

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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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 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.*

E-mail: aka@geo.ku.dk

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

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

Herta Effenberger, *Institut für Mineralogie und Kristallographie, Universität, Vienna, Austria.*

E-mail: herta.silvia.effenberger@univie.ac.at

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 $M1^{1+,2+,3+ [8-10]}$ = Na, K, Rb, Ag, NH_4 , Tl, Ca, Pb, Bi; $M2^{2+,3+ [6, 4+2]}$ = Cu, Zn, Co, Ni, Mg, Al, Fe^{3+} , Mn^{3+} , $\text{X}^{5+,6+ [4]}$ = 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 M_2O_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

group. The O atoms maintain a close packed arrangement. The *M1* sites and the other hydrogen bonds link the layers. Astonishingly, this structural motive is found in compounds with quite different chemical formulas. They are worth mentioning because of some unique structural features. In medenbachite, $\text{Bi}_2\text{FeCu}(\text{AsO}_4)_2(\text{O},\text{OH})_2(\text{OH})_2$, the Bi and (O,OH) atoms are intercalated between the brucite-like layers. In $\text{KCu}_3(\text{OH})_2[(\text{AsO}_4)\text{H}(\text{AsO}_4)]$ some of the vacant positions are occupied by $\text{Cu}^{[2+4]}$ cations, an extremely rare environment for Cu^{2+} atoms. Again, a symmetry restricted hydrogen bond occurs, but it links between the brucite-like layers. In $\text{Cu}_2\text{O}(\text{SO}_4)$ (dolerophanite) all hydrogen and *M1* atoms are missing; in addition to the *M2* and XO_4 tetrahedra, two trigonal bipyramidally coordinated Cu^{2+} atoms share a common O-O edge in the centre of a vacant cation position.

Keywords: tsumcorite; H_3O_2 group; $\text{Cu}^{[2+4],5}\text{O}_6$ coordination figures

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Charge and Orbital Ordering in Layered Perovskites. Markus Braden^a, O.J. Schumann^a, M. Cwik^a, M. Kosmala^a, M.T. Fernandez-Diaz^b, M. Meven^c, A. Cousson^d. ^a*II. Physikalisches Institut, Köln, Germany.* ^b*Institut Laue Langevin, Grenoble, France;* ^c*FRM-II, Garching, Germany.* ^d*Laboratoire Léon Brillouin, Saclay, France.*

E-mail: braden@ph2.uni-koeln.de

Charge and orbital order is observed in many transition-metal oxides in a wide range of doping. The most famous examples are the stripe phases in the cuprates and the charge and orbital ordered states in manganates that exhibit colossal magneto resistivity. At least in the latter materials, the key role of the charge and orbital ordering for the understanding of the main physical mechanism has been well established. In spite of the large interest in these phenomena, there have been very little precise crystallographical studies determining the small structural distortions related with the electronic ordering. We have performed several single-crystal diffraction experiments mostly using neutrons in order to analyze the charge and orbital order in layered perovskites, $\text{La}_{2-x}\text{A}_x\text{MeO}_4$ (A=Sr, Ca and Me=Mn, Ni and Co), focusing on the half-doping concentration range. By analyzing the weak superstructure reflections we may clearly establish the character of the charge order in single-layered cobaltates, manganates and nickelates as well as that of the orbital order in manganates and in cobaltates. The precise analysis of the charge and orbital order in $\text{La}_{2-x}\text{A}_x\text{MeO}_4$ allows one to quantitatively understand the magnetic ordering schemes appearing in all these phases and, in the case of the manganates, yield an insight why these materials can so easily switch between ferromagnetic metallic and antiferromagnetic insulating states.

Keywords: charge and orbital order; neutron diffraction; electronic structure and magnetism

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Novel Li Vacancy Ordered Structure of Stage-2 $\text{Li}_{0.38}\text{BC}$ Phase. Bora Kalkan^a, Engin Ozdas^a.

^a*Advanced Materials Research Group, Department of Physics, Hacettepe University.*

E-mail: kalkan@hacettepe.edu.tr

The existence of several borocarbides with crystal structures highly related to MgB_2 , in which one of these, the layered LiBC has been predicted based on the electronic structure calculations that this compound should become superconducting on doping with holes. However, the superconducting features for Li off-stoichiometric borocarbide compounds have not been observed in any experimental studies, because of the difficulties in the sample preparation. In this work, the effects of synthesis conditions on the structure of Li_xBC samples with the different Li content and the phase stability were investigated. The structural studies showed that the intercalation process has a staging behavior as Li intercalated graphite and a novel Li vacancy ordered structure for off-stoichiometric stage-2 $\text{Li}_{0.38}\text{BC}$ phase. The temperature dependence of the conductivity shows semiconducting behavior over the whole temperature range and the hopping type conduction improved by the hole doping.

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Keywords: layered materials; solid-state reactions; novel structures