American Mineralogist, Volume 82, pages 512–516, 1997

Incorporation of rare earth elements in titanite: Stabilization of the *A*2/*a* dimorph by creation of antiphase boundaries

JOHN M. HUGHES,[1] ERICH S. BLOODAXE,[1] JOHN M. HANCHAR,[2]* AND EUGENE E. Foord[3]

[1]Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.
[2]Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York 12180–3590, U.S.A.
[3]U.S. Geological Survey, P.O. Box 25046, MS 905, Denver Federal Center, Denver, Colorado 80225, U.S.A.

ABSTRACT

The atomic arrangement of a natural rare-earth-rich titanite and two synthetic rare-earth-doped titanites have been refined in space group *A*2/*a*, and the atomic arrangement of an undoped $P2_1/a$ synthetic titanite was also refined for comparison.

Previous work has shown that titanite possesses a domain structure, with domains formed of like-displaced Ti atoms in the [100] octahedral chains. $P2_1/a$ titanite results when the crystal is formed of a single domain, but as Ti-reversal sites occur in the octahedral chain the apparent *A*2/*a* structure results from the average of antiphase domains. Antiphase boundaries occur at O1, which is alternately overbonded or underbonded at the boundaries, depending on the displacement of the neighboring Ti atoms. Type 2 antiphase boundaries exist where two Ti atoms are displaced away from the intervening O1 atom and are energetically unfavorable because of underbonding of that O1 atom. However, substitution of a trivalent rare earth element in the adjacent Ca^{2+} site relieves that underbonding, favoring the creation of type 2 antiphase boundaries and stabilization of the *A*2/*a* dimorph. The results of high-precision crystal structure analyses demonstrate that rare earth substituents for Ca stabilize the *A*2/*a* dimorph at lower substitution levels than required for octahedral substitutions.