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Comparative Structural Evolution and Surface Characteristics of Solid-State Synthesized Pr_2NiO_4 and Pr_2CoO_4 Oxides

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Abstract

Rare-earth mixed oxides have attracted considerable attention because of their structural adaptability, oxygen transport capability, and promising catalytic characteristics. In the present investigation, Pr_2NiO_4 and Pr_2CoO_4 oxide materials were synthesized through a conventional solid-state ceramic route followed by calcination at different temperatures. Their crystal structures and surface characteristics were systematically examined using powder X-ray diffraction (PXRD) and Brunauer-Emmett-Teller (BET) surface area measurements. PXRD analysis confirmed the successful formation of orthorhombic crystalline phases for both oxide systems. The Pr_2NiO_4 sample exhibited lattice parameters of $a = 5.380 \text{ \AA}$, $b = 7.626 \text{ \AA}$, and $c = 5.419 \text{ \AA}$, whereas Pr_2CoO_4 possessed lattice constants of $a = 5.344 \text{ \AA}$, $b = 7.578 \text{ \AA}$, and $c = 5.377 \text{ \AA}$. Comparative crystallographic analysis indicated a higher degree of structural ordering for Pr_2CoO_4 , with crystallinity reaching 67.40%, compared with 51.73% for Pr_2NiO_4 . Nitrogen adsorption-desorption measurements demonstrated mesoporous characteristics for both materials, with average pore diameters between 5 and 9 nm. The maximum BET surface area of Pr_2NiO_4 was $2.646 \text{ m}^2 \text{ g}^{-1}$ at 800°C , whereas Pr_2CoO_4 exhibited its highest surface area of $3.357 \text{ m}^2 \text{ g}^{-1}$ at 1000°C . These findings indicate that transition-metal substitution significantly affects crystal growth, pore development, and accessible surface area. The combined structural and surface analyses demonstrate that Pr_2CoO_4 exhibits superior physicochemical characteristics under the investigated synthesis conditions, suggesting its greater potential for catalytic and adsorption-related applications.

Keywords: Pr_2NiO_4 , Pr_2CoO_4 , Rare-earth mixed oxides, Solid-state ceramic synthesis, Powder X-ray diffraction, BET surface area, Mesoporous materials, Crystallinity, Surface properties

1. Introduction

Rare-earth transition-metal oxides constitute an important class of inorganic functional materials because they combine structural stability with tunable electronic, catalytic, and oxygen-transport properties. Their ability to accommodate different oxidation states and oxygen non-stoichiometry makes these compounds attractive for applications in heterogeneous catalysis, electrochemical energy conversion, oxygen-permeable membranes, gas sensors, and environmental remediation technologies. Continuous advances in oxide chemistry have demonstrated that the functional performance of these materials strongly depends on crystal structure, microstructural evolution, and surface characteristics developed during synthesis. Among rare-earth oxides, praseodymium-based compounds have received particular attention because praseodymium can readily undergo reversible oxidation-state changes, thereby facilitating oxygen defect formation and lattice oxygen mobility. These characteristics improve redox behaviour and contribute significantly to catalytic activity and electrochemical performance. When praseodymium is combined with transition metals such as nickel or cobalt, distinct oxide phases with different crystal architectures and physicochemical characteristics are produced. Pr_2NiO_4 belongs to the Ruddlesden-Popper family and possesses a layered K_2NiF_4 -type crystal framework. The alternate stacking of perovskite-like and rock-salt layers provides efficient pathways for oxygen diffusion, making this compound attractive for solid oxide fuel cells, catalytic oxidation, and oxygen transport

applications. In contrast, Pr_2CoO_4 crystallizes in an orthorhombic perovskite structure that exhibits excellent structural stability, high oxygen mobility, and favourable redox properties. These characteristics have made cobalt-containing rare-earth oxides promising candidates for oxidation catalysis, environmental applications, and electrochemical devices. The preparation route plays a decisive role in determining the final properties of oxide materials. Among various synthesis techniques, the conventional solid-state ceramic method remains one of the most reliable approaches because of its simplicity, reproducibility, and suitability for producing thermally stable crystalline oxides. Calcination temperature directly influences diffusion kinetics, phase formation, crystallite growth, pore evolution, and particle agglomeration. Consequently, understanding the relationship between synthesis temperature, crystal structure, and surface properties is essential for optimizing material performance. Powder X-ray diffraction (PXRD) is widely employed to determine phase composition, crystal symmetry, lattice parameters, and crystallinity, whereas nitrogen adsorption-desorption measurements based on the Brunauer-Emmett-Teller (BET) theory provide valuable information regarding specific surface area, pore volume, and pore diameter. The combined interpretation of these techniques offers a comprehensive understanding of the structure-surface relationship governing oxide behaviour.

