[1] G. Nalini, T.N.G. Row, *Chem. Mater.* **2002**, *14*, 4729-4735. [2] D. Swain, T.N.G. Row, *Chem. Mater.* **2007**, *19*, 347-349. [3] A. Paytan, *Science* **2000**, *288*, 626-627. [4] C. Palache, H. Berman, C. Frondel, *The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana*, 7th ed.; John Wiley and Sons, Inc: New York, **1951**; Vol. II.

Keywords: mineral, bimetallic sulfates, phase transition

MS54.P04

Structural analysis of new mineral phases

Marcin Stachowicz,[a] Jan Parafiniuk,[b] Boguslaw Baginski,[b] Raymond Macdonald,[b] Krzysztof Wozniak,[a] [a]*Chemistry Department, University of Warsaw.* [b]*Geology Department, University of Warsaw. (Poland).* E-mail: marcin.stachowicz@chem.uw.edu.pl

Redikortsevite, NH_4MgCl_3 x6H_2O, from the burned dumps of the Chelabinsk coal basin in Russia, described by Chesnokov et al. (1988), has not been submitted to IMA for approval and it is not recognized as a valid mineral species. The occurrence of this phase has also been noticed on burning waste dumps of one of the Upper Silesia coal mines in Poland. Redikortsevite forms there aggregates and fine crystals suitable for structural study. We have determined its 3D structure and performed chemical and mineralogical analysis necessary for the approval process.

Alumohydrocalcite is hydrated calcium and aluminium carbonate. It is ascribed to have chemical formula $CaAl_2(CO_3)_2(OH)_4$ x3H_2O and commonly forms compact fine-crystalline aggregates. This mineral still does not have reliable crystal structure although it has been known since 1926. The reason of such a situation is difficulty in finding single crystals of a good quality and adequate size. We have acquired a unique sample of this mineral from its classic occurrence site at Nowa Ruda, Sudetes Mts., Poland. It consists of spherulitic needle aggregates. Crystals are very well formed and large enough for X--ray structural investigations. They reach length even up to decimal parts of millimeter and are suitable for synchrotron sources rather than laboratory ones. For this mineral, powder diffraction and chemical analysis have been performed for the sake of its identification.

The chevkinite group of minerals are found as accessory phases in a wide variety of parageneses, including igneous rocks ranging from gabbros to peralkaline granites, fenites, ore deposits, granulite facies gneisses and metacarbonates [1]. The composition of the majority of occurrences closely approaches the ideal formula $A_4BC_2D_2Si_4O_{22}$, where A = REE, Ca, Sr, Th; B = Fe^{2+};
C = Ti, Al, Fe^{2+}, Fe^{3+}, Mn, Mg, Zr, Nb; and D = Ti, but there is a wide range of compositionally different species. The geochemical importance of chevkinite group is that they are strong REE-concentrators; total REE_2O_3 contents are up to 50 wt%. They can be the dominant REE-bearing phase in any given rock. The REE are being increasingly used in a host of green technologies, such as the production of novel wind turbines, low-energy light bulbs also mobile phones. Additionally neodymium, one of the most common REE, is a key part of neodymium-iron-boron magnets used in hyperefficient motors and generators. Published work has shown that compositional variations in the group are mirrored in the structure but there is still no consensus as to how. Further, several species within the group have not been structurally determined. We are attempting to define the complete composition-structure relationships in the group.

[1] R. Macdonald, H.E. Belkin, *Mineralogical Magazine* **2002**, *66(6)*, 1075-1098.

