

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

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Quantitative Analysis of Poorly Crystalline Fe₂O₃ Specimens

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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

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Revisitation of the Structural Models for Ferrihydrites

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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

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Crystal Structure of New Lanthanide Diphosphates

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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

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Roman Ceramics in the Transylvanian Basin (Romania)

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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

orientation of the grains in the marginal and central zones of the walls or the lack of the preferential orientations, associated with some obvious directional changes in the very limited spaces. emphasizing in such way different techniques of moulding-fashioning of the ceramic paste. No engobe has been identified.

Though, they have been found in the same area and they are considered contemporary, the mineralogical aspects emphasize (i) different historical periods, (ii) the same period, but some changes in the processing of ceramic material could taken place, or (iii) different geographical areas, for their origin.

Keywords: ceramics, mineralogy, properties

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Cobalt Incorporation in Mullite

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Mullite (nominally $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is technologically important material for advanced ceramics applications. Depending on the synthesis procedure, mullite is able to incorporate considerable amounts of transition metal cations [1]. While Cr^{3+} , Fe^{3+} and V^{3+} have the strongest tendency of incorporation in mullite, only low or very low amounts of Fe^{2+} , Co^{2+} , Mn^{2+} and Zr^{4+} ions can enter the mullite structure. A major goal of this work is to determine upper limit of Co^{2+} incorporation in mullite. The samples of pure mullite and of Cr-doped mullite were derived from diphasic precursors and sintered at 1600 °C for two hours. Four samples were prepared containing 0, 1, 2 and 3 at% Co. They were examined by XRD at room temperature. Samples contained mullite phase and small amounts of $\alpha\text{-Al}_2\text{O}_3$ and CoAl_2O_4 . Unit-cell parameters of the mullite phase were refined by the whole-powder-pattern fitting method [2]. They increased just slightly with increase of cobalt content in the samples. Quantitative phase analysis showed that the samples with 1, 2, and 3 at% Co contained 0.8, 2.5 and 5.1 wt% CoAl_2O_4 , respectively. These means that ~0.6 at% Co was incorporated in mullite. Same value of upper limit of Co^{2+} incorporation in mullite was obtained on the basis of intensity ratio $I_{(311, \text{CoAl}_2\text{O}_4)} / I_{(111, \text{mullite phase})}$, which was linearly dependent on the Co content in the examined samples.

[1] Schneider H., *Ceramics Transactions*, 1990, 6,135. [2] Toraya H., *J. Appl. Cryst.*, 1986, 19, 440.

Keywords: co-doped mullite, X-ray diffraction, fitting methods

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Rietveld Refinement of Solid Solutions of La_2TiO_5 and $\text{La}_4\text{Ga}_2\text{O}_9$

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Orthorhombic (Pnam) La_2TiO_5 and monoclinic (P2₁/c) $\text{La}_4\text{Ga}_2\text{O}_9$ were found to form solid solutions in the whole concentration range. Samples of $\text{La}_2\text{Ti}_{(1-x)}\text{Ga}_x\text{O}_{(5-x/2)}$ with $x = 0.00, 0.20, 0.50, 0.70, 0.90, 0.95$ and 1.00 were prepared by solid state reaction of oxides at 1300 °C in air (fired and remixed several times for 60 h, until no change).

Structure of La_2TiO_5 has already been known, while $\text{La}_4\text{Ga}_2\text{O}_9$ was found in this study to be isostructural with $\text{Y}_4\text{Al}_2\text{O}_9$, $\text{Eu}_4\text{Al}_2\text{O}_9$ and $\text{Pr}_4\text{Ga}_2\text{O}_9$, and was successfully refined from the $\text{Y}_4\text{Al}_2\text{O}_9$ model.

Laboratory data in the range of 10-120 °2θ were used for an unrestrained Rietveld refinement (TOPAS). Results were consistent and showed random replacement of Ti^{4+} by Ga^{3+} ions in the solid solutions, coupled with oxygen vacancies, most probably preferably occurring at one site. Vacancies at this site are not ordered till $x = 0.90$ and the structures up to this composition are orthorhombic, obeying Vegard's law. Increase of a and c and decrease of b was explained considering ionic radii and shifts of ions towards the vacant site.

Ordering of the oxygen vacancies on one oxygen site at $x = 0.95$ and 1.00 causes doubling of the unit cell and lowering of the

symmetry to monoclinic. In pure $\text{La}_4\text{Ga}_2\text{O}_9$ ($x = 1.00$) the total population at this site reaches 0.5 and the ordering (1 full : 1 empty) produces the superstructure. The structural relationship between the end members (orthorhombic and the other monoclinic) was also clarified by finding the transformation matrix between the two.

Keywords: solid solution, Rietveld refinement, ceramics

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Comparative Study between Synthesized $\text{Zn}_{2-x}\text{Co}_x\text{SiO}_4$ and Cobalt-base Pigments

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Except V-ZrSiO_4 , all commercial ceramic pigments are cobalt-base. Most compounds used are Co_2SiO_4 , Co_2SnO_4 , and CoAl_2O_4 type. Although these pigments show an intense blue color, they present two major disadvantages: the high cost of cobalt and its toxicity. We can reduce these problems by introducing a small quantity of cobalt into chemically and thermally stable crystalline matrix of Zn_2SiO_4 .

In this work, we have synthesized blue $\text{Zn}_{2-x}\text{Co}_x\text{SiO}_4$ pigments with low cobalt content. The powder obtained was characterized by several techniques: X-rays diffraction powder, IR and UV-Visible spectroscopy, LAB color measurement, and Scanning Electron Microscopy. Comparative study was made between our synthesized pigments and the most used commercial pigments produced by different companies.

Keywords: ceramics, pigments, cobalt

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Rietveld Analysis in Biological Apatite Composite Tissues

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A Rietveld analysis has been carried out for two types of hard tissues: bone and dentin. As it is well known, both bone and dentin are composite materials having the presence of an organic matrix (type I collagen) and nanometric crystals of biological apatite. In Rietveld Refinement, the description of the Bragg intensity peaks can be carried out without serious difficulties. In any case, the microstructural contribution must be settled carefully, by introducing an instrumental resolution function. In the correction for absorption we have taken into account the contribution for air scattering, according to Ottani et al. [1]. As part of the background, we have considered the incoherent scattering using the analytical expression published by Smith et al. [2] and the thermal diffuse scattering [1]. The amorphous contribution has been described using the scattering of a pure amorphous collagen, and the Debye equation. This possibility is available in program FULLPROF [3] in which we have used six terms to fit the collagen contribution to the background. The possibility of perform a quantitative analysis in this kind of composite materials is analyzed. A structural study of several biological apatites from bones of humans and animals is presented.

[1] Ottani S., Riello P., Polizzi S., *Powder Diffraction*, 1993, 8, 149-154. [2] Smith V. H., Thakkar A. J., Chapman D. C., *Acta Cryst.*, 1975, A31, 391-392. [3] Rodríguez-Carvajal J., Roisnel T., FullProf.98: New Windows 95/NT Applications for Diffraction, *Newsletter N°20*, 1998.

Keywords: Rietveld analysis, biological apatites, amorphous compounds

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Structural Characterization of $\text{CdCO}_3\text{-CdS}$ by X-ray

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