High-pressure behavior and structural transition of beryl-type johnkoivulaite, Cs(Be$_2$B)Mg$_2$Si$_6$O$_{18}$

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ABSTRACT

The beryl-group mineral johnkoivulaite, Cs(Be$_2$B)Mg$_2$Si$_6$O$_{18}$, was compressed hydrostatically in a diamond-anvil cell up to 10.2 GPa. In situ Raman spectroscopy and X-ray crystallography revealed a P6/mcc-to-$P$3c1 (second-order) phase transition on isothermal compression at the critical transition pressure $P_\tau = 4.13 \pm 0.07$ GPa. The elastic parameters determined for the volume elasticity of the two polymorphs correspond to a Birch-Murnaghan equation of state with $K_0 = 148 \pm 2$ GPa and $K' = 0$ for $P < P_\tau$ and $K_0 = 75.5 \pm 0.9$ GPa with $K' = 4$ for $P > P_\tau$. The low-$P$ polymorph shows anomalously linear compression behavior, as reported for several other beryl-derived framework structures. The high-$P$ polymorph, which was found to follow a $d'' = a''/\sqrt{3}$, $c' = c$ superstructure according to $P$3c1, is almost twice as compressible as its low-$P$ form. This is unique for any beryl-derived structure and can be attributed to the high degree of freedom for atomic displacements in the superstructure. The reduced symmetry can also be understood as the effect of the driving mechanism of the transformation. The extra-framework Cs channel components counteract any lateral deformation of the channels parallel to [0001] within the microporous framework and, similar to pezzottaite, are responsible for maintaining the trigonal/hexagonal lattice metrics.

Keywords: Beryl-type structure, johnkoivulaite, high pressure, structural transition, second-order phase transition, superstructure; Microporous Materials: Crystal-chemistry, Properties, and Utilizations

INTRODUCTION

The beryl-type structure is an outstanding structure representing a non-holotetrahedral framework, with a pronounced one-dimensional porosity in the form of channels running along [0001]. It is represented in nature by several beryllium silicate minerals, such as beryl Be$_3$Al$_2$(Si$_6$O$_{18}$), stoppaniite Be$_3$Fe$_2$(Si$_6$O$_{18}$), and bazzite, Be$_3$Sc$_2$(Si$_6$O$_{18}$), whose crystal structures consist of the symmetry-determining [Si$_6$O$_{18}$]$^{12-}$ silicate ring units that predetermine the hexagonal archetype microporous framework (e.g., Bragg and West 1926; Gibbs et al. 1968; Artioli et al. 1993; Armbruster et al. 1995; Ferraris et al. 1998; Della Ventura et al. 2000). Any deviation from the beryl-aryistotype P6/mcc symmetry originates from stoichiometric substitution, such as in cordierite Al$_3$Mg$_6$(AlSi$_3$O$_{10}$) and sekaninaite Al$_2$Fe$_2$(AlSi$_3$O$_{10}$), where the substitution of 1/3 of the silicon atoms on the T2 site within the ring units, and the simultaneous occupation of Si on the T1 site, lead to symmetry-breaking orthorhombic Cmcm cation distribution (Armbruster 1985a; Redfern et al. 1989; Daniels et al. 1994; Malcherek et al. 2001). While the cation redistribution on the tetrahedral T1, T2 and the octahedral M sites does not affect the total charge balance of the framework, both in pezzottaite, Cs(Be$_2$Li)Al$_2$Si$_6$O$_{18}$, and johnkoivulaite, Cs(Be$_2$B)Mg$_2$Si$_6$O$_{18}$, the stoichiometric substitution of one third of the Be by either lithium or boron at the T1 position leads to a formal charge deficiency within the framework (Yakubovich et al. 2009; Gatta et al. 2012; Lambruschi et al. 2014; Palke et al. 2021). This, in turn, requires charge balance through additional extra-framework cations located within the one-dimensionally infinite channel mentioned above. The structures of pezzottaite and johnkoivulaite are characterized by the intercalation of a significant fraction of alkali cations, preferably high Cs contents, within the cavities of the existing one-dimensional channels. At least for pezzottaite, a resultant lower symmetry and the formation of a trigonal superstructure, according to the $R\bar{3}c$ space group, could be demonstrated for the existing Li-Be cation ordering.

The ability to incorporate Cs in the microporous framework makes beryl-type compounds of interest in the materials science community. In particular, immobilization of Cs-137 makes the physicochemical properties of this potential host structure important for possible technological applications. Thermodynamic properties and phase stabilities are an important focus of research. The two most prominent representatives of this mineral group, i.e., cordierite and beryl, moreover are characterized by their petrological importance. Cordierite is a stable phase in contact metamorphic pelitic rocks or in high-grade regionally metamorphosed schists, gneisses, and granulites. Beryl is a host of Be, a rare lithophile element, in highly evolved S-type