Keywords: minerals, structure, diffraction

MS54.P05

The crystal structure of huemulite

Fernando Colombo,[a] Ricardo Baggio,[b] Anthony R. Kampf,[c] [a]*Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba, Córdoba (Argentina).*[b]*Departamento de Física (Lab. TANDAR), Comisión Nacional de Energía Atómica. San Martín, Buenos Aires (Argentina).* [c]*Natural History Museum of Los Angeles County, Los Angeles, California (USA).* E-mail: fosfatos@yahoo.com.ar

The crystal structures of natural (from the West Sunday Mine, Utah, USA) and synthetic huemulite, $Na_4Mg(V_{10}O_{28})\cdot24H_2O$, have been solved and refined to $R_1 = 0.0313$ (for 3535 unique $F_o > 4\sigma F$ reflections) and 0.0246 (for 3672 unique $F_o >_- 4\sigma F$ reflections), respectively. Huemulite is triclinic, space group $P\bar{1}$, with Z = 1; unit-cell dimensions of the natural sample are a 9.0453(2), b 11.3337(3), c 11.7372(8) Å, α 105.223(7), β 97.383(7), γ 100.790(7)°, V 1120.30(9) Å³, whereas those of the synthetic sample are a 9.0425(2), b 11.3303(2), c 11.7353 (8) Å, α 105.222 (7), β 97.377 (7), γ 100.791 (7)°, V 1119.47(8) Å³. The structure consists of decavanadate oxyanions $(V_{10}O_{28})^{6-}$ linked via an interstitial complex composed of isolated $[Mg(H_2O)_6]^{2+}$ octahedra and an $[Na_4(H_2O)_{14}]^{4+}$ cationic group (defining an infinite zig-zag chain). There are also four isolated H_2O groups, two of them positionally disordered. All except 4 H atoms have been located, showing a network of H-bonds that further links the interstitial complex and the structural unit, stabilizing the atomic arrangement. The Lewis acidity of the interstitial complex (0.18) is almost coincident with the upper limit of basicity of the structural unit (0.17), thus showing that the valence-matching principle is maintained in this structure.

It is probable that the X-ray pattern and the unit-cell dimensions informed in the original description of huemulite [1] were measured using a mixture that included fully hydrated and partially dehydrated material.

Huemulite is closely related to a synthetic family of general formula $Na_4M^{2+}(V_{10}O_{28})\cdot23H_2O$ (M=Ni,Mg) [2] [3], the main difference (in addition to having $\approx$ 23 H_2O molecules instead of $\approx$ 24) being that the latter compounds have a unit cell with doubled volume. Unit cell and atomic positions of huemulite are related to those of the synthetic family by the transformation matrix M = [1 0 0 / 0 1 1 / 0 $\bar{1}$ -1]. After the transformation, the space group of huemulite becomes $A\bar{1}$. Some of the symmetry restrictions (inversion centers, cell centering, etc.) present in huemulite are relaxed, with the consequence that fewer atoms are symmetry-related in the synthetic family.

[1] C.E. Gordillo, E. Linares, R.O. Toubes, H. Winchell, H. *American Mineralogist* **1966**, *51*, 1–13. [2] Z.-G. Sun, L.-S. Long, Y.-P. Ren, R.-B. Huang, L.-S. Zheng, S.W. Ng. *Acta Crystallographica* **2002**, *E58*, 34-36. [3] H.N. Miras, R.G. Raptis, N. Lalioti, M.P. Sigalas, P. Baran, T.A. Kabanos, *Chemistry – A European Journal* **2005**, *11*, 2295–2306.

Keywords: mineralogy, vanadium, valence-matching principle

MS54.P06

Structural Investigations of Synthetic Analogues of Murataite

Anna S. Pakhomova,[a] Sergey V. Krivovichev,[a] Sergey V. Stefanovsky,[b] Sergey V. Yudintsev,[c] [a]*Departament of Crystallography, Saint-Petersburg State University, Saint-Petersburg.* [b]*MosNPO Radon, Moscow.* [c]*Institute of Geology of Ore deposits, Petrograghy, Mineralogy and Geochemistry, Moscow (Russia).* E-mail: a.s.pakhomova@mail.ru

Synthetic analogues of rare mineral murataite, a complex oxide of titanium, iron, rare earth and other elements, attract special attention as perspective matrixes for the radioactive waste streams with complex composition. Murataite ceramics are usually obtained either by solid-phase sintering at 1200–1300 °C, or by melting at 1500–1600 °C with subsequent melt crystallization. Transmission electron microscope studies [1] allowed to identify four synthetic murataite varieties with 3×3×3, 5×5×5, 7×7×7 and 8×8×8 fluorite cubic supercells referred as murataite-3C, -5C, -7C and -8C. Structural investigations reveal that these varieties can be considered as members of murataite-pyrochlore polysomatic series based upon incorporation of high-actinide pyrochlore nanoclusters into modified murataite-like frameworks [2]. Here we report results of structural analysis of the synthetic murataite-3C.

