

PS18.03.20 RAMAN AND X-RAY ANALYSES ON CHALCEDONY AND CHRYSOPRASE by Shu-Cheng Yu, Heng-Ying Su and Jiann-Shing Lee, Department of Earth Sciences, National Cheng-Kung University, Tainan, Taiwan

An X-ray diffraction study and a Raman spectroscopic analysis at elevated pressure conditions have been carried out on two cryptocrystalline silica minerals, chalcedony and chrysoprase. The chalcedony samples are of fibrous variety and the chrysoprase specimens are granular in microstructure. X-ray diffraction measurements indicate that the crystallinity index of the chalcedony is inferior to that of the chrysoprase. The variation in crystallinity between these two samples is also consistent with the Raman spectroscopic analysis. At ambient conditions, a principal Raman peak of the chrysoprase has a wavenumber of 466.1 cm⁻¹ instead of 464.3 cm⁻¹ for a crystalline quartz specimen. With increasing pressure, this Raman peak shifts toward a higher wavenumber region, and its FWHM value increases. At 15 GPa, this 466.1 cm⁻¹ peak has moved to 565.0 cm⁻¹. The peak has significantly broadened in peak width, indicating the deterioration of the crystallinity of the sample.

No obvious structural phase transformations were observed within the studied pressure range for both cryptocrystalline silica samples. The pressure effect on amorphization of cryptocrystalline SiO₂ is more profound for chalcedony than for chrysoprase.

PS18.03.21 THE STRUCTURAL PRESSURE DEPENDENCE OF MICROCLINE (KAISi₃O₈) TO 7 GPa. D. R. Allan, R. J. Angel, Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

Members of the feldspar group of minerals are the most abundant constituents of igneous rocks and form a major component of the Earth's crust. A knowledge of their high-pressure and high-temperature behaviour is, therefore, crucially important for the understanding of crustal chemical and thermodynamic processes. Previous high pressure single-crystal x-ray diffraction studies of well-ordered K-rich microcline have identified discontinuities in the pressure dependence of the α and β unit-cell angles at approximately 3.8 GPa while, in contrast, the rate of change of g was found to be continuous. The volume reduction accompanying this change in behaviour was found to be too small to be measurable and studies conducted above ~3.8 GPa did not reveal a change in symmetry. We have now repeated these earlier unit-cell measurements, but over a pressure range extended from ~4.8 GPa to ~7.1 GPa and we have also determined the underlying pressure-induced changes in the crystal structure for the first time.

Our preliminary results confirm the findings of the previous study and indicate that the structural changes with pressure are remarkably strong. The potassium atom, for example, initially undergoes a large continuous shift which is principally directed along the a -axis and at pressures above 3.8 GPa there is an abrupt change with a strong additional c -axis component. Accompanying the potassium atom displacement some of the key Si(Al)-O-Si(Al) linking bond angles exhibit very large changes of up to 18° at 7.1 GPa. Indeed, the sudden change in the pressure dependence of some of the linking bond angles at 3.8 GPa may partly account for the discontinuity in the rate of change of the unit-cell angle β at the same pressure.

PS18.03.22 THE STRUCTURAL PRESSURE BEHAVIOUR OF PARAGONITE. Comodi P., Zanazzi P.F., Department of Earth Sciences, University of Perugia, Perugia, Italy

Structural and volume compressibility data for paragonite (Na_{0.9}K_{0.1}Al₃Si₃O₁₀(OH)₂) were determined by single-crystal X-ray diffraction in a diamond anvil cell up to a pressure of 40.5 kbar.

From the unit-cell data the volume variation with P was best described by the equation $V/V_0 = 1 - 0.00153(4)P$ (bulk modulus = 650(20) kbar). The mean compressibility coefficients of the cell edges were $\beta_a = 3.5(1) \cdot 10^{-4}$, $\beta_b = 3.6(1) \cdot 10^{-4}$, $\beta_c = 8.3(3) \cdot 10^{-4}$ kbar⁻¹, with a very anisotropic compressional pattern: $\beta_a : \beta_b : \beta_c = 1:1.03:2.37$.

The main features of the deformation mechanism resulting from the structural refinements at pressures of 0.5, 25.4, 40.5 kbar were:

- the different variation of sheet thickness indicated that the compression of the c parameter was due entirely to the interlayer thickness (Δt) reduction (Δt changed from 3.13 Å at 0.5 kbar to 2.76 Å at 40.5 kbar);
- the compressibility of the octahedra (average octahedral bulk modulus \approx 600 kbar) being larger than that of tetrahedra, the dimensional misfit between the tetrahedral and octahedral sheet increased with P and therefore the tetrahedral rotation angle (α) increased from 15° at 0.5 kbar to 21.6° at 40.5 kbar;
- the basal surface corrugation (Δz) of the tetrahedral layer, due to the different dimensions of M1 and M2 octahedra and to the octahedral distortion, decreased with P ($\Delta z = 0.19$ and 0.12 Å at 0.5 and 40.5 kbar respectively).

By comparing the new data on paragonite with the data of a K-muscovite and a Na-rich muscovite (Comodi and Zanazzi, 1995) a clear trend toward the decrease of compressibility when Na substitutes for K atoms in the interlayer cavity can be pointed out. The results may yield important insights on the thermodynamic properties of dioctahedral micas along the muscovite-paragonite join.

Comodi P. and Zanazzi P. F. (1995) Phys. Chem. Minerals, 22:170-177.

PS18.03.23 STRUCTURAL PRESSURE DEPENDENCE OF SYNTHETIC BRAUNITE, Mn²⁺Mn³⁺₆O₈SiO₄. R. Miletich, D. R. Allan, R. J. Angel, Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

Investigations of the high-pressure crystal chemistry of synthetic braunite, Mn²⁺Mn³⁺₆O₈SiO₄ ($I4_1/acd$; $a = 9.4226(5)$ Å, $c = 18.6952(7)$ Å, $V = 1661.26(18)$ Å³ at 0.0001 GPa), allow the study of the pressure dependence of the polyhedral geometries of Jahn-Teller (JT) distorted Mn³⁺O₆ octahedra. A high-pressure single-crystal X-ray diffraction study was carried out in a diamond-anvil cell (DAC); the crystal structures were determined at ~1.5 GPa intervals while the unit-cell parameters were measured at ~0.3-0.5 GPa pressure increments. The equation of state (EOS) of synthetic braunite was fitted from an experimentally determined P-V data set yielding $K = 175 \pm 3$ GPa and $K' = 11 \pm 3$ with the Birch-Murnaghan function.

As expected for JT distorted octahedra, anisotropic behaviour was observed for the Mn³⁺O₆ polyhedral compression. The compression mostly affects the four short Mn-O bonds of the [4+2] coordinations whereas the weaker axial Mn-O bonds are not affected significantly. Therefore the distortion of the uniaxially elongated octahedra increases as a function of pressure. This pressure-induced change can be observed for all three independent octahedral Mn³⁺ sites in the structure.

The relatively low compressibility compared to other oxygen-based transition metal compounds can be related to the structural topology. Most of the Mn³⁺O₆ octahedra, as well as the Mn²⁺O₈ polyhedra, are interconnected by sharing common edges. The only interconnections via corners are for the SiO₄ units. As a result only the Mn³⁺-O₃-Si bond angle has a small but significant change with pressure. In addition, all three oxygen atoms are coordinated by four cations which appear to constrain the oxygen atom positions.