

Poster Presentation

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Symmetry reduction in thortveitites: incommensurability and polytypism

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For many years periodicity was the defining property of crystalline materials. The discovery of numerous aperiodic materials like incommensurately modulated phases or quasi-crystals led to a paradigm shift and since 1992 crystallinity is defined by the IUCr via the discreteness of the diffraction pattern [1]. A different class of materials lacking periodicity in three dimensions, albeit following strict building principles, are polytypes. Polytypes are composed of modules that can be arranged in different but energetically similar ways. On the example of the thortveitite family of compounds it will be shown that these seemingly disparate phenomena can be linked to the same underlying cause, namely symmetry reduction. Many bivalent transition metal diphosphates(V), diarsenates(V) and divanadates(V) of general formula $M_2X_2O_7$ ($X=P, As, V$) crystallize in the thortveitite structure type. The high temperature β - $M_2X_2O_7$ phases feature one crystallographically unique X_2O_7 group located on a centre of inversion. Due to the unfavourable X-O-X angle of 180° these phases transform on cooling into lower symmetry structures. Thus, numerous superstructures based on the thortveitite aristotype have been described. Incommensurate structures can be considered as superstructures with symmetry reduction by an index of ∞ . The first example in the thortveitite family was described by Palatinus et al. [2]. Since then we found several other incommensurate thortveitites with varying modulation functions and phase-transition behaviour. If the symmetry reduction leads to layers with different local symmetry, the resulting structures are order-disorder (OD) polytypes [3], resulting in twinning or diffuse scattering. In $(Co,Ni)_2As_2O_7$ both features, incommensurate modulation and systematic twinning, are combined. An overview of the crystal-chemistry and the complex phase-transition behaviour of the incommensurately modulated and/or polytypic thortveitite phases will be given.

[1] *International Union of Crystallography, Acta Cryst., 1992, A48, 922-946*, [2] *L. Palatinus, M. Dušek, R. Glaum, B. El Bali., Acta Cryst., 1992, B62, 556-566*, [3] *K. Dornberger-Schiff & H. Grell-Niemann., Acta Cryst., 1961, 14, 167-177*

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