Natural murataite [3] (*Mu*-3C), space group $F\overline{4}3m$, $a = 14.89$ Å, $Z = 4$, has the ideal and simplified formula $R_6M1_{12}M2_4TX_{43}$ (R = Y, Na, Ca, Mn; M1 = Ti, Fe; M2 = Fe, Ti; T = Zn; X = O, F). The crystal structure contains four cation sites: R site is [8]-coordinated, M1 site is octahedrally coordinated, M2 site is [5]-coordinated by a triangular bipyramid and T site is tetrahedrally coordinated. The structure is based upon a nanoporous 3D framework consisting of polymerized α-Keggin $[Zn^{[4]}Ti^{[6]}_{12}O_{40}]^{30-}$ clusters with T_d symmetry. Polymerization of Keggin units results in a creation of two types of voids that can be characterized as a truncated tetrahedron 3^46^4 and cubooctahedron 4^66^8. The framework accommodates complex fluorite-like substructure of Y, Fe and Na cations and O^{2-} and F^- anions.

The crystal chemical formula of synthetic murataite derived from structure refinement and determined on the basis of site-scattering power of cation sites is $[Ca_{3.24}Mn_{2.66}Ti_{1.90}Tb_{1.20}Fe_{0.76}{}_{0.24}](Al_{0.71}Fe_{0.29})(Ti_{3.92}Al_{0.08})$ $(Ti_{9.96}Zr_{2.04})O_{42}$ or $Ca_{3.24}(Mn_{2.66}Fe_{1.06})_{\Sigma=3.72}Ti_{15.78}Tb_{1.20}Al_{0.79}Zr_{2.04}O_{42}$ which is in reasonable agreement with the formula derived from chemical analysis. In comparison with the natural murataite, the synthetic material has noticeably less quantities of vacancies in the cation substructure. Structural investigations reveal that, in contrast to natural murataite, its synthetic analogue contains five instead of four cation positions. The additional site is [8]-coordinated and contains Ca^{2+} и Tb^{3+}. Structural and chemical differences between synthetic and natural murataites is the consequence of the significant amounts of fluoride present in natural samples, which compensates the absence of additional cation site in its structure.

[1] N.P. Laverov, A.I. Gorshkov, S.V. Yudintsev, A.V. Sivtsov, M.I. Lapina *Dokl. Earth Sci.* **1998**, *363*, 1272-1274. [2] S.V. Krivovichev, S.V. Yudintsev, S.V. Stefanovsky, N.I. Organova, O.V. Karimova, V.S. Urusov *Angewandte Chemie* **2010**, *49*, 9982-9984. [3] T.S. Ercit, F.C. Hawthorne *Can.Mineral.* **1995**, *33*, 1223-1229.

Keywords: murataite, complex oxides, titanates

MS54.P07

Crystal structure of vanadate garnet $Ca_2NaCd_2V_3O_{12}$

Akira Yoshiasa,[a] Shinobu Nishimiya,[a] Akihiko Nakatsuka,[b] Kazuake Iishi,[b] Maki Okube,[c] Hiroki Okudera,[d] [a]*Graduate School of Sciences and Technology, Kumamoto University, Kumamoto 860-8555 (Japan).* [b]*Department of Advanced Materials Science and Engineering, Yamaguchi University, Ube 755-8611(Japan).* [c]*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-850 (Japan).* [d]*Graduate School of Natural Science, Kanazawa University, Kanazawa, 920-1192 (Japan).* E-mail: yoshiasa@sci.kumamoto-u.ac.jp

Vanadate garnets provide important information for the general understanding of the structural stability of garnets, such as the effect of the cation-cation repulsion across the shared edges of the polyhedron.

