Effect of B-site substitution on the structural properties of La$_{0.2}$Na$_{0.8}$Al$_{0.3}$M$_{0.7}$O$_3$(M=Mg and Mn) perovskite oxides

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This study focuses on solar-based thermochemical methods to obtain hydrogen, which is a clean energy source, at a low cost in one step without the need for a secondary separation process [1]. For this purpose, non-stoichiometric perovskite oxides with high redox capacity, stable and fast reaction kinetics were preferred [2].

The effect of B-sites substitution on the structural properties of La$_{0.2}$Na$_{0.8}$Al$_{0.3}$M$_{0.7}$O$_3$ (M=Mg and Mn) perovskite oxides were investigated in this study. La$_{0.2}$Na$_{0.8}$Al$_{0.3}$Mn$_{0.7}$O$_3$(LNAMn-2837), La$_{0.2}$Na$_{0.8}$Al$_{0.3}$Mg$_{0.7}$O$_3$ (LNAMg-2837) were synthesized by the Pechini method to observe the effect of structural properties on hydrogen production.

As precursors La(NO$_3$)$_3$, 6H$_2$O, Na(NO$_3$), Al(NO$_3$)$_3$, 9H$_2$O, Mn(NO$_3$)$_2$, 4H$_2$O, Mg(NO$_3$)$_2$, 6H$_2$O were used to synthesize the perovskite powders. Citric acid was added as a chelating agent where ammonium solution was used to adjust the pH of the solution. After pre-calcination of the powders synthesized at 250 °C for 2 hrs, calcination was carried out at 900 °C, 1100 °C and 1300 °C for 6 hrs.

X-ray diffraction (XRD) was performed to determine the crystal structure of perovskite materials synthesized. XRD patterns were collected with a scan rate of 2°/min as shown in Figure 1 and 2. It was observed that while rhombohedral and orthorhombic structures were formed by Mn substitution, whereas Mg substitution resulted in rhombohedral and hexagonal structures for perovskites synthesized under the same experimental conditions.

LNAMn-2837 and LNAMg-2837 were synthesized via the Pechini method to be used as active materials in two-step thermochemical water splitting to evaluate hydrogen production amount. XRD studies revealed that B-site dopant has an influence on the final structure. It was observed that both perovskite oxide LNAMn2837 and LNAMg2837 structures were initially rhombohedral structures containing a small amount of orthorhombic and hexagonal structure secondary perovskite structures, respectively. It was also confirmed by decreasing orthorhombic and hexagonal secondary perovskite oxide structures that the rhombohedral structure became more stable for both compositions with increasing calcination temperature. Results of thermochemical water splitting tests were used to correlate the structural results with hydrogen production.

References