The objective of the present work is to perform a comparative investigation of Pr_2NiO_4 and Pr_2CoO_4 synthesized by the conventional solid-state ceramic route. Particular emphasis is placed on evaluating crystallographic characteristics, crystallinity, surface area, pore structure, and the influence of transition-metal chemistry on the structural evolution of both oxide systems. The results contribute to a better understanding of how compositional variation affects the physicochemical properties of rare-earth mixed oxides and may provide useful guidance for their utilization in catalytic and adsorption-related applications.

2. Experimental

2.1 Materials

All starting chemicals employed in this investigation were of analytical reagent (AR) grade and were used without further purification. Praseodymium oxide (Pr_6O_{11} , $\geq 99.9\%$), nickel(II) oxide (NiO , $\geq 99.9\%$), and cobalt precursor (used for Pr_2CoO_4 synthesis according to the experimental design) were selected as the raw materials. High-purity reagents were chosen to minimize impurity-induced phase formation during high-temperature calcination. Stoichiometric quantities of each precursor were accurately weighed before the synthesis procedure.

2.2 Synthesis Procedure

The oxide materials were synthesized using a conventional solid-state ceramic method. Appropriate stoichiometric amounts of precursor oxides were weighed and thoroughly mixed using an agate mortar and pestle to achieve homogeneous mixing. The powder mixtures were subjected to repeated grinding and calcination in air. Calcination was carried out at 800, 900, 1000 and 1100 °C to investigate the

effect of temperature on phase formation and surface development.

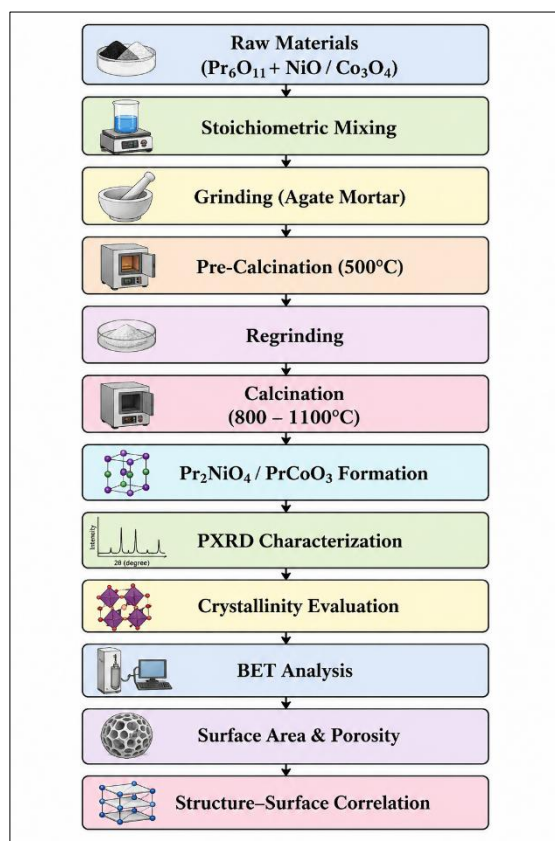


Fig 1: Schematic representation of the solid-state ceramic synthesis route.

2.3 Powder X-ray Diffraction (PXRD)

Phase identification and crystallographic characterization of the synthesized oxide powders were carried out using powder X-ray diffraction (PXRD) with Cu K α radiation ($\lambda = 1.5406$ Å). Diffraction patterns were recorded over an appropriate 2θ range using a constant scanning rate to obtain well-resolved diffraction peaks. The diffraction data were indexed using standard crystallographic databases and analysed to determine lattice parameters, crystal symmetry, unit-cell dimensions, and crystallinity. Structural refinement was performed by comparing the experimental diffraction profiles with reference crystallographic data available in the COD database. The diffraction results were further utilized to evaluate the influence of calcination temperature on phase evolution and crystal growth.

