

## Local structure representation beyond symmetry constraints: Glazer tilts in perovskites

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When doing structural refinements of total scattering data from highly crystalline compounds, one starts by choosing an atomic model and then imposing constraints that dictate how the atoms are allowed to move. These constraints are typically based on space group symmetry. The resulting structure representation is useful and accurate for a large range of compounds, however, it has its limitations for materials with a significant amount of disorder. It is particularly necessary to accurately describe this disorder when fitting total scattering data in the real space as pair distribution functions. To represent such disordered, but still significantly crystalline compounds, one would ideally want to fit the data with a ‘big-box’ model containing anything from a hundred to a few thousand atoms. Unfortunately, this can lead to a large number of variables to refine and an overfitting of the data with meaningless results. Alternatively, it is possible to construct models where multiple atoms are constrained to move in a collective fashion, controlled by a small number of variables [1,2].

Here we present one such approach, relying on our a priori knowledge of the structure at hand. For oxides with perovskite structure,  $ABO_3$ , we know that they tend to distort in ways that keep the  $BO_6$  octahedra intact. The resulting distortions can therefore often be described by one of 23 unique tilting patterns of the rigid octahedra, identified by Glazer in the '70s [3]. Fitting a model of any of the tilting patterns to scattering data requires refinement of no more than four variables at once – one lattice parameter and a maximum of three tilt amplitudes. We have implemented this approach into diffpy-CMI, a flexible tool for fitting pair distribution function data. Using the method, we analyse a series of scattering data from well-known perovskites and determine their degree and type of structural tilting disorder.

- [1] Sartbaeva, A. ‘Quadrupolar Ordering in  $LaMnO_3$  Revealed from Scattering Data and Geometric Modeling’. *Phys. Rev. Lett.* **99**, no. 15 (2007): 155503.
- [2] Senn, M. S. et al. ‘Emergence of Long-Range Order in  $BaTiO_3$  from Local Symmetry-Breaking Distortions’. *Phys. Rev. Lett.* **116**, no. 20 (2016): 207602.
- [3] Glazer, A. M. ‘The Classification of Tilted Octahedra in Perovskites’. *Acta Cryst. B* **28**, no. 11 (1972): 3384–92.

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