Reversible Oxygen Exchange and Composition-Structure Relationships in High-Entropy Perovskites

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High-entropy oxides (HEOs) typically contain five principal elements randomly distributed over a single crystallographic site. These compositionally complex solid solutions provide exceptional flexibility for tuning functional properties and show strong potential for industrially relevant applications. For example, HEOs exhibit tunable magnetic behavior [1], high proton conductivity [2], and excellent catalytic activity for the oxygen evolution and reduction reactions [3]. At the same time, their expanded compositional space compared to conventional solid solutions presents significant synthetic challenges.

In this study, we have investigated composition-structure relations of rare-earth ABO_3 HEOs. Depending on the elemental combinations at the A and B sites, the materials crystallize in bixbyite, orthorhombic perovskite, or hexagonal perovskite structures. Remarkably, the structural symmetry can be tuned by slight compositional modifications. For example, substituting Yb with Tb in $(Dy_{0.2}Y_{0.2}Ho_{0.2}Er_{0.2}Yb_{0.2})MnO_3$, changes the symmetry of the perovskite from hexagonal to orthorhombic. Furthermore, while $(Dy_{0.2}Y_{0.2}Ho_{0.2}Er_{0.2}Tb_{0.2})MnO_3$ forms an orthorhombic perovskite and $(Dy_{0.2}Y_{0.2}Ho_{0.2}Er_{0.2}Tb_{0.2})InO_3$ adopts a bixbyite structure, intermediate solid solutions $(Dy_{0.2}Y_{0.2}Ho_{0.2}Er_{0.2}Tb_{0.2})Mn_{1-x}In_xO_3$ (x = 0.25 - 0.75) surprisingly form hexagonal perovskites instead. In selected compositions, we observe a reversible oxygen loss (~2 wt%) and uptake process starting at temperatures as low as 280 °C, evidenced by temperature-dependent X-ray diffraction and thermogravimetric analysis. This process is both composition- and structure-dependent.

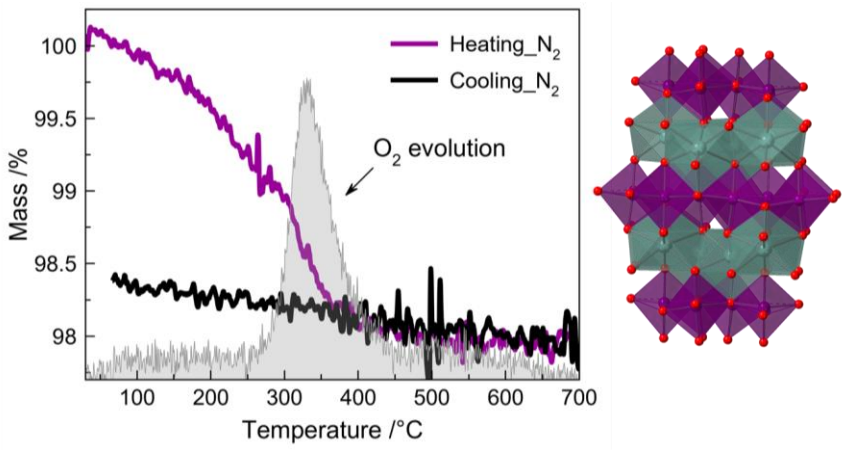


Figure 1. *Temperature-dependent oxygen loss of hexagonal perovskite* $(Dy_{0.2}Y_{0.2}Ho_{0.2}Er_{0.2}Tb_{0.2})Mn_{0.75}In_{0.25}O_3$

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[3] Wang, X., Singh, H., Nath, M., Lagemann, K., Page, K. ACS Mater. Au (2024) 4, 274