in evacuated quartz tubes. The crystal structures of the compounds have been determined by single crystal and powder X-ray diffraction. Depending on synthesis conditions (pressure and temperature) these phases crystallize either in a tetragonal structure (P41/m/mnm) with statistical distribution of metal ions on one site (rutile-type), with cation ordering along c-axis (trirutile-type), or in a monoclinic rutile-like structure (C2/m) with ordering of Cr- and Re-cations and metallic Re-Re bonds. The “a” parameter of the tetragonal unit cell increases with increasing Re content whereas the “c” parameter decreases, indicating a strengthening of the Re-Re-bond. The thermal expansion of CrReO₄ is anisotropic with a larger expansion coefficient in the “c” direction. Tetragonal CrReO₄ with 0.31 ≤ x < 0.54 order antiferromagnetically at low temperatures with Tᵣ depending on the Cr-content x.


Keywords: rutile-like structures; re-re metallic bond; antiferromagnetic ordering

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The Crystal Chemical Role of Fe-Mn Substitution in the Epidote Family. Anna Katerinopoulou¹, Tonci Balic-Zunic², Jochen Kolb³, Karsten Secher⁴.

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New occurrences of red coloured minerals from the epidote family A1A2M1M2M3[O:OH/SiO2/Si2O7] have been found in Greenland and their structures have been solved. They are all monoclinic members of the ternary Al-Fe-Mn solid solution series with end members clinozoisite-piemitite-epidote [1]. Although they do not incorporate enough amount of Mn³⁺ to be classified as piemitite, their color varies from pink to intense red. We encounter both Mn³⁺-enriched clinozoisite and Mn³⁺-enriched epidote. As expected, Fe³⁺ and Mn³⁺ are substituting Al³⁺ exclusively in the M3 octahedra.

The distortion of the M3 polyhedron increases with increasing content of Mn, an effect that can be attributed to the Jahn-Teller effect of the 3d⁴ electron configuration of Mn⁴⁺ [2]. The Fe/Al and Mn/Al substitutions influence the distortions of other coordination polyhedra as well. The monoclinic structures can incorporate more Fe and/or Mn than the orthorhombic structure of zoisite. The distortions of atomic coordinations connected to atomic substitutions are reviewed to explain this difference. We also apply them for the quantification of the relative content of Mn and Fe in the structures of minerals from the epidote family.


Keywords: epidote; crystal structure determination; X-ray diffraction

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The Crystal Structure of M1M2₄(XO)₄(O,OH)₄ Compounds and Topological Relations. Herta Effenberger. Institut für Mineralogie und Kristallographic, Universität, Vienna, Austria.

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Natural occurring compounds with the general chemical formula M1M2₄(XO)₄(O,OH)₄ belong either to the tsumcorite or to the natrocalcite series. Meanwhile about 30 minerals and synthetic compounds are known with M1=Ca, Sr; M2=Fe, Mn; X=As, V, S, Se, Mo). For each of the cation sites M1, M2 and X at least two different valences are possible; the coupled exchange at these cation positions and adjusting the ratio OH:H₂O ensures electro-neutrality. However, compounds known so far reveal that extensive solid solution is very common for the M₂ site, less common for the X site, and very rare for the M₁ site. The crystal structure is noticeable due to a number of facts. The most striking one is a H atom between two hydroxyl groups forming a strong and symmetry restricted hydrogen bond in the H₂O group in case of OH:H₂O = 1:1 which represents the parental structure and is in most compounds verified (monoclinic ‘tsumcorite type’). Two triclinic structure variants are known: two H₂O molecules per formula unit require an avoidance of the symmetry-restricted hydrogen bond (‘helmutwinklerite type’). Mixed occupations at the M₂ site requiring individual environments (octahedral coordination besides Jahn-Teller distorted [4+2] coordination) cause a splitting of the M₂ site (‘gartrellite type’). SrCo₄(AsO₄)(AsO₄OH)(OH)₂H₂O forms the ‘Sr-Co type’ which maintains monoclinic symmetry but represents the first proof of (partial) protonated arsenate groups; an nearly complete solid solution series Ca₄Bi₂Bi₄O₁₂ has been identified with statistical distribution of error; no conspicuous anisotropy of the displacement parameters is observed. In addition, the symmetry restriction of the hydrogen bond is given up. The formation of protonated arsenate groups is controlled by the pH and Eh conditions. Astonishingly, a nearly complete solid solution series Ca₄Bi₂Bi₄O₁₂ was verified within the series cobaltolithomayéreite – schneebergite; most Bi³⁺ atoms exhibit steric active lone-pair electrons which is incompatible with the centro-symmetric site; here the site symmetry 2/m for the M₁ site is maintained within limits of error; no conspicuous anisotropy of the displacement parameters is observed.

The parental structure of the tsumcorite - natrocalcite series is topologically related to brucite layers; only parts of the cation site are occupied resulting in edge sharing rows of MZO₄ polyhedra; they are linked by XO₄ tetrahedra facing vacancies of the cation site at both sides of the layers and by the symmetry restricted hydrogen bond of the H₂O₄.