

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 ($P4_2/mnm$) 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 $\text{Cr}_x\text{Re}_{1-x}\text{O}_2$ is anisotropic with a larger expansion coefficient in the “c” direction. Tetragonal $\text{Cr}_x\text{Re}_{1-x}\text{O}_2$ with $0.31 \leq x < 0.54$ order antiferromagnetically at low temperatures with T_N depending on the Cr-content x.

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The Crystal Chemical Role of Fe-Mn Substitution in the Epidote Family. Anna Katerinopoulou^a, Tonci Balic-Zunic^a, Jochen Kolb^b, Karsten Secher^b. ^a*Department of Geography and Geology, University of Copenhagen, Denmark.* ^b*Department of Economic Geology, Geological Survey of Denmark and Greenland.*

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New occurrences of red coloured minerals from the epidote family $\text{A1A2M1M2M3}[\text{O}/\text{OH}/\text{SiO}_2/\text{Si}_2\text{O}_7]$ 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-piemontite-epidote [1]. Although they do not incorporate enough amount of Mn^{3+} to be classified as piemontite, their colour varies from pink to intense red. We encounter both Mn^{3+} -enriched clinozoisite and Mn^{3+} -enriched epidote. As expected, Fe^{3+} and Mn^{3+} are substituting Al^{3+} 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 $3d^4$ electron configuration of Mn^{3+} [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.

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The Crystal Structure of $M1M2_2(\text{XO}_4)_2(\text{O},\text{OH})_2$ Compounds and Topological Relations.

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Natural occurring compounds with the general chemical formula $M1M2_2(\text{XO}_4)_2(\text{O},\text{OH})_2$ belong either to the tsumcorite or to the natrocalcite series. Meanwhile about 30 minerals and synthetic compounds are known with $M1^{1+,2+,3+ [8-10]} = \text{Na, K, Rb, Ag, NH}_4, \text{Ti, Ca, Pb, Bi}$; $M2^{2+,3+ [6, 4+2]} = \text{Cu, Zn, Co, Ni, Mg, Al, Fe}^{3+}, \text{Mn}^{3+}, \text{X}^{5+,6+ [4]} = \text{P, As, V, S, Se, Mo}$. 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 $\text{OH}:\text{H}_2\text{O}$ 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 H_3O_2 group in case of $\text{OH}:\text{H}_2\text{O} = 1:1$ which represents the parental structure and is in most compounds verified (monoclinic ‘tsumcorite type’). Two triclinic structure variants are known: two H_2O molecules per formula unit require an avoidance of the symmetry-restricted hydrogen bond (‘helmutwinklerite type’). Mixed occupancies at the $M2$ site requiring individual environments (octahedral [6] coordination besides Jahn-Teller distorted [4+2] coordination) cause a splitting of the $M2$ site (‘gartrellite type’). $\text{SrCo}_2(\text{AsO}_4)(\text{AsO}_3\text{OH})(\text{OH})\cdot\text{H}_2\text{O}$ forms the ‘Sr-Co type’ which maintains monoclinic symmetry but represents the first proof of (partial) protonated arsenate groups; an increase of the unit cell volume enables that the As-atom site splits into two crystallographically independent sites. 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 $\text{Ca}^{2+}\text{Bi}^{3+}$ was verified within the series cobaltharmeyerite – schneebergite; most Bi^{3+} atoms exhibit steric active lone-pair electrons which is incompatible with the centrosymmetric 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 $M2\text{O}_6$ polyhedra; they are linked by XO_4 tetrahedra facing vacancies of the cation site at both sides of the layers and by the symmetry restricted hydrogen bond of the H_3O_2