

rays which are insensitive to the scattering of light atoms and hence neutron diffraction data on a single crystal sample are essential in determining precisely the atomic co-ordinates during this possible transition. Previously only data up to 2.0 GPa have been collected using single crystal neutron diffraction. We present structures determined from a single crystal of 4 mm³ using time-of-flight Laue diffraction on the SXD instrument at the ISIS Facility at Rutherford Appleton Laboratory in the UK.

[1] Endo S. et al, *Nature*, **340**, 452, 1989.

Keywords: high pressure, single crystal diffraction, neutron diffraction

P.10.04.12

Acta Cryst. (2005). A61, C375

Compression of Oxygen Vacancy Type Al-bearing MgSiO₃ Perovskite

Yasuo Ohishi^{a,b}, Kei Hirose^c, Hiroshi Kojitani^d, Tetsu Watanuki^e, Masaki Takata^{a,b}, ^aJapan Synchrotron Radiation Research Institute, Hyogo. ^bCREST-JST. ^cDepartment of Earth and Planetary Science, Tokyo Institute of Technology. ^dDepartment of Chemistry, Gakushuin University, Tokyo. ^eJapan Atomic Energy Research Institute, Hyogo, Japan. E-mail: ohishi@spring8.or.jp

MgSiO₃ perovskite is believed to be a dominant constituent of the Earth's lower mantle. Experimental results on the effect of Al on the compressibility of MgSiO₃ perovskite have been pretty controversial. Two kinds of the Al substitution mechanisms are expected: 2Al³⁺ = Mg²⁺ + Si⁴⁺ and 2Al³⁺ = 2Si⁴⁺ + (as a vacancy site) O²⁻ [1]. Theory predicts that the latter mechanism significantly increases the compressibility [2].

Recently, Kojitani et al (2005) demonstrated the structural differences between these two types of Al-bearing MgSiO₃ perovskite on the basis of Rietveld analyses. In this work, the volume compression measurements were performed on the oxygen vacancy type Al-MgSiO₃ perovskite by using synchrotron radiation x-rays. Data were collected under hydrostatic conditions using helium pressure transmitting medium. Preliminary results show that the isothermal bulk modulus is reduced due to the incorporation of Al₂O₃ in perovskite with oxygen vacancy.

[1] Navrotsky A., Shoenitz M., Kojitani H., Xu H., Zhang J., Weidner D. J., Jeanloz R., *J. Geophys. Res.*, 2003, **108-B7**, ECV2-1. [2] Yamamoto T., Yuen D.A., Ebisuzaki T., *Earth Planet. Sci. Lett.*, 2003, **206**, 617.

Keywords: perovskite, high pressure mineralogy, synchrotron X-ray diffraction

P.10.04.13

Acta Cryst. (2005). A61, C375

New High-pressure Phase of Calcite at Room Temperature

Kenji Hagiya, Masanori Matsui, Masahiro Obata, *School of Science, University of Hyogo, Japan*. E-mail: hagiya@sci.u-hyogo.ac.jp

A new high-pressure phase of calcite (CaCO₃) has been found by single-crystal X-ray analyses. Recently we determined the crystal data of calcite III (monoclinic C-centered lattice, Z=8) using single-crystal X-ray diffraction methods at 300K and pressures between 2.3 and 4.1 GPa [1]. The present studies have been carried out to determine the crystal data of calcite at room temperature and higher pressures.

The samples are single crystals of natural calcite from Creel, Chihuahua, Mexico. For high-pressure experiments, the Merrill-Bassett type diamond-anvil-cells were used. Pressures were estimated based on the ruby-fluorescence method. X-ray diffraction measurements were performed using an Enraf-Nonius CAD-4 diffractometer with MoK α radiation monochromatized by graphite. A film cassette for a flat imaging plate was attached on the diffractometer.

On the oscillation photographs taken at 2.5GPa, all the reflections could be assigned as calcite III being composed two twinned individuals. By increasing the sample pressure to 4.5GPa, several reflections disappeared. Then remained reflections were re-indexed and the cell parameters were determined with the angular data of 25 reflections. The triclinic unit-cell are $a=3.855(3)$, $b=4.815(2)$, $c=6.165(5)\text{\AA}$, $\alpha=84.10(4)$, $\beta=72.15(5)$, $\gamma=88.73(5)$, $Z=2$ at 300K and

4.5GPa. The cell parameters were determined at pressures between 4.3 and 5.6GPa. Thus the phase transition from calcite III to the new phase may occur at 4.1-4.3GPa.

[1] Hagiya K., Matsui M., Kimura Y., Akahama Y., *J. Mineralogical and Petrological Sciences*, 2005, **100**, 31.

Keywords: calcium compounds, carbonates, high-pressure phase

P.10.04.14

Acta Cryst. (2005). A61, C375

High-pressure Single-crystal Study of Chlorite

Sabrina Nazzareni, P. Comodi, M. Montagnoli, P. F. Zanazzi, *Dipartimento di Scienze della Terra, Università di Perugia, Italy*. E-mail: crystal1@unipg.it

Chlorite is a major constituent of hydrated oceanic crust, and may represent an important water carrier in subducting slabs. In this context, its stability under high pressure has relevant implications on rheology and melting behaviour of mantle rocks.

The structural effects of pressure on a natural chlorite from Val Malenco (Italy) [clinoclhor, polytype IIb-4, S.G. C-1, pseudomonoclinic metric, composition (Mg_{7.82}Al_{3.36}Fe²⁺_{0.52}Fe³⁺_{0.30})(Si_{7.70}Al_{0.30})O₂₀(OH)₁₆] have been studied by X-ray diffraction on single-crystal mounted in a DAC. Pressure was calibrated through the EoS of α -quartz.

