

carbon was studied in detail. For the samples distinguished by genesis, rows of dependence nanostructures features from geological conditions of finding, PT-parameters of processes of formation have been constructed. Possible mechanisms of structurization of globules are analyzed on ideas about aggregation of colloidal particles.

**Keywords:** AFM-STM studies of minerals and glasses, amorphous materials characterization, nanostructures

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#### Distinct Local Environments for Ca in Pyrope-Grossular Garnets: a New Model Based on XRD and EXAFS Studies

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A multi-technique approach (based on electron microprobe analysis, X-ray structure refinement, and EXAFS analysis at the Ca K-edge) was used to characterise the local geometry of Ca in synthetic and natural garnet compositions referable to the pyrope-grossular solid-solution. Multi-shell fits of the EXAFS data indicate that Ca assumes the standard [4 + 4]-fold coordination (the polyhedral shape being a triangular dodecahedron) when Ca > 1.50 atoms per formula unit (apfu), but assumes a nearly regular [8]-fold coordination when Mg + Fe > 1.50 apfu. In the latter situation, both Ca-O bonds converge towards the value of the longer Mg-O bond in pyrope.

This anomalous change of coordination may explain the strong non-ideality of many structural features and geochemical and thermodynamic properties observed along the pyrope-grossular solid solution, which is the one most relevant for the use of garnets in petrogenetic studies of igneous and subduction environments.

This feature must be taken into account when building theoretical models of the garnet solid solutions, which are at the moment the most promising approach to calculate thermodynamic properties and to interpret and predict trace-element behaviour in this crucial mineral phase.

**Keywords:** EXAFS, XRD, garnet solid solutions

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#### Analysis of Microporous Crystal Structures with Voronoi-Dirichlet Polyhedra

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The methods for computer characterization of voids in crystal structures by means of Voronoi-Dirichlet polyhedra are extended to microporous mineral phases and synthetic ionic conductors. It is shown that these methods allow one to appropriately visualize cavities, cages, and channels, and estimate their geometrical properties, such as size and shape. Some typical minerals (sodalite, olivine, pyroxene, sheelite, anortite, etc) are considered to analyze the systems of pores, and the methods are found to be an effective tool for predicting type and positions of interstitial cations. Moreover, the absence of some phases with large alkali cations (e.g. Sc-containing olivines or pyroxenes with Na, K, Rb, or Cs cations) is successfully explained by comparing typical cation sizes and shapes with those for crystal structure cavities. In addition, several ionic conductors are tested, such as Nasicon, Liphos, Na<sub>15</sub>Y<sub>3</sub>[Si<sub>12</sub>O<sub>36</sub>], etc, to visualize the conductive channels, assess their size, and find possible paths of ion migration. Special attention is paid to framework rare-earth silicates and germanates, possessing high conductivity and/or ion-exchange properties. The principal advantage of the proposed methods is their independence of any empirical parameters (such as ionic or van der

Waal radii) and, hence, the possibility of being used for hosts and guest atoms or molecules of any chemical composition and geometry. This work was financially supported by the Russian Foundation for Basic Research (project 04-02-16851).

**Keywords:** Voronoi-Dirichlet polyhedron, pore, ionic conductor

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#### Langasite Crystals: Growth, Composition and Physical Properties

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Single crystals with melt composition La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub> (growth atmosphere – Ar) (I) and La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub> (II), La<sub>3</sub>Ga<sub>5.14</sub>Si<sub>0.86</sub>O<sub>14</sub> (III), La<sub>3</sub>Ga<sub>5</sub>Si<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>14</sub> (IV) (growth atmosphere 99±98%Ar+1±2% O<sub>2</sub>) are grown by the Czochralski method in the <0001> direction. It was found that growth conditions change structural parameters, type and concentration of point defects and also physical properties in the volume of crystals.

For all crystals in the temperature range from 20 to 600 °C the level of activation is E=0.94 (±0.02) eV. Specific resistance of crystals at 350 °C changes depending on the initial composition of melt and growth conditions: from 4.6 · 10<sup>5</sup> Ohm·cm (crystal I) to 1.26 · 10<sup>7</sup> Ohm·cm (crystals II-IV). Anisotropy of tangent of dielectric losses angle was found: in the <0001> direction the value of temperature maximum of relaxational losses is shifted by 20 ° into the high temperature area compared to direction <11-20>. This is connected with the influence of structural defects having polarization in electric field (for example: inclusions, vacancies etc). Treatment of crystals at 1000 °C in vacuum leads to decreasing oxygen vacancies what is accompanied by shifting of temperature maximum of dielectric losses from 310 °C to 430 °C.

**Keywords:** langasite crystals, structure, electric properties

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#### Ponomarevite, K<sub>4</sub>Cu<sub>4</sub>OCl<sub>10</sub>, a Naturally Occurring Mineral with a [Cu<sub>4</sub>O] Core –Ancestor of Many Synthetic Cluster Compounds

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The crystal structure of the title compound was determined by de Boer et al.[1]. Later the mineral Ponomarevite has been identified in fumarole deposits in Kamchatka, Russia, its crystal structure being essentially identical with that of the synthetic compound [2]. The Russian authors, however, appear to have not known the earlier work.

Ponomarevite is composed of Cu<sub>4</sub>OCl<sub>10</sub> clusters with a Cu<sub>4</sub> tetrahedron centered by oxygen. The two-valent copper has fivefold distorted trigonal-bipyramidal coordination by one terminal and three bridging chlorine atoms and the centering oxygen.

Many other related compounds with clusters of the type [Cu<sub>4</sub>OCl<sub>6</sub>X<sub>4</sub>], with X being always terminal and mainly organic or halogen, have been reported without making reference to Ponomarevite. All these cluster compounds are in principle very interesting from a magnetic point of view.

In this paper the crystal structure of the new compound [Me<sub>4</sub>N]<sub>4</sub>[Cu<sub>4</sub>O(OCN)<sub>10</sub>] is reported (a=16.632, b=12.632, c=20.557Å, β=101.34, SG. P2<sub>1</sub>/a, Z=4). In this compound the cluster differs from all the ones known by having only two cyanato ligands with oxygens bridging opposite edges of the [Cu<sub>4</sub>O] tetrahedron, while the other eight cyanato groups are terminal. The copper has thus a quadratic coordination by four oxygens.

[1] De Boer J.J. et al., *Acta Cryst.*, 1972, B28, 3436. [2] Semenova T. F. et al., *Doklady Akademii Nauk SSSR* 1989, 304, 427.

**Keywords:** mineral chemistry, copper, complexes