

# Anion structures of fluorite-type high entropy materials and their effects on ion transport and catalysis

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## Topics

Structure-property relationship

## Communication type

Oral

## Abstract

High entropy oxides are attracting attention for catalysis, but there are few studies on their precise structure, hampering true detailed investigations on fundamental properties. Using combined synchrotron X-ray and neutron scattering, we have looked at the structure of high-entropy  $(\text{La,Ce,Pr,Nd,Y})\text{H}_{1.5}\text{O}_{0.75}$  and  $(\text{La,Ce,Pr,Nd,Y})\text{O}_{1.68}$ . Together, these offer contrasting examples of anion-excess and anion-deficient fluorites, respectively. While they roughly adopt fluorite-type structures, the anion coordination sites are somewhat different from their low-entropy analogues.

With the oxyhydride  $(\text{La,Ce,Pr,Nd,Y})\text{H}_{1.5}\text{O}_{0.75}$ , we find additional hydride interstitials not present in low-entropy analogues such as  $\text{SmH}_{1.5}\text{O}_{0.75}$  or  $\text{La}_{1.5}\text{H}_{0.75}$ . As a result, bond valence sum energy mapping shows low activation barriers for hydride diffusion, and impedance measurements also show a correspondingly low activation barrier of 46 kJ/mol.

Anion-deficient  $(\text{La,Ce,Pr,Nd,Y})\text{O}_{1.68}$  exhibits a structure (Ia-3) similar to  $\text{CeO}_{1.68}$ ; however, oxide position shifts result in a large difference of cation coordination polyhedra volumes. Here too, bond valence sum energy mapping shows more facile oxygen diffusion pathways compared to  $\text{CeO}_{1.68}$ ,  $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_{2-????}$ ,  $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_{2-????}$ . All of these latter materials are known as oxygen storage materials in oxidation catalysis. Our own results show enhanced methane oxidation activity and oxygen storage capacity of  $(\text{La,Ce,Pr,Nd,Y})\text{O}_{1.68}$ . This is due to high-entropy induced resistance to sintering, and full utilization of Ce/Pr oxidation range as a result of the enhanced oxygen diffusion.

## Annexes

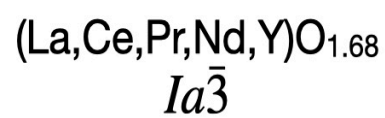
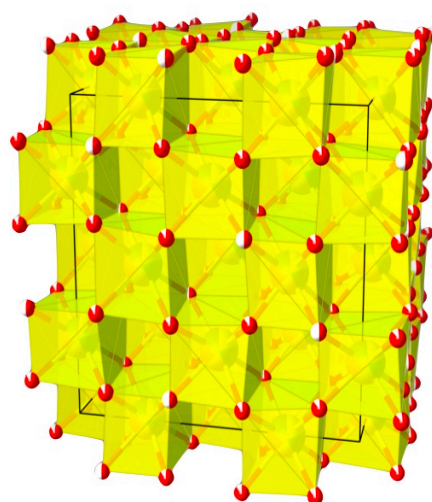
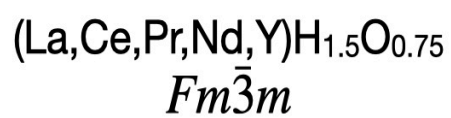
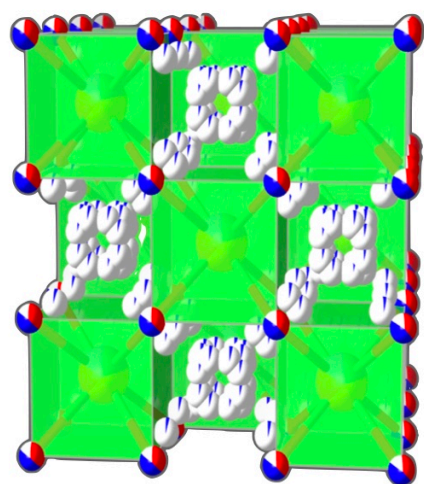


Figure 1: Fig. 1. Structures of  $(\text{La,Ce,Pr,Nd,Y})\text{H}_{1.5}\text{O}_{0.75}$  and  $(\text{La,Ce,Pr,Nd,Y})\text{O}_{1.68}$ .