crystIT: Quantification of Crystal Structure Complexity via Information Theory[1]

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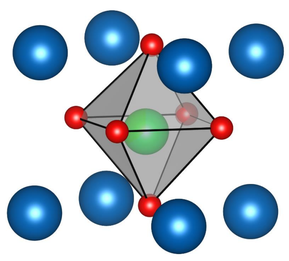
How to Quantify Crystal Structure Complexity?

1

The unbiased quantification of crystal structure complexity that not only captures various aspects of the crystal's architecture but also reflects the chemist's intuition is a challenging task. Recently, the Shannon Information I_G (derived from Information Theory) was introduced as a concise concept by S. Krivovichev.[2] This poster introduces an extension of the original formula by consideration of partial occupancies and vacancies, allowing for the complexity quantification of disordered crystal structures.

$$I_G\left[\frac{\text{bit}}{\text{position}}\right] = -\sum_a \frac{m_a \cdot occ_a}{P} \cdot \log_2 \frac{m_a \cdot occ_a}{P}$$

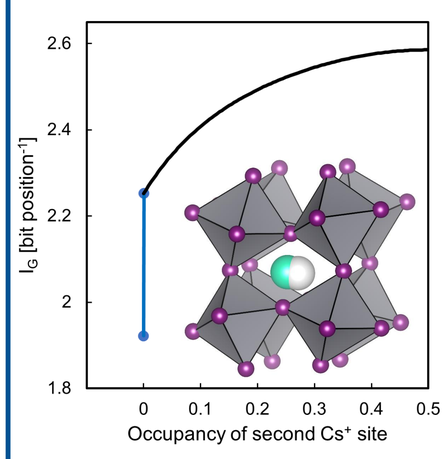


$PbTi_{0.35}Zr_{0.65}O_3$

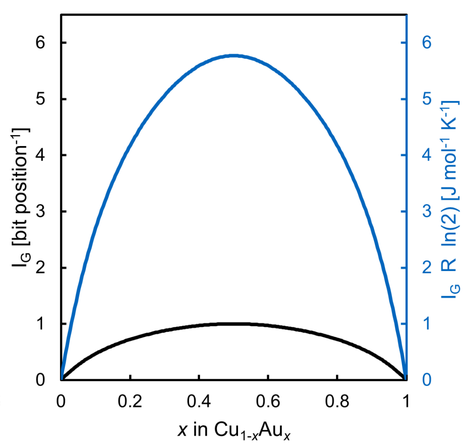
a – species (unique combination of element and crystallographic orbit)
m – multiplicity of crystallographic orbit
occ – occupancy of species
P – number of positions / reduced unit cell

3 crystallographic orbits are occupied in the lead zirconate titanate $PbTi_{0.35}Zr_{0.65}O_3$.[3] O occupies a 6*b* Wyckoff position with multiplicity 6, whereas Pb is located at 2*a*. Ti and Zr occupy a shared 2*a* position ($occ_{Ti} = 0.35$ and $occ_{Zr} = 0.65$). All in all, there are 4 species, distributed among 6+2+2 = 10 positions. Inserting into the above equation, we obtain an information content (complexity) of I_G = 1.56 bit · position^{-1}.

2 Effects of Occupancy Consideration

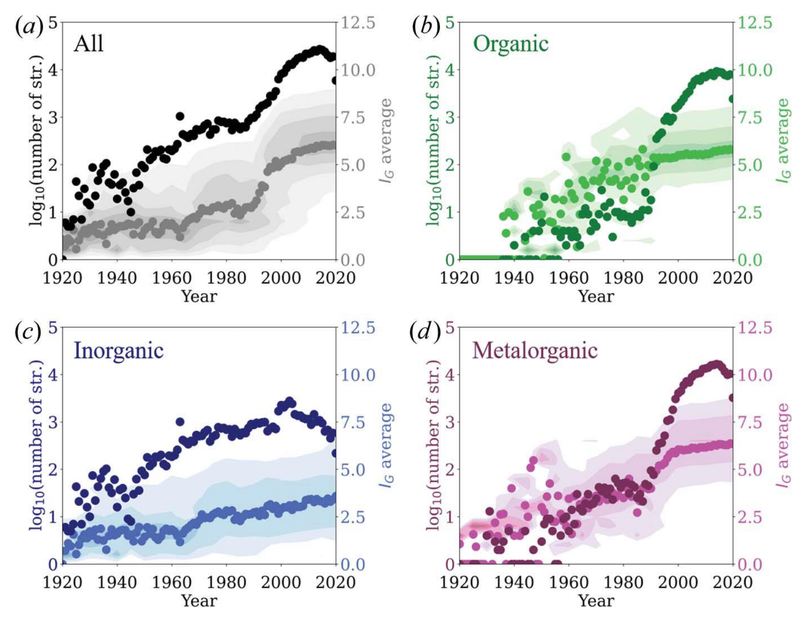


Discontinuous behavior of I_G on emergence of 2nd Cs$^+$ site in **CsPbI$_3$** is counterintuitive; jump at $\lim_{occ\to 0} I_G$ due to vacancy that instantly fills 2nd position (1-*occ*).



