

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 $F\bar{4}3m$, $a = 14.89 \text{ \AA}$, $Z = 4$, 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 $[Ca_{3.24}Mn_{2.66}Ti_{1.90}Tb_{1.20}Fe_{0.76}O_{0.24}](Al_{0.71}Fe_{0.29})(Ti_{3.92}Al_{0.08})(Ti_{9.96}Zr_{2.04}O_{42}$ 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.

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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 $m\bar{3}m$ to give 448 independent reflections. The final R index is 2.5 %. The structure is subjected to the geometric constraints 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, $Ca_2NaCd_2V_3O_{12}$

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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 $Ia\bar{3}d$) 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]_⊥), 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]:

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

where $\langle u^2 \rangle_{\text{static}}$ is the temperature-independent static disorder component, $\langle u^2 \rangle_{\text{dynamic}}$ 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 $\langle u^2 \rangle_{\text{static}}$ values of V^{5+} are 0.0062(2) Å² in [100] and 0.0001(1) Å² in [100]_⊥; thus, the V static disorder is

suggested to occur in [100]. From consider of the interaction between the dodecahedral and tetrahedral cations, it is inferred that a part of V^{5+} occupies the 48*f* site ($x, 0, 0.25$), off-centered along [100], and the remainder stays at the 24*d* site ($0.375, 0, 0.25$), the average position. To confirm the presence of the V static disorder, the refinement based on this split-atom model was conducted at 96 K by applying isotropic ADPs (U_{iso}) only in V^{5+} at the 24*d* and 48*f* sites under the constraint of $U_{iso}(24d) = U_{iso}(48f)$. The electron density distribution was better fitted by this refinement, and the isotropic ADP of V^{5+} [$U_{iso} = 0.00283(16) \text{ \AA}^2$] resulted in the smaller value than that [$U_{eq} = 0.00457(3) \text{ \AA}^2$] from the refinement on the normal model, assigning V^{5+} only to the 24*d* site. Moreover, the resulting V positional parameter at the 48*f* site is $x = 0.3835(3)$, significantly deviating from the 24*d* site. The displacement quantity from the 24*d* site to this 48*f* position is $0.107(4) \text{ \AA}$, agreeing approximately with $\sqrt{\langle u^2 \rangle_{static}} [= 0.079(1) \text{ \AA}]$ of V^{5+} . Thus, we conclude that the peculiar atomic displacement behavior of V^{5+} is due to its static disorder along [100].

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Keywords: vanadate garnet, static disorder, Debye model

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HT-behavior of fettelite: Fast ion conduction and ionic phase-transition

Silvio Menchetti^b, Luca Bindi,^a ^aNatural History Museum of Florence, (Italy). ^bDipartimento di Scienze della Terra, Univ. Firenze, (Italy). E-mail: crystal@unifi.it

Bindi et al. ([1] references therein) have showed that the minerals belonging to the pearceite-polybasite group, general formula $[(Ag,Cu)_6M_2S_7][Ag_9CuS_4]$ with $M = As$ and Sb , exhibit a fast ion conductivity character. These authors also elucidated the atomic structures and the ionic phase transitions of all the members of the group by means of DSC (differential scanning calorimetry) and CIS (complex impedance spectroscopy) studies and *in situ* single-crystal X-ray diffraction experiments. Based on these results, we have attempted to determine whether there are any minerals, strictly related to those of the pearceite-polybasite group, which could behave as fast ion conductors. Although not belonging to this group, fettelite, $[Ag_6As_2S_7][Ag_{10}HgAs_2S_8]$, bears structural similarities to members of this group. Such a mineral, indeed, has been recently structurally characterized with data collected from a twinned crystal from Chañarcillo, Copiapó Province, Chile [2] and shows strong structural analogies with the minerals belonging to the pearceite-polybasite group. On the whole, the structure can be described as a regular succession of two module layers stacked along the *c*-axis: a first module layer (labeled *A*) with composition $[Ag_6As_2S_7]^{2-}$ and a second module layer (labeled *B*) with composition $[Ag_{10}HgAs_2S_8]^{2+}$. The *A* module layer of fettelite (both at RT and HT) is identical to that described for the minerals belonging to the pearceite-polybasite group.

