

Understanding the Formation of Defect-Structured Hibonite in Chondritic Meteorites: A FIB/TEM Study

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Hibonite ($\text{CaAl}_{12}\text{O}_{19}$) is a primary refractory phase occurring in many refractory inclusions from chondritic meteorites, and is predicted to condense as the second major phase, after corundum, from a cooling gas of solar composition [1]. Our previous transmission electron microscope (TEM) studies of hibonite in Ca-Al-rich inclusions (CAIs) and their rims revealed the presence of numerous stacking defects along the (001) plane and correlated non-stoichiometry, which are interpreted as complex intergrowths of stoichiometric and non-stoichiometric, Mg-rich hibonites [2,3]. In this study, we present the TEM analyses of hibonite found from carbonaceous chondrites and synthesized from a set of annealing experiments. Our goals were to better understand the effect of Mg and Ti on the formation of stacking defects in hibonite and the site occupancy and substitution mechanism of Mg and Ti in defect-structured hibonite.

We studied hibonite from CM, CO, CV carbonaceous chondrites that contains a range of MgO and TiO_2 contents up to ~4 wt% and ~8 wt%, respectively, and often shows fine scale zoning [2-4]. In addition, our experimental hibonite samples were prepared by reacting $2\text{CaO-Al}_2\text{O}_3$ eutectic melt \pm 5 wt% MgO \pm CaTiO_3 with a pure alumina crucible at 1530°C for 4 hours or 5 days, followed by air quenching [5,6]. All FIB sections were examined using a JEOL 2500SE field emission scanning TEM at NASA JSC.

Hibonite in the reaction zone of run products contains a range of stacking defect densities and correlated compositional variations in Mg and Ti contents [5,6]. There are several important TEM observations: (1) electron diffraction patterns show streaking along the *c* axis, and lattice fringe images show random intergrowths of 2.6 nm (001) spacing within prominent 2.2 nm (001) spacing; (2) Mg-bearing hibonite contains significantly higher densities of stacking defects compared to Ti-bearing hibonite; and (3) stacking defects are linked to an increase in MgO contents and a decrease in TiO_2 contents. These features are comparable to those observed in hibonite from different carbonaceous chondrite groups, and can be interpreted as complex intergrowths of stoichiometric and non-stoichiometric (Mg-enriched and Ti-depleted) hibonites [2-6]. Such defect-structured hibonite appears more stable than the thermodynamically predicted equilibrium assemblages of stoichiometric hibonite with corundum or spinel in high-temperature environment [3].

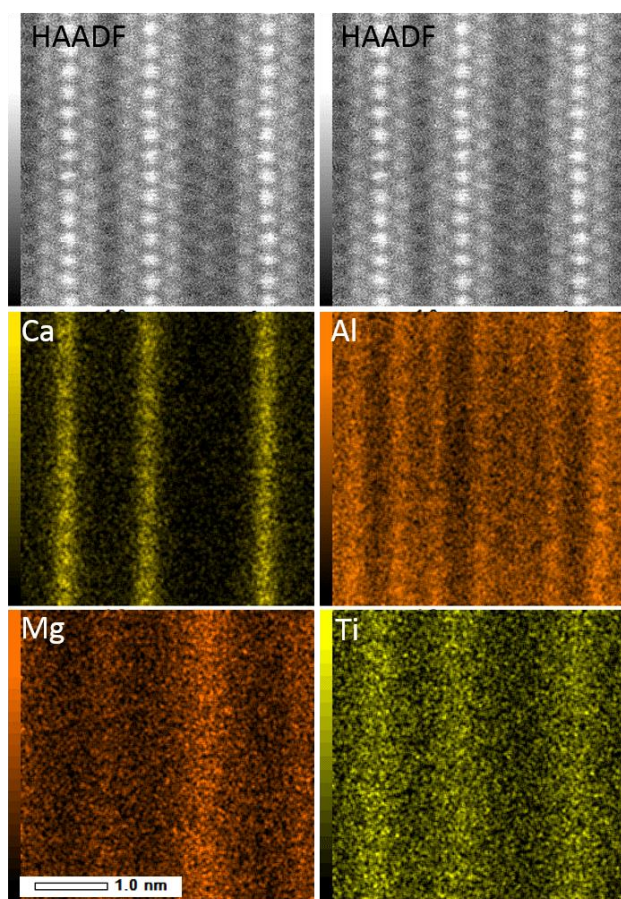
Hibonite consists of spinel blocks alternating with Ca-containing blocks normal to the *c* axis. There are five Al sites that can be substituted with various amounts of Mg and Ti: three octahedral sites (M1, M4, and M5), a trigonal bipyramidal site (M2), and a tetragonal site (M3). The tetrahedral (M3) and octahedral (M1 and M5) layers are arranged in spinel blocks, which are separated by Ca-containing blocks comprising the M2 and M4 sites. Mg is predicted to occupy the M3 site only in spinel blocks, whereas Ti appears to have a range of possible sites, but has been reported to preferentially occupy the M2 and M4 sites in Ca-containing blocks [7].

Our TEM observations of hibonite both from different carbonaceous chondrite groups and our

experimental samples imply that the introduction of Mg during the formation of hibonite stabilized the formation of wider spinel blocks, possibly due to the substitution of Mg with Al in the M3 sites. However, the role of Ti-Al substitution in the formation of wider Ca-containing blocks is unclear. The Ti-Al substitution may be not important in the formation of stacking defects in hibonite, but only required for the charge coupled substitution with Mg²⁺ (Ti⁴⁺ + Mg²⁺ = 2Al³⁺) [2-6].

Hibonites from a compact Type A CAI from the Allende CV carbonaceous chondrite and our experimental samples were analyzed using a JEOL F200 STEM at JEOL in Japan, and their high angle annular dark-field (HAADF) images and corresponding X-ray maps (**Figure 1**) provide new details on the atomic distribution of Mg and Ti in defect-structured hibonite. Mg is largely concentrated in the defects, and occupies the M3 sites and possibly the neighboring M5 sites. In contrast, Ti is concentrated in the M2 sites where Ca occupies, but also appears to occupy the M4 sites. We infer that defects can be explained as additional (M1+M3) and M5 layers, forming wider spinel blocks that contain twice as many M1 and M3 sites, and 50% more M5 sites as spinel blocks in stoichiometric hibonite [8].

Our extended TEM studies of synthetic and meteoritic hibonite have consistently shown that stacking defects in hibonite are unique microstructural characteristics that accommodate greater Mg substitution only with Al preferentially in the M3 sites, forming defect-structured, Mg-enriched hibonite. Kinetics (e.g., fast cooling rate) or other thermal effects may also exert a strong control on the formation of stacking defects in hibonite [9].



References:

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Figure 1. HAADF images and corresponding X-ray maps for Ca, Al, Mg, and Ti in meteoritic hibonite.