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) Å^2] resulted in the smaller value than that [U_{eq} = 0.00457(3) Å^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) Å, agreeing approximately with $\sqrt{\langle u^2\rangle_{static}}$ [= 0.079(1) Å] 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

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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 *C*2), and a fast ion conducting, trigonal, disordered HT-form (space group *P*-3*m*1) 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

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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, 18ºC) and with different methods of the preparation of tetraethyl ortosilicate (TEOS) [2]. Three series of experiments were conducted. The first series was conducted under 18ºC, all the preparation of tetraethyl ortosilicate came to its preliminary purification through distillation. The second series was conducted like the first one but under 8ºC. The third series was conducted using TEOS processed with combined method [2], in concentration interval (0.04÷4.75) mole/dm^3 for NH_3 and (1.5÷31.8) mole/dm^3 for H_2O, with the constant concentration of tetraethyl ortosilicate of 0.28 mole/dm^3 and of the temperature at 18ºC. 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/dm^3 for NH_3 and (2.75÷6.4) mole/dm^3 for H_2O 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 occured.

The oscillation of dependence of particle sizes on the concentration of the system components: TEOS-C_2H_5OH-NH_3-H_2O 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

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