Single crystals of vanadate garnet $Ca_2NaCd_2V_3O_{12}$ were synthesized by a floating zone method. A single crystal ground into a sphere of 0.15 mm in diameter was used for measurements of X-ray diffraction measurements. The measurements were carried out using a four circle diffractometer (Rigaku AFC-7). A total of 1326 reflections was measured and averaged in Laue symmetry m3m to give 448 independent reflections. The final R index is 2.5 %. The structure is subjected to the geometric constrains similar to that of silicate garnets. The geometric constraints force the tetrahedral-dodecahedral shared edge to become shorter than the unshared tetrahedral edge. The other palenzonite garnets have unusual structure features, which like grossular-type garnets, for instance the dodecahedral- dodecahedral shared edge length is longer than the unshared dodecahedral edge length and the octahedral-dodecahedral shared edge length is as long as the unshared octahedral edge length. On the other hand, the vanadate garnet $Ca_2NaCd_2V_3O_{12}$ has a normal structure feature, which like pyrope-type garnets, in that dodecahedral-dodecahedral share edge length is shorter than the unshared dodecahedral edge length.

Keywords: vanadate garnet, Ca2NaCd2V3O12

MS54.P08

Static disorder of vanadium ion in $NaSr_2Mg_2V_3O_{12}$ garnet

Akihiko Nakatsuka,[a] Hikaru Tsukamoto,[a] Mami Shimokawa,[a] Noriaki Nakayama,[a] Akira Yoshiasa,[b] [a]*Graduate School of Science and Engineering, Yamaguchi University, Ube, (Japan).* [b]*Graduate School of Science and Technology, Kumamoto University, Kumamoto, (Japan).* E-mail: tuka@yamaguchi-u.ac.jp

Garnets ($X_3Y_2Z_3O_{12}$) have attracted much attention in extensive research fields from solid state physics to earth science because of their interesting physical properties and their importance as major constituents in the earth's interior. They usually crystallize in cubic symmetry (space group *Ia*3*d*) and have three symmetrically distinct cation sites: the dodecahedral X site, the octahedral Y site and the tetrahedral Z site. In most of reported garnets, the mean square displacements (MSDs) of Z cations are the smallest in [100], in which adjacent X cations exist, and the largest in the directions perpendicular to this ($[100]_\perp$), in which no adjacent atoms are not present. However, we recently found that this is not the case for some of vanadate garnets such as $NaSr_2Mg_2V_3O_{12}$ and $NaPb_2Mg_2V_3O_{12}$; the tetrahedral V^{5+} has the largest MSD in [100]. We here conduct the structure refinements of $NaSr_2Mg_2V_3O_{12}$ garnet single-crystal synthesized by a floating zone (FZ) method in the range of 96–873 K to examine the peculiar atomic displacement behavior of V^{5+} in this garnet.

According to the Debye model, MSD can be described as follows [1]:

$$\text{MSD} = \left\langle u^2 \right\rangle_{\text{static}} + \left\langle u^2 \right\rangle_{\text{dynamic}}$$
$$= \left\langle u^2 \right\rangle_{\text{static}} + \frac{3\eta^2 T}{mk_B\Theta_D^2}\left[\Phi\left(\frac{\Theta_D}{T}\right) + \frac{1}{4}\frac{\Theta_D}{T}\right] \qquad (1)$$
$$\Phi\left(\frac{\Theta_D}{T}\right) = \frac{T}{\Theta_D}\int_0^{\frac{\Theta_D}{T}} \frac{x}{\exp(x)-1}dx$$

where $<u^2>_{\text{static}}$ is the temperature-independent static disorder component, $<u^2>_{\text{dynamic}}$ the temperature-dependent dynamic disorder component, m the mass of atoms, k_B the Boltzmann constant, $\hbar$ the Planck constant, Θ_D the Debye temperature and T the absolute temperature. The static disorder component and the Debye temperature were determined by fits of MSDs to Eq. (1). The resulting $<u^2>_{\text{static}}$ values of V^{5+} are 0.0062(2) Å^2 in [100] and 0.0001(1) Å^2 in $[100]_\perp$; thus, the V static disorder is