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 $F\bar{4}3m$, $a = 14.89$ 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

Acta Cryst. (2011) A**67,** C574

Crystal structure of vanadate garnet $Ca_2NaCd_2V_3O_{12}$

Akira Yoshiasa,[a] Shinobu Nishimiya,[a] Akihiko Nakatsuka,[b] Kazuaki 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

Acta Cryst. (2011) A**67,** C574-C575

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]:

$$\begin{aligned}\mathrm{MSD} &= \left\langle u^2 \right\rangle_{\mathrm{static}} + \left\langle u^2 \right\rangle_{\mathrm{dynamic}} \\ &= \left\langle u^2 \right\rangle_{\mathrm{static}} + \frac{3\eta^2 T}{mk_{\mathrm{B}}\Theta_{\mathrm{D}}^2}\left[\Phi\left(\frac{\Theta_{\mathrm{D}}}{T}\right) + \frac{1}{4}\frac{\Theta_{\mathrm{D}}}{T}\right] \qquad (1)\end{aligned}$$

$$\Phi\left(\frac{\Theta_{\mathrm{D}}}{T}\right) = \frac{T}{\Theta_{\mathrm{D}}}\int_0^{\frac{\Theta_{\mathrm{D}}}{T}} \frac{x}{\exp(x)-1}dx$$

where $\langle u^2 \rangle_{\mathrm{static}}$ is the temperature-independent static disorder component, $\langle u^2 \rangle_{\mathrm{dynamic}}$ 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 $\langle u^2 \rangle_{\mathrm{static}}$ 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