Supplementary Information: Self-assembly of a space-tessellating structure in the binary system of hard tetrahedra and octahedra[†]

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Structure analysis with bond order diagrams

The crystal structures observed in this study were analyzed primarily by visual inspection. However, bond-orientational order diagrams (BODs)[1] were also found to be instructive, especially when investigating structural subtleties. In the binary structure, the BODs were also generated both for the mixture of polyhedra and for tetrahedra and octahedra separately. In the binary crystal, the centers of the tetrahedra form a simple cubic lattice, and the octahedra form a face-centered cubic lattice. The BODs of the binary structure and the octahedra packings are shown in Fig. S1, the ones of the dodecagonal quasicrystal in Fig. S2. The quasicrystal of tetrahedra has a particular signature in the BOD, resembling a cylinder and resulting in dark spots aligned with the 12-fold axis of the dodecagonal structure.

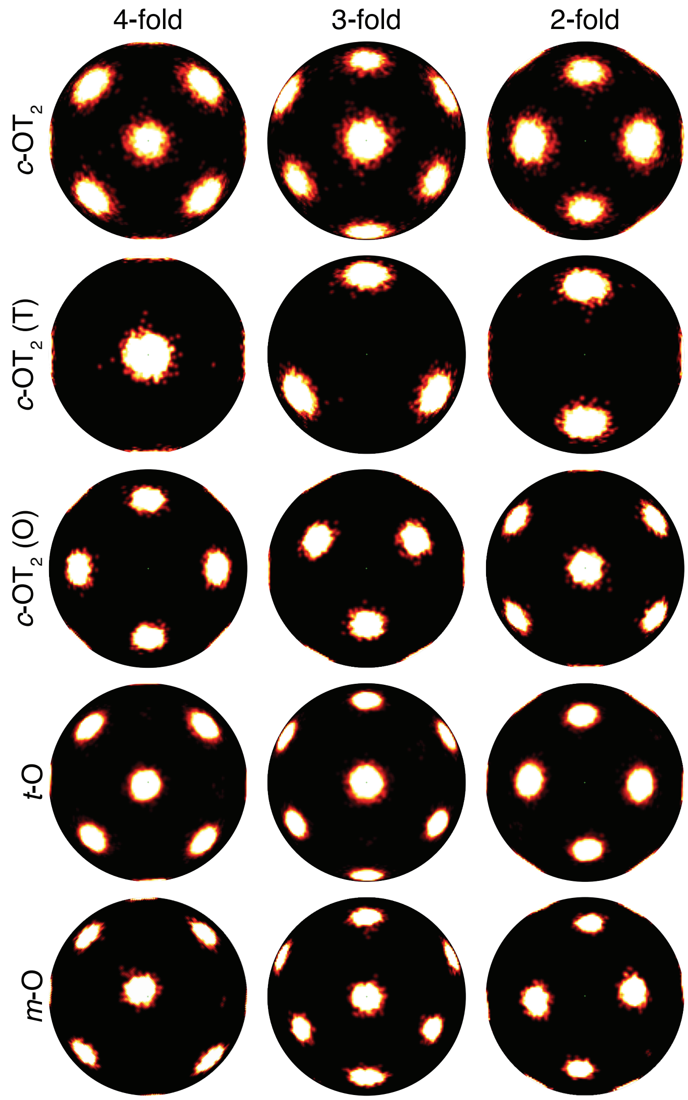

Fig. S1: Bond-orientational order diagrams (BODs), from top to bottom, of the full binary structure *c*-OT_2, as well as of only the tetrahedra (T), only the octahedra (O), and of the trigonal and monoclinic octahedra packings, *t*-O and *m*-O, respectively. Shown are the 4-fold / pseudo-4-fold, 3-fold / pseudo-3-fold, and 2-fold crystallographic directions.

Quasicrystal binary-crystal coexistence

Small numbers of octahedra that are present in a simulation of mainly tetrahedra have a preferred alignment within the quasicrystal. In some cases, they form five-rings, alternating with pentagonal bipyramids of tetrahedra, similar to a model of dodecagonal Al–Mn[2–4], as shown in Fig. S3.

Binary crystal structure

The binary crystal consists of layers of alternating tetrahedra and octahedra that share faces with each other, *i.e.*, with only O–T nearest neighbor contacts. This leads to each octahedron having six neighbors within the layer (all tetrahedra) and each tetrahedron having three neighbors within the layer (all octahedra). The remaining faces – two per octahedron and one per tetrahedron – form a triangular lattice on the outside of the layer and are again arranged alternatingly. The ratio of octahedral to tetrahedral faces in this tiling is O:T = 1:1; each octahedron contributes two triangles and each tetrahedron contributes one, but their 1:2 composition overall and in the layer results in equal numbers on the outside of the layer (see Fig. 1 in the main text).

The resulting triangular lattices can be aligned alternatingly, joining octahedral faces with tetrahedral ones and

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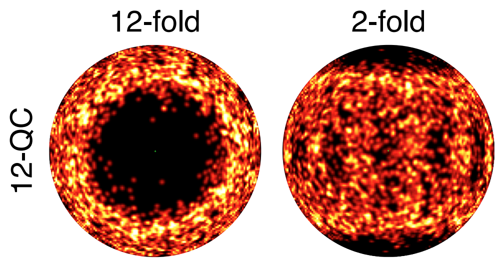

Fig. S2: Bond-orientational order diagrams (BODs) of the dodecagonal structure 12-QC made up of tetrahedra. Shown are the 12-fold and 2-fold crystallographic directions.

