Dehydration dynamics of analcime by in situ synchrotron powder diffraction

GIUSEPPE CRUCIANI1,* and ALESSANDRO GUALTIERI1

1Istituto di Mineralogia, Università di Ferrara, Ferrara, Italy
2Dipartimento di Scienze della Terra, Università di Modena, Modena, Italy

ABSTRACT

The continuous structural transformation of tetragonal analcime (\(\text{Na}_{15.87}\text{Al}_{15.20}\text{Si}_{32.64}\text{O}_{96} \cdot 16.3\text{H}_{2}\text{O}\)) upon dehydration was studied, using Rietveld structure analysis of temperature-resolved powder diffraction data collected using synchrotron radiation. The variation of the \(a-c\) axis length difference and normalized intensity of the (200) reflection as a function of temperature suggest that tetragonal analcime evolves toward a cubic structure at high temperature. The removal of water was accompanied by a spreading of the initial Na sites into many positions bonded to the framework O atoms. The migration of H\(_2\)O molecules through the [111] channels during dehydration caused the six-member ring apertures to open as widely as possible: this was accompanied by a twisting of the tetragonal prism, constituting the analcime framework, which led to an opposite tilting of tetrahedra connecting the prisms. These modifications induced by water diffusion are not energetically favored because they would increase the elastic energy of the system, and require a substantial thermal activation energy. The analcime framework reached a maximum distortion at about 650 K, the temperature of complete water loss, then underwent a relaxation process during which the T-O-T angles were restored to the starting value. The relative variation of cell volume associated with the opening of wide six-member ring channels during water migration, and then due to the framework relaxation process after complete dehydration, provides an explanation of the “negative thermal expansion” (i.e., volume contraction) effect in dehydrated analcime, which is complementary to that based on the Rigid Unit Modes theory.

INTRODUCTION

Analcime is a zeolite (and feldspathoid) having a complex aluminosilicate framework that is common to all leucite-type feldspathoids (Merlino 1984). The maximum topological symmetry of analcime is cubic, \(Ia\3d\) (Taylor 1930; Calleri and Ferraris 1964; Knowles et al. 1965; Ferraris et al. 1972). However, deviations from cubic symmetry are well known (Mazzi and Galli 1978; Hazen and Finger 1979). Regarding the genetic conditions, analcimes have been divided into five groups (Luhar and Kysler 1989): primary igneous analcimes (called P-type); those formed by cation exchange from leucite (L-type or X-type); hydrothermal analcimes (H-type); sedimentary analcimes (S-type); and metamorphic analcimes (M-type). X-type analcimes are typically cubic, whereas H-type analcimes have tetragonal, rhombohedral, or orthorhombic symmetry (Kapusta and Włodyka 1997).

Dehydration of analcime is a one step process, as evidenced by the DTA and TG curves that show only one maximum at roughly 620 K; this corresponds to the removal of H\(_2\)O molecules in the sole symmetry-independent site in the cubic structure (Gottardi and Galli 1985). Kim and Burley (1971; 1980) suggested that a structural phase transition occurs upon dehydration, which leads to a stable high-temperature dehydrated phase (high-analcime) with a unit-cell volume smaller than that of low-analcime. The kinetics of the dehydration process in H-type (hydrothermal) and X-type (cation exchange from leucite) cubic analcimes studied by DTA methods show apparent activation energies for the H-type analcimes that are four times greater than for X-type analcimes (Giampaolo and Lombardi 1994; Line et al. 1995). Cubic analcime has recently been the subject of a series of papers, given its similarity to the structure of leucite that has displacive phase transitions currently of great interest (Palmer et al. 1996). Putnis et al. (1993) reported that cubic analcime transformed to tetragonal upon heating at a temperature of about 600 K, depending on the atmosphere, mainly due to the \(c\) axis contraction. After dehydration, the unit cell became cubic again, due to the increase of the \(c\) axis, and it remained cubic until analcime turned to amorphous. Line (1995) found no displacive phase transition associated to the high-temperature dehydration process of cubic analcime. Line et al. (1996) also studied the low-temperature behavior of analcime by high-resolution neutron powder diffraction in the range 30–300 K, and found no sign of any phase transition.

The present investigation strives to (1) give a more