

s7.m23.o4 **A New Geometrical Approach to Configurational Stability of Layered Structure Types.** Dmitri O. Charkin, Department of Materials Sciences, Moscow State University, Moscow 119992, Russia. E-mail: charkin@inorg.chem.msu.ru

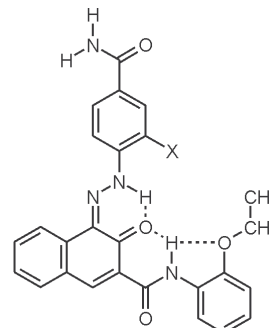
Keywords: Layered Structures; Configurational Stability; Geometrical Approach

Layered (2D) fluorites and perovskites constitute a huge class of inorganic and hybrid organic-inorganic materials famous for the amazing versatility of both their crystal chemistry and applied properties. Their crystal chemistry is rich with non-trivial phenomena like stabilization of unusual oxidation states, including otherwise unstable redox pairs, non-ambient and even unknown polymorphs (in the form of 2D fragments). Many representatives are known as bi-dimensional ionic conductors, ferroelectrics, superconductors, catalysts for water photolysis, ion exchangers (including traps for toxic and radioactive ions), etc. One should also mention high percentage of complicated intergrowth structures. The family represents a wide field for structural design and targeted synthesis of novel materials with desired crystal structures as well as applied properties. Two important questions arise: the compositional and structural stability of known structure types and formulation of stability criteria which are particularly necessary upon structure modeling and predicting the chemical composition for representatives of novel, yet unknown structures. Up to now, several attempts have been made in the area [1-3]; their common problems are narrow specificity, i.e. validity within a relatively small group of isostructural or closely structurally related compounds and comparatively weak predictive power. We report a new semi-quantitative geometrical approach to configurational stability of tetragonal and pseudotetragonal layered structure types. It is based on the concept of limiting deformations of coordination polyhedra constituting the layers, and the deformation is induced by agreement of geometrical parameters of the layers forming a commensurate structure. Provided a numerical expression of deformation, existence of a new compound may be predicted in a rather simple way: if the estimated deformations of all contributing layers do not exceed the tolerance limit (which we denote as the critical deformation), the compound is likely to exist and be synthesized; if any limit is exceeded, the probability of existence decreases sharply. The approach has been applied not only to description of stability areas for some known structure types, but also to prediction of new structure types of different complexity. Over 200 predicted compounds crystallizing in 15 novel structure types were found to exist. Crystal structures of selected representatives have been determined to confirm the expected atomic arrangements. The new compounds are interesting as new ferroelectrics and ion conductors. We discuss the precision of our approach dependent on the kinds of the polyhedra involved and complexity of the structure. We also consider the possibilities of its further development into the realm of other symmetries.

- [1] I.D. Brown, *Acta Cryst. B* **48** (1992) 553-572.
 [2] B.A. Popovkin, A.M. Kusainova, V.A. Dolgikh, L.G. Akselrud, *Russ. J. Inorg. Chem.* **43** (1998) 1471-1475.
 [3] T. Kikuchi, *Mater. Res. Bull.* **14** (1979) 1561-1569.

s7.m23.o5 **Structure Determination from Powder Diagrams by Crystal Structure Prediction.** Christian Buchsbaum, Martin U. Schmidt, Institute for Inorganic and Analytical Chemistry, Goethe-University Frankfurt, Marie-Curie-Str. 11, D-60439 Frankfurt am Main, Germany

Keywords: Crystal structure prediction; Powder diagrams; Pigments



1: X=H (Pigment Red 170)
 2: X=CH₃

Pigment Red 170 is a commercial pigment used for the coloration of plastics and laquers. The metastable α phase resulting from synthesis shows always an X-ray powder diagram of very low quality (12 distinguishable peaks), which could not be indexed. The powder diagram of the isotopic compound **2** is slightly better, but can only partially be indexed: 30 of the occurring 33 peaks could be described as $hk0$ peaks; thus information about c , α , β , space group and crystal system were missing. The structure of **2** was solved using FlexCryst [1,2] by crystal structure prediction (lattice energy minimization in various space groups) using trained potentials and comparing simulated and experimental X-ray powder diagrams. The structure was optimized by force field calculations taking into account the molecular flexibility (program CRYSCA [3]). Finally a Rietveld refinement with restraints was performed (program GSAS [4]). The refinement converged with $R_p=4.99\%$, $wR_p=6.4\%$, red. $\chi^2=3.96$ and $R(F^2)=18.25\%$. Compound **2** crystallizes in a layer structure in space group $P2_12_12_1$ with $a=24.6208(9)$, $b=22.8877(9)$, $c=3.9388(2)\text{\AA}$. Based on these results, the crystal structure of α -1 was refined with rigid body Rietveld methods (GSAS).

Acknowledgements: The authors wish to thank D.W.M. Hofmann for calculations with FlexCryst, S. Ruehl for help on using GSAS, and Clariant GmbH for financial support.

- [1] J. Apostolakis, D.W.M. Hofmann, T. Lengauer, *Acta Cryst. A* **57** (2001), 442-450.
 [2] D.W.M. Hofmann, M.U. Schmidt, in preparation.
 [3] M.U. Schmidt, H. Kalkhof: CRYSCA, *Program for crystal structure calculations of flexible molecules*, Frankfurt am Main, 1997-2002.
 [4] A.C. Larson, R.B. van Dreele, General Structure Analysis System (GSAS), *Los Alamos National Laboratory Report LAUR* (2000), 86-74.