Ulexite, NaCaB$_5$O$_6$(OH)$_6$·5H$_2$O: structure refinement, polyanion configuration, hydrogen bonding, and fiber optics

SUBRATA GHOSE, CHE'NG WAN

Department of Geological Sciences, University of Washington
Seattle, Washington 98195

AND JOAN R. CLARK

U. S. Geological Survey, 345 Middlefield Road
Menlo Park, California 94025

Abstract

The crystal structure of ulexite, NaCaB$_5$O$_6$(OH)$_6$·5H$_2$O, triclinic, PI, has been refined to a conventional $R = 0.046$ using least-squares methods, partially block-diagonal, for 4911 reflections collected on a single-crystal diffractometer with graphite-monochromatized Mo radiation. All 16 hydrogen atoms in the asymmetric unit were located, and all form hydrogen bonds. Refined cell constants are: $a = 8.816(3)$, $b = 12.870(7)$, $c = 6.678(1)$ A, $\alpha = 90.36(2)^\circ$, $\beta = 109.03(2)^\circ$, $\gamma = 104.98(4)^\circ$. $V = 688.4(4)$ A$^3$. $Z = 2$, density (calc) = 1.955 g/cm$^3$. The structure contains isolated pentaborate-type polyanions composed of three tetrahedra and two triangles, plus chains of Na octahedra and chains of Ca polyhedra, all cross-linked by polyanion bonds to the cations and by a network of hydrogen bonds. Average bond distances (A) are: B–O, tetrahedral 1.475; triangular 1.367; Na–O, 2.421; Ca–O, 2.484; hydrogen bonds, O–H 0.80, H···O 2.08, O···O 2.852. The octahedral and polyhedral chains are parallel to c, the elongation direction, and cause the fibrous habit of ulexite crystals that is essential to the optical fiber bundles. The hydrogen bonds range from strong with a minimum O···O distance of 2.595(3) A to very weak and possibly bifurcated with O···O distances of 3.082(4) and 3.194(3) A. The water molecule environments are normal; each contacts at least one Na or Ca on its lone-pair side. Bond strengths calculated using the observed O–H and H···O values agree fairly well with those obtained from an empirical relationship. A good cleavage parallel to (120), rather than to (010) as previously suggested, breaks hydrogen and Na–OH(5) bonds only; a reproducible fracture surface is parallel to (001).

Introduction

According to Dana's System of Mineralogy (Palache et al., 1951, p. 345-348), ulexite has been recognized as a valid species since about 1840. Its formula, Na$_2$O·2CaO·5B$_2$O$_5$·16H$_2$O, assigned by chemist George Ludwig Ulex for whom the mineral was named, has been associated with the mineral almost as long. Ulexite occurs in salt plays and dry saline lakes and has also been found associated with gypsum deposits. Frequently it occurs in bundles of fibers matted together to resemble a cotton ball, and this habit is known as "cottonball ulexite." Less frequently the fibers are oriented in parallel bundles that transmit an optical image with remarkable clarity and resolution. This phenomenon was investigated by Weichel-Moore and Potter (1963), who conclude their paper with the sentence "The discovery and study of ulexite show that it is possible to find in Nature a device almost as good as a man-made [optical] fibre bundle."

The crystallography of ulexite was studied by Murchoch (1940) and reexamined by Clark and Christ (1959), who also gave indexed X-ray diffraction powder data. Clark and Appleman (1964) solved the structure, but published only a brief report because the data were too numerous to be refined economically at that time. Even today the dimensions of the structure refinement are too large to be treated economically by the usual full-matrix least-squares method. In the present work with new data, we have been able to determine all the hydrogen positions and