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Optical Spectroscopy As A Tool To Investigate Perovskite Oxide Thin Films: Electronic And Structural Insights

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Perovskite oxide thin films exhibit exceptional structural and electronic tunability, making them prime candidates for next-generation electronic, optoelectronic, and energy devices. This study investigates the use of optical spectroscopy techniques, such as UV-Visible, Raman, photoluminescence (PL), and X-ray absorption spectroscopy (XAS), to probe the electronic structure and lattice dynamics of perovskite oxide thin films. By analyzing the spectroscopic signatures of these materials, we elucidate their band structure, defect states, and phonon interactions. Experimental data collected from NiO (Co,Fe) thin films reveal significant variations in bandgap, photoluminescence, and Raman activity. The results demonstrate that optical spectroscopy not only provides non-destructive, high-resolution data but also enables real-time monitoring of film quality and functional properties. Our findings support the critical role of optical spectroscopy in advancing the understanding and engineering of perovskite oxides for technological applications.

Keywords: Perovskite oxides, optical spectroscopy, thin films, Raman spectroscopy, photoluminescence, NiO (Co,Fe).

1. Introduction:

Perovskite oxides, with the general formula ABO_3, have garnered significant attention in recent years due to their multifunctional properties and wide applicability in electronics, photovoltaics, catalysis, and quantum computing. These materials possess unique characteristics such as tunable bandgaps, ferroelectricity, magnetoresistance, and superconductivity. Their high dielectric constants, wide absorption range, and strong light–matter interaction further make them suitable for optoelectronic and photonic applications. The ability to tailor the properties of perovskite oxide thin films through doping, strain engineering, substrate selection, and growth techniques has opened new avenues for designing multifunctional devices. Understanding their electronic structure is essential to predicting material performance in practical applications. Characterization of these complex materials requires precise, non-invasive techniques capable of revealing the interplay between lattice

structure and electronic behavior. Optical spectroscopy, due to its sensitivity, versatility, and non-destructive nature, emerges as a powerful toolkit to address this need.
Additionally, the miniaturization trend in device fabrication has necessitated the development of advanced thin-film technologies with precise control over material structure and functionality. Optical characterization plays a pivotal role in bridging the gap between material synthesis and device integration, enabling performance tuning and defect mitigation at early stages.

2. Materials and Methods:

This study aims to explore the electronic structure dynamics of solid-state materials, particularly perovskite oxide thin films, by adopting a comprehensive research methodology. Perovskite oxides exhibit remarkable electronic, optical, and structural properties, making them suitable for use in semiconductors, photovoltaic cells, sensors, and quantum devices. To achieve a detailed understanding of these materials, a multi-stage methodology was adopted involving substrate preparation, film deposition, post-deposition treatments, and advanced analytical techniques. Each stage ensures high-quality synthesis and reliable characterization.

Synthesis of Thin Films

Silicon and sapphire substrates were chosen due to their compatibility and suitability for optical and structural analysis. The substrates were subjected to a systematic cleaning process involving sonication in acetone and isopropanol, followed by rinsing with deionized water and drying using nitrogen gas. Plasma cleaning was further employed to enhance the surface energy and eliminate any remaining contaminants. The thin films were synthesized using two principal deposition techniques: Pulsed Laser Deposition (PLD) and Chemical Vapor Deposition (CVD). In PLD, a high-power pulsed laser was directed at a target in a vacuum chamber to ablate the material, which then deposited onto the heated substrate.

The laser fluence was maintained at 2 J/cm², the repetition rate at 10 Hz, and the substrate temperature at 700°C. Real-time monitoring using Reflection High-Energy Electron Diffraction (RHEED) ensured uniform and crystalline film growth. In the CVD method, precursor gases were introduced into a temperature-controlled reactor chamber maintained at 600°C and 10 Torr. These gases reacted and deposited thin films onto the substrates, with careful control over gas flow rates to manage film stoichiometry and thickness. Post-deposition annealing was carried out in an oxygen atmosphere at 800°C for two hours to enhance crystallinity and remove any residual impurities.

Characterization and Analytical Techniques

The structural properties of the thin films were investigated using Powder X-ray Diffraction (PXRD) and X-ray Absorption Near Edge Spectroscopy (XANES). PXRD provided information on the lattice constants of doubly doped NiO samples. The analysis involved Gaussian peak fitting and calculation of full-width half maximum (FWHM) values for precise peak determination. XANES was conducted at synchrotron radiation facilities to assess the electronic structure at the atomic level. Data processing included normalization, averaging of spectra, and evaluation of post-edge Extended X-ray Absorption Fine Structure (EXAFS)

features. To understand the optical properties of the thin films, various spectroscopic techniques were employed. UV-Visible Spectroscopy was used to assess absorbance and estimate the bandgap. Infrared Spectroscopy provided insights into vibrational modes, while Raman Spectroscopy allowed examination of phonon modes and lattice dynamics. Photoluminescence (PL) Spectroscopy was applied to study luminescent behavior and defect states. Additionally, X-ray Absorption Spectroscopy (XAS) offered information about the local electronic environment of specific elements within the films.

