Effect of temperature on structural properties and photocatalytic performance of Ni- and Mn-doped $LaCoO_3$

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$LaCoO_3$ (LCO) perovskites excel in photovoltaics, catalysis, and energy storage due to their robust chemical stability and durability [1,2]. Their crystal structure exhibits trigonal symmetry (space group *R*-3*c*) resulting from cooperative rotations of oxygen octahedra, based on the archetypal cubic ABX_3 perovskite ($A = La^{3+}$, $B = Co^{3+}$, $X = O^{2-}$). Doping with transition metals at the A- and/or B-sites enhances their structural, chemical, and electrical properties, thereby unlocking novel functionalities and improving performance in a wide range of applications. This study investigates the (micro)structural evolution of undoped $LaCoO_3$, $LaCo_{1-x}Ni_xO_3$ (x = 1.3, 2.9 at.%), and Mn-doped $LaCo_{1-x}Mn_xO_3$ (x = 1.7, 2.8 at.%) hydrothermally synthetized powders upon heating to 1000 °C and subsequent cooling to ambient temperature. We employed in situ laboratory powder X-ray diffraction (PXRD) with controlled heating and slow cooling to probe cation ordering across key temperature ranges. In addition to analysing diffraction peak broadening, we detail temperature-driven shifts in the oxygen positional parameter, La–O and Co/Ni(Mn)–O bond lengths, and Co/Ni(Mn)–O–Co/Ni(Mn) bond angles within constrained structural models during Rietveld refinements. Field-emission scanning electron microscopy (FE-SEM) of as-heated, slowly cooled, and pre-treated samples reveals the impact of thermal treatment on the microstructure and morphology of LCO samples. PXRD revealed that all samples were nanocrystalline, maintaining hexagonal symmetry across the entire temperature range. Although there is a relative possibility of pseudo-symmetry (space group *Pm*-3*m*) in pure LCO, the doublet peak splitting at 69° 2θ eliminates this possibility. At room temperature, Ni- and Mn-doped LCO showed expanded unit cell parameters and broader diffraction peaks, yet cation ordering remained largely stable with heating. Heating undoped and doped LCO to 1000 °C followed by reverse cooling results in well-resolved doublet peaks in the PXRD patterns. Heating reduces lattice microstrain, sharpens doublet reflection splitting, and significantly alters oxygen positional features and metal–oxygen distances, which are responsible for the catalytic properties of LCO. It has been shown that doping with Ni and Mn clearly enhances photocatalytic activity; however, temperature has a dual impact on the photocatalytic process. Larger crystallites formed at elevated temperatures are expected to reduce the degradation efficiency of cefixime (used as an organic model pollutant). Nevertheless, despite the formation of a small percentage of the additional La_2O_3 phase, its presence has a positive influence on catalysis, slightly increasing the degradation efficiency.

[1] S. Jayapandi et al, J. Sustain. Technol. Mater. (2025). 43, e01225.
[2] Y.S. Orlov et al, Dalton Trans. (2025). 54, 4530-4541.

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