

Substitution of Ti^{3+} and Ti^{4+} in hibonite (CaAl_2O_9)

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ABSTRACT

The structures of eight synthetic samples of hibonite, with variable Ti oxidation state and Ti concentration (2.4–15.9 wt% TiO_2) that span the range reported for natural hibonite found in meteorites, were determined by Rietveld refinements of neutron powder diffraction data. Ti^{3+} was found to exclusively occupy the octahedral face-sharing M4 site irrespective of the presence or absence of Ti^{4+} . Ti^{4+} partitions between the trigonal bipyramidal M2 site and the M4 site. The ratio (Ti^{4+} on M2):(Ti^{4+} on M4) appears to be constant for all the samples, with an average of 0.18(2) irrespective of the concentrations of Ti^{3+} and Ti^{4+} . These substitutional sites were shown to be the most stable configurations for Ti in hibonite from calculations using density functional theory, although the predicted preference of Ti^{4+} for M4 over M2 is not as strong as is observed. This is attributed to the different Ti contents of the experimental and calculated structures and suggests that the Ti site occupancies might change between these concentrations. Furthermore, it is shown that Ti has a preference to occupy neighboring M4 sites such that Ti-Ti interactions occur with stabilization energies of 83 kJ/mol for Ti^{3+} - Ti^{3+} and at least 15 kJ/mol for Ti^{4+} - Ti^{4+} . Features in optical spectroscopy and electron spin resonance data from meteoritic and synthetic hibonites that have been used to infer $\text{Ti}^{3+}/\text{Ti}^{4+}$ are shown to actually derive from these Ti-Ti interactions. The amount of Ti^{4+} in hibonite can be determined from the unit-cell parameters if ΣTi is determined independently. $\text{Ti}^{3+}/\text{Ti}^{4+}$ in hibonite may record the oxygen fugacity (f_{O_2}) of the early solar nebula, however, the existence of Ti^{3+} - Ti^{3+} and Ti^{4+} - Ti^{4+} interactions and the potential for Ti^{4+} - Ti^{3+} interactions need to be considered when interpreting spectroscopic data in terms of Ti valence state and f_{O_2} . Hibonite as a single-mineral oxybarometer must be used with caution due to the potential role of crystal chemistry (including Ti-Ti interactions) to stabilize Ti oxidation states independently of f_{O_2} .

Keywords: Hibonite, titanium substitution, site occupancy, CAI, neutron diffraction, density functional theory, oxygen fugacity