

triangles. Sheet f is composed of [9]-coordinated (Ca,REE, Y) polyhedra, Si tetrahedra and B triangles. In sheet g, [6]-coordinated sites are 67% occupied by Ti and Nb, and B triangles are only 17% occupied by B. In sheet h, [6]-coordinated sites are only 17% occupied by Ti, they are coordinated by OH and H₂O groups. Two identical h sheets are connected via common vertices of 17% occupied Ti octahedra which are H₂O groups. In sheet k, the [8]-coordinated sites are 22% occupied by Ba. The structure is a framework of cation polyhedra which can be considered an intercalation of three domains: one fully ordered with full occupancy of cation sites, and two partly ordered with cation-site occupancies of 67% and 17%, respectively. To acknowledge the extreme chemical and structural complexity of this mineral, we chose the name byzantievite. "Byzantine" means "intricately involved". For 12 centuries (374-1453), the Byzantine Empire was home to many different peoples and religions. The structure of the Empire was extremely complex but the state functioned very efficiently, and shaped Europe and modern civilization.

Keywords: byzantievite; framework; new mineral

FA2-MS01-O6

A Few Applications of the Superspace Approach in Mineralogy. Alla Arakcheeva. *Laboratoire de Cristallographie, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.*

E-mail: Alla.Arakcheeva@epfl.ch

It is fair to claim that the development of crystallography was initiated by mineralogy. First the crystal forms and later crystal structure determinations did primarily instigated the mathematical description of minerals. Crystal chemistry is essentially based on the large amount of structure determinations of natural minerals. It is not surprising that precisely the minerals natrite, Na₂CO₃ [1] and calaverite [2] have played a fundamental role in the development of the superspace theory. Currently, the superspace concept is successfully applied for the determination and description of a many incommensurately modulated crystal structures (IMCS) including minerals. For example, investigations of minerals like fresnoite, melilite, laszurite, akermanite, sartorite, labradorite, srebrodolskite, tridymite, quartz (between α and β modifications) could only be meaningful with the superspace symmetry approach. The IMCSs of minerals give the possibility to study details of their crystal chemistry, which can be used for a better understanding of their genesis. For instance, the determination of IMCSs in the calaverite-sylvanite group, Au_{1-x}Ag_xTe₂, [2, 3] reveals different degrees of valence fluctuations on the Au-position, which are due to different degree of the Ag ordering on the Au position. The IMCSs of two different occurrences of natrites allow to distinguish specific characteristics of Na and CO₃, although their average structures are identical. In material science, mineral names are used to characterize of structure types. With the superspace approach, the structure type (ST) concept can be generalised in (3+1)D symmetry space [4] (3+1)D ST can be used not only to predict 3D structures but also to identify them [4]. In addition to the

pioneering scheelite (3+1)D ST [4], the calaverite (3+1)D ST [3] is able to characterize calaverite, sylvanite, kostovite and krennerite minerals as well as NbTe₂, TaTe₂, VTe₂, synthetic compounds based on the unique *C2/m*($\alpha 0\gamma$)(0s) superspace group with identical basic structures. The (3+1) D ST concept permits also a unified symmetry approach for group-subgroup considerations in phase transitions [5]. The superspace approach born from the study of mineralogical samples now is an effective tool, which can be applied to the needs of mineralogy. The precise characterization of isomorphic substitution is greatly facilitated with IMCSs determination. Investigation of IMCSs allows to predict series of 3D structures and, sometimes, polymorphic modifications [6]. The extension of the ST concept in (3+1) D space appears to be an effective way to identify structure-relation properties.

[1] Brouns, E., Visser, J.W. & de Wolff, P.M., *Acta Cryst.*, **1964**, 17, 614; Van Aalst, W., Van den Hollander, J., Peterse, W.J.A.M. & De Wolff, P.M., *Acta Cryst.*, **1976**, B32, 47; De Wolff, P.M., *Acta Cryst.*, **1974**, A30, 777. [2] Goldschmidt, V., Palache, C., Peacock, M., *N. Jahrbuch, f. Mineralogie* **1931**, 63(A), 1; Janner, A., Dam, B., *Acta Cryst.* **1989**, A45, 115; Schutte, W.J., De Boer, J.L., *Acta Cryst.* **1988**, B44, 486. [3] Bindi, L., Arakcheeva, A., Chapuis, G. *Amer. Min.*, **2009** (accepted article). [4] Arakcheeva, A., Chapuis, G., *Acta Cryst.*, **2008**, B64, 12. [5] Stokes, H.T., Campbell, B.J., Hatch, D.M., *Acta Cryst.*, A63, 365. [6] Arakcheeva, A., Chapuis, G. *Acta Cryst.*, B62, 52.

Keywords: mineralogy and crystallography; incommensurately modulated structures; classification of crystal structures

FA2-MS01-O7

Cr_xRe_{1-x}O₂ Oxides with Different Rutile-like Structures: Changes in the Electronic Configuration and Resulting Physical Properties.

Daria Mikhailova^{a,b}, Helmut Ehrenberg^{a,b}, Dmytro Trots^c, S. Oswald^a, H. Fuess^b. ^a*IFW Dresden*, ^b*TU Darmstadt*. ^c*HASYLAB Hamburg, Germany.*

E-mail: d.mikhailova@ifw-dresden.de

Rutile type crystal structures and their derivatives are based on the same topology: straight chains of edge-sharing MO₆ octahedra for the cations M are connected via corner-sharing to four surrounding chains [1]. Rutile-derivatives show ordering of cations, anions or distortions of coordination polyhedra.

Several complex oxides of Cr³⁺ with rutile, trirutile or rutile-like structure exist, because the ionic radius of Cr³⁺ (0.62 Å) is close to the one of Ti⁴⁺ (0.61 Å) for octahedral oxygen coordination. Ternary oxides in the system Cr – Re – O are less intensively investigated, although these systems offer an additional degree of freedom due to the ability of the Re ion to adopt formal oxidation states between +4 and +7 in complex oxides with different resulting properties. Both end members, CrO₂ [2] and the monoclinic modification of ReO₂ [3], have a rutile-like structure.

In our work [4], mixed chromium-rhenium oxides, Cr_xRe_{1-x}O₂ with 0.31 ≤ x ≤ 0.66, have been synthesized for the first time by high-pressure high-temperature synthesis and

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.

[1] W. H. Baur, *Crystallography Reviews*, 13, **2007**, 65-113. [2] P. Porta, M. Marezio, J. P. Remika, P. D. Dernier, *Mat. Res. Bull.* 7, **1972**, 157-162. [3] H. P. S. Correa, I. P. Cavalcante, L. G. Martinez, C. G. P. Orlando, M. T. D. Orlando, *Brazilian Journal of Physics*, 34, **2004**, 1208-1210. [4] D. Mikhailova, H. Ehrenberg, D. Trots, G. Brey, S. Oswald, H. Fuess, *Solid State Chem. in print*.

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

FA2-MS01-O8

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.

[1] Liebscher, A.; Franz, G. (ed), *Epidotes, Reviews in Min and Geoch.* **2004**, 56. [2] Langer, K.; Tillmanns, E.; Kersten, M.; Almen, H.; Armi, R.K. *Z.Kristallogr.* **2002**, 217.

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

FA2-MS01-O9

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