Elastic behavior and phase stability of pollucite, a potential host for nuclear waste

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ABSTRACT

The elastic behavior and the phase stability of natural pollucite, (Cs,Na)16Al8Si32O80·nH2O, were investigated at hydrostatic pressure by in situ single-crystal X-ray diffraction with a diamond-anvil cell. Pollucite experiences a P-induced phase transition, not previously reported in the literature, at P = 0.66 ± 0.12 GPa from cubic (Ia3d) to triclinic symmetry (P). The phase transition is completely reversible and without any appreciable hysteresis effect. No further phase transition has been observed up to 9 GPa. Fitting the pressure-volume data of the low-pressure cubic polymorph with a second-order Birch-Murnaghan Equation-of-State (BM-EoS), we obtain V0 = 2558.3(4) Å3, K10 = 41(2) GPa, and K′ T0 = 4.6(5). For the high-pressure triclinic polymorph, a third-order BM-EoS fit gives V0 = 2577.5(40) Å3, K10 = 25.1(9) GPa, and K′ T0 = 6.5(4). The axial bulk moduli of the high-pressure triclinic polymorph were calculated with a third-order “linearized” BM-EoS. The EoS parameters are a0 = 13.699(12) Å, K10(a) = 25.5(17) GPa, and K10(b) = 6.8(6) for the a axis; b0 = 13.728(12) Å, K10(b) = 23.2(15) GPa, and K10(c) = 7.7(7) for the b axis; c0 = 13.710(7) Å, K10(c) = 25.2(10) GPa, and K′ T0(c) = 6.8(4) for the c axis [K10(a):K10(b):K10(c) = 1.10:1:1.09]. Brillouin light-scattering was used to investigate the single-crystal elastic properties of pollucite at ambient conditions. The aggregate adiabatic bulk modulus (K) and shear modulus (G), calculated using the Voigt-Reuss-Hill averaging procedures, are K = 52.1(10) GPa and G = 31.5(6) GPa. The elastic response of pollucite and other isotypic materials (e.g., analcime, leucite, and wairakite) is compared. The high thermo-elastic stability of pollucite, reflected by the preservation of crystallinity at least up to 9 GPa (at room T) and 1470 K (at room P) in elastic regime, the large amount of Cs hosted in this material (Cs2O ~ 30 wt%), the immobility of Cs at high-temperature and high-pressure conditions, and the extremely low leaching rate of Cs, make of this open-framework silicate a functional material with potential use for fixation and deposition of Cs radioisotopes in high-level nuclear waste.

Keywords: Pollucite, single-crystal X-ray diffraction, high-pressure, compressibility, phase transition, nuclear waste disposal material

INTRODUCTION

Pollucite is a zeolite mineral (Coombs et al. 1997), although it is commonly defined as a feldspathoid, with ideal formula (Cs,Na)16Al8Si32O80·nH2O (with Cs + n = 16). Pollucite occurs mainly in Li-Cs-rich granitic pegmatites in association with quartz, muscovite, K- and Na-feldspars, spodumene, petalite, lepidolite, elbaite, eucryptite, and apatite.

Pollucite is isotypic with analcime (Na16Al8Si32O80·16H2O), leucite (K16Al8Si32O80), wairakite (Ca9Al10Si32O80·16H2O), and hsianghualite (Li4Al10Si32O80·16H2O) (Gottardi and Galli 1985; Armbruster and Gunter 2001; Baerlocher et al. 2001), and forms a complete solid-solution series with analcime (Černý 1974; Legache 1995; Teerstra and Černý 1995). The (open) tetrahedral framework of this group of isotopic minerals (i.e., the “analcime group”) results from the combination of two “secondary building units” (SBU, Baerlocher et al. 2001), constituted by 4- and 6-membered rings of tetrahedra (ANA topology, Baerlocher et al. 2001) (Fig. 1). The topological symmetry of such a framework type is cubic, with space group Ia3d (Baerlocher et al. 2001).

At room conditions, the general symmetry of pollucite is cubic Ia3d, with a ~ 13.68 Å. In cubic pollucite, there is a disordered Si/Al-distribution in the tetrahedral framework, with only one independent tetrahedral site (at x,y,z,1/8, Wyckoff position 48g).

Cesium, Na, and H2O represent the extra-framework content. According to the structural model of Beger (1969) (i.e., “model 1”), water molecules and Cs atoms share the only extra-framework site (i.e., Cs/W-site, Fig. 1) lying in the 6-membered ring channels (6mR) along [111] (at 1/8,1/8,1/8, Wyckoff position 16b), whereas sodium atoms are located out from the 6mR-channels (at 1/4,1/8,0, Wyckoff position 24c), in the distorted 8-membered ring of tetrahedra that connect the 6mR-channels.

Cesium atoms are coordinated by 12 O atoms belonging to the tetrahedral framework (6 Cs-O ~ 3.39 Å and 6 Cs-O ~ 3.56 Å, Beger 1969). The H2O-molecules and the sodium atoms occupy the same site positions as they do in analcime, but they occur only in randomly distributed clusters of atoms forming interrupted ·[H2O-Na-H2O]·· chains, with H2O/Na ≤ 2 (Beger 1969). On