68 eV, located at 1072.66 eV after application of the uniform -2.02 eV shift. This signal qualitatively confirms that sodium remains at the material surface after heat treatment.

The corrected position is compatible with sodium bound to oxygen. However, the energy intervals corresponding to NaOH, Na₂CO₃, possible Na₂O-like species, and Na–O–C interfacial configurations overlap. Na 1s therefore cannot unequivocally differentiate these species or determine their relative proportions.

The probable assignment of a carbonated sodium fraction is supported mainly by XRD reflections and consistency with the preparation route. C 1s and O 1s provide complementary information on an oxygenated carbon surface but do not independently identify Na₂CO₃.

Consequently, Na 1s confirms surface sodium in oxygen-containing environments without establishing one exclusive chemical species. The collective NaO_x designation is therefore retained for the possible sodium species present in Sample B.

Structural, thermal, and surface correlation

Joint interpretation of TG–DTG/DTA, XRD, and XPS indicates that heat treatment transforms the La, Ce, and Na precursors and partially modifies oxygen-containing functionalities of the carbonaceous matrix. XRD identifies mainly fluorite CeO₂ and, with moderate confidence, domains compatible with La₂O₃. XPS confirms the surface persistence of C, O, La, Ce, and Na in different chemical environments.

The complementarity of these techniques means that a dispersed, minor, or structurally low-order surface species may not produce clearly identifiable XRD reflections. Taken together, the results support a multiphase architecture comprising a low-order, partially functionalized C_x matrix, crystalline CeO₂ domains, La³⁺–O species, and surface NaO_x species that are probably partially carbonated.

The coexistence of these components permits possible C_x/oxide, CeO₂/La–O, and NaO_x/oxide contact regions to be proposed. However, the available data do not directly demonstrate electron transfer, oxygen-vacancy concentration, or formation of specific Na–O–C, Na–O–La, or Na–O–Ce interfacial bonds. These aspects constitute complementary lines of study for a deeper understanding of relationships among structure, surface chemistry, and functional properties.

Therefore, the Na 1s signal is conservatively assigned to surface sodium species in oxygen-containing environments, with a possible carbonated fraction. In correlation with XRD and the C 1s, O 1s, Ce 3d, and La 3d regions, the results support a multiphase model consisting of a functionalized C_x matrix, crystalline CeO₂ domains, La³⁺–O species, and probably partially carbonated NaO_x species. The evidence has a higher level of confidence for the functionalized C_x matrix and CeO₂, and a moderate level of confidence for the La–O and carbonated sodium species. The presence of adsorbed molecular oxygen cannot be established from the available data.

DISCUSSION

The combined results show that non-isothermal treatment converts the impregnated precursors into a hybrid, multiphase architecture. TG–DTG/DTA was performed on uncalcined Sample A, whereas XRD and XPS were performed on Sample B after gradual heating in air from approximately 25 to 600 °C, including a 2 h trajectory from 300 to 600 °C without an isothermal hold. The correlation therefore links global thermal behavior to the final post-treatment structure but does not establish the temperature at which each phase formed.

TG–DTG behavior revealed several transformation stages. The first event, with a maximum at 56.10 °C and an approximate mass loss of 2.10%, was attributed mainly to desorption of physically adsorbed water and partial elimination of water associated with the hydrated precursors. The second stage, with an approximate loss of 9.12% between 200 and 400 °C and a DTG maximum at 324.12 °C, was related to decomposition of the La and Ce precursors, evolution of sodium species, and transformation of carbon-surface functionalities. The broad

exothermic event with a DTA maximum near 469.6 °C reflects the superposition of carbon-matrix oxidation and reorganization of the inorganic components.

Above 600 °C, thermal analysis of Sample A showed an approximate 30.29% mass loss, mainly associated with oxidation and combustion of residual carbon. Nevertheless, the C_x contributions in the XRD pattern and C 1s region of Sample B demonstrate that the treatment used to obtain this sample did not completely eliminate the carbonaceous matrix.

The most consistent crystallographic evidence corresponds to cubic fluorite CeO_2 , identified through the (111), (200), and (220) reflections. Their joint agreement permits a high-confidence assignment. Reflections compatible with La_2O_3 overlap more extensively with CeO_2 , the carbon matrix, and other secondary phases; its presence is therefore considered probable with moderate confidence. A possible $La(OH)_3$ contribution remains provisional because its reflections overlap and because lanthanum species are susceptible to hydration during cooling and environmental exposure.

XRD signals compatible with Na_2CO_3 and consistency with the preparation route support a probable carbonated sodium fraction. Na 1s confirms surface sodium in oxygen-containing environments but cannot unequivocally distinguish NaOH, Na_2CO_3 , possible Na_2O -like species, and interfacial configurations. The C 1s region likewise does not resolve an independent CO_3^{2-} component. Consequently, the Na_2CO_3 assignment is supported mainly by XRD and the chemical plausibility of NaOH carbonation, rather than by an independent XPS identification.

XPS confirmed the surface persistence of C, O, Na, La, and Ce. Corrected C 1s components at 284.80, 286.18, and 291.06 eV were associated with C–C/C=C, C–O/C–OH/C–O–C functionalities, and a $\pi-\pi^*$ shake-up satellite, respectively. These results indicate that Sample B retains a structurally low-order carbon matrix containing aromatic or conjugated domains and oxygen-containing surface groups.