Entropy of mixing as $\Delta S_{mix} = I_G \cdot R \cdot \ln(2)$ equals Boltzmann $\Delta S = k_B \ln(\Omega)$
Example: $Cu_{1-x}Au_x$

3 Complexity Development Over Time: Database Screening



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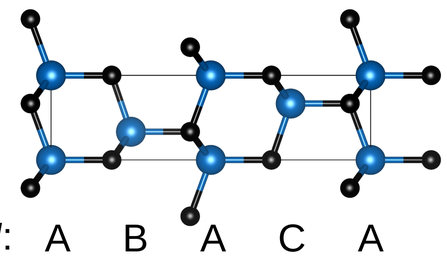
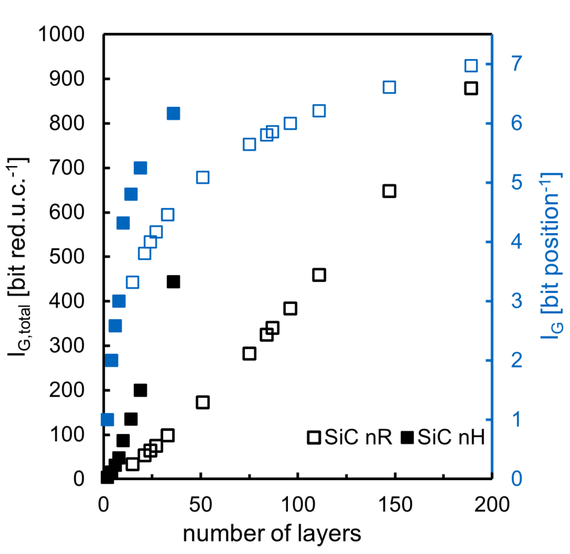
Crystallography Open Database[4]

4 I_G vs Intuition



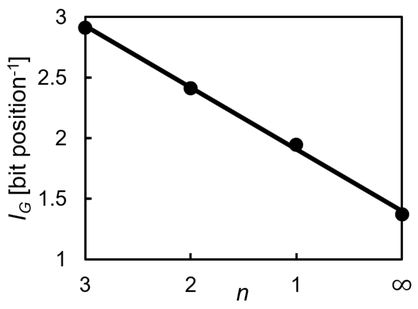
SiC 4*H*: A B A C A

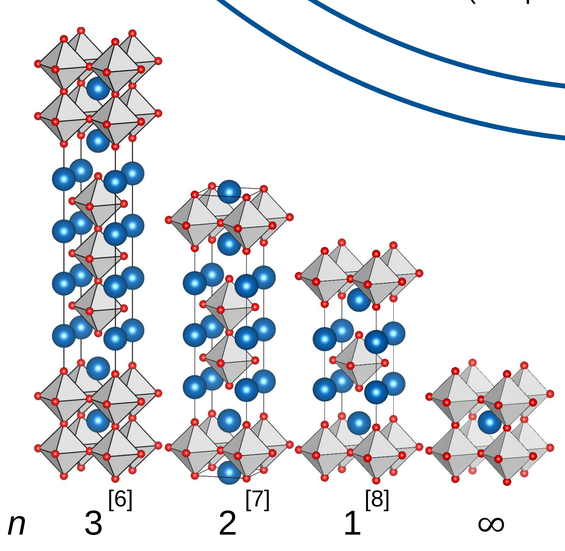


There is a large number of SiC stacking polytypes:[5] (AB, ABC, ABAC, …). I_G per layer strongly depends on spacegroup because of different amounts of lattice points in ***H***exagonal and ***R***hombohedral centering
→ counterintuitive

5 I_G vs Intuition

Right: Ruddlesden-Popper-Series based on **SrTiO$_3$** (general: $A_{n+1}B_nX_{3n+1}$)
Bottom: linear correlation of *n* and I_G follows intuition





6 Conclusion

- Ruddlesden-Popper & complexity increase with time are intuitive
- Counterintutive I_G discontinuity and SG-dependence
- *Outlook*: Establish relationship between I_G and configurational entropy for application in materials science

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References
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