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$Bi_2M_4O_9$ compounds are known to have potential as electrolytes in solid oxide fuel cells (SOFC) [1]. The conducting properties could be related to an increased number of oxygen vacancies due to the requirement of charge neutrality with the substitution of Bi^{3+} by Sr^{2+} [2]. The samples were synthesized using the glycerin method as described in [3] and finely washed with nitric acid to remove impurity phases. Two different heating procedures were used for samples having an initial Sr content of x = 0.2. Heating steps of 353 K (1/2 h), 473 K (1/2 h) and 1023 K (2h) were used for one sample (#173) and the strontium free reference (#174), whereas the faster heated sample (#172) was treated at 473 K (1/4 h) and 1023 K (2h). The unit-cell volumes calculated from X-ray powder diffraction data of all samples calculated against silicon as internal standard show only a very small variation around 357.3(5) 10^{-6} pm^3. Whereas small amounts of Bi_2O_3 and $SrAl_4O_9$ were found in the as synthesized samples no indication for these impurities were detected in the washed samples. To prove the incorporation of Sr into the mullite-type structure small crystals of a sample with an initial Sr content of x = 0.2 (#172) were selected in a HRTEM. Suitable crystallites were analyzed by EDX in a scanning TEM mode using a spot size of approximately 300 pm. Several particles were evaluated showing a variation of x between 0.05 (often) and 0.24 (rare). A line scan on a crystal having a high Sr content (x = 0.244) shows homogeneous strontium distribution. If strontium is incorporated into the $Bi_2Al_4O_9$ structure two possibilities for charge balance have to be discussed. On one hand oxygen deficiency with vacant oxygen positions are possible. On the other hand for incorporating 2 Sr^{2+} ions 1 Bi^{3+} could be oxidized to Bi^{5+}. To exclude the latter possibility XPS investigations were carried out on two samples with x = 0.2 (#172, #173) and $Bi_2Al_4O_9$ (#174) and Bi_2O_3 as references. No indication was found that Bi^{5+} is formed during the strontium incorporation. Nevertheless, for the fast synthesized sample (#172) the Bi4f photoelectron peaks are much more asymmetric than in the slowly synthesized compound (#173). X-ray powder heating experiments between 298 K and 1272 K for $Bi_2Al_4O_9$ show a (nearly) linear thermal expansion in all three orthorhombic lattice directions without any changes during the heating and cooling runs. For the strontium doped samples an irreversible deviation for the thermal expansion was observed at ~1085 K (#172) and ~1135 K (#173) for the as synthesized and at ~1185 K for both washed samples. Adding 15 wt-% Bi_2O_3 to the latter sample (#173) the expansion deviation was observed at ~1035 K. In all cases the refined (Rietveld method) strontium content on the bismuth position was reduced from 15(3)% to zero at these temperatures.

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Keywords: mullite-related phases, high temperature, strontium doping

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FA2-MS16-P28

Polytypism in $Na[C_6H_4Cl(SO_3)]\cdot H_2O$ analysed by Order-Disorder (OD) Theory. <u>Jürgen Glinnemann</u>, Alexandra K. Wolf, Martin U. Schmidt. *Goethe-University, Institute of Inorganic and Analytical Chemistry, Max-von-Laue-Str. 7, D-60438 Frankfurt am Main, Germany.*
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Ordered and disordered crystal structures of the title compound are built up by two chemically rather distinct kinds of alternating layers: (1) hydrophilic $NaSO_3(H_2O)$, and (2) hydrophobic C_6H_4Cl layers [1].
The hydrophilic layers are ordered and act like templates on the hydrophobic layers. Due to this steric condition, the C_6H_4 rings have to be mutually perpendicular aligned in their respective layers. These have an orthogonal metric with layer-group symmetry $C1m1$, layer orientation (001). The ability for different stacking sequences of these layers gives rise to a family of structures, ordered and disordered ones. Their discussion will follow the lines of order-disorder (OD) theory [2, 3], and starts with the OD groupoid family symbol:

$$C \quad 1 \quad m \, (1)$$
$$\{ 1 \quad 2_s \quad 1 \quad \}$$
$$\{ 2_{r'} \quad 1 \quad n_{r',s'} \}$$

