

Fine structure tuning for strongly correlated functionalities in high entropy oxides

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Background incl. aims

Strongly-correlated phenomena, such as, colossal magnetoresistance (CMR) and metal-insulator transitions (MIT), exhibited by perovskite manganites are accompanied and reinforced by coexistence of competing magneto-electronic phases [1]. Such magneto-electronic inhomogeneity is governed by the intrinsic lattice-charge-spin-orbital correlations, which are conventionally tailored via chemical substitution, charge doping or strain engineering. Alternately, the recently discovered high entropy oxides (HEOs), owing to the presence of multiple-principal cations on a given sub-lattice, exhibit indications of an inherent magneto-electronic phase separation encapsulated in single crystallographic phase. In this abstract we present the structure characterization at atomic resolution for a series of single-phase orthorhombic HE-manganites, $(\text{Gd}_{0.25}\text{La}_{0.25}\text{Nd}_{0.25}\text{Sm}_{0.25})_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0 - 0.5$), which combines high entropy (HE) concept with standard property control by Sr^{2+} (hole) doping, with the aim to extend the HE based approach to design strongly-correlated systems. High resolution scanning transmission electron microscopy (HR-STEM) and integrated differential phase contrast (iDPC) imaging have been used to determine the crystal structure variations in HEO introduced by different Sr concentrations. Electron energy-loss spectroscopy (EELS) has used to reveal the Mn valence change with Sr doping levels. We aim to correlate the atomically resolved geometric and electronic structures to the finely tuned electromagnetic properties of the series of Sr doped HEOs.

Methods

The powder samples were synthesized using nebulized spray pyrolysis (NSP) technique. The details of the synthesis procedure can be found elsewhere [2]. A double aberration corrected transmission electron microscope Themis Z (Thermo Fisher) equipped with a Super-X energy dispersive X-Ray detector and Gatan GIF Continuum 970 HR + K3 IS camera (operated at 300 kV) were used to examine the specimens.

Results

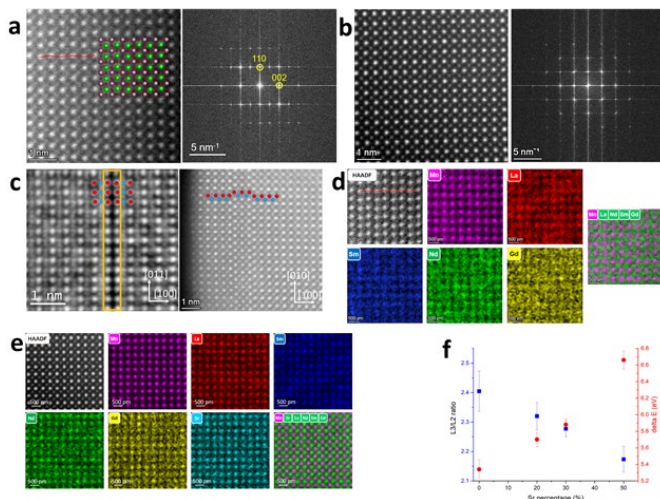
From the high-angle annular dark-field (HAADF) STEM images, the strong orthorhombic distortion can be identified for $x = 0$ (Figure 1a). The distortion becomes weak with increasing the Sr concentration. For $x = 0.5$ system (Figure 1b), the crystal structure is very close to pseudo-cubic. However, the higher symmetric phase shows noticeably higher density of different types of lattice defect, including twin boundaries and Ruddlesden-Popper faults, as revealed by iDPC and HAADF images in Figure 1c along $[01-1]$ and $[001]$ zone axis, respectively. Figure 1d and 1e present the HAADF STEM image and the corresponding atomically resolved elemental distribution maps for $x = 0$ and $x = 0.5$. A homogenous distribution of the rare-earth cation (and Sr for $x = 0.5$) on the A-site (RE) sub-lattice along with presence of Mn on the B-site sub-lattice, without any observable segregation at the atomic length scales, can be confirmed. The change in the oxidation state of Mn can be evaluated from the integrated area ratio of the Mn L3 to L2 edges (L3/L2 ratio) and the energy difference (ΔE) for the O K-edge features between the Mn 3d feature (~ 530 eV) and the RE 5d/Sr 4d feature (~ 536 eV). The changes in the Mn L3/L2 ratio and ΔE as a function of Sr^{2+} doping (Figure 1f)

unambiguously confirms that increasing amount of Sr²⁺ doping results in change of Mn valence state from ~3.1+ for 0%Sr to ~3.6+ for 50% Sr. The quantitative EELS analysis indicates that the separation of the antiferromagnetic ferromagnetic phases mainly depends on the ratio of the Mn³⁺ and Mn⁴⁺. More Mn⁴⁺ enhances the double-exchange interaction between Mn³⁺ – O – Mn⁴⁺, which increases the ferromagnetic component.

Conclusion

This initial study signals excellent potential to achieve complex magneto-electronic phase diagram with unique temperature dependencies that stem from competing magneto-electronic interactions. The unique subtle properties can be tuned by the merger of the high entropy-based design approach with the strongly correlated electron systems. The tunable electromagnetic properties are attributed to the structure changes by the high-resolution imaging and EELS analyses showing an increase in the amount of Mn⁴⁺ and a corresponding decrease in Jahn–Teller effect and the degree of orthorhombic distortion upon increasing amount of Sr²⁺ doping [3].

Graphic:



Keywords:

high entropy oxide, STEM, EELS

Reference:

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