Here we report a combined high-temperature single-crystal X-ray diffraction (HT-SCXRD), differential scanning calorimetry (DSC), and complex impedance spectroscopy (CIS) study on a sample of fettelite from Chañarcillo, Copiapó Province, Chile. DSC and conductivity measurements pointed out that fettelite shows a ionic-transition at about 380K. HT-SCXRD experiments confirmed the phase transition toward a disordered phase having a trigonal symmetry with the *a* and *b* unit-cell parameters halved. In the HT-structure, the disorder is located in the *B* layer where the Ag-Hg cations are found in various sites corresponding to the most pronounced probability density function locations of diffusion-like paths. This indicates that at least two

polytypes could exist for fettelite, the ordered, monoclinic RT-structure (space group *C2*), and a fast ion conducting, trigonal, disordered HT-form (space group *P-3m1*) with *a* and *b* parameters halved. The two unit-cell types (corresponding to two different polytypes) could be also found in nature. Slightly different chemical compositions for different fettelite samples (e.g., different Ag/Hg ratios) could play a crucial role as driving forces for different unit-cell stabilizations.

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Hierarchical self-organization: the case of monodispersed spherical silica particles

Dmitry V. Kamashev, Institute of Geology, Komi Science Centre, Ural Branch, Russian Academy of Sciences, Syktyvkar (Russia). E-mail: kamashev@geo.komisc.ru

The problems of study of supermolecular structures generation arouse a certain interest, since recently they find a more broad application in different spheres of chemistry, physics, including their application as matrices for nanocomposite materials. The available data on the mechanism of formation of permolecular structures and their components is insufficient.

In the present work, on the basis of experimental data, we considered the influence of different physical and chemical conditions of permolecular structures synthesis on the sizes and morphology of resulting silica particles, and also the features of their precipitation into well-ordered structure. On the basis of the obtained results we suggested the model of spherical particle structure.

The formation of monodisperse silica spheres was based on Stober-Fink method [1], which we improved [2]. The synthesis was carried out under different temperatures (8, 18°C) and with different methods of the preparation of tetraethyl ortosilicate (TEOS) [2]. Three series of experiments were conducted. The first series was conducted under 18°C, all the preparation of tetraethyl ortosilicate came to its preliminary purification through distillation. The second series was conducted like the first one but under 8°C. The third series was conducted using TEOS processed with combined method [2], in concentration interval (0.04÷4.75) mole/dm³ for NH₃ and (1.5÷31.8) mole/dm³ for H₂O, with the constant concentration of tetraethyl ortosilicate of 0.28 mole/dm³ and of the temperature at 18°C. Just in this series we were able to obtain monodisperse silica spheres in the wide ratio of the system components: (0.2÷0.8) mole/dm³ for NH₃ and (2.75÷6.4) mole/dm³ for H₂O and hence in the wide size range of 235-765 nm. At lower temperatures and also beyond the suggested concentration interval the disturbance of both monodisperses and of spherical form of particles occurred.

The oscillation of dependence of particle sizes on the concentration of the system components: TEOS-C₂H₅OH-NH₃-H₂O along with the discreteness of sizes of resulting particles (division into strata during gravitational precipitation, polymodality in distribution of particles according to their sizes) let us suppose the following mechanism of spherical particle structure. According to concepts of cluster self-organization of matter at nanolevel, ultradisperse particles of the size, typical for opal balls, are composed of much smaller particles than mentioned above 10 nm. The sizes of these particles depend on the satiety of solution and in amorphous state can reach about 2.4 nm. Accordingly all the compact amorphous formations can be formed resulting from hierarchical aggregation. In the first case, when clusters are located around the central one, cluster aggregation of the 1st