The OD approach results in three maximum degree of order (MDO) polytypes and in the disordered family structure, all structures consisting of four layers (1) and (2) in their respective unit cells. Two of the MDO structures have space-group type $P12_1/c1$ (Z = 8) (layer orientation (010)) with the same lattice parameters. The third MDO structure has space-group type $C1c1$ (Z = 16), with an orthogonal metric (layer orientation (001)). The disordered family structure ('average structure') is orthorhombic, space-group type $Pnma$ (Z = 4) (layers parallel (100)).
One of the MDO '$P2_1/c$ polytypes' could be identified by X-ray single-crystal analysis, yet with severe disorder, as exemplified by streaks of diffuse scattering in direction perpendicular to the structural layers [1]. Moreover is this structure twinned, the twin laws reflecting the two mirror planes of the point group of the orthorhombic family structure perpendicular to the layers.
In addition to the three MDO polytypes and the disordered family structure, all with a periodicity of four layers, less-ordered structures with larger periodicities or disordered ones without any stacking periodicity may occur. Altogether these polytypes establish the OD family of structures of the title compound.

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Keywords: polytypes, order-disorder (OD) theory, sodium *p*-chlorobenzenesulfonate monohydrate

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FA2-MS16-P29

RT and high T crystal structure of ferroelastic $(TMA)_2[TiF_6]$ <u>Ole F. Göbel</u>, Gerrit van Hummel, Johan E. ten Elshof. *Inorganic Materials Science, University of Twente, the Netherlands.*
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$(TMA)_2[TiF_6]$ is pseudocubic rhombohedral and ferroelastic at RT. It is isostructural with $(TMA)_2[OsF_6]$ [1]. Crystals grown from aqueous solution exhibit birefringence and twinning along the pseudocubic {110} and {100} faces. By applying shear stress, the lattice of a single crystal could be reoriented.

[1] Küppers, H.; Göbel, O.; Bruhn, C.; Schmahl, W.W. *Z. Krist.* 2001, 216, 354.

Keywords: $(TMA)_2[TiF_6]$, RT structure, Ferroelasticity

FA2-MS16-P30

A structural study of the lithiophilite-sicklerite series. <u>Frédéric Hatert</u>[a]. [a]*Laboratory of Mineralogy, University of Liège, Belgium.*
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Minerals of the triphylite-lithiophilite series, $Li(Fe^{2+},Mn^{2+})PO_4$-$Li(Mn^{2+},Fe^{2+})PO_4$, are primary phosphates which occur in the geological context of rare-element granitic pegmatites. The oxidation processes, affecting the pegmatites during their evolution, provoke a progressive oxidation of triphylite in ferrisicklerite $[Li_{1-x}(Fe^{3+},Mn^{2+})PO_4]$ and in heterosite $[(Fe^{3+},Mn^{3+})PO_4]$, and of lithiophilite in sicklerite $[Li_{1-x}(Mn^{2+},Fe^{3+})PO_4]$ and in purpurite $[(Mn^{3+},Fe^{3+})PO_4]$ [1,2]. These phosphates exhibit the olivine structure, but the detailed structural modifications induced by these oxidation processes were not previously investigated. It is noteworthy that these olivine-type phosphates are good candidates for the development of new cathode materials for Li-ion batteries.

In this study, we investigated a natural sample from the Altai Mountains, China, in which a progressive transition from lithiophilite to sicklerite is observed. Under the polarizing microscope, lithiophilite is colorless, whereas sicklerite shows a deep orange color. Several grains show intermediate colors, suggesting a progressive transition from lithiophilite to sicklerite. This progressive transition if confirmed by SIMS (Secondary Ion Mass Spectrometry) analyses, which indicate Li values from 0.96 to 0.69 Li atoms per formula unit (*p.f.u.*).

