

A first-principles investigation on the enthalpy landscape for the hibonite solid solution: Implications for a nebular barometer

PIERRE-MARIE ZANETTA^{1,*†}, ABHISHEK KUMAR THAKUR², VENKATESWARA RAO MANGA^{1,2}, KRISHNA MURALIDHARAN^{1,2}, AND THOMAS J. ZEGA^{1,2}

¹Lunar and Planetary Laboratory, University of Arizona, 1629 E. University Boulevard, Tucson, Arizona 85721, U.S.A.

²Materials Science and Engineering, University of Arizona, 1235 E. James E. Rogers Way, Tucson, Arizona 85721, U.S.A.

ABSTRACT

Hibonite, nominally CaAl_2O_9 , is among the first minerals thermodynamically predicted to have formed in the early history of our solar system. It can incorporate significant amounts of Ti (≤ 15 wt%, ~ 2 cations per formula unit) into its crystal structure, as both Ti^{4+} and Ti^{3+} . The main pathways for Ti incorporation in the solar nebula include a direct substitution of Ti^{3+} replacing Al^{3+} and a coupled substitution in which Ti^{4+} and Mg^{2+} replace two Al^{3+} . Additionally, the formation of oxygen vacancies can also reduce a Ti^{4+} cation to Ti^{3+} by trapping a free electron. The relative amounts of these cations potentially reflect the fugacity of oxygen (f_{O_2}), a fundamental thermodynamic parameter, that prevailed when hibonite first formed or last equilibrated. However, the Ti content and its oxidation state in hibonite does not depend solely on f_{O_2} . The composition of the system is, thus, a key factor in changing the $\text{Ti}^{4+}/\Sigma\text{Ti}$ ratio of the structure concurrently with the f_{O_2} . Therefore, it is necessary to understand the energetics, complex crystal chemistry, and substitution reactions of hibonite to relate the Ti oxidation state to the f_{O_2} of the nebular system in which it condensed.

To that end, we report DFT calculations (0 K) to determine the ground-state energies and the enthalpy of formation (ΔH) of hibonite solid solutions that span the range reported in meteorites. Our results show that coupled substitution is energetically favored ($\Delta H = -96.70$ kJ·mol⁻¹, from oxides). In comparison, the formation of oxygen vacancies is energetically unfavorable, though similar to Ti^{3+} direct substitution for Al^{3+} ($\Delta H = \sim 60$ kJ/mol, from oxides), which is commonly observed in hibonite. It is therefore necessary to consider oxygen vacancies as a potential mechanism for controlling the incorporation of Ti^{3+} into hibonite, in addition to direct replacement reactions. We provide here the first reliable estimation of the formation enthalpies for the hibonite solid solution that includes solutes and point defects. The results presented herein constitute a significant advance toward the establishment of a comprehensive Gibbs free energy description of the hibonite solid solution, which is ultimately required for accurate modeling of its thermodynamic stability within the early solar nebula.

Keywords: Hibonite, density functional theory, enthalpy of formation, titanium, oxidation state, oxygen vacancies, early solar system