High-pressure behavior of bikitaite: An integrated theoretical and experimental approach

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ABSTRACT

Pressure-induced structural modifications in the zeolite bikitaite are studied by means of in situ synchrotron X-ray powder diffraction and ab initio molecular dynamics. The experimental cell parameters were refined up to 9 GPa, at which pressure we found reductions of 4.5, 4.5, 6.3, and 15% in a, b, c, and V, respectively. Minor variations were observed for the cell angles. Complete X-ray amorphization is not achieved in the investigated P range, moreover the P-induced effects on the bikitaite structure are completely reversible. Because it was possible to extract only the cell parameters from the powder patterns, the atomic coordinates at 5.7 and 9.0 GPa were obtained by means of Car-Parrinello simulations using the unit-cell parameters experimentally determined at these pressures. Analysis of the computational results for increasing pressures showed that the volume contraction is essentially due to rotations of the tetrahedra; the 8-ring channels become more circular; the pyroxene chain becomes more corrugated in the b-c plane; and the mean Li-O bond distances and coordination polyhedral volumes decrease with increasing pressure without significant distortion of the internal angles. The peculiar aspect of the bikitaite structure, i.e., the presence in the channels of a “floating” one-dimensional water chain, is only partially maintained at high pressure; the compression brings framework O atoms close enough to water hydrogen atoms to allow the formation of host-guest hydrogen bonds, without, however, destroying the one-dimensional chain.

INTRODUCTION

Bikitaite [Li2(Al2Si4O12)·2H2O, s.g. P1] is a high-density zeolite with Li as the extra-framework cation. Its topology, also observed in the synthetic aluminosilicate compound C80,35Al8,35Si1,65O4 (Annehed and Fälth 1984), is characterized by parallel sheets with hexagonal tiling, connected by pyroxene chains developing along b. Also parallel to b, the structure is characterized by a system of mono-dimensional non-crossing channels, each delimited by 8-membered rings. This channel system alternates along a with high-density b-c layers. The two Li cations present in the bikitaite unit cell are coordinated to one water molecule and three framework O atoms, although the two water molecules are hydrogen bonded to each other and form a peculiar one-dimensional chain, parallel to the channel direction. No hydrogen bonds have been found between water and the framework (Stähl et al. 1989). Recent studies (Quartieri et al. 1999; Fois et al. 1999) demonstrated the high rigidity and stability of the water chain and excluded room temperature rotational motion of water molecules, therefore justifying the naming of such a water system as “one-dimensional ice.” Moreover, the same authors demonstrated that the water-chain system is stabilized by host-guest interactions based on the antiparallel dipole moments of the framework and the water chain.

Bikitaite represents an example of confinement of a low-dimensionality system in an ordered matrix (Fois et al. 2001a, 2001b), which could be of technological relevance for the tailoring of new kinds of materials with particular chemical and physical properties. In this respect, it is highly desirable to study the stability of this system under different physico-chemical conditions, in order to understand how low-dimensional species can be introduced and stabilized in materials like zeolites. To this aim, we undertook a multi-technique investigation on the structural modifications in bikitaite at high-temperatures (HT) (Vezzalini et al. 2001b) and high-pressures (HP).

Although the thermal behavior of zeolites has been extensively studied (see for example Bish 1995), the scientific literature on the effects of pressure, using penetrating or non-penetrating pressure-transmitting media, is limited. Little information is available on the structural properties and on the possible pressure-induced polymorphic phases, although more effort has been dedicated to the study of the amorphization processes and of pressure-induced effects on ionic conductivity. Most of the available information is on fibrous zeolites (Belitsky et al. 1992; Gillet et al. 1996; Bazhan et al. 1999; Goryainov and Smirnov 2001; Lee et al. 2002; Moroz et al. 2001; Ballone et al. 2002), analcime and wairakite (Hazen and Finger 1979; Velde and Besson 1981; Goryainov et al. 1996, 1999), heulandite (Comodi et al. 2001; Vezzalini et al. 2001a), and synthetic zeolites A and Y (Hazen 1983; Hazen and Finger 1984; Huang 1998; Secco and Huang 1999).