

Abstract

Reliable detection of climate-critical atmospheric pollutants - carbon dioxide (CO_2), sulfur dioxide (SO_2), methane (CH_4), carbon monoxide (CO), hydrogen (H_2), and nitrogen dioxide (NO_2) remains constrained by the cost, complexity, and single-gas limitation of existing sensor technologies. This thesis presents the systematic development of inorganic perovskite oxide (ABO_3) gas sensors as a unified material platform for multi-gas atmospheric monitoring, demonstrating that the compositional flexibility, defect tolerance, and tunable surface chemistry of the perovskite structure can be deliberately engineered to achieve sensitive, selective, and long-term stable detection of six target gases.

The investigation centres on bismuth ferrite (BiFeO_3) and lanthanum ferrite (LaFeO_3) based systems, synthesized via sol-gel auto-combustion, hydrothermal, and chemical co-precipitation routes. Three complementary engineering strategies are pursued: B-site valence engineering through mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ oxidation states, controlled oxygen vacancy incorporation, and morphology-directed synthesis - each targeting specific gas-surface interaction mechanisms.

For carbon monoxide detection, crystallographically tuned BiFeO_3 nanojunction structures were developed, where oriented crystal planes and engineered interfacial contacts enhance charge transport, achieving a response of ~ 6 at 30 ppm CO with stable operation over repeated exposure cycle. A dual-gas sensing platform based on phase-pure $\text{Bi}_2\text{Fe}_4\text{O}_9$ (mullite) demonstrates simultaneous CO_2 (down to 40 ppm) and SO_2 (down to 50 ppb) detection at 250°C using a single sensing element, enabled by coexisting mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ valence states and high oxygen vacancy concentration. The two gases interact through distinct chemical pathways - carbonate formation for CO_2 and Fe^{2+} oxidation with sulfate formation for SO_2 producing distinguishable adsorption-desorption kinetics. A kinetic-index-based discrimination approach exploiting these differences demonstrates reliable gas identification across single-gas and mixed-gas scenarios through principal component analysis and blind validation testing. The sensor maintains operational stability over 180 days with minimal humidity interference, and this dual-gas capability has been granted Indian Patent.

Morphology-controlled BiFeO_3 nanocubes were investigated for hydrogen sensing, achieving a response of ~ 5 at 1000 ppm H_2 , where shape-dependent crystal facet exposure correlates with the enhanced response characteristics. Rare-earth modified BiFeO_3 (Nd-doped) compositions demonstrate nitrogen dioxide sensitivity down to 0.25 ppm with a measurable response of 1.3, establishing A-site substitution as a viable selectivity-tuning strategy.

For methane, the most technically challenging target due to the chemical inertness of CH_4 , oxygen vacancy engineering in LaFeO_3 with a controlled vacancy concentration of $26 \pm 3\%$ enables detection down to 1

ppm at 250°C, with only 8.7% humidity degradation compared to 40–60% typical of conventional binary oxides. Langmuir–Freundlich kinetic modelling validates the vacancy-mediated sensing mechanism, while stability testing over 200 days confirms a degradation time constant of ~361 days with reproducibility across ten independent devices.

Comprehensive characterisation combining XRD, FESEM, XPS, HRTEM, EPR, and UV-Vis spectroscopy establishes quantitative structure–property–performance relationships throughout the work. This thesis demonstrates that the ABO_3 perovskite architecture functions as a programmable material platform where A-site composition, B-site valence, oxygen sub lattice defects, and nanostructure morphology serve as independent engineering parameters, capable of addressing multi-gas, field-deployable sensing demands for climate monitoring, industrial safety, and environmental assessment.

Keywords: Perovskite oxide gas sensors; oxygen vacancy engineering; dual-gas detection; methane sensing; $BiFeO_3$; $LaFeO_3$; $Bi_2Fe_4O_9$; chemiresistive sensing; atmospheric pollutant monitoring; long-term stability