

Peculiarity and defect structure of the natural and synthetic zeolite mordenite: A single-crystal X-ray study

PETRA SIMONCIC AND THOMAS ARMBRUSTER*

Laboratorium für Chemische und Mineralogische Kristallographie, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

ABSTRACT

Single-crystal X-ray data were collected from a natural fibrous mordenite crystal of composition $\text{K}_{2.99}\text{Ca}_{1.85}\text{Na}_{1.06}\text{Al}_{7.89}\text{Si}_{40.15}\text{O}_{96}\cdot 28\text{H}_2\text{O}$ and from a platy synthetic mordenite crystal of composition $\text{Na}_6\text{Al}_{6.02}\text{Si}_{42.02}\text{O}_{96}\cdot 19\text{H}_2\text{O}$. Diffraction data were measured with a point detector using a sealed X-ray tube and an image plate using synchrotron radiation, respectively. Both structures exhibit the same defect features visible in difference-Fourier maps. Domains of the entire *Cmcm* framework structure are reproduced by a non-crystallographic (001) mirror plane at $z = 0$ and $z = 1/2$. An identical description is a shift of framework domains $1/2$ along the **c** axis. The concentration of this defect domain is 2.7(2) and 3.1(1)% for the natural and synthetic mordenite crystals, respectively. Reproductions of reciprocal layers from synchrotron image-plate data reveal diffuse scattering for *hkl* layers with $l = 2n + 1$. The diffuseness of these layers is not homogeneous but concentrates in the form of halos around selected reflections allowed for C-centering. Diffuse features in electron diffraction patterns of natural and synthetic mordenite have been described before and were interpreted either as evidence of $c/2$ faults or intergrowth with different mordenite-related structure-types. We have modeled a (100) defect layer that is modified from the mordenite characteristic puckered sheet of six-membered rings and allows coherent intergrowth of identical structural subunits shifted by $c/2$. These defect domains do not influence or obstruct the 12-membered ring-channels characteristic of this zeolite. The major difference in Si,Al distribution between the two samples is that the natural crystal has Al strongly enriched at T3, which is part of the four-membered rings. We suggest that a synergetic effect between extraframework cations and Si, Al ordering during crystal growth is responsible for Al enrichment in natural mordenite with ca. 2 Ca p.f.u. close to T3.