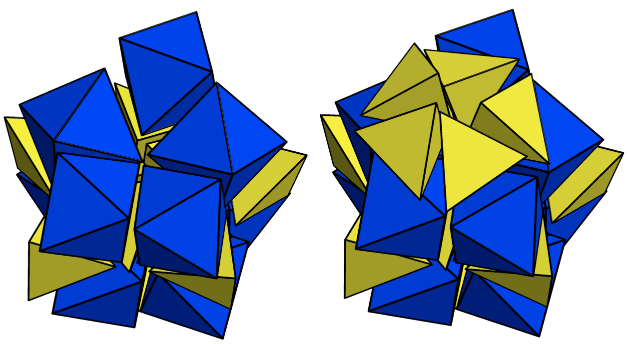

Fig. S3: An intergrowth motif of octahedra with the 12-QC structure, consisting of a ring of five octahedra that can be stacked with pentagonal bipyramids of tetrahedra.

vice versa, creating the same contacts that already occur within the layer. Alternatively, they can be rotated by 60° around any vertex so that each octahedral face joins another octahedral face and tetrahedral faces from different layers join one another, forming a mirror plane between layers. As is the case with different stacking variants in sphere-packings, both arrangements can be combined in an infinite number of ways.

If only the first kind of stacking – resulting in alternating polyhedral arrangements between layers – is employed, the alternated cubic honeycomb emerges. A honeycomb is a space-filling tessellation. Both of the honeycombs discussed in this manuscript are also uniform or vertex-transitive, *i.e.*, all vertices are equivalent, as well as convex, as they are built from convex polyhedra. The alternated cubic honeycomb structure is also edge-transitive, while the gyrated, hexagonal structure has two kinds of edges. A structure composed solely of the second kind of stacking results in the gyrated honeycomb. Edges in the alternated cubic honeycomb are shared by a tetrahedron, an octahedron, another tetrahedron, and another octahedron, respectively. The gyrated, hexagonal honeycomb also exhibits this configuration, however, there is also a second kind of edge located between neighboring layers, shared by, in the following order, a tetrahedron, another tetrahedron, an octahedron, and a second octahedron.

The crystallographic structure type corresponding to the alternated cubic honeycomb is fluorite CaF_2: the space group is $Fm\bar{3}m$ (no. 225), octahedra occupy the Ca-Wyckoff position $4a$ 0, 0, 0 and tetrahedra the F-position $8c$ 1/4, 1/4, 1/4. The gyrated honeycomb structure has no atomic equivalent; its crystallographic description can be derived from the cubic structure equivalent to the analogy between cubic-close and hexagonal-close packings *ccp* and *hcp*. The space group is $P6_3/mmc$ (no. 194) with octahedra occupying Wyckoff position $2a$ 0, 0, 0 and tetrahedra $4f$ 1/3, 2/3, 5/8.

Within the stability range of the binary OT_2 phase, the cubic c-OT_2 structure is dominant, but is interspersed with a few stacking faults, which come in the form of the hexagonal h-OT_2 structure. The short bond length between face-sharing tetrahedra that are located between layers can be used to easily map these stacking faults within the c-OT_2 structure.

As expected, the binary crystal seems to form best at the ideal stoichiometry of O:T = 1:2 and at a packing fraction of 60%. This was determined by the clarity of the BOD, as well as the highest number of particles that were identified as having a crystalline environment with the employed Steinhardt order parameter.

Octahedra crystal structure(s)

The two octahedra structures are shown in Fig. S4. The m-O structure can be understood as a packing of octahedra with tetrahedral voids [T] in a stoichiometry O:[T] = 1:4, where the edge length of the tetrahedral voids is $1/2$ the edge length of the octahedra. The octahedra are arranged in stacked trigonal layers that allow for a parallel shear plane (the layers can be sheared with respect to one another) and another perpendicular shear plane that can move along one direction. The t-O structure, also termed the Minkowski phase, can be thought of as a packing of octahedra with O:[T] = 1:6, where the edge length of the tetrahedral voids [T] is $1/3$ the edge length of the octahedra. The re-tessellations of tilings of octahedra and tetrahedra with different edge lengths – here introduced as packings of octahedra with tetrahedral voids – were described in detail by Gabbrielli *et al.*[5].

References

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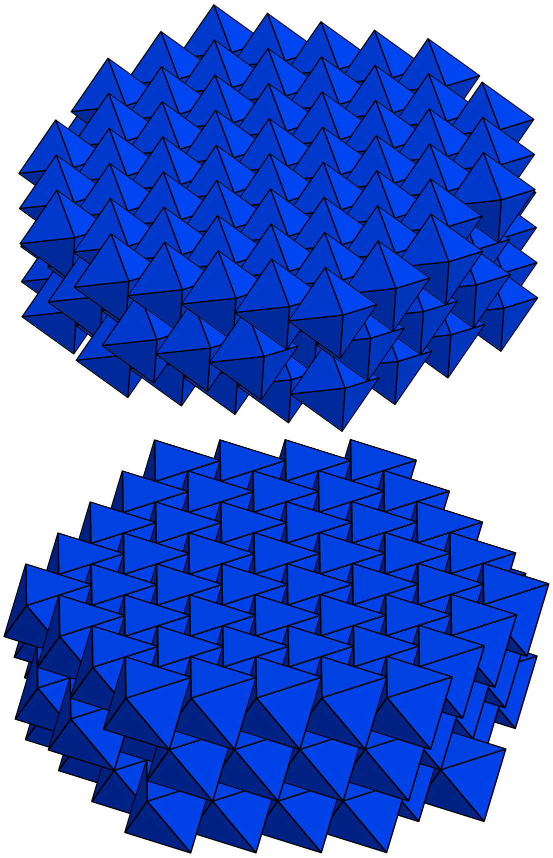

Fig. S4: Two packings of octahedra: the trigonal closest packing of octahedra, *t*-O structure *(top)* and the monoclinic layered structure *m*-O *(bottom)*.

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