American Mineralogist, Volume 99, pages 1413–1419, 2014

Z-contrast imaging and ab initio study on "*d*" superstructure in sedimentary dolomite

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Abstract

Nano-precipitates with tripled periodicity along the ***c***-axis are observed in a Ca-rich dolomite sample from Proterozoic carbonate rocks with "molar tooth" structure. This observation is consistent with previous description of *d* reflections. High-angle annular dark-field STEM imaging (or Z-contrast imaging) that avoids dynamic diffraction as seen in electron diffraction and high-resolution TEM imaging modes, confirms that *d* reflections correspond to nanoscale precipitates aligned parallel to (001) of the host dolomite. The lamellae precipitates have a cation ordering sequence of Ca-Ca-Mg-Ca-Ca-Mg along the ***c*** direction resulting in a chemical composition of $Ca_{0.67}Mg_{0.33}CO_3$. This superstructure is attributed to the extra or *d* reflections, thus is referred to as the *d* superstructure in this study. The structure can be simply described as interstratified calcite/dolomite. The crystal structure of the *d* superstructure calculated from density functional theory (DFT) has a space group of *P*31*c* and has *a* and *c* unit-cell parameters of 4.879 and 16.260 Å, respectively, values between those of dolomite and calcite. The detailed structural characteristics and parameters obtained from ab initio calculations are also reported in this paper. The method of combining Z-contrast imaging and ab initio calculations can be used for solving structures of other nano-precipitates and nano-phases.

Keywords: Dolomite, *d* superstructure, Z-contrast imaging, density functional theory, molar tooth carbonate