2.4 BET Surface Area Analysis

Surface characteristics of the synthesized materials were investigated through nitrogen adsorption-desorption measurements based on the Brunauer-Emmett-Teller (BET) method. Before analysis, each powder sample was degassed under vacuum at an elevated temperature to eliminate adsorbed moisture and atmospheric contaminants. The adsorption isotherms were used to calculate the specific surface area, while pore volume and average pore diameter were determined using standard adsorption models. The obtained parameters were employed to examine the influence of calcination temperature on pore development and surface evolution. Comparative evaluation of BET results was performed to establish correlations between structural

ordering observed from PXRD and the corresponding surface properties of both oxide systems.

3. Results and Discussion

3.1 Structural Evolution of Pr_2NiO_4

The phase formation and crystallographic characteristics of the synthesized Pr_2NiO_4 samples were investigated using powder X-ray diffraction analysis. The diffraction patterns obtained for samples calcined at different temperatures exhibited sharp and well-defined reflections, indicating successful formation of a crystalline oxide phase. As the calcination temperature increased, the diffraction peaks became progressively sharper and more intense, suggesting enhanced crystal growth and improved long-range structural ordering. The diffraction peaks were indexed using

HighScore Plus software and compared with the corresponding COD reference data. The obtained diffraction pattern was successfully assigned to an orthorhombic crystal structure belonging to the Pnma space group. The calculated lattice parameters were $a = 5.380 \text{ \AA}$, $b = 7.626 \text{ \AA}$ and $c = 5.419 \text{ \AA}$, with a unit-cell volume of $222.33 \text{ \AA}^3$. These values are in good agreement with those reported for Pr_2NiO_4 -type layered nickelates in previous investigations^[5]. The strongest reflection was observed near $2\theta \approx 33.18^\circ$, corresponding to a highly ordered crystalline plane. Additional reflections were indexed to the characteristic planes of orthorhombic Pr_2NiO_4 , confirming phase purity and successful synthesis through the solid-state route. No significant secondary phases were detected within the detection limit of the instrument.

Table 1: PXRD indexing data of Pr_2NiO_4 .

Peak No.	hkl	d observed (Å)	d theoretical (Å)	2θ observed ($^\circ$)	Relative intensity (%)
1	11	4.417	4.417	20.085	0.2
2	101	3.818	3.818	23.28	16.6
3	20	3.813	3.813	23.31	9
4	111	3.414	3.414	26.08	3.4
5	2	2.71	2.71	33.034	24.9
6	121	2.698	2.698	33.179	100
7	220	2.208	2.208	40.823	12.8
8	40	1.909	1.909	47.596	27.1

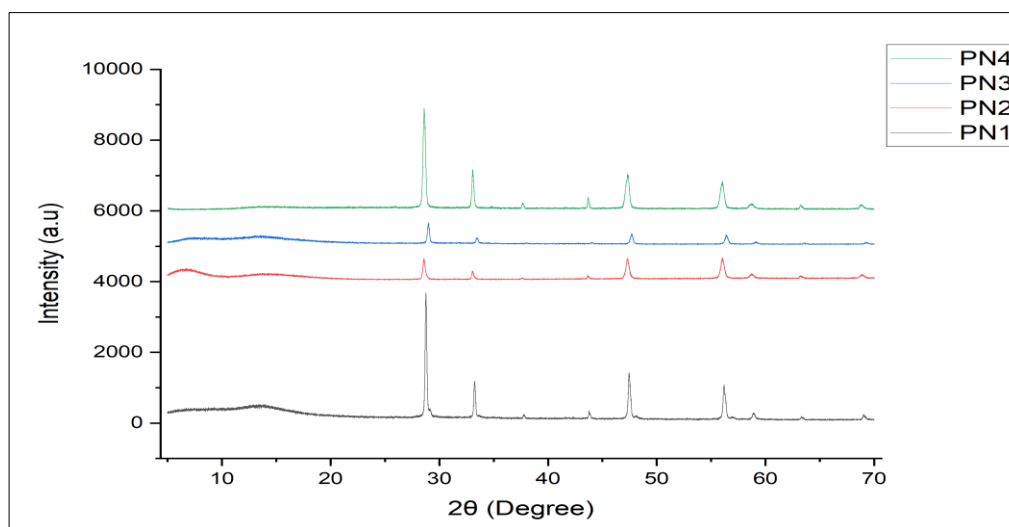


Fig 2: PXRD patterns of Pr_2NiO_4 samples calcined at different temperatures.

