Topological approach in prediction of new crystal structures: application to simple sulfates, selenates, sulfides and selenides

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Using the program package ToposPro [1], topological analysis and classification of 69 simple sulfates and 33 selenates into 22 and 13 topological types, respectively, have been carried out. All cases of topological similarity of cation arrays of ternary anhydrous salts $M_y(XO_4)_z$ and binary compounds M_yX_z (X = S, Se) were found and discussed. The influence of pressure, temperature, size of the ions on the topology was considered.

The following main regularities were revealed. Increase of pressure leads to increase the coordination of the structural units. At ambient conditions the topology of the structures with larger ions often corresponds to that of the structures with smaller ions under high pressure. We have found correlations between structure topologies in the series M_yX_z and $M_y(XO_4)_z$.There are different ways of behaviors of the compounds at higher temperatures: (i) the high-temperature polymorphs have the structures with less coordinated structural units than the title compound at ambient conditions; (ii) the topological type changes but the coordination of structural units is preserved; (iii) the coordination of structural units increases. In some cases, more uniform and symmetric polyhedra $M[X]_n$ than in the initial structure are formed at high temperatures. We have found that the overall topology of the structures strongly depends on the geometrical forms of coordination figures of structural units. In some cases, the cation arrays of the $M_y(XO_4)_z$ salts correspond to binary compounds M_yX_z.

Our comparative topological analysis of simple anhydrous salts and binary compounds predicted new polymorphs of CaS and CaSe, whose stability was confirmed by DFT simulation.

The results show the effectiveness of the combined application of topological and quantum mechanical approaches for prediction of new compounds and crystalline polymorphic forms.

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Bibliography

[1] V. A. Blatov, A. P. Shevchenko, D. M. Proserpio, *Cryst. Growth Des*., **14**, 3576 – 3586 (**2014**)