American Mineralogist, Volume 97, pages 1749–1763, 2012

Second-order $P\bar{6}c2$-$P31c$ transition and structural crystallography of the cyclosilicate benitoite, $BaTiSi_3O_9$, at high pressure

Clivia Hejny,[1,*] Ronald Miletich,[2] Andreas Jasser,[3] Pascal Schouwink,[3,4] Wilson Crichton,[5] and Volker Kahlenberg[1]

[1]Institut für Mineralogie und Petrographie der Universität Innsbruck, Innrain 52, 6020 Innsbruck, Austria
[2]Institut für Mineralogie und Kristallographie der Universität Wien, Althanstrasse 14, 1090 Wein, Austria
[3]Institut für Geowissenschaften der Universität Heidelberg, Im Neuenheimer Feld 234, 69120 Heidelberg, Germany
[4]Laboratoire de Cristallographie de l'Université de Genève, 24, quai Ernest-Ansermet, 1211 Geneva 4, Switzerland
[5]European Synchrotron Radiation Facility, ESRF, 6 Rue Jules Horowitz, 38043 Grenoble, France

Abstract

Experimental high-pressure investigations on benitoite in the diamond-anvil cell reveal a second-order phase transition at a critical transition pressure $P_c = 4.24(3)$ GPa, as determined from synchrotron powder diffraction, single-crystal X-ray diffraction, and Raman spectroscopy. Diffraction experiments indicate a non-isomorphous transition from $P\bar{6}c2$ to $P31c$ space-group symmetry with $a' = a\sqrt{3}$ and $c' = c$ relative to the $P\bar{6}2c$ subcell below P_c. The high-pressure polymorph is characterized by a larger compressibility compared to the compressional behavior of benitoite below P_c. Fitting second-order Birch-Murnaghan equations of state to the experimental data sets, the parameters obtained are $V_0 = 372.34(4)$ Å^3, $K_0 = 117.9(7)$ GPa, with $a_0 = 6.6387(3)$ Å, $K_a = 108.1(7)$ GPa, and $c_0 = 9.7554(4)$ Å, $K_c = 143.3(1.1)$ GPa for the low-pressure form ($P < P_c$), and $V_0 = 376.1(4)$ Å^3, $K_0 = 88.9(1.6)$ GPa, with $a_0 = 11.516(4)$ Å, $K_a = 95.4(1.8)$ GPa, and $c_0 = 9.826(4)$ Å, $K_c = 77.2(1.6)$ GPa for the high-pressure form ($P > P_c$). One of the most significant structural changes is related to the coordination of Ba atoms, changing from an irregular [6+6] coordination to a more regular ninefold. Simultaneously, the Si_3O_9 rings are distorted due to no longer being constrained by mirror-plane symmetry, and the Si atoms occupy three independent sites. The higher compressibility along the **c**-axis direction is explained by the relative displacement of the Ba position to the Si_3O_9 rings, which is coupled to the lateral displacement of the non-bridging O2-type atoms of the ring unit. A symmetry mode analysis revealed that the transition is induced by the onset of a primary order parameter transforming according to the K_6 irreducible representation of $P\bar{6}c2$.

Keywords: Benitoite, crystal structure, phase transition, high pressure, diamond-anvil cell, X-ray diffraction, Raman spectroscopy, symmetry mode analysis