The progressive increase in peak intensity and reduction in peak broadening indicate that higher calcination temperatures promote atomic diffusion and facilitate the formation of a more ordered crystal lattice. Similar observations have been reported by Takeda *et al.*^[5], who demonstrated that thermal treatment significantly influences structural ordering in rare-earth nickelate systems.

3.2 Structural Evolution of Pr_2CoO_4

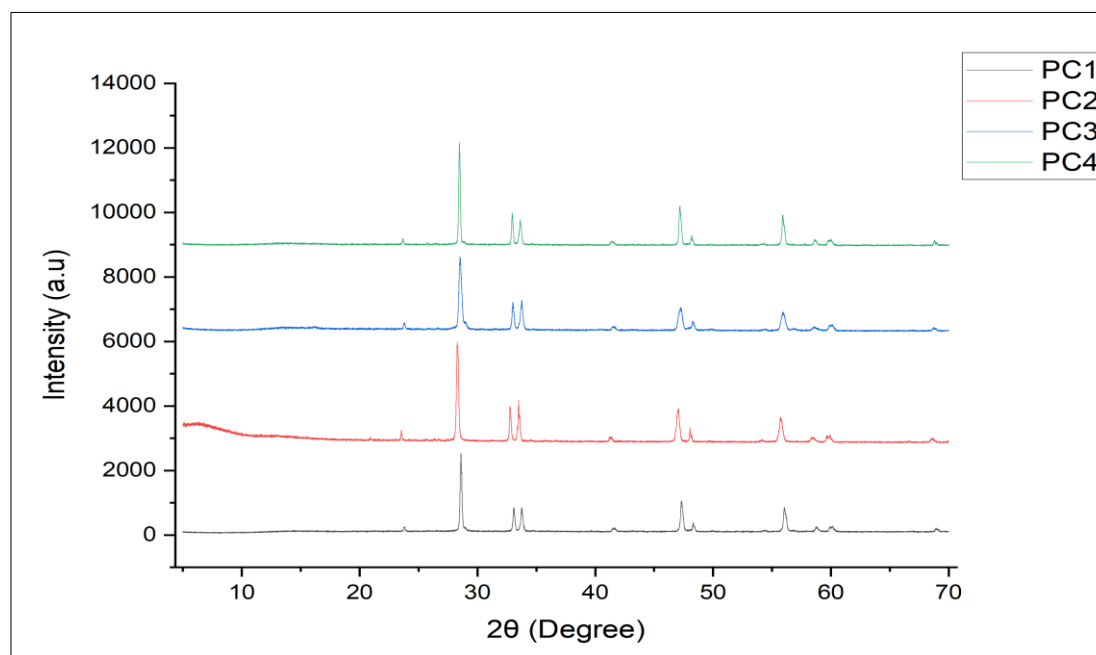
The PXRD patterns of the cobalt-containing samples exhibited sharp diffraction peaks characteristic of a highly crystalline oxide phase. Phase identification and indexing using COD reference data indicated that the diffraction

pattern corresponds to orthorhombic Pr_2CoO_4 with Pnma symmetry.

The refined lattice parameters were determined as $a = 5.344 \text{ \AA}$, $b = 7.578 \text{ \AA}$ and $c = 5.377 \text{ \AA}$, with a unit-cell volume of $217.75 \text{ \AA}^3$. These values are consistent with previously reported structural parameters for rare-earth cobaltite perovskites^[26]. The strongest diffraction peak was observed near $2\theta \approx 33.41^\circ$, accompanied by several intense reflections in the higher-angle region. Compared with Pr_2NiO_4 , the diffraction peaks of Pr_2CoO_4 appeared sharper and more intense, indicating superior crystallinity and improved long-range structural ordering.

