

$(\text{TMA})_2[\text{TiF}_6]$  is pseudocubic rhombohedral and ferroelastic at RT. It is isostructural with  $(\text{TMA})_2[\text{OsF}_6]$  [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:**  $(\text{TMA})_2[\text{TiF}_6]$ , RT structure, Ferroelasticity

## FA2-MS16-P30

**A structural study of the lithiophilite-sicklerite series.** Frédéric Hateri<sup>a</sup>. <sup>a</sup>Laboratory of Mineralogy, University of Liège, Belgium.

E-mail: [fhateri@ulg.ac.be](mailto:fhateri@ulg.ac.be)

Minerals of the triphylite-lithiophilite series,  $\text{Li}(\text{Fe}^{2+}, \text{Mn}^{2+})\text{PO}_4$ - $\text{Li}(\text{Mn}^{2+}, \text{Fe}^{2+})\text{PO}_4$ , 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 [ $\text{Li}_{1-x}(\text{Fe}^{3+}, \text{Mn}^{2+})\text{PO}_4$ ] and in heterosite [ $(\text{Fe}^{3+}, \text{Mn}^{3+})\text{PO}_4$ ], and of lithiophilite in sicklerite [ $\text{Li}_{1-x}(\text{Mn}^{2+}, \text{Fe}^{3+})\text{PO}_4$ ] and in purpurite [ $(\text{Mn}^{3+}, \text{Fe}^{3+})\text{PO}_4$ ] [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 is 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 $\alpha$ ). 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.** Rolf Heinemann<sup>a</sup>, Diedrich Stöckelmann<sup>a</sup>, Herbert Kroll<sup>a</sup>, Wolfgang Hoffmann.

<sup>a</sup>Institut für Mineralogie, WWU Münster.

E-mail: [rhein\\_03@uni-muenster.de](mailto:rhein_03@uni-muenster.de)

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 bicone, 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

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

where  $\eta$ ,  $\kappa$  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  $\eta$  and  $\kappa$  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.

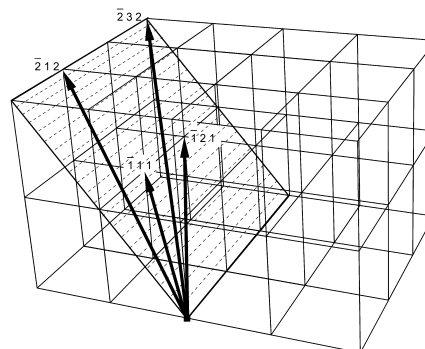


Figure 1: Zone configuration

[1] [1] Runge, C., *Phys. Zeitschr.*, 1917,18, 291-301. [2] Wolff, P.M. de, *Acta Crystallogr.* 1958, 11, 664-665. [3] Wolff, P.M. de, *Advances in X-Ray Analysis*, 1963, 6, 1-17.

**Keywords:** reciprocal lattice geometry, metrical invariants, powder pattern indexing