Report

A natural sample of bloedite from the Natural History Museum of Denmark No. 1922.144 from Leopoldshall, Strassfurt, Germany, was selected for this investigation. The sample was chemically characterized by using a LEO 1525 – ZEISS field emission electron microscope equipped with a GEMINI column installed at the Perugia University using 15 kV accelerating voltage and 10 nA beam current. The sample appears to be chemically homogeneous and the chemical composition averaged over ten points was: SO_3.= 48.5%, Na_2O = 15.8 % and MgO = 13.7 wt%. The amount of H_2O (22 wt%) was obtained by thermogravimetric analysis. The sample was tested with an Xcalibur (Agilent Technologies) single-crystal diffractometer equipped with a CCD detector , operating at 50 KV and 40 mA and using graphite monochromated Mo radiation ($\lambda_{K\alpha1}$ = 0.7093 Å). Diffraction data were collected at room conditions from a crystal fragment (100x80x60 μm) in air using a combination of ω and φ scans, with a step size of 0.4° and a counting time of 30 s/frame for a total of 1800 frames to maximize the reciprocal space coverage. Data were corrected for absorption with the program SADABS (Sheldrick 1996).

The H*P* synchrotron single-crystal X-ray diffraction experiments were carried out at ID-09 beamline dedicated to the determination of structural properties of solids at high pressure using angle-dispersive-diffraction with Diamond Anvil Cells (DAC) at ESRF (Grenoble). A membrane-type DAC equipped with 300 micron diamond culets was used. Helium was used as pressure transmitting medium, to carry out the measurements under hydrostatic pressure. The choice of the hydrostatic medium was based on results of Singh (2012) who showed that the strength of solid helium under high pressure, responsible for non-hydrostatic stresses that can develop in the sample, remains very low at pressures below 20GPa, in comparison with the strength of argon, another usually used medium, which acquires several times the strength of helium.

Ruby chip was loaded as *P* calibrant together with the bloedite sample (30x30x20 μm) in the pre-indented Inconel steel gasket with a 80 μm hole. Pressure was measured before and after each data collection. The X-ray beam was monochromatized to a wavelength of 0.4133 Å and focused down to 5x5 μm area. Data were collected rotating the DAC of 60° round the ω-axis (from -30 to +30°) with an angular step of 2° and counting time of 2s per step. The scattered radiation was collected by a Mar555 flat panel detector, which has a 430 The extraction and correction of the intensity data, merging of reflections, and the refinements of the crystal lattice parameters were done with the CrysAlis program (Agilent technologies) for the whole set of measurements (12 data collections).

The structure refinements were carried out with SHELXL (Sheldrick 2008) integrated into the WingX system, on F^2, starting from atomic coordinates of the non-hydrogen atoms from Hawthorne (1985a). Due to difficulties in performing satisfactory structure refinements, data collected at 2.07GPa, 5.95 GPa and 11.2 GPa were not finally processed. Scattering curves for neutral atoms were used. The insufficient quality of the data and the reduced number of reflections due to the diamond anvil cell, prevented us from refining the H positions.

x 350 mm (555mm diagonal) active area.

The volume-pressure data, collected up to 11.2 GPa, were fitted by a second and a third-order Birch-Murnaghan equations of state (EOS), yielding V_0 = 495.6(7) $Å^3$ with K_0 = 39.9(6) GPa, and V_0 = 496.9(7) $Å^3$, K_0 = 36(1) GPa and K' = 5.1 (4) GPa^{-1} respectively. The axial moduli were calculated using a Birch-Murnaghan EOS truncated at the second order, fixing K' equal to 4, for a and b axes and a third order Birch-Murnaghan EOS for c axis. The results were a_0 = 11.08(1) and K_0 = 56(3) GPa, b_0 = 8.20(2) and K_0 = 43(3) GPa and c_0 = 5.528(5), K_0 = 40(2) GPa, K' = 1.7(3) GPa^{-1}. The values of the compressibility for a, b and c axes are β_a = 0.0060(3) GPa^{-1}, β_b = 0.0078(5)GPa^{-1}, β_c = 0.0083 (4) GPa^{-1} with an anisotropic ratio of β_a:β_b:β_c = 0.72:0.94:1. The evolution of crystal lattice and geometrical parameters indicates no phase transition up to 11 GPa.

The evolution of crystal lattice and geometrical parameters indicates no phase transition up to 11 GPa. Sulphate polyhedra are incompressible, whereas Mg polyhedral bulk modulus is 95 GPa. Sodium polyhedron is the softest part of the whole structure with a bulk modulus of 41 GPa. Pressure decreases significantly the distortion of Na coordination. Up to 10 GPa, the donor-acceptor oxygen distances decrease significantly and the difference between the two water molecules decreases with an increase in the strengths of hydrogen bonds. At the same time, the bond lengths from Na and Mg to oxygens of the water molecules decrease faster than other bonds to these cations suggesting that there is a coupling between the Na-Ow and Mg-Ow bond strengths and the "hydrogen transfer" to acceptor oxygens.