Table 2: PXRD indexing data of Pr_2CoO_4 .

Peak No.	hkl	d -observed (Å)	d-theoretical (Å)	2θ observed (°)	Relative intensity (%)
1	121	2.68	2.68	33.411	100
2	200	2.672	2.672	33.511	23.6
3	10	2.52	2.52	35.599	2.6
4	220	2.184	2.184	41.312	12.7
5	131	2.102	2.102	42.995	11.7
6	40	1.895	1.895	47.964	27.6
7	42	1.551	1.551	59.578	21.1
8	232	1.544	1.544	59.847	15.4

**Fig 3:** PXRD patterns of Pr_2CoO_4 samples calcined at different temperatures.

The cobalt-containing oxide was synthesized with the intended composition of Pr_2CoO_4 using the conventional solid-state ceramic route. PXRD analysis and comparison with the corresponding COD reference data confirmed the formation of the Pr_2CoO_4 phase under the employed calcination conditions. The observed diffraction peaks were consistent with the characteristic crystalline structure of Pr_2CoO_4 , confirming the successful formation of the desired cobalt-containing oxide. The progressive sharpening and intensification of the diffraction peaks with increasing calcination temperature indicate enhanced crystallization and structural ordering of the Pr_2CoO_4 phase during thermal treatment. Similar phase stabilization has been reported by Alonso *et al.* [26].

3.3 Comparative Crystallographic Analysis: A comparison of crystallographic parameters reveals significant differences between the nickel-containing and cobalt-containing oxide systems. Both materials crystallized in orthorhombic symmetry; however, Pr_2CoO_4 exhibited slightly smaller lattice parameters and lower unit-cell volume compared with Pr_2NiO_4 .

The reduction in unit-cell volume may be attributed to differences in metal-oxygen bond lengths and crystal packing efficiency. Such structural variations directly influence defect concentration, oxygen mobility and physicochemical properties.

Table 3: Comparative crystallographic parameters of Pr_2NiO_4 and Pr_2CoO_4 .

Parameter	Pr_2NiO_4	Pr_2CoO_4
Crystal system	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma
a (Å)	5.38	5.344
b (Å)	7.626	7.578
c (Å)	5.419	5.377
Unit cell volume (Å ³)	222.33	217.75
Crystallinity (%)	51.73	67.4

3.4 Crystallinity Analysis

Crystallinity calculations were performed using integrated peak-area analysis. The crystalline peak area and total diffraction area were used to estimate the degree of crystallinity of both oxide systems. The calculated

crystallinity values were 51.73% for Pr_2NiO_4 and 67.40% for Pr_2CoO_4 . These results clearly indicate that the cobalt-containing oxide possesses a significantly higher degree of structural ordering.

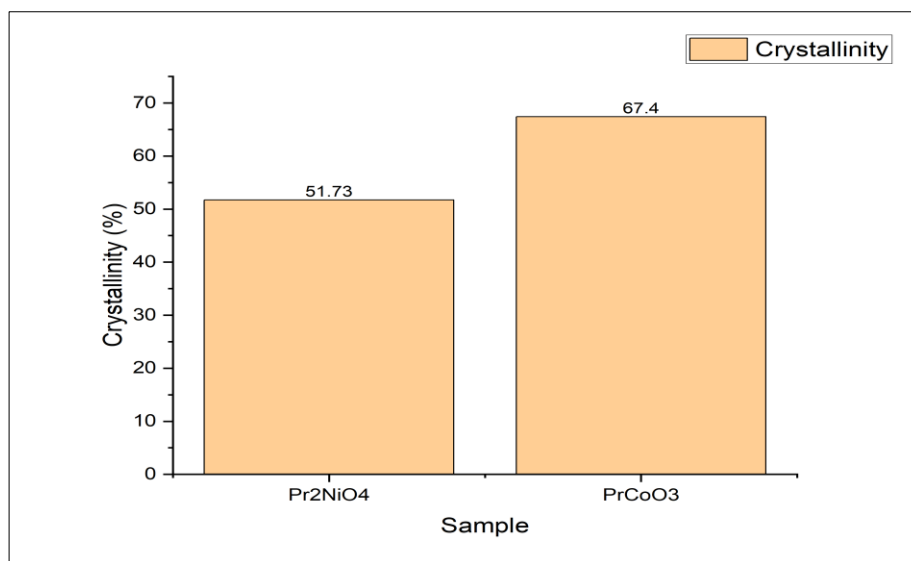


Fig 4: Comparative crystallinity of Pr_2NiO_4 and Pr_2CoO_4 .

