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Modulating the O-binding energies of Mn-based perovskites towards the maximization of solar thermochemical hydrogen (STCH) production

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Solar thermochemical hydrogen (STCH) production is a potential method for the clean evolution of H_2 from H_2O and solar energy through a two-step redox cycle. In the first step, a transition metal oxide (TMO) is thermally reduced, releasing O_2 from the crystal lattice and subsequently forming oxygen vacancies (O_v). In the second step of a STCH cycle, the metal oxide is thermally oxidized in steam, forming H_2 gas as a product. During this redox cycle, the formation of O_v in the crystal lattice of the TMO are stabilized by the ability of the transition metal to adopt difference valence states. For example, manganese is well known for its ability to change oxidation states between $Mn^{4+}/Mn^{3+}/Mn^{2+}$ during redox cycling. While Mn-based perovskites have been reported as promising materials for STCH production, little mechanistic insight into how to further improve on the overall H_2 production in these systems is known. Ideally, modulating the Mn-O binding energy in a complex metal oxide or perovskite would promote both O_v formation during reduction and the subsequent oxidation of O_v in steam to maximize water-splitting activity. However, the ability to independently modify both maximize reduction of a perovskite while also promoting oxidation of the material in steam has not yet been realized.

Here we explore two methods for modifying O_v energies in the Mn-based perovskite $BaCe_{0.25}Mn_{0.75}O_3$ (BCM), a highly active material for STCH production. First, the formation of twin defects during redox cycling in BCM creates local chemical environments that modify the O_v formation energy. The structure of these twins and the corresponding O_v formation energies, calculated from density functional theory (DFT), are shown in Figure 1 for BCM. Alternatively, by substituting for Ce in BCM with other cations, a family of related materials in the form of $BaX_{0.25}Mn_{0.75}O_3$ (BXM), where X = Pr or Nb, was recently synthesized (Figure 2) and tested for their H_2 production activity in a stagnation flow reactor. Interestingly, BCM demonstrated the highest H_2 production activity, especially under high conversion conditions (H_2O:H_2 1333:1) relative to both BNM and BPM. Combining information obtained from X-ray diffraction (XRD), X-ray absorption (XAS), and STEM-EELS analysis we probed the compositional, structural, and electronic changes that occurred in these materials during redox cycling. Material was analyzed ex situ after STCH cycling in the flow reactor. and during in situ reduction in the TEM. The H_2 production in this class of BXM materials depends on both the chemical environment and density of twin boundaries present during STCH cycling, which further provide nucleation sites for phase transformations that affect the overall water-splitting activity observed in these systems. High energy and spatial resolution microscopy is necessary to enable observations of the important microstructural features in these materials important for renewable energy production.

