Charoite: The Enigmatic Structure of “Unnaturally Beautiful” Gemstone

Charoite is a rare mineral first described in 1978 and named after the Chara River (Murmansk, Kukutka, Siberia, Russia). Charoite is translucent lavender to purple in color with a pearly lustre. Charoite is strictly massive in nature, and fractures are conchoidal. It has an unusual swirling, fibrous appearance, sometimes chatoyant, and that, along with its intense color, can lead many to believe at first that it is synthetic or enhanced artificially. Charoite is used as an ornamental stone and sometimes a gemstone, generally as cabochons set into pendants. However, Charoite is a discrete mineral rather than a rock.

Despite many attempts to solve the charoite structure, or at least to construct a convincing structural model, the structure and stoichiometry have remained enigmatic due to the presence of secondary phases, polymorphism and pseudosymmetries. Selected area electron diffraction (SAED) patterns of different fibres along [010] have revealed the presence of four structural arrangements, presenting polytypism. The two simplest polytypic structures have clearly related cell parameters and monoclinic symmetry. These are described as ‘charoite-96’ and ‘charoite-90’, on the basis of their β angles, respectively 96° and 90°. A third polytypic structure (‘charoite-2a’) was detected that presents a doubling of the a-parameter in all h0l diffraction lines in SAED patterns. The presence of diffuse streaks along h0l (l = 2n+1) lines and of disordered intergrown fine lamellae in HRTEM images suggests a fourth disordered sequence of OD layers (‘charoite-d’).

3D electron diffraction tomography “coupled” to beam precession (PED) allowed an almost complete quasi-kinematic electron diffraction intensity collection from a single nanocrystal, allowed the structure determination of charoite for the first time.

The intensities extracted from the precessed diffraction tomography tilt series show unambiguously that charoite-90 and charoite-96 are both monoclinic, despite the β angle of 90° for charoite-90.

The angle β of 96° in the charoite-96 unit cell is produced by a shift by c/2 in comparison to the unit cell of charoite-90. Due to the spatial relationship between the octahedral bands and dreier chains this means that in charoite-96 the tetrahedral chains are shifted by c/2 along the octahedral bands in each subsequent unit cell.

Both polytypes are composed of three different silicate chains parallel to the z axis: a dreier double chain, [Si₈O₂₆]⁴⁻, a tubular loop-branched dreier triple chain, [Si₈O₂₆]⁴⁻ and a tubular hybrid dreier quadruple chain, [Si₈O₂₆]⁴⁻. The chains share their apical oxygens with bands of (Ca, Na) octahedra. The K⁺ and Sr⁺ cations and H₂O molecules are located inside the channels formed by the silicate chains.

After more than 50 years of attempts to determine the enigmatic nature of the charoite structure the problem has been solved using the 3D electron diffraction tomography together with PED strategy.

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Crystal Structure

Experimental data

charo-90 / charo-96

tilt range: ±60° / ±60° step: 1°
No ind. reflections 2876 / 3353
No ind. atoms 90 / 89
R = 17% / 22%

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Figure 1

Crystal used for ADT measurements.
[010] 3D reconstructed Reciprocal Space

Figure 2

Charoite-96 and Charoite-90 Polytype viewed along [010].
The red line emphasizes the shift of the chain along c.

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