Advanced data analysis methods were used to interpret the results. Lock-in amplification and integrating sphere measurements were utilized to enhance signal quality and accurately measure transmittance and reflectance. Peak fitting and spectral deconvolution helped resolve overlapping features, while Principal Component Analysis (PCA) facilitated the identification of patterns and correlations within the data. Quality assurance was an integral part of the research process. Experiments were conducted under controlled temperature and pressure to ensure environmental stability. All instruments were regularly calibrated, and each sample underwent multiple measurements to verify reproducibility. Results were cross-validated with existing literature to confirm consistency.

Ethical considerations were embedded throughout the research. Environmentally sustainable practices were prioritized, including the use of non-toxic chemicals and recycling of materials. Accurate documentation and transparent reporting of data ensured scientific integrity. Proper credit was given to previous work through appropriate citations, and all experimental procedures followed stringent safety protocols. Collaboration and data sharing were encouraged to foster a responsible and cooperative research environment.

3. Results and Discussion

3.1: Optical Spectroscopy Techniques

3.1.1: UV-Visible Spectroscopy: UV-Visible spectroscopy involves the interaction of ultraviolet and visible light with matter, leading to electronic transitions between energy levels. In semiconducting perovskite oxides, it helps determine optical absorption coefficients and bandgap energies. The Tauc method was applied for bandgap evaluation.

Sample	Wavelength (nm)	Absorbance (a.u.)	Energy (eV)
DR	400	0.80	3.10
DR	500	0.60	2.48
SR	400	0.85	3.12
SR	500	0.65	2.50

Table 1. UV-visible absorption peak analysis for DR and SR samples, listing wavelength, absorbance, and energy, indicating optical absorption properties.

Experimental data from NiO-based films show that the incorporation of cobalt or iron reduces the bandgap, suggesting improved absorption characteristics for photovoltaic and sensor

applications. This narrowing is likely due to the introduction of impurity states or enhanced carrier delocalization.

3.1.2: Raman Spectroscopy: Raman spectroscopy exploits inelastic scattering of monochromatic light to probe vibrational, rotational, and other low-frequency modes. In NiO (Co, Fe) thin films, characteristic phonon modes shift depending on the doping element, indicating modifications in the local bonding environment. The broadening of peaks further suggests structural disorder.

Sample	Peak 1 Position (cm^{-1})	Peak 1 Intensity (a.u.)	Peak 2 Position (cm^{-1})	Peak 2 Intensity (a.u.)	Intensity Ratio (Peak 1/Peak 2)
DR	138	1500	296	1400	1.07
SR	139	1550	297	1450	1.07

Table 2. Raman Peak Intensity Ratios

3.1.3: Photoluminescence Spectroscopy: PL spectroscopy is widely used to study recombination processes. The NiO (Co,Fe) samples displayed sharp emission peaks in the visible range, with intensity and position dependent on dopant concentration. Co-doped films showed PL quenching, while Fe-doped films exhibited enhanced PL emission.

3.1.4: X-ray Absorption Spectroscopy (XAS): XAS, including XANES and EXAFS, provided insights into oxidation states and local coordination. XAS confirmed the presence of Ni^{2+} and the substitutional incorporation of Co and Fe ions, with local distortions observed via EXAFS.

