

MS23-P13 Simulation of X-ray diffraction scattering for nanostructured aluminum oxides

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The metastable g-, h-, c-Al₂O₃ polymorphs prepared by low-temperature decomposition of the various aluminum hydroxides are the nanocrystalline systems with complex hierarchical nanostructure [1]. They are widely used as catalysts and supports. Therefore, the investigation of the relationship between physicochemical properties, atomic structure and nanostructure of materials is an actual problem.

However, the structure determination of alumina by the powder scattering data is a significant challenge due to the complexity of the diffraction patterns. Specific shape of primary nanocrystallites and their type of coherent ordering in the nanostructure are cause of significant and, moreover, anisotropic broadening of the diffraction peaks. The purpose of this report is the illustration of possibilities of the method associated with the creation of an nanostructured systems and the subsequent calculation of the diffraction pattern.

The method is based on the Debye equation and known in the literature as Debye Function Analysis (DFA) [2]. It is full-profile method which is applicable for any an arbitrary atoms collection, and therefore can be used for crystalline materials or nano-structured objects. The calculations were performed on the DIANNA program [3], which is public-domain software and available on the website: www.sourceforge.net/projects/dianna.

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Keywords: X-ray analysis, XRD, modeling, nanostructure, Debye scattering equation, DFA

MS23-P14 Structure determination of molecular nanocomposites by combining pair distribution function analysis and solid-state NMR

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Transparent mesoporous silica monoliths of well controlled porosity and a narrow pore size distribution around 6 nm have been used to elaborate sodium nitroprusside (SNP) nanocomposites. The obtained nanomaterials could be characterised using X-ray total scattering coupled to atomic pair distribution function analysis (PDF) and solid-state NMR spectroscopy. The PDF analysis allows for a structural description of the confined species as well as for the identification of various existing phases: SNP isolated molecules and SNP crystalline nanoparticles. The model obtained suggests that the nanocrystals have the same molecular structure as the bulk crystalline material and measure about 6 nm in diameter. This result is quite exceptional since the space available inside the pores is only about ten times the size of the molecules. The multi-nuclei Solid State NMR investigation confirms the structural model proposed by the PDF analysis and assigns the isolated molecules to dynamic disorder of a solvated phase. The latter approach additionally provides quantitative information on the relative ratio between the dynamic molecules and the rigid nanocrystals. This result is exploited to study the evolution of the two confined SNP phases with respect to solvating water molecules. We show that the confined SNP nanocrystals can be easily dissolved when storing the nanocomposites at increasing atmospheric relative humidity.

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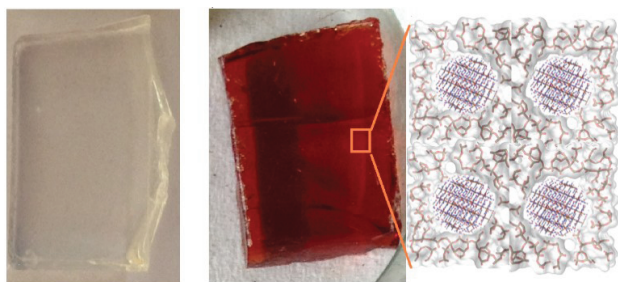


Figure 1. Photographs of transparent empty silica monolith (left) and SNP-silica nanocomposite (right) and schematic representation of encapsulated nanoparticles.

Keywords: total scattering, NMR, nanocrystalline material, molecular compounds

MS23-P15 Tailoring phase composition and microstructural features of $\text{Ba}_4\text{Nb}_2\text{O}_9$ polymorphs *via* thermal decomposition route

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Synthesis of nanoparticles with a controlled size has been found to be crucial for tailoring desired material properties since thermal, electric, optical, catalytic, and magnetic properties are strongly composition-, structure-, but also, size- and shape-dependent.^{1,2} It is well known that $\text{Ba}_4\text{Nb}_2\text{O}_9$ exhibits mixed electronic, oxide ion, and proton conductivity, which makes it especially attractive in the field of fuel cells, steam electrolyzers, and humidity sensors.³ Especially, the γ - $\text{Ba}_4\text{Nb}_2\text{O}_9$ phase exhibits several orders higher conductivity than α - $\text{Ba}_4\text{Nb}_2\text{O}_9$ due to a faster protonic and oxide ionic transport.^{3,4} Up to now, the γ polymorph was metastable at room temperature (RT) and so could be isolated only by quenching the sample from high temperatures, because slow cooling led to a transformation to α phase.³ In the present study the mixed Ba^{II} - Nb^{V} containing oxides were prepared using $\{\text{Ba}_2(\text{H}_2\text{O})_2[\text{NbO}(\text{C}_2\text{O}_4)_3]\text{HC}_2\text{O}_4\} \cdot \text{H}_2\text{O}$ as a single-molecular precursor.² A systematic study of preparation conditions was carried out, namely, tuning the final structural and microstructural parameters by (i) the holding time (2, 1 and 0.5 h) at 1175 °C and (ii) the cooling rate (3, 7 and 12 °C min⁻¹) from 1175 °C back to RT. Nanocrystalline products obtained by thermal decomposition of the precursor were investigated by X-ray powder diffraction at RT. Size and strain analysis were obtained in the course of the Rietveld refinement. Since all samples prepared by a cooling rate of 12 °C min⁻¹ contained only the γ - $\text{Ba}_4\text{Nb}_2\text{O}_9$ polymorph, it was evident that faster cooling prevented the $\gamma \rightarrow \alpha$ phase transition, which resulted in the retention of the high-temperature γ - $\text{Ba}_4\text{Nb}_2\text{O}_9$ phase at RT. Shortening of the time period for which γ - $\text{Ba}_4\text{Nb}_2\text{O}_9$ containing samples were held at 1175 °C had no impact on their phase composition. All samples were found to be strain free. Crystallite sizes were ~20 nm for γ - $\text{Ba}_4\text{Nb}_2\text{O}_9$ prepared with a holding time of 2 h while it decreased to ~5 nm with shortening of the holding time to 0.5 h.

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Keywords: phase composition, size and strain analysis, Rietveld refinement