The enhanced crystallinity of Pr_2CoO_4 suggests improved crystal growth kinetics and reduced amorphous content during calcination. Higher crystallinity is generally associated with improved thermal stability, lower defect concentration and enhanced structural durability [5]. The present findings are consistent with the observations of Zhang *et al.* [10], who reported that improved crystallinity in mixed oxide systems often leads to superior physicochemical performance.

3.5 BET Surface Area Development

The BET surface area measurements were carried out to investigate the influence of calcination temperature on surface development. The obtained values indicate that both materials possess relatively low but measurable specific surface areas characteristic of solid-state synthesized ceramic oxides.

Table 4: BET surface area, pore volume and pore diameter of Pr_2NiO_4 and Pr_2CoO_4 .

Calcination Temperature	Total Pore volume		Average pore Diameter		Surface area	
	PC (Pr_2CoO_4)	PN(Pr_2NiO_4)	PC (Pr_2CoO_4)	PN(Pr_2NiO_4)	PC(Pr_2CoO_4)	PN(Pr_2NiO_4)
800	4.464e-03 cc/g	5.810e-03 cc/g	7.00360e+00 nm	8.78184e+00 nm	2.549	2.646
900	3.429e-03 cc/g	4.689e-03 cc/g	6.02694e+00 nm	7.31923e+00 nm	2.276	2.563
1000	6.241e-03 cc/g	5.766e-03 cc/g	7.43552e+00 nm	9.15723e+00 nm	3.357	2.519
1100	3.141e-03 cc/g	3.593e-03 cc/g	5.51111e+00 nm	6.78021e+00 nm	2.280	2.119

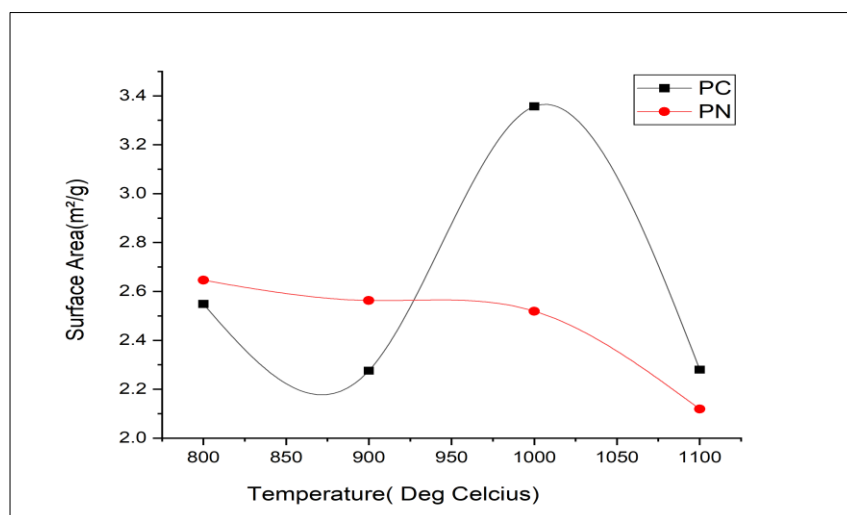


Fig 5: Variation of BET surface area with calcination temperature.

For Pr_2NiO_4 , the specific surface area decreased gradually from $2.646 \text{ m}^2 \text{ g}^{-1}$ at 800°C to $2.119 \text{ m}^2 \text{ g}^{-1}$ at 1100°C . This reduction is attributed to grain growth, particle agglomeration and thermal densification during high-temperature calcination. In contrast, Pr_2CoO_4 exhibited a maximum surface area of $3.357 \text{ m}^2 \text{ g}^{-1}$ at 1000°C before decreasing at

1100°C . This behaviour suggests that 1000°C provides an optimum balance between crystallization and pore preservation. Similar temperature-dependent trends have been reported for rare-earth mixed oxides by Li *et al.* [7] and Kumar *et al.* [8].