Structural refinements were performed at 0, 0.8, 1.8, 2.7, 3.5, 4.4, 5.1 GPa with intensity data collected on a CCD Xcalibur diffractometer (Oxford Instr.) equipped with monochromatized MoK α . Lattice parameters were measured with the point-detector mounted on the same instrument.

The compressibility data of chlorite (bulk modulus K= 83(1) GPa, K'= 4) are in fair agreement with data based on powder neutron [1] and synchrotron diffraction methods [2,3]. Axial moduli are 102(2), 97(3) and 63(1) GPa respectively for a , b and c axes. The main structural deformations affect the interlayer region where the hydrogen bonds are relevant to the structural properties of the phase. The OH-O distances decrease of about 4% in the 0-5 GPa range. Work is in progress and further details will be presented at the conference site.

[1] Welch M.D., Marshall W.G., *Am. Mineral.*, 2001, 1380. [2] Pawley A.R., Clark S.M., Chinnery N.J., *Am. Mineral.*, 2002, 1172. [3] Welch M.D., Crichton W.A., *Eur. J. Min.*, 2002, 561.

Keywords: high-pressure diffraction, chlorite, compressibility

P.10.05.1

Acta Cryst. (2005). A61, C375-C376

Research of Nanostructured X-ray Amorphous Minerals by AFM

Yevgeniy A. Golubev, *Institute of Geology, Russian Academy of Sciences, Syktyvkar, Russia*. E-mail: golubev@geo.komisc.ru

Among products of geological processes the noncrystal substances are distributed. Before among geomaterials the basic attention was given to research of crystal mineral substance and microdisperse mineral phases. Progress of methods of research has allowed to find out and considerably to expand last decade ideas about nanodisperse mineral phases. Their study causes interest due to active influence of nanoconstitution on properties, to detection of some new unique forms in mineral substances.

In our work an attempt of search characteristics of nanoconstitution of various noncrystal mineral substances will be undertaken. Among them simple substances (ex., fullerene shungite Karelia), oxides (ex., natural photonic crystals – opals), complex substances (ex., solid hydrocarbons). Nanoconstitution visualized on a fractures surface off by atomic force and electronic microscopies. The quantitative superstructural data were received by a combination of microscopic researches with diffractational and statistical-geometrical analysis of morphological features.

As a result of the carried out researches local and global characteristics of supermolecular structures, in particular, a degree of orderliness of a relative positioning of elements nanostructures have been established. The multilevel fullerene-like structure of shungite

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

P.10.05.2

Acta Cryst. (2005). A61, C376

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

Maria Chiara Dalconi^a, Roberta Oberti^b, Simona Quartieri^c, Federico Boscherini^d, Gianluca Iezzi^e, Massimo Boiocchi^f, ^a*Dipartimento di Scienze della Terra, Università di Ferrara, Italy.* ^b*CNR, Istituto di Geoscienze e Georisorse, Pavia, Italy.* ^c*Dipartimento di Scienze della Terra, Università di Messina, Italy.* ^d*INFN and Dipartimento di Fisica, Università di Bologna, Italy.* ^e*Dipartimento di Scienze della Terra, Università di Chieti, Italy.* ^f*Centro Grandi Strumenti, Università di Pavia, Italy.* E-mail: dmc@unife.it

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

P.10.05.3

Acta Cryst. (2005). A61, C376

Analysis of Microporous Crystal Structures with Voronoi-Dirichlet Polyhedra

Olga A. Blatova^a, Vladislav A. Blatov^b, Gregory D. Ilyushin^c, Lyudmila N. Dem'yanets^c, ^a*Samara State Architectural University, Samara.* ^b*Samara State University, Samara.* ^c*Institute of Crystallography of RAS, Moscow, Russia.* E-mail: olga_blatova@mail.ru

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, Na₁₅Y₃[Si₁₂O₃₆], 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

P.10.05.4

Acta Cryst. (2005). A61, C376

Langasite Crystals: Growth, Composition and Physical Properties

Elena Domoroshchina^{a,b}, Alexander Dubovskiy^b, Galina Kuz'micheva^a, Galina Semenkovich^b, ^a*Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia.* ^b*Russian Research Institute for the Synthesis of Minerals, Aleksandrov, Russia.* E-mail: elena2078@list.ru

Single crystals with melt composition La₃Ga₅SiO₁₄ (growth atmosphere – Ar) (I) and La₃Ga₅SiO₁₄ (II), La₃Ga_{5.14}Si_{0.86}O₁₄ (III), La₃Ga₅Si_{0.9}Ge_{0.1}O₁₄ (IV) (growth atmosphere 99±98%Ar+1±2% O₂) 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 · 10⁵ Ohm·cm (crystal I) to 1.26 · 10⁷ 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

P.10.05.5

Acta Cryst. (2005). A61, C376

Ponomarevite, K₄Cu₄OCl₁₀, a Naturally Occurring Mineral with a [Cu₄O] Core –Ancestor of Many Synthetic Cluster Compounds

Herbert Boller, Rahima Dilshad, Kurt Klepp, *Institut für Allgemeine und Anorganische Chemie, Johannes-Kepler-Universität-Linz, Linz, Austria.* E-mail: Herbert.Boller@jku.at.

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 Cu₄OCl₁₀ clusters with a Cu₄ 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 [Cu₄OCl₆X₄], 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 [Me₄N]₄[Cu₄O(OCN)₁₀] is reported (a=16.632, b=12.632, c=20.557Å, β=101.34, SG. P2₁/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 [Cu₄O] 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