Superstructure of Challis mordenite with doubled monoclinic unit cell

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ABSTRACT

A new superstructure was found in mordenite (Na5.59Ca1.80Al9.19Si38.81O96·nH2O) from Challis Valley, Idaho—a zeolite widely used in previous studies. The occurrence of the superstructure reflections were observed in 12 specimens from two rock samples, at the midpoint of layers in the oscillation photographs around the a* and b* axes, but not around the c* axis. The apparent 2a, 2b, and c axes are orthogonal. In spite of yielding an apparent orthorhombic cell, careful observation of the intensities revealed that the superstructure is monoclinic with twice the volume of the orthorhombic cell: a' = 27.356(9), b' = 27.356(9), c' = 7.517(2) Å, β' = 97.14(4)°, and V' = 5582(4) Å³.

The presence of the superstructure was examined for specimens from ten other localities and a synthetic sample but there was no evidence for extra spots of the superstructure, indicating that the occurrence is not common.

The large displacement factors of O8 oxygen, and its associated 180° T-O-T angle that is energetically unfavorable, are basic to the mordenite structure. In the monoclinic superstructure the O8 oxygen is decomposed into several asymmetric O atoms by the symmetry reduction. The large displacement smearing of O8 oxygen perpendicular to the straight T-O-T, are explained by the superposition of decomposed O atoms.

The extra spots are predominantly observed in the reciprocal planes with l = odd in the same way as diffuse streaks. The observation of extra spots and diffuse streaks suggests that there are three kinds of domains in the mordenite, one in the ordered form and two others in the random form of c/2 linear displacements. The domain in the ordered form represents the superstructure. Thus, we propose a model for the superstructure in which the c/2 displacement occurs alternatively in the two basic unit cells slightly modified in the superstructure, yielding the periodic arrangements.

Keywords: Mordenite, superstructure, monoclinic cell, diffuse streak, linear displacement, ordered form

INTRODUCTION

Mordenite, ideally NaAl2Si18O50·2H2O, is a member of zeolite group with the most siliceous composition of any zeolite. Its structure is characterized by 12-membered and 8-membered rings running along the c axis, and another 8-membered rings running along the b axis; these channels accommodate extraframework cations and water molecules. The mineral, especially synthetic varieties, has many industrial applications such as isomerization catalysts. The structure has an orthorhombic unit cell (a = 18.1 Å, b = 20.5 Å, and c = 7.5 Å) with topological space group symmetry Cmcm. Meier (1961) first determined the crystal structure of a Na-exchanged mordenite from Challis Valley, Idaho in Cmcm space group, suggesting that the ordered Al/Si distributions would reduce the symmetry to acentrosymmetrical Cmc21. After Meier’s determination, several structural analyses were performed for both natural and synthetic mordenites as summarized by Armbruster and Gunter (2001).

In the course of these studies, several additional space groups for different polotypes of mordenite-related structures have been proposed, such as: Immm, Cmmm, and Imcm (Kerr 1963; Sherman and Bennett 1973), but these hypothetical space groups were determined to be experimental artifacts resulting from diffuse halos of adjacent layers (Simoncic and Armbruster 2004a). Current research indicates that the original Cmcmm and Cmc2 are the correct space group for mordenite; however, dehydrated, cation-exanged forms occur with Pbnm space group (Mortier et al. 1978; Schlenker et al. 1978, 1979). The structures of hydrated, cation-, and molecule-exchanged samples (e.g., Se, thionin blue and methylene blue dyes), have been refined in the lower symmetry monoclinic space group Cc because of the better fits but there is no direct experimental evidence for monoclinic symmetry (Simoncic and Armbruster 2004b, 2005; Simoncic et al. 2004).

Diffuse reflections in mordenite have been observed in X-ray and electron diffraction photographs (e.g., Sherman and Bennett 1973; Sanders 1985; Simoncic and Armbruster 2004a). The diffuse scattering extends perpendicular to the e axis and is restricted...