

s6.m2.p1 Crystal structure of the triclinic high-pressure polymorph of CaSnOSiO_4 malayaite. St. Rath & M. Kunz, *Laboratorium für Kristallographie, ETH Zürich, Switzerland*.

Keywords: malayaite, high-pressure phase transition.

The mineral malayaite is isostructural to the aristotype of titanite (CaTiOSiO_4 , space group: $A2/a$). Phase transitions in titanite, whether temperature- or pressure-induced are well known. However no pressure dependent data is available for malayaite up to now.^{1,2}

A single crystal high-pressure diffraction study in an ETH diamond –anvil cell shows that under hydrostatic conditions monoclinic malayaite transforms into a triclinic structure. No discontinuity in the relative cell axes and volume occurred. Instead, the phase transformation reveals itself at 5 GPa by deviations of the alpha and gamma angles from 90° to 91.2° and 89.2° . In contrast to this, calculations of the principal components for the spontaneous strain indicate a phase transition already at 3 GPa. This suggests the existence of an intermediate phase between 3 and 5 GPa.

Structure refinements of malayaite at 7.3 GPa reveal structural details of the triclinic (P-1) phase. The behavior of the Ca polyhedra seems to be the most important component in the phase transition: The CaO_7 polyhedra, which in $A2/a$ form chains parallel [101] polymerize to sheets parallel (-111). They do this by moving towards to and away from the octahedral chains, which separates the SnO_6 octahedral chain into two symmetrically distinct chains. The octahedral pivot angle (Sn-O1-Sn) changes from 132° to 133.63° or 129.21° , respectively.

s6.m2.p2 Modelling the crystal packing and conformation of $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{NO}_2]^{2+}2\text{Cl}^-$ in a range of pressures. A.V. Dzyabchenko^a, and E.V. Boldyreva^b. ^aKarpov Institute of Physical Chemistry, 10 Vorontsovo pole, 103064 Moscow, Russia. ^bInstitute of Solid State Chemistry RAS, Kutateladze 18, Novosibirsk 128, 630128, Russia.

Keywords: crystal structure prediction, high pressure, $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{NO}_2]^{2+}2\text{Cl}^-$.

The crystal structure of $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{NO}_2]^{2+}2\text{Cl}^-$ is known in a range of pressures up to 33.5 kbar from the single crystal X-ray structure determination.¹ In the present theoretical study, we used those data to probe our approach to the crystal structure prediction of the metal complexes, whose coordination geometry and ligand conformation depends on the crystal packing. The Co and Cl- atoms and the ligand molecules from four formula units of the unit cell were treated as independent particles whose positions and orientations together with the cell parameters determined the crystal lattice energy.

The energy was calculated with pairwise atom-atom potentials, in which the same analytical form ('6-12 LJ plus Coulomb') was taken to describe both the weak non-bonded interactions and the much stronger coordination bonds. Minimization using a recent version of the PMC program² has been repeatedly carried out with various trial sets of the potential parameters r_0 (equilibrium distance) and ϵ (minimum depth), with the aim to find the one giving the smallest deviation of the predicted structure from the observed.

The best parameter set reproduced the most significant features of the observed structure, including the cell parameters, the coordination geometry of the complex cation, and the orientations of all ligands. Remarkably, although no symmetry constraints except the translation symmetry was imposed on the crystal, the optimized structure demonstrated the observed $C2/c$ space group, including the twofold symmetry in the arrangement of the six ligands around each Co atom.

Then we calculated the effect of pressure on the crystal structure by minimization of the enthalpy function. The calculated changes in the theoretical structure with pressure were found in remarkably good agreement with the observed data. Thus, the model reproduced fairly well the anomalous change in the cell parameters and the change in the torsion angle of the NO_2 ligand.

Thus, by this example we have demonstrated for the first time that the pressure-dependent structure of a crystalline complex can be effectively modelled with rather simple atom-atom potentials.

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