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Crystal structures of laihunite and intermediate phases between laihunite-1*M* and fayalite: Z-contrast imaging and ab initio study

HUIFANG XU[1,*], ZHIZHANG SHEN[1], HIROMI KONISHI[1], PINGQIU FU[2] AND IZABELA SZLUFARSKA[3]

[1]NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin-Madison, Madison, Wisconsin 53706, U.S.A.
[2]Institute of Geochemistry, The Chinese Academy of Sciences, Guiyang, Guizhou 550002, P.R. China
[3]Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, U.S.A.

ABSTRACT

Crystals of laihunite from Xiaolaihe of Liaoning Province, northeast China, were studied using selected-area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM), and Z-contrast imaging. Z-contrast images directly reveal ordered vacancies in M1 sites. The results confirm early structural models for 1-layer laihunite (or laihunite-1*M*) with ideal stoichiometry of $\square_{0.5}Fe^{2+}_{0.5}Fe^{3+}SiO_4$. 2-layer laihunite and 3-layer laihunite are found to be chemically different from laihunite-1*M*. The 2-layer laihunite can be viewed as a periodic intergrowth of laihunite and fayalite in the 1:1 ratio. The 3-layer laihunite can be considered to be a periodic intergrowth of laihunite and fayalite in the 1:0.5 ratio along the ***c***-axis. Ideal stoichiometries for the 2-layer structure and the 3-layer structure are $\square_{0.5}Fe^{2+}_{2.5}Fe^{3+}[SiO_4]_2$ and $\square_{1.0}Fe^{2+}_{3.0}Fe^{3+}_{2.0}[SiO_4]_3$, respectively. The structural intergrowth of the 3-layer laihunite and the 1-layer lahunite results in chemical compositions falling within the range between the two aforementioned structures, such as the chemical formula of $\square_{0.4}Fe^{2+}_{0.8}Fe^{3+}_{0.8}SiO_4$, reported earlier in the literature.

The crystal structures of the 1-layer laihunite (1*M*), the 2-layer laihunite (2*M*), and the 3-layer laihunite (3*Or*) determined from Z-contrast images and ab initio calculations using the density functional theory (DFT) have space groups of $P2_1/b$, $P2_1/b$, and *Pbnm*, respectively. The previously reported monoclinic symmetry for the 3-layer laihunite may be an artifact due to overlapping diffraction spots from both, the laihunite-3*Or* and the laihunite-1*M*. Our study demonstrates that the method of combining Z-contrast imaging and ab initio calculation can be effectively used for identifying structures of nano-phases in host crystals. Perhaps more importantly, Z-contrast imaging provides a powerful means for direct observation of vacancies and other defects, and may be utilized to map vacancies in Fe^{3+}-bearing olivines, the alignments of which can greatly affect anisotropic diffusion in such structures.

Keywords: Laihunite, vacancy ordering, Z-contrast imaging, DFT, HRTEM, superstructure, olivine, oxidation