

ammonium ions, size and precipitation speed of the globules.

In fact, at high pH values we have spherical silica particles surrounded by a dense shell of gegenions that results in their electrostatic repulsion. As a result, during precipitating of particles on the surface of a supramolecular crystal, their position in the structure is conditioned by the repulsion of precipitating particles from the surface analogous to charged globules in the structure. It results in maximal filling of space. The situation is changed at low pH values and low sizes (less 400 nm) of particles which results in reducing their surface and the greater reduction of the concentration of gegenions, and as a consequence, of the force of their electrostatic repulsion. Forming here hydrogen bonds prevent the precipitation of the particles in the most favorable positions which results in reducing the filling ratio of the particles.

In the framework of the experiment conducted by us, the packing type of spheric particles in opal matrixes depends on the sol pH and silica sphere sizes. At pH 7.5–8.0 a primitive cubic packing of particles is realized. The increase of pH up to 8.5–9.0 results in the formation of hexagonal packing with a corresponding increase of particle sizes. At a higher pH values the closest packing formed which is characteristic for natural noble opal.

Keywords: amorphous materials, supramolecular crystals, spherical silica particles

P.11.05.3

Acta Cryst. (2005). A61, C389

Quantitative Analysis of Poorly Crystalline Fe₂O₃ Specimens

Tomas Grygar^a, Petr Bezdecka^a, Veronika Simova^a, Oldrich Schneeweiss^b, Radek Zboril^c, ^a*Institute of Inorganic Chemistry AS CR, Rez, Czech Republic.* ^b*Institute of Physics of Materials AS CR, Brno, Czech Republic.* ^c*Palacky University, Olomouc, Czech Republic.* E-mail: grygar@iic.cas.cz

We analyzed amorphous and nanocrystalline natural and synthetic ferric oxides by X-ray diffraction (XRD), Mossbauer and UV-Vis spectroscopies, voltammetry of microparticles, and thermoanalytical methods. The quantitative analytical methods were tested with intermediates of the thermal conversion of ferrihydrite to nanocrystalline hematite.

The XRD measurement with the addition of a known amount of reference material (Si) is not applicable when the mean coherence is only a few nm. Mossbauer spectroscopy and voltammetry of microparticles of such poorly ordered solids should be supported by the results of other methods, but under optimal conditions they are expected to "see" both amorphous and crystalline components with a comparable sensitivity permitting their determination. However, the minimal particle size of the target compounds is not known for Mossbauer spectroscopy and voltammetry of microparticles, and it seems to be equal or even larger than mean coherence length enabling XRD measurement. Diffuse reflectance spectroscopy can only be used to qualitative analysis, because the spectra of ferrihydrite and almost amorphous Fe₂O₃ are hardly interpretable.

The results indicate a lack of the knowledge on a local structure of 2-line ferrihydrite and XRD amorphous ferric oxides.

Keywords: amorphous materials, nanocrystalline materials, iron oxides

P.11.05.4

Acta Cryst. (2005). A61, C389

Revisitation of the Structural Models for Ferrihydrites

Gabriele Navarra, Maria F. Casula, Gabriella Pinna, *Department of Chemical Sciences, University of Cagliari, Cagliari, Italy.* E-mail: navarra@unica.it

Ferrihydrite is a generic term for various poorly ordered Fe(III) oxyhydroxides. They are also characterized by small particle size, as evident from X-ray diffraction patterns. They in fact consist of a number of broad peaks varying from 2 to 6; the extreme forms are referred to as 2-line and 6-line ferrihydrite, while the 4-line one is better known as ferroxhyte. The lack of experimental details causes concern about the uniqueness of structural interpretation of XRD data.

In spite of this [1,2], several models have been proposed:

however, the agreements with the experiments were reached assuming a mixture of two or three crystalline structures which made use of sets of rather unreasonable atomic occupancies. Besides, some Fe-Fe distances obtained from EXAFS analysis are not consistent with those interpretations.

We present here structural models for the three forms of ferrihydrites in which the oxygen atoms have unitary weights and the iron atoms, with half weights according to the oxide stoichiometry, are set in all the available octahedral sites.