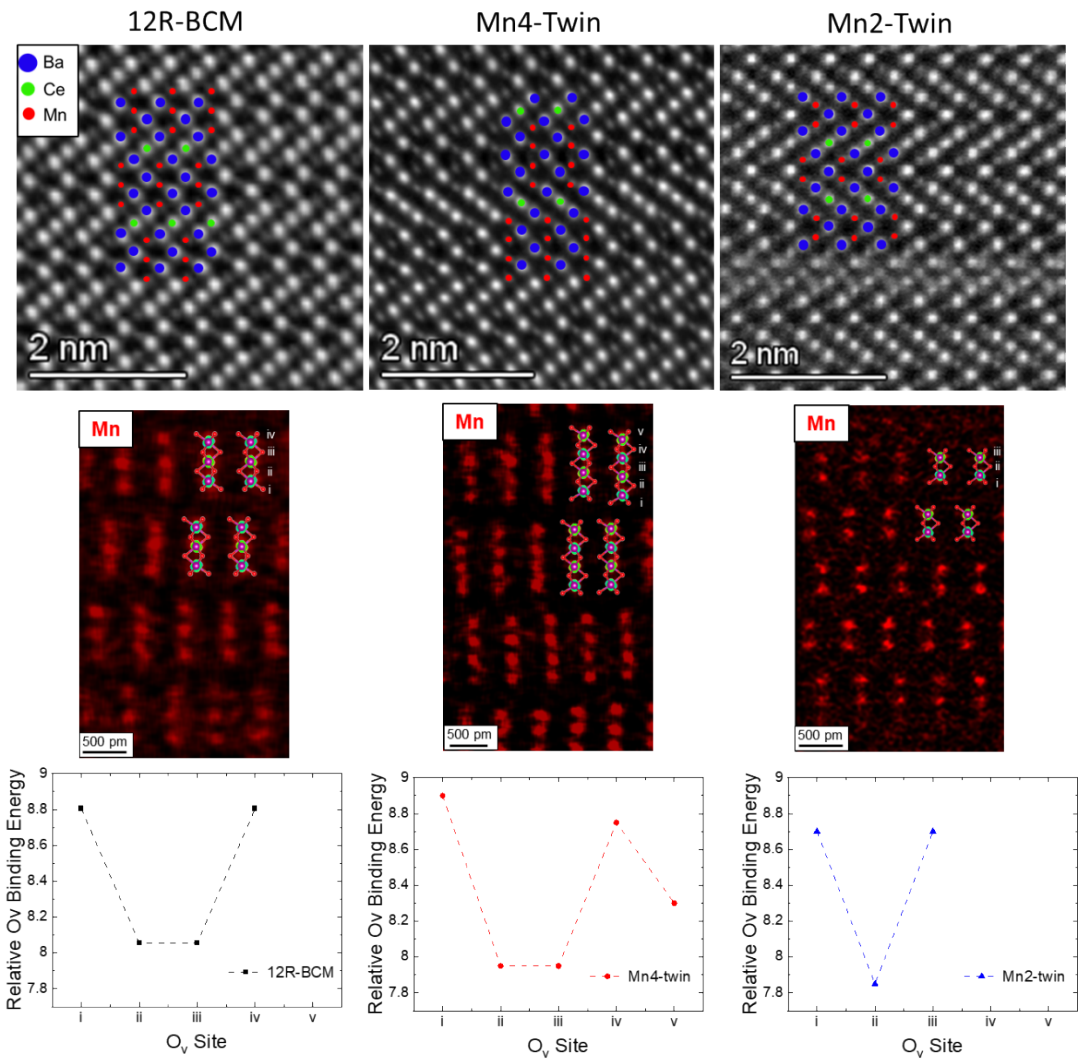
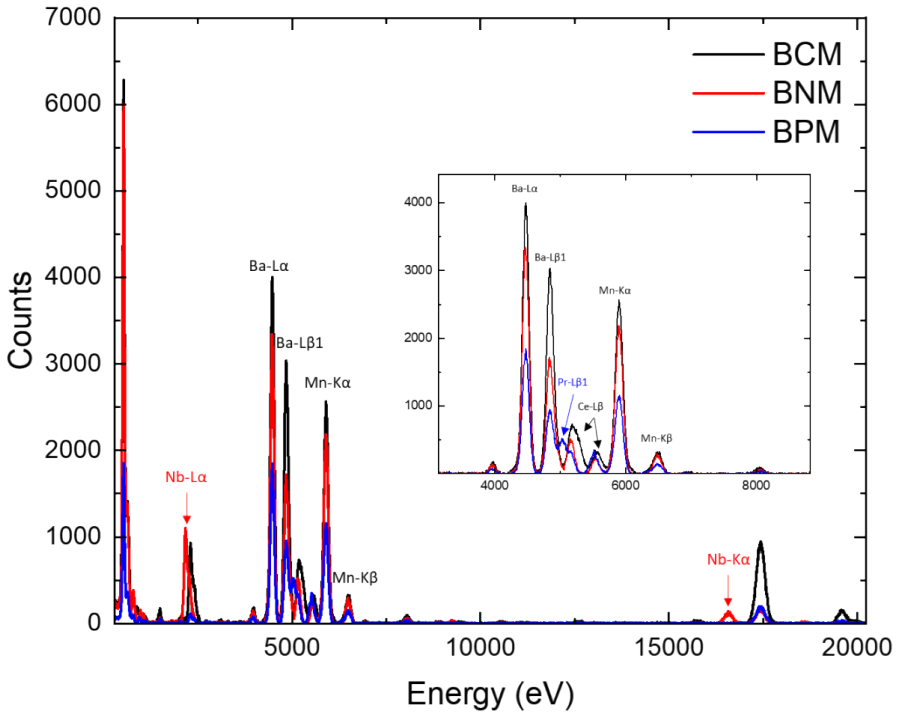


Figure 1. (top row) Atomic-resolution STEM images and structural model overlays, (middle row) EDS maps of the Mn-signal with structural model overlays (including O) of the Mn trimers, quadrimers, and dimers and (bottom row) scatter plots of the O_v formation energies of each of the O-binding sites designated in the EDS maps as i-v of (left column) 12R-BCM , (middle column) Mn4-twins, and (right column) Mn2-twins. 12R-BCM and the Mn4-twins are present in oxidized BCM while the Mn2-twin is present in the reduced state.



Element	BCM	BNM	BPM
O	61±2	59±2	58±2
Ba	22±2	20±2	20±2
X = Ce, Nb, Pr	5±1	5±1	5±1
Mn	17±2	16±2	16±2

Figure 2. Table showing EDS spectra of BCM, BNM, and BPM with corresponding elemental compositions for O, Ba, X (Ce, Nb, or Pr, respectively), and Mn.

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