3.6 Adsorption-Desorption Behaviour and Pore Structure

Nitrogen adsorption-desorption analysis was used to evaluate pore characteristics and adsorption behaviour. Both oxide systems exhibited adsorption profiles typical of mesoporous

materials. The average pore diameter values ranged approximately from 5 to 9 nm, placing both materials within the mesoporous region according to IUPAC classification [8, 9].

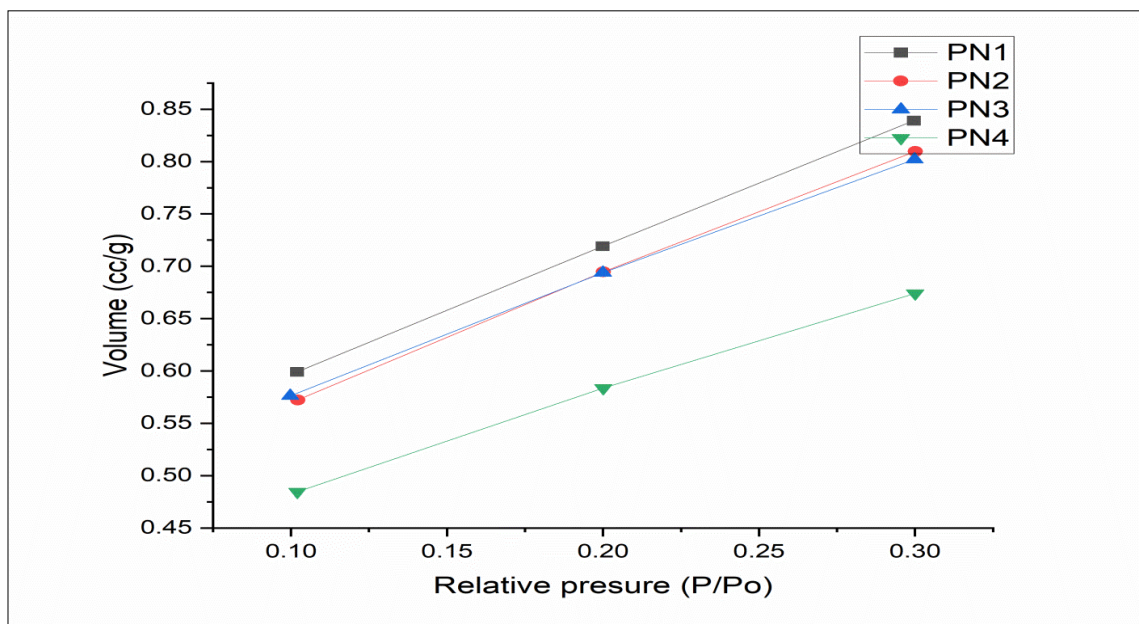


Fig 6: Nitrogen adsorption-desorption isotherm of Pr_2NiO_4 .

