MS23-P16 Facile route for preparation of nanocrystalline $ZnMn_2O_4$: effect of preparation conditions on structure and microstructure

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Traditional synthesis of spinel materials such as solid-state route involving grinding and firing of a mixture of oxides, nitrates or carbonates which requires elevated temperatures and prolonged process times have been abandoned. Indeed, majority of papers on manganese spinels are focused on low cost preparation methods which proceed at moderate temperatures (600 °C) with enhanced reaction kinetics [1,2]. Interestingly, Liu *et al.* reported a room temperature route for preparation of AMn_2O_4 (A=Zn, Co, Cd) from metal acetates [3]. Although synthetic route proposed by Liu *et al.* represents a facile and very efficient route for low temperature synthesis of spinel materials, in order to utilize this route for the targeted design of nanomaterials it is necessary to establish, very precisely, correlations between specific preparation conditions (concentration of NaOH, aging period, and temperature of additional heat treatments), structure, microstructure and properties. Detailed structural investigation using X-ray powder diffraction (XRPD) and Raman spectrocopy have been carried out in order to correlate specific structural and microstructural features with changes in preparation conditions. $ZnMn_2O_4$ was prepared by precipitation with NaOH (c=0.25-0.8 M) from solution of Zn and Mn acetates. Also, sample obtained by 0.8 M NaOH was additionaly heat treated at T=300, 400 and 500 °C. Pronounced difference in crystallinity was observed with increase in concentration of NaOH. Based on the results of Raman spectroscopy a model described by the formula: $[Zn^{2+}_{1-x}Mn^{2+}_{x}]_{tetra}[Zn^{2+}_{x}Mn^{3+}_{2-2x}Mn^{4+}_{x}]_{octa}O_4$ has been proposed and tested upon structural data. It was shown, based on Rietveld structure refinement, that unit-cell constants as well as the inversion parameter of spinel lattice increase with the increase in temperature of thermal treatment.

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Keywords: manganese spinels, XRPD, microstructure

MS23-P17 Synthesis and characterization of ultrasmall zirconia particles prepared via nonhydrolytic route

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Zirconia has been applied to various fields in materials science due to its noteworthy electronic, mechanical and thermal properties. These properties become distinctive for ultrasmall particles which are neither that of atomic nor bulk characteristics[1]. Structure determination of ultrasmall nanoparticles is at the forefront of modelling their properties and is still at its infancy[2]. In order to help in getting their structural models it is crucial that we synthesize quality ultrasmall particles. However, synthesis of ultrasmall particles with good control over the size and phase purity is not easily done. One way is to use nonhydrolytric route which is advantageous in terms of purity and homogeneity[3]. In this work, we were able to synthesize well crystallized ultrasmall particles using a modified nonhydrolytic route without surfactants. Average structural and morphological characterizations via classical X-ray diffraction and transmission electron microscopy were done on the samples. Results show that we were able to manipulate the phase purity of our samples from dual phase to single phase. Also, we observed a good control over the size of our particles which are in the nanoscale range from ~5.0 to ~1.0 nm and appear to have a spherical shape. Furthermore, the modified nonhydrolytic approach allowed us to produce nanoparticles at low temperatures from ~210 down to ~100°C with good compositional purity. One of the reasons why we were able to achieve these results is due to the fine tuning of the ratio of precursors to adjust the alkalinity of the solution. Whereas the average structure of our ultrasmall particles is consistent to that of a tetragonal phase zirconia, the atomic-pair distribution function analysis reveal that the particles demonstrate local structural distortions to that of the ideal tetragonal phase zirconia.

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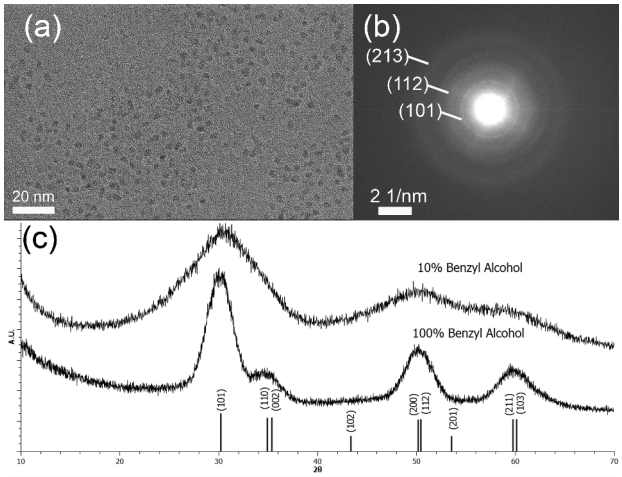

Figure 1. TEM image (a), selected area electron diffraction image (b) and XRD images of tetragonal phase zirconia (c) prepared via nonhydrolytic route

Keywords: ultrasmall, nanoparticles, nonhydrolytic sol-gel, zirconia, pair distribution function

MS23-P18 Combining fast-XANES and SAXS for time-resolved studies on the formation mechanism of iron oxide nanoparticles

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Iron oxide nanoparticles find application in different areas like sensing [1], catalysis [2], magnetic storage media [3], and biomedicine [4,5], due to their magnetic properties and environment-friendliness. Different synthesis routes are intensively studied, one of which is the co-precipitation. The synthesis is performed by precipitating the iron precursor in an alkaline, aqueous solution. Despite many studies based on *ex situ* investigations, information on the particles formation mechanism in the aqueous solution is still scarce [6,7]. Time-resolved *in situ* investigations allow to clarify the pathways and intermediates occuring during the formation. In the present contribution, we report on the *in situ* investigation of an iron oxide nanoparticle synthesis by coupled X-ray absorption near-edge structure (XANES) and small-angle X-ray scattering (SAXS) (Fig. 1). The combination provides simultaneously information about the size and shape of particles (SAXS) and on the oxidation state and the local structure of the iron atoms (XANES). The co-precipitation synthesis was exemplary studied, using a stabilization agent to decelerate the fast precipitation of the iron oxides. This allows to detect intermediates *in situ*. The measurements were performed using a custom-made acoustic levitator as sample holder. From the data, a mechanism was derived indicating different phases of particle formation and oxidation state changes. The information obtained provided the basis for an improved control of the product of the synthesis.

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