$BaCe_{0.25}Mn_{0.75}O_3$ structures for the 12R and 10H polytypes

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Within the HydroGEN Energy Materials Network, $BaCe_{0.25}Mn_{0.75}O_3$ (BCM) is of interest for Solar Thermo-Chemical Hydrogen (STCH) generation. The purpose of this dataset is to provide explicit structure models for both the 12R (ground state) and 10H (metastable at ambient temperature) polytypes of BCM. These structure models can be used for further electronic structure calculations and comparisons with experimental data.

The experimental crystal structures of the 12R and 10H polytypes have been published in Refs. [1] and [2], respectively, and the respective crystallographic information files (CIF) are available from the Inorganic Crystal Structure Database (ICSD) [3]. However, these structures cannot directly be used for electronic structure calculations, since the magnetic (12R and 10H) and configurational (10H) degrees of freedom are averaged. For an explicit structure model, magnetic configurations (spin arrangements) of the Mn^{4+} ions are assigned via Monte-Carlo sampling. In case of the 10H polytype, there is a Wyckoff position that is shared between Mn and Ce ions with fractional occupancies. Explicit Mn/Ce arrangements are determined. Further, the structure information for the 10H polytype reported in the original article [2] exhibits inconsistencies which are resolved. Structural relaxation and total energies were determined by density functional theory (DFT) calculations.

12R polytype (antiferromagnetic): Starting from the experimental CIF, a 20 atom rhombohedral primitive cell was created. Since this structure contains 3 Mn ions and only a single Mn1 site, it does not accommodate a well defined antiferromagnetic (afm) configuration. Three different 40 atom supercells were constructed by expanding the primitive cell within the basal plane, and the energies of different afm configurations were evaluated. The structure with the lowest DFT energy is included in the dataset. It is noted that the search was not extensive, and it is possible that afm configurations with still lower energy exist. More details about the supercell construction are given in the README files contained in the dataset.

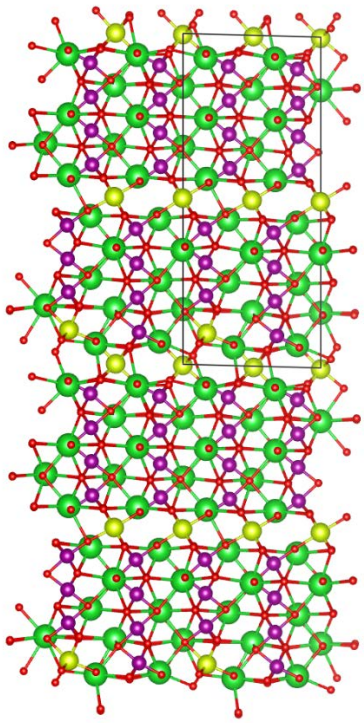

Figure 1: Representative structure of BCM in the 10H polytype, showing Ba (green), Ce (yellow), Mn (purple), and O (red).

12R polytype (paramagnetic): At the temperatures of interest for STCH, BCM is paramagnetic (pm). In order to create pm samples, a 160 atom supercell was generated and MC sampling of pm configurations was performed with a temperature of 1000 °C. The equilibrated configurations for 5 different MC seeds are included in the dataset.

10H polytype (paramagnetic): The crystallographic parameters published in Ref. [2] are inconsistent, requiring a correction before constructing explicit structure models. Specifically, the O1 parameters for the 6h site are given in table 1 of Ref. [2] as (x = 0.1764, y = –0.1925, z = 0.25), whereas, in the hexagonal space group # 194, the 6h site requires the format (x, $-x$, 0.25) by symmetry (see, e.g., the Bilbao crystallographic server [4]). In one approach, the x and y parameters were averaged to x = 0.1844. A second correction approach is suggested by the CIF, where in deviation of the original reference, O1 was defined as a 12j site, but with a fractional O occupancy of 0.5. Additionally, minor

inconsistencies in the O2 and O3 sites were also corrected. Unit cells with 50 atoms were generated for both approaches. Since the 12j site occurs in close pairs with only 0.1 Å distance, occupancies were searched for that avoid such close O-O pairs. The resulting nearest neighbor distances and coordinations agree with table 2 in Ref. [2], except for Ba1-O1 = 2.899 instead of 2.852 in case of the first correction approach using the 6h site. The original and corrected cif files are included in the dataset.

In order to accommodate the Mn2/Ce2 distribution on a shared 4f site, two 200 atom supercells were generated, and different Mn2/Ce2 configurations were sampled with a 7:1 ratio of Mn2:Ce2. Based on the DFT total energy ordering in a ferromagnetic (fm) configuration, two Mn2/Ce2 configurations were selected for each supercell type. Both correction approaches described above gave similar structures, but the approach using the 6h site gave the lowest energy, and the 12j approach did not give any new structures not contained in 6h set. In order to determine paramagnetic configurations, MC calculations were performed for 1000 °C, similarly as above for the 12R polytype. The dataset includes 3 different pm configurations for each atomic configuration, resulting in a total of 12 structures and their corresponding DFT calculations. A representative structure of the 10H polytype is shown in Figure 1.

Methods: DFT calculations were performed using the vasp code [5] using the generalized gradient approximation and DFT+U with U = 3 eV for Mn-d. Unit cells were generated from CIF files using the cif2cell code [6], and CIF files were generated from DFT relaxed supercells using the findsym code [7]. Figure 1 was generated using the vesta code [8]. Supercell generation and MC simulations were performed using custom codes.

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