Chemical Equitable Partitions of Inorganic Lattices

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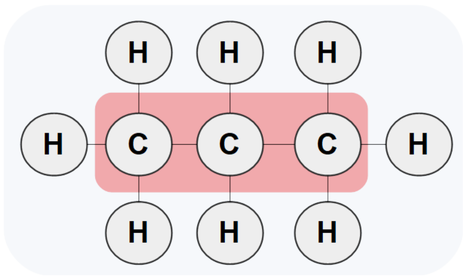
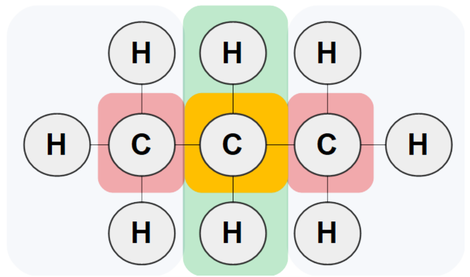
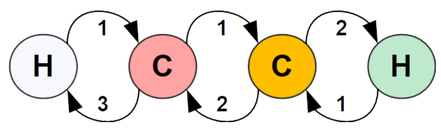


(a) Split atoms into cells according to their chemical element *and* node degree (in the case of molecular graphs: chemical valence).



(b) Split further until eliminating all violations of same cell-to-cell out-degree condition. The resulting partition is easily shown to be an EP.



(c) Q*uotient graph*, *QG(CEP)*. Atoms (graph vertices) are *classified* to cells according to their connectivity to their neighbours.

***Fig*. 1 Definition of CEP** [1] **and an algorithm for its derivation, drawing from existing work on detection of graph isomorphism** [3, 4, 5]**. Example: the molecule of *n*-propane. In crystal unit cells, periodicity is also accounted for**

$$\%CR = \left(100\,\frac{n_{QG}}{n_G}\right)\frac{a_{QG}}{m_G}\,Z\,f$$

***Fig*. 2 Definition of compression ratio of a given graph, *G*, ref.** [1]
QG denotes the CEP quotient graph; n is the number of nodes in G or QG; a_{QG} is the number of arcs in QG; m_G is the number of edges in G; Z is the number of formula units in the conventional unit cell; and f is the number of lattice points per cell [11,12]. Low $\%CR$ indicates rich symmetry and high information compression.

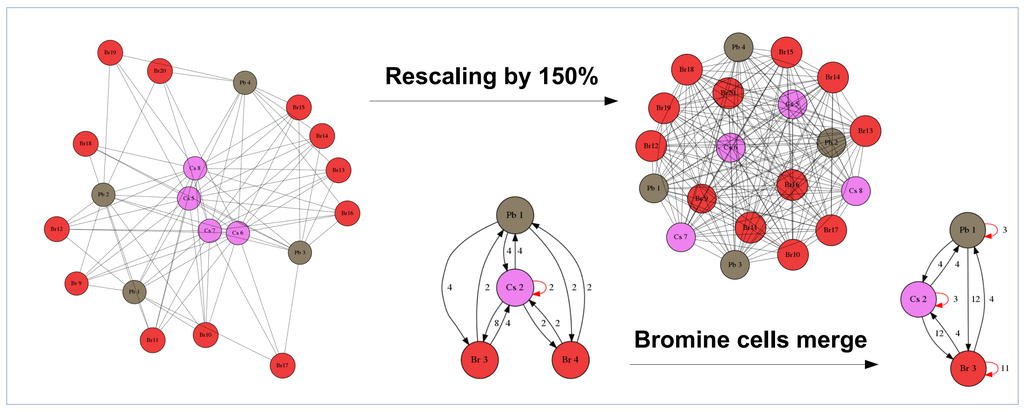


***Fig*. 3 Chemical Composition Graphs (CCG); example: $CsPbBr_3$ (*Pnma*)**
By bloating atomic radii, all atom pairs overlap and graphs become regular. At this point, CEP cells coincide with the initial partition (CP) and the quotient graph (now, termed CCG) gets considerably simplified. CCGs offer a baseline for CEP quotient graphs, highlighting by comparison the latters' complexity (or lack thereof).

Introduction: Graph-theoretical approaches in the study of materials, can shed new light on their structure-property relationships. Here, a novel concept termed Chemical Equitable Partition (CEP) [1,2] was used as a means to look at crystal symmetries and classify atoms accordingly.

An ***Equitable Partition* (EP)** [6] of a graph G is a partition $\pi = (V_1, ..., Vp)$ of its vertex set with the property that for each i and j from 1 to p, each atom in cell V_i is connected to the same non-negative number, say b_{ij}, of atoms in cell V_j. The corresponding directed multigraph is the ***quotient graph*** QG of π.

Given a partition of a graph based on chemical elements and valences (Chemical Partition, CP) we can define ***Chemical Equitable Partition* (CEP)** as the unique coarsest EP that **refines** CP. CEP has been defined for molecules and crystal unit cells, and it has been associated with a measure of information reduction, which quantifies the system's generalised symmetry and was aptly termed ***Compression Ratio* (CR)** [1, 2].

This study focused on inorganic lattices (perovskites, salts, oxides) without partial or mixed occupancies. Atom pairs were marked as adjacent when the sum of the atoms' radii exceeded the pair distance, respecting unit-cell periodicity. Various sets of atom radii such as in [7–10] were used. The atoms' connectivity profiles were processed as described by Michos and Raptis [1] to derive Chemical Equitable Partitions. Electrostatic lattice site potentials were calculated using VESTA's built-in functionality. CEP cells were compared to the atom groups defined by Wyckoff symbols and positions, on the one hand, and lattice site potentials, on the other.