[1] Drits V.A., Sakharov B.A., Salyn A.L., Manceau A., *Clay Minerals*, 1993, **28**, 185. [2] Jansen E., Kyek A., Schafer W., Schwertmann U., *Appl. Phys. A*, 2002, **74**, S1004.

Keywords: ferrihydrite, disordered systems, xrd

P.11.06.1

Acta Cryst. (2005). A61, C389

Crystal Structure of New Lanthanide Diphosphates

Francesco Capitelli^a, Brahim El Bali^b, Juan F. Piniella^c, ^a*IC-CNR, Bari, Italy.* ^b*Dépt. de Chimie, Faculté des Sciences Dhar Mehraz, BP 1796 Atlas, 30000 Fès, Morocco.* ^c*Dept. of Geology, Universitat Autònoma de Barcelona, Bellaterra, Spain.* E-mail: francesco.capitelli@ic.cnr.it

In the context of a general study on synthetic phosphates [1-2], the crystal structures of three new lanthanide diphosphates are presented: KLnP₂O₇·2H₂O, where Ln is Gd, Tb and Yb. Suitable monocrystals were grown after the synthesis carried out using equimolar proportions of K₄P₂O₇ (dissolved in HCl) and LnCl₃·6H₂O as reagents. The structures, solved by X-ray diffraction methods (SIR97) and refined by full-matrix least squares (SHELXL-97), resulted to be isostructural within space group P2₁/c. In table 1 are presented the unit-cell parameters, the volumes and the final R₁ (I ≥ 2σ(I)) values. The three-dimensional frameworks are made by zig-zag chains of KO₉ polyhedra down c, sharing edges with discrete LnO₇ polyhedra and P₂O₇ units; intricate hydrogen bonding networks complete the arrays.

Table 1

Ln	a(Å)	b(Å)	c(Å)	β(°)	V(Å ³)	R ₁ (%)
Gd	7.7522(2)	10.6732(8)	10.1375(7)	93.308(5)	837.39(9)	4.31
Tb	7.7380(6)	10.6360(8)	10.1060(7)	93.283(6)	830.37(11)	3.85
Yb	7.6791(3)	10.4992(7)	9.9554(9)	93.214(6)	801.39(10)	5.42

[1] Capitelli F., Brouzi K., Harcharras M., Ennaciri A., Moliterni A. G. G., Bertolasi V., *Z. Kristallogr.* 2004, **219**, 93-98. [2] Capitelli F., Khaoulaf R., Harcharras M., Ennaciri A., Habyby S. H., Valentini V., Mattei G., Bertolasi V., *Z. Kristallogr.*, 2005, **220**, 25-30.

Keywords: diphosphate, lanthanide, X-ray single crystal diffractometry

P.11.06.2

Acta Cryst. (2005). A61, C389-C390

Roman Ceramics in the Transylvanian Basin (Romania)

Ion Nicolae Robu^a, L. Robu^a, A. Pescaru^b, G. Verdes^c, A. Ursoi^c, ^a*Geological Institute of Romania, Caransebes str. 1, 012271-Bucuresti, Romania.* ^b*Museum of Dacic and Roman Civilization, Decebal str. 2, Deva, Romania.* ^c*Gold Museum, Independentei str. 3, Brad, Romania.* E-mail: inrobu@yahoo.com

Some ceramic objects, as pots, have been found in some graves, emplacement in the Muncelu-Ruda zone from the Apuseni Mountains, Transylvania Region. They are associated with high burnt bones, quartz crystals, burnt ore, silver coins and funeral monuments, belonging to Roman Period (II-III).

Some fragments of pots belonging to different pots have been investigated for their mineralogical properties: thinness, color, porosity, engobe, and technique of moulding-fashioning of the ceramic paste.

The investigated fragments are characterized by different porosity (high-low), variation of burning degree intensity, its effect being recognized in both wells of the pots as very parallel different red-brownish tints of strip. The structural aspects consist in the parallel