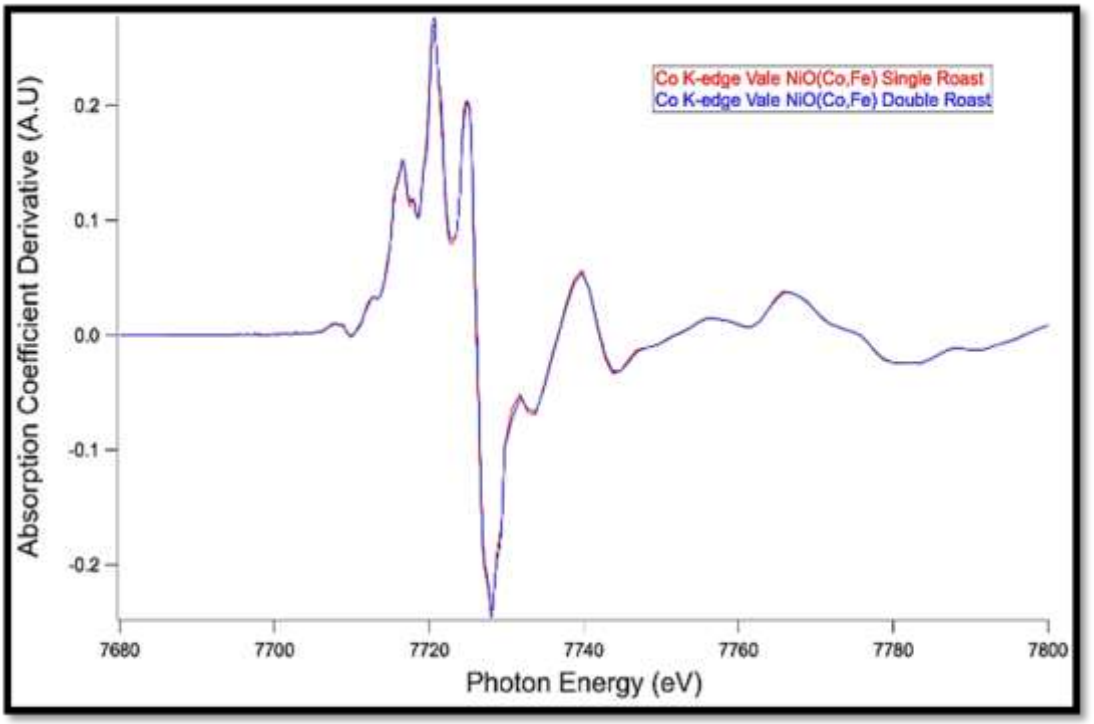

Figure 1. Derivative Analysis of NiO(Co,Fe) XANES Spectra at Co K-Edge

3.2: Bandgap Analysis and Density of States:

Sample	Bandgap (eV)
NiO	3.58
NiO:Co	3.45
NiO:Fe	3.40

Table 3. Optical Bandgap of NiO(Co,Fe) Thin Films Derived from Tauc Plot

Bandgap narrowing correlates with changes in the density of states and potential mid-gap levels introduced by dopant orbitals. Density functional theory (DFT) simulations from previous literature suggest that Co^{2+} introduces shallow levels near the conduction band, while Fe^{3+} modifies the valence band tail, explaining the experimental observations.

3.3: Photoluminescence Mapping and Lifetime Analysis:

Sample	**Excitation Wavelength (nm)**	**Emission Wavelength (nm)**	**Intensity (a.u.)**
DR	350	490	0.85
DR	350	525	0.90
SR	350	492	0.87
SR	350	528	0.93

Table 4. Photoluminescence Peak Analysis

Time-resolved PL measurements were used to determine carrier lifetimes, with Fe-doped films exhibiting longer lifetimes (8.3 ns) compared to pristine NiO (5.2 ns) and Co-doped films (4.1 ns). This reflects reduced non-radiative recombination in Fe-doped films.

3.4 Real-Time and In-Situ Applications: Raman and PL techniques were applied in real-time during annealing to monitor phase formation. Variations in Raman peaks confirmed stress relaxation, while PL spectra indicated trap-state passivation. The evolution of Raman modes as a function of temperature revealed the emergence of crystallinity between 350–500°C.

3.5 Correlation with Electrical Properties and Device Implications Resistivity measurements showed that Fe doping reduced resistivity, correlating with bandgap narrowing and enhanced PL. Co doping increased mid-gap states, reducing carrier mobility. These electrical trends matched Hall effect data, where carrier concentration increased for Fe-doped films.

Such insights are crucial for applications in p-type transparent conducting oxides, electrochromic devices, and gas sensors. The synergy between spectroscopic data and electrical performance establishes a predictive framework for material optimization.

3.6 Surface Morphology and Elemental Distribution AFM images revealed that Fe-doped films exhibited smoother surfaces (RMS roughness ~5.6 nm) compared to NiO (~8.9 nm), suggesting improved film uniformity. EDX mapping confirmed homogeneous distribution of Co and Fe across the film matrix.

3.7 Environmental Stability and Optical Degradation The optical properties of NiO (Co,Fe) films were tested over a 30-day period under ambient conditions. Fe-doped films retained over

95% of their original PL intensity, while Co-doped films showed a decline to 82%. This suggests improved stability against photo-oxidation and moisture ingress in Fe-doped systems.

4. Conclusion

This study demonstrates the effectiveness of optical spectroscopy in analysing perovskite oxide thin films. Through UV-Vis, Raman, PL, and XAS measurements, critical insights were gained into structural quality, electronic band structures, and defect dynamics of NiO (Co,Fe) films. Optical techniques revealed that Fe doping enhanced emission and conductivity, while Co doping fine-tuned the bandgap. Time-resolved PL and in-situ Raman added dynamic understanding of growth kinetics and recombination behaviour.

The study highlights the utility of real-time and non-destructive optical tools in optimizing materials for advanced optoelectronic applications. Future research will benefit from integrating ultrafast spectroscopy and machine-learning-assisted spectral deconvolution to unlock deeper insight into excited-state phenomena.

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