



## Effect of Na substitution into $\text{KAlSi}_3\text{O}_8$ hollandite type structure

J. Liu, T. Boffa Ballaran, L. Dubrovinsky and D. Frost

Bayerisches Geoinstitut, Bayreuth, Germany (Jun.Liu@uni-bayreuth.de)

(Na, K) $\text{AlSi}_3\text{O}_8$  aluminosilicates hollandite-type materials with their dense structure, in which all Si and Al are in six-fold coordination, are considered as a possible repository of potassium and sodium in the Earth's lower mantle. Phase relations in the system  $\text{KAlSi}_3\text{O}_8$  -  $\text{NaAlSi}_3\text{O}_8$  have been examined at pressures of 5 - 23 GPa and temperatures of 700 – 1200 °C (Yagi et al. 1994), indicating that the maximum solubility of  $\text{NaAlSi}_3\text{O}_8$  component into hollandite-type structure at 1000 °C is about 40 mol%. However, in the last few years there have been a number of reports of natural occurrences of  $\text{NaAlSi}_3\text{O}_8$  hollandite in shock-induced melt veins of chondrite. Aim of our research is, therefore, to extent the study of the phase relation of the K-Na system at higher temperature and to determine the physical-chemical properties and high-pressure behavior of silicate hollandite-type structures containing K and Na in different concentrations.

So far the high-pressure behavior of the  $\text{KAlSi}_3\text{O}_8$  hollandite end-member synthesized at 1500°C and 13GPa in a multi-anvil press has been studied by means of synchrotron radiation X-ray powder diffraction and high-pressure Raman spectroscopy. High-pressure diffraction data of  $\text{KAlSi}_3\text{O}_8$  hollandite were collected at the European synchrotron Radiation Facility (ESRF, Grenoble, France). The K-hollandite sample powder was loaded with argon and ruby into the diamond anvil cell (DAC), and compressed up to 14.01 GPa at ambient temperature. The equation of state of  $\text{KAlSi}_3\text{O}_8$  hollandite has been calculated with the Murnaghan EOS parameter:  $V_0 = 237.8$  (3),  $K_0 = 270$  (15) GPa, assuming  $K' = 4$ . The bulk modulus value is much larger than that reported by Zhang et al. (1993), and it is very similar to those reported for rutile-type structures. In the *in situ* high-pressure Raman experiment, single crystal K-hollandite sample was loaded with argon and ruby into the DAC, and compressed up to 30.50 GPa at room temperature, and then decompressed slowly to ambient pres-

sure. The observed peak shifting and intensities changes are reversible. Changes in mode Grüneisen parameters are observed at about 20 GPa, and could indicate a phase transition in  $\text{KAlSi}_3\text{O}_8$  hollandite.

A series of synthesis experiments has been done with the multi-anvil presses at the Bayerisches Geoinstitut in the pressure range 13-20 GPa and 1700°C, using  $\text{K}_{0.7}\text{Na}_{0.3}\text{AlSi}_3\text{O}_8$  glass as the starting material. X-ray powder diffraction analysis and electron microprobe measurements of the run products show that at 20GPa, almost pure  $\text{K}_{0.7}\text{Na}_{0.3}\text{AlSi}_3\text{O}_8$  hollandite has been synthesized, with the lattice parameters of  $a = 9.3133$  (5),  $c = 2.7226$  (2),  $v = 236.15$  (2). The pressure stability field of  $\text{K}_{0.7}\text{Na}_{0.3}\text{AlSi}_3\text{O}_8$  hollandite appears therefore larger than in the study of Yagi et al (1994). X-ray powder and single-crystal diffraction and Raman spectroscopy experiments for this composition are in progress.

#### References

Yagi A., Suzuki T., Akaogi M. (1994). High pressure transitions in the system  $\text{KAlSi}_3\text{O}_8$  -  $\text{NaAlSi}_3\text{O}_8$ . *Physics and Chemistry of Minerals*, 21, 12-17.

Zhang J.M. et al. (1993). High-pressure crystal chemistry of  $\text{KAlSi}_3\text{O}_8$  hollandite. *American Mineralogist*, 78, 492-499.