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SYNTHESIS AND STRUCTURAL ANALYSIS OF HIGH-ENTROPY OXIDE $(CoCrFeMnNi)_3O_4$

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Abstract
Technological developments and the demand for innovative products in catalysis and energy conversion/storage have driven the development of high entropy alloys (HEAs) and high entropy oxides (HEOs). HEAs, formed by combining four or more elements in nearly equal ratios, and HEOs have become prominent research topics for the above-mentioned technologies. HEOs are typically synthesized through solid-state reactions due to easy processability. In this study, high entropy oxide was designed and optimized using atomic level modeling [(density functional theory (DFT)] to guide synthesis studies. Accordingly, synthesis of $(CoCrFeMnNi)_3O_4$ high entropy oxide with AB_2O_4 type spinel structure having Fd-3m cubic space group symmetry was carried out using solution combustion synthesis (SCS).

1. Introduction

HEOs exhibit exceptional structural and functional properties, making them ideal for applications in catalysis, energy storage, and electronics. This study focuses on synthesizing $(CoCrFeMnNi)_3O_4$ spinel structured HEO using SCS and computational methods. SCS enables the rapid formation of high-purity, fine-grained oxides through the exothermic combustion of metal nitrates and fuel. Cluster expansion (CE) together with special quasirandom structures (SQS) may be used to generate relevant atomic configurations and perform DFT calculations which are used to determine the electronic structure, magnetic properties, and phase stability of the target HEO.

2. Materials and Methods

Synthesis of the HEO was carried out by solution combustion synthesis (SCS) using metal nitrates as oxidants and glycine ($C_2H_5NO_2$), urea (CH_4N_2O) and citric acid ($C_6H_8O_7$) as fuels. The precursors were dissolved in distilled water and heated up to combustion temperature. Selected combustion reaction products were calcined at three different temperatures for 1 hour. The products obtained after combustion and calcination were characterized by Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS) and X-ray Diffraction (XRD) analyses.

In the unit cell of the HEO, the five cations (i.e. Cr, Mn, Fe, V, Ni) were randomly distributed in slightly off-stoichiometric ratios. The lowest energy configuration of the random structures were used in DFT calculations for guiding experiments.

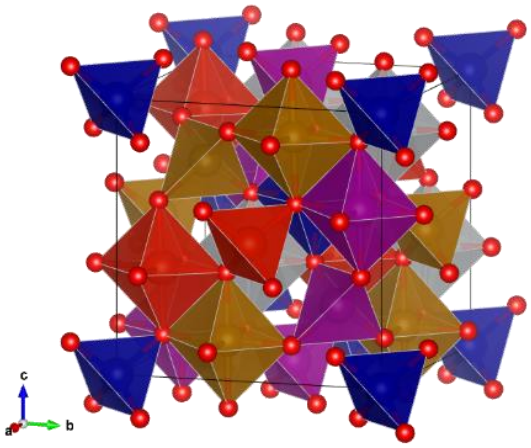

Figure 1. Crystal structure of HEO. Cr: blue, Mn: purple, Fe: brown, V: red, Ni: grey color.

Conclusion

Characterization of SCS products shows that when comparing fuel types (glycine, urea and citric acid), glycine gives better results in terms of combustion efficiency and product quality. Furthermore, XRD analysis reveals a strong similarity between the patterns of 5 randomized crystal structures after geometry optimization and that of the Fe_3O_4 crystal structure.

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