The O 1s contribution at 532.73 eV is compatible mainly with an overlapping envelope of C–O, C–OH, and C–O–C functionalities, although it may also contain unresolved M–OH, carbonate, and adsorbate contributions. The high-energy component at 537.23 eV remains an unresolved secondary signal with no specific chemical assignment. The absence of a clearly resolved independent component between 529.0 and 530.5 eV does not contradict CeO_2 and La–O species because these are supported by XRD and by the Ce 3d and La 3d regions.

The La 3d region is compatible with lanthanum predominantly as La^{3+} in oxygen-containing environments, but it cannot unequivocally differentiate La_2O_3 , $La(OH)_3$, oxycarbonates, carbonates, or other surface La^{3+} –O species. Ce 3d qualitatively confirms cerium in oxidized environments and agrees with the crystallographic identification of CeO_2 . However, the available resolution does not permit reliable quantification of Ce^{3+}/Ce^{4+} or determination of the oxygen-vacancy concentration.

Taken together, the techniques support a general C_x – CeO_2 –La–O– NaO_x structural model rather than formation of a homogeneous La–Ce–Na crystalline phase. Sample B consists of a functionalized, low-order carbon matrix, crystalline CeO_2 domains, La–O species, and surface sodium species that are probably partially carbonated.

This heterogeneity could favor adsorption-related properties, acid–base interactions, electron transfer, and redox behavior. These properties were not demonstrated in the present study. The Ce^{3+}/Ce^{4+} ratio, oxygen vacancies, interfacial bonds, and potential performance in catalysis, CO_2 conversion, oxidation, gas detection, and electrochemical storage must be evaluated through specific experiments addressing activity, selectivity, stability, adsorption, and electrical or electrochemical response.

Scope and Analytical Considerations

This study presents the physicochemical characterization of Sample B. The BET surface area of 1200–1300 m² g^{−1}

characterizes the activated carbon used as the starting material, while the La and Ce amounts correspond to the proportions employed during material preparation.

The results obtained allow the system to be described as a multiphase C_x - NaO_x -La-O- CeO_2 association and provide an experimental basis for future research. Further studies may focus on evaluating the porosity of the final product, determining its relative La:Ce:Na composition, and investigating its functional properties using comparative materials.

Additional research directions include a detailed investigation of the Ce^{3+}/Ce^{4+} ratio, oxygen vacancies, interfacial electron transfer, the nature of the evolved gases, and the specific temperatures associated with phase formation. These studies will enable the assessment of potential synergistic effects and a more precise correlation among the material's composition, structure, and properties.

CONCLUSIONS

A multiphase hybrid material based on a carbonaceous matrix modified with Ce, La, and Na species was obtained and characterized. Sample B was prepared through a single non-isothermal heat treatment in air, consisting of gradual heating from approximately 25 to 600 °C, with a 2 h trajectory between 300 and 600 °C and no isothermal holding stage.

TG-DTG/DTA analysis of Sample A revealed multistep thermal behavior. An initial mass loss of approximately 2.10%, with a DTG maximum at 56.10 °C, was attributed mainly to removal of water and weakly retained species. The 9.12% loss between 200 and 400 °C, with a maximum at 324.12 °C, was related to transformation of the inorganic precursors and surface functionalities. The DTA maximum near 469.6 °C was interpreted as the result of overlapping carbon-matrix oxidation and inorganic-component reorganization. Above 600 °C, an approximate 30.29% loss was observed and attributed predominantly to residual-carbon oxidation.

XRD analysis of Sample B identified fluorite-type CeO_2 with high confidence through the (111), (200), and (220) reflections. La_2O_3 was considered probable with moderate confidence because of reflection overlap. Na_2CO_3 was assigned as a probable phase from XRD and consistency with the chemical route, whereas $La(OH)_3$ remained a provisional and possibly minor contribution.

XPS confirmed persistence of a functionalized carbonaceous matrix and the surface presence of Na, La, and Ce in predominantly oxygen-containing environments. C 1s showed C-C/C=C domains, oxygen functionalities, and local electronic conjugation. Na 1s confirmed surface sodium, while O 1s revealed heterogeneous oxygen-containing surface chemistry. Nevertheless, these regions did not permit unequivocal differentiation among NaOH, Na_2CO_3 , possible Na_2O -like species, or interfacial configurations. C 1s likewise did not resolve an independent CO_3^{2-} contribution.

La 3d was compatible with lanthanum predominantly as La^{3+} in oxygen-containing environments, although no exclusive surface species could be distinguished. Ce 3d confirmed cerium in oxidized environments and was consistent with CeO_2 determined by XRD, but the available data did not permit reliable quantification of Ce^{3+}/Ce^{4+} or the oxygen-vacancy concentration.

Overall, the results support a multiphase architecture consisting of a functionalized low-order C_x matrix, crystalline CeO_2 domains, La-O species, and probably partially carbonated NaO_x species. This study establishes a physicochemical reference for the material but does not demonstrate catalytic, adsorption, sensing, electrical, or electrochemical performance. Assessment of these properties will require application-specific tests, suitable controls, quantitative elemental analysis, and complementary methods capable of resolving morphology, porosity, oxidation states, structural defects, conductivity, and component interactions.

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