American Mineralogist, Volume 107, pages 1470–1476, 2022

The interplay between twinning and cation inversion in $MgAl_2O_4$-spinel: Implications for a nebular thermochronometer

Venkateswara Rao Manga[1,2,*], Krishna Muralidharan[1,2], and Thomas J. Zega[1,2]

[1]Lunar and Planetary Laboratory, University of Arizona, 1629 E. University Boulevard, Tucson, Arizona 85721, U.S.A.
[2]Department of Materials Science and Engineering, University of Arizona, 1235 E. James E. Rogers Way, Tucson, Arizona 85721, U.S.A.

Abstract

We report a first-principles-based thermodynamic investigation of the interplay between cation inversion and twinning in $MgAl_2O_4$ spinel (MAS). We examine the atomic-scale structure of (111) twins and characterize the local octahedral and tetrahedral distortions. We observe that the asymmetric nature of polyhedral distortions about the (111) twin plane causes anisotropy in cation inversion energies near the planar fault. The predicted enthalpies and entropies of inversion reveal that in comparison to the Kagome layer, the anti-site occupancies of Al and Mg, i.e., cation inversion, on the mixed-cation-layer near the twin boundary are more favorable and stable in the entire range of temperature of twin stability. Structurally, such a stable inversion is necessitated by the minimization in the polyhedral distortions, especially by the octahedral distortion, which exhibits a reduction of four orders of magnitude relative to the polyhedra with no inversion. The fundamental understanding obtained on the thermodynamics of the twin-cation inversion interplay in conjunction with the kinetics of inversion was used as a basis for developing a thermochronometer for deducing the temperature of twinning in MAS. This work serves as an important steppingstone for experimental characterization of MAS structures within a host of Earth and planetary materials. In the case of the latter, our results enable the use of planar faults, such as twins, as important markers for deducing the physical and chemical landscape that MAS experienced in its evolution and transport within the solar protoplanetary disk.

Keywords: Spinel twins, cation inversion, thermodynamics, order parameter, nebular thermochronometer