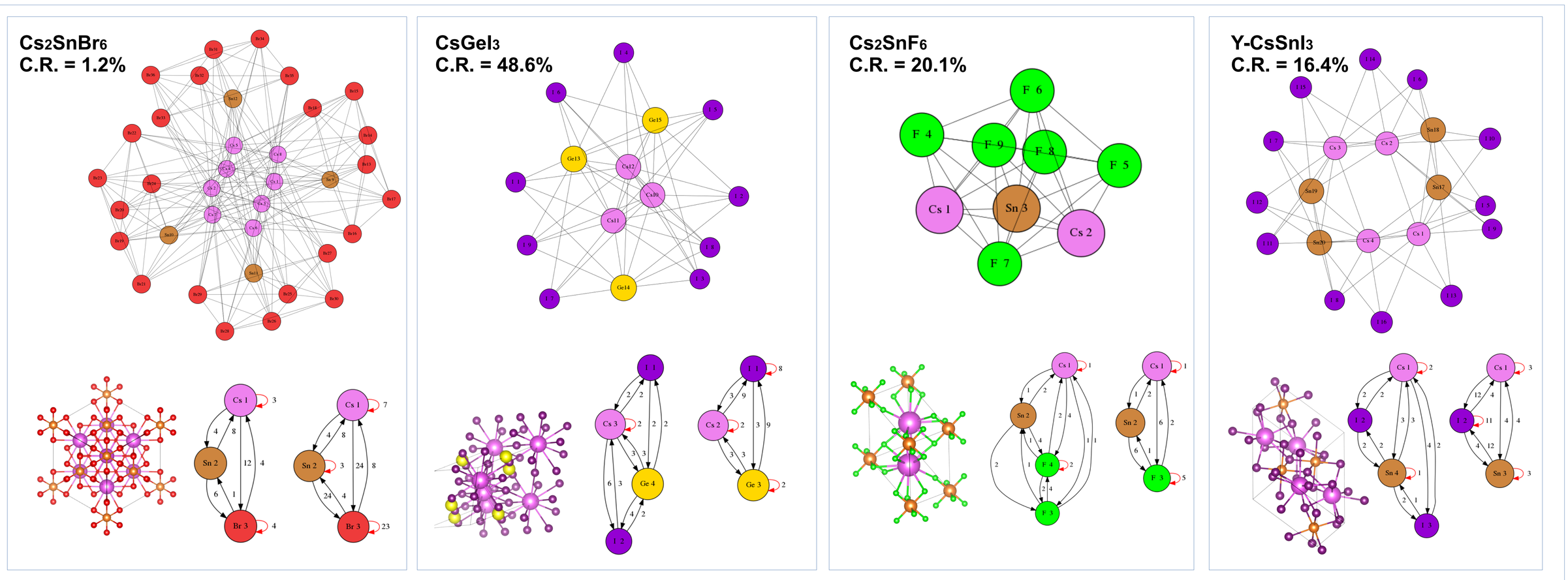
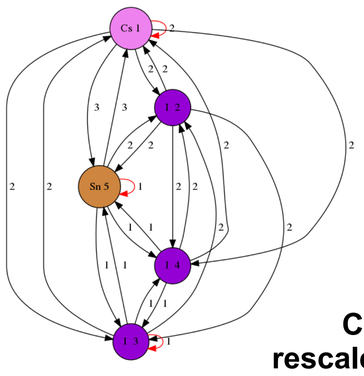


***Fig*. 4 Examples of graph-theoretic depictions of inorganic lattices.**
Two 'defect perovskite' (Cs_2SnBr_6, Cs_2SnF_6) and two perovskite ($CsGeI_3$, $CsSnI_3$ yellow polymorph) inorganic lattices are depicted. In each pane, top row: structural graph of the lattice unit cell where atom-pair adjacency respects toroidal boundary conditions; bottom row, from left to right: conventional unit cell, quotient graph of the chemical equitable partition, GQ(CEP), chemical composition graph (CCG). Higher symmetry corresponds to higher information compression reflected in lower % compresssion ratio values.

***Fig*. 5 Hidden complexity.**
Electrostatic lattice site potentials in the conventional unit cells, were computed using VESTA's built-in calculator of Madelung energy [13]. Ions with same potential formed classes that coincided with CEP cells, with few exceptions where partitioning by potential refined CEP. In the latter case, rescaling the radii reshaped QGs and modified CEP, which featured more cells in alignment with the potential classes, thus revealing an underlying complexity of the crystal structure.



Y-CsSnI3
C.R. = 28.8%
rescaled by 110%
(compare with Fig. 4, rightmost pane)

Results. Highly symmetric cells feature identical partitions, according to CEP; Wyckoff-symbols; and lattice site potentials, whereas CEP in less symmetric systems is a refinement of the partitions according to electrostatic potentials and Wyckoff symbols. However, partition according to Wyckoff *orbits* (positions) and lattice site potentials, compares to CEP in a manner dependent on the selection of radii.
Conclusions. CEP provides an alternative perspective on crystal structure and symmetry. When scanning the range of ion radii, CEP is modified revealing different aspects of structural complexity, which are also reflected in the physical properties of individual ions.

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