A Comprehensive Validation and Reassessment Of The Rutile Aristotype's Distortion Tree Using Representational Analysis And Crystal Chemistry Concepts

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This work shows how subtly distorted crystal structures can be identified, classified, and validated using advanced group theory tools combined with crystal chemistry concepts. The work is applied to the rutile (TiO_2) structure type and its 20 to 30 distorted subtypes that together span hundreds of distinct compounds. There are many examples to date of representative materials that are complicated by ambiguous assignment of distortion type that have yet to be resolved. Representative compounds are of interest in a wide range of applications including solar cells, electrodes, and optical and magnetic device. Some, such as VO2, are also notable platforms for studying the fundamental physics of electrostructural phase transitions.

Presented is a detailed and comprehensive review of the known compounds, their reported structure types, and the isotropic group-subgroup relationships. We show how representational analysis can be applied to the reported compounds to provide a straightforward template for interpreting observables when assigning a distorted rutile structure type. Most probably primary order parameters (POPs) are identified for each structure type, which is necessary to discriminate between similar distortion modes that differ in crystal system or space group. Additionally, we identify several reported subtypes that are likely incorrect and suggest alternative choices. So far we have experimentally verified at least one of these predictions, β-NbO_2. β-NbO_2 was originally reported in the $I4_1$ space group, which requires two POPs. We synthesized the compound and found that its crystal structure is better described using our predicted subtype, which is a single POP supergroup of the original report.

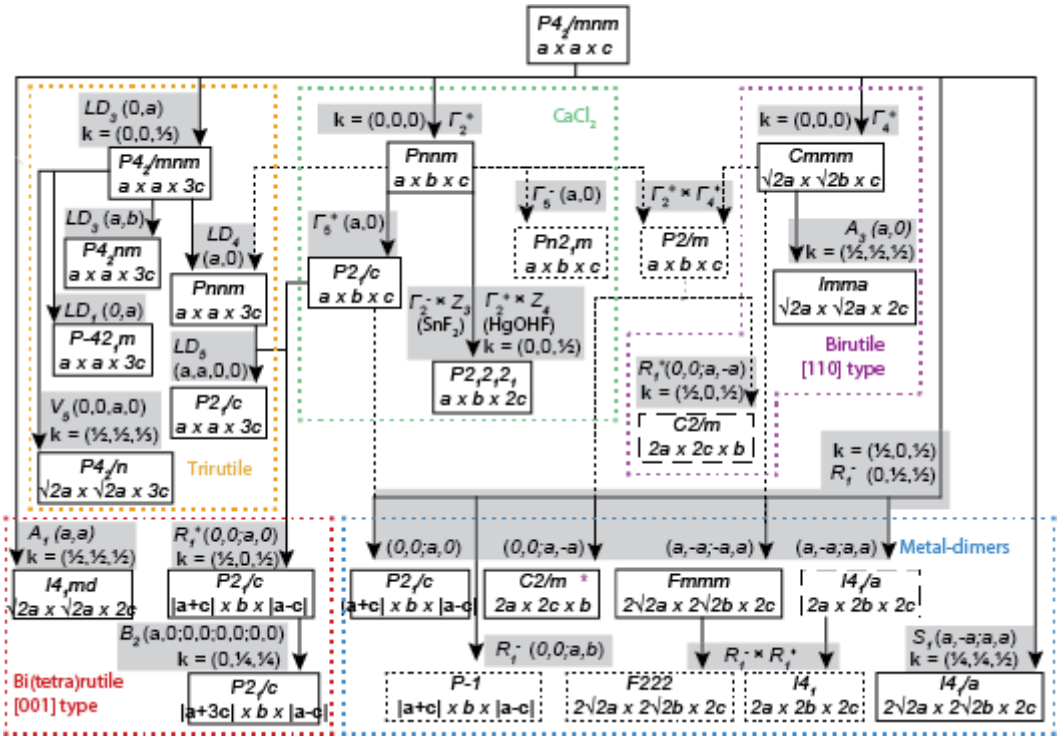

Figure 1