Five single-crystals, corresponding to zones with different colors, were extracted from the sample and investigated by single-crystal X-ray diffraction techniques (Oxford Diffraction Gemini PX Ultra 4-circle diffractometer, 50 kV, 40 mA, MoK_a). The samples are orthorhombic, space group *Pbnm*, with unit-cell parameters ranging from $a = 4.736(1)$, $b = 10.432(2)$, $c = 6.088(1)$ Å (lithiophilite) to $a = 4.765(1)$, $b = 10.338(2)$, $c = 6.060(1)$ Å (sicklerite). Surprisingly, the oxidation of lithiophilite in sicklerite provokes an increase of the a parameter, whereas b and c decrease significantly.

The structures were refined to R_1 values ranging from 2.19 to 2.94 %, and show a topology identical to that of olivine-type phosphates reported in the literature [3]. Li occurs on the M(2) site, and shows occupancy factors from 0.99 Li *p.f.u.* (lithiophilite) to 0.75 Li *p.f.u.* (sicklerite). These values are in good agreement with the values measured by SIMS.

[1] Quensel P., *Geologiska Föreningens I Stockholm Förhandlingar*, 1937, 59(1), 77. [2] Mason B., *Geologiska Föreningens I Stockholm Förhandlingar*, 1941, 63, 117. [3] Loosey A., Rakovan J., Hughes J.M., Francis C.A., Dyar M.D., *Can. Mineral.*, 2004, 42, 1105.

Keywords: lithiophilite, sicklerite, olivine-type phosphates, crystal structure

FA2-MS16-P31

Invariant relations between the moduli squares of reciprocal lattice vectors. <u>Rolf Heinemann</u>[a], Diedrich Stöckelmann[a], Herbert Kroll[a], Wolfgang Hoffmann. [a]*Institut für Mineralogie, WWU Münster.*
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A system of 1-, 2- and 3-dimensional metrically independent relations between the squared moduli of reciprocal lattice vectors (Q values) is developed. The relations generalize and thereby resolve the earlier special Runge-de Wolff approach to indexing unknown powder patterns. Given the background of trial-and-error-methods employed in recent automatic powder pattern indexing, we suggest an alternative route based on a generalization of the original Runge-de Wolff approach. [1], [2], [3], For this purpose, a system of five metrically invariant relations between the Q values of reciprocal lattice vectors is developed that encompasses the earlier special relations. The five invariant relations correspond to a line, a zone, a bizone, a cone and a pencil configuration. In particular, the zone configuration relates four vectors H_i being arbitrarily distributed in a plane. The respective equation reads

$$(\frac{\eta_1}{\eta_2} - \frac{\kappa_1}{\kappa_2})Q(H_1) + (\frac{\eta_2}{\eta_1} - \frac{\kappa_2}{\kappa_1})Q(H_2).$$
$$-\frac{1}{\eta_1\eta_2}Q(\eta_1H_1 + \eta_2H_2) + \frac{1}{\kappa_1\kappa_2}Q(\kappa_1H_1 + \kappa_2H_2) = 0 \quad (1)$$

where η, κ are rational coefficients. Equation (1) combines any four lattice vectors extending from the zero point that span a plane (Fig. 1). It is a powerful equation because systematic variation of the coefficients η and κ allows to identify among a measured set of Q values any four reciprocal lattice vectors that are *arbitrarily* distributed in a plane rather than representing a special configuration. The equation may thus be termed the general planar indexing equation and as such it is suited to become a cornerstone in an indexing procedure that in contrast to the current indexing programs would be strictly based on metrical invariants.
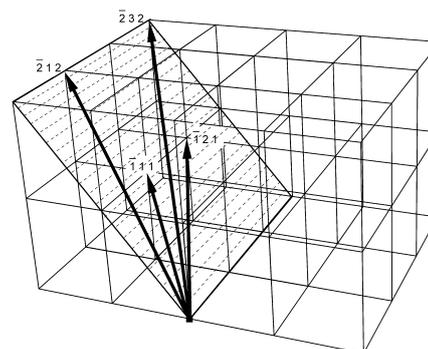
Figure 1: Zone configuration

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