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High-pressure single-crystal synchrotron x-ray diffraction of kainite

S. Nazzareni (1), P. Comodi (1), and M. Hanfland (2)

(1) Perugia, Earth Sciences, Perugia, Italy (sabrina.nazzareni@unipg.it), (2) ESRF, Grenoble, France

Kainite (KMg(SO_4) Cl $3H_2O$) is a K-Mg sulphate of marine evaporitic origin first noted in the salt deposits of Stassfurt (Germany). It belongs to a group of evaporitic minerals more soluble than Ca-sulphate hydrate and NaCl. A new interest in these systems arose from the findings of sulphates hydrate in planets of our solar system (e.g. Mars).

Kainite is monoclinic (sp. gr. $C\ 2/m$) with a crystal structure characterised by Mg- and K-octahedra and sulphur tetrahedra to form sheets that are linked together by Mg(3) octahedra, producing a perfect {100} cleavage. Nevertheless the sheet-like structure is only apparent. Chlorine anions are linked to K1 and K2 to form 8-fold coordination and to K3 in nine-fold coordination [1].

We performed high-pressure single-crystal X-ray diffraction experiments at ESRF (Grenoble), to study the compression behaviour of kainite structure. Single-crystal was loaded in a DAC with a ruby chip as pressure calibrant, and He as pressure transmitting media. HP single-crystal XRD experiments were carried out at ID09 beamline (Grenoble, France) up to 12 GPa.

Kainite remains stable over the investigated pressure range and no phase transition was recognised. The kainite bulk modulus is K_0 = 31.8(3) GPa V0= 3045(4), (K' fixed to 4), as obtained by fitting the P-volume data with a 2^{nd}-order Birch-Murnaghan EoS. The axial bulk moduli were obtained by fitting the lattice parameters with a 2nd-order of the BM EoS (K' fixed to 4): K_{0a}= 38(5) Gpa, a_0 = 19.731(4) Å; K_{0b}= 38(1) GPa, b_0= 16.217(3) Å, K_{0c}= 23.3(2) GPa, c_0= 9.532(2) Å and $K_{0\beta}$= 150(3) GPa, β_0= 94.92(3) Å. The axial compressibility was calculated using the relation β_{axis}= -1/3K_{T0axis} and resulted β_a = -8.8 10^{-3}GPa and β_β= -8.8 10^{-3}GPa β_c= -14.1 10^{-3}GPa β_β= -2.2 10^{-3}GPa. The anisotropy of the lattice parameters is β_{0a}: β_{0b} : β_{0c}= 1:1:1.6.

Structure refinements showed a strong compression of the K1 and K3 polyhedra with a decrease of the K1-Cl2 bond distance of about 13%, of the K1-Cl1 bond distance of about 10%, of the K3-Ow6 and K3-O8B of 9%. S-tetrahedra are almost incompressible and among the Mg-octahedra M1, M2 and M4 a similar behaviour with a decrease of bond distances between 2-4% is observed. In the Mg(3) octahedron two bond distances (Mg3-O7 and Mg3-Ow6) decrease of the same amount whereas Mg3-Ow3 remains unchanged. Mg(3) links together the T-O sheets with the Mg3-Ow3 bond pointing toward the cavity where K2 is located. The complex structural configuration explains the axial compressibility (with c direction softer than a and b directions) that seems to contrast with the (100) cleavage. Still unknown is the role of the H-bonds.

[1] Robinson et al.(1972) American Mineralogist, 57,1325-1332