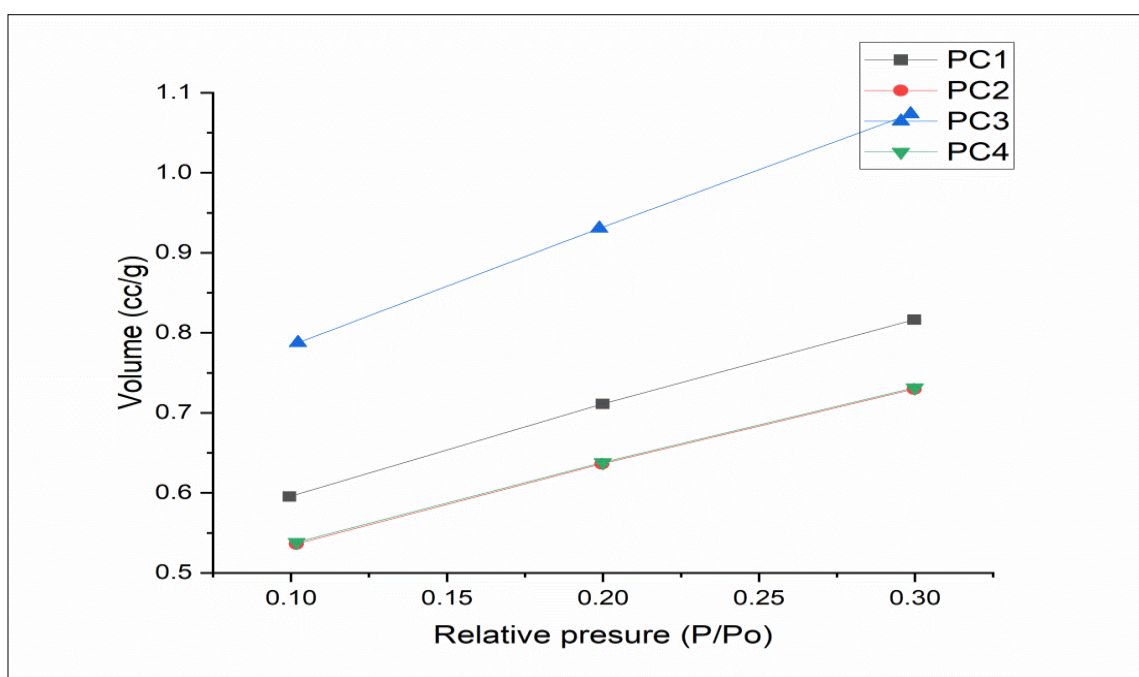


Fig 7: Nitrogen adsorption-desorption isotherm of Pr_2CoO_4 .

The adsorption curves indicate the presence of accessible pore channels and interconnected pore networks. The cobalt-containing oxide exhibited comparatively higher adsorption volume, suggesting improved pore accessibility and surface development. Mesoporous structures are advantageous

because they provide a larger number of accessible active sites and facilitate diffusion of adsorbate molecules. Consequently, these materials may be suitable for adsorption and catalytic applications.

3.7 Structure-Surface Property Correlation

One of the most significant outcomes of the present investigation is the clear relationship between crystallinity and surface development. Pr_2CoO_4 exhibited both higher crystallinity (67.40%) and higher BET surface area ($3.357 \text{ m}^2 \text{ g}^{-1}$) compared with Pr_2NiO_4 , which showed crystallinity of 51.73% and maximum surface area of $2.646 \text{ m}^2 \text{ g}^{-1}$.

This observation suggests that cobalt incorporation promotes both crystal growth and favourable pore evolution during calcination. The improved structural ordering of Pr_2CoO_4 appears to be accompanied by enhanced surface accessibility and pore preservation. Wang *et al.* [10] reported that structural ordering and surface development are closely interconnected in rare-earth oxide systems. The present findings strongly support this conclusion. The combined PXRD and BET results demonstrate that transition-metal chemistry plays a decisive role in controlling crystallinity, pore architecture and surface characteristics. Under identical synthesis conditions, the cobalt-containing oxide exhibited superior physicochemical properties compared with the nickel-containing oxide.

4. Conclusion

Pr_2NiO_4 and Pr_2CoO_4 oxide materials were successfully synthesized using a conventional solid-state ceramic route followed by high-temperature calcination. Powder X-ray diffraction confirmed the formation of well-crystallized orthorhombic phases without significant secondary impurities under the selected synthesis conditions. Comparative crystallographic analysis showed that Pr_2CoO_4 possesses a higher degree of crystallinity (67.40%) than Pr_2NiO_4 (51.73%), indicating superior structural ordering. BET measurements further demonstrated that both oxides exhibit mesoporous characteristics, although their surface evolution differs because of the influence of the transition-metal cation on crystal growth and pore development. The integration of PXRD and BET results establishes a clear relationship between crystal structure, crystallinity, and surface properties. The improved structural ordering and favourable surface characteristics of Pr_2CoO_4 suggest that this material may provide enhanced performance in catalytic, electrochemical, and adsorption-related applications. The present investigation contributes to a better understanding of the influence of transition-metal substitution on the structural evolution of rare-earth mixed oxides synthesized by the conventional ceramic route and provides a useful basis for the future design of advanced functional oxide materials.

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