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Preparation and characterization of Sb₂S₃ nanorods and nano particles via hydrothermal condition.

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Single-crystalline antimony trisulfide (Sb₂S₃) nano materials with nano particle and rod-like morphologies were successfully synthesized via hydrothermal method by the reaction of antimony trichloride (SbCl₃) and carbon disulfide with high yield in 24h at 180 °C. The powder X-ray diffraction pattern shows the Sb₂S₃ crystals belong to the orthorhombic phase with calculated lattice parameters a=1.120nm, b=1.128nm and c=0.383nm. The quantification of energy dispersive X-ray spectrometry analysis peaks give an atomic ratio of 2:3 for Sb:S. Scanning electron microscopy (SEM) images show that diameter of Sb₂S₃ nano particles is around 80-150nm, and rod-like Sb₂S₃ possess a diameter around 70-140nm and length up to 3µm, respectively. X-ray powder diffraction, scanning electron microscopy, atomic force microscopy, optical measurements, UV-Vis analyses were used to characterize the products. UV-Vis analysis and emission spectra indicates that band gap of Sb₂S₃ is around 2.82eV, indicating a considerable blue shift relative to the bulk. The effects of reaction time and reaction temperature on the growth of nano materials with different morphologies were also investigated.

Keywords: antimony sulfide, nanorods, nano particles, Hydrothermal

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Synthesis of nanocrystalline intermediate phase between cancrinite and sodalite.

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Syntheses in the system Na₂O-SiO₂-Al₂O₃-Na₂CO₃-H₂O were carried out under various experimental conditions with the aim to synthesize nanocrystalline cancrinite, a mineral with zeolite-like behaviour.

After synthesis of a cancrinite reference from the educt zeolite A and well-known high-temperature conditions at 200°C, an aluminosilicate-gel was used to produce amorphous aluminosilicate precursor phases for crystal growth at 60°C. This low-temperature hydrothermal synthesis resulted in the formation of an intermediate phase between sodalite and cancrinite with one dimensional stacking disorder of aluminosilicate layers along the [001] direction, first described in [1]. A second series of syntheses with the addition of the Al³⁺-complexing additive triethanolamine (TEA) was performed to investigate the effect on crystal growth and structure-upgrade at 60°C [2]. Additionally the hydrothermal stability of the nanocrystalline intermediate phase was tested. Therefore the material was treated in water at 80°C for times up to 24h.

The products were analysed by FTIR-spectroscopy, X-ray powder diffraction and scanning electron microscopy.

Temperature dependent FTIR-spectroscopy as well as heating experiments in a muffle furnace up to 600°C and thermogravimetry (TGA) with differential-thermoanalysis (DTA) up to 1400°C supplied further informations.

The nanocrystalline intermediate phase shows interesting zeolitic behaviour. Properties like water content and thermal stability are higher than in pure-phase carbonate cancrinite, whereas the hydrothermal stability of the intermediate phase is less than those of the cancrinite-phase.

Furthermore the crystal growth under addition of TEA yield to formation of aggregates of nanocrystalline material of intermediate phase [3]. Beside the time dependent deceleration of nucleation of aluminosilicate by TEA a recrystallisation of big Na₂CO₃ crystals occurred. Later nanoparticle formation of the intermediate phase by heterogeneous nucleation on the surface of the Na₂CO₃ crystals is responsible for the aggregate formation (Fig. 1).

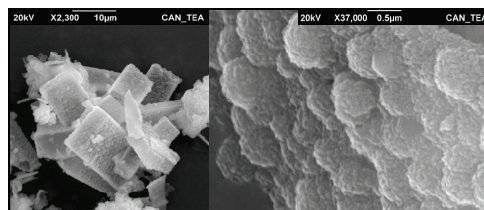


Fig. 1: Nanoparticles on Na₂CO₃-crystals, left: magnification 2300x, right: 37000x.

[1] Hermeler, G.; Buhl, J.-Ch.; Hoffmann, W. *Catalysis Today*, 1991, 8, 415. [2] Charnell, J.F. *J. Crystal Growth*, 1971, 8, 291-294. [3] Grader, C. *diploma thesis*, 2009, Institut für Mineralogie, Universität Hannover.

Keywords: nanocrystallites, intermediate zeolite, hydrothermal stability

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Hydrogen Thin structure of nano-dispersed powders of rare earth oxides and fluorides produced from amorphous precursors.

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The nano-dispersed rare earth simple oxides Lu₂O₃, Gd₂O₃, Y₂O₃, La₂O₃ and Eu₂O₃, garnets Y₃Al₅O₁₂ and Y₃Ga₅O₁₂, perovskites YAlO₃ and LaAlO₃, borates LuBO₃, GdBO₃ (Lu_xGd_(1-x))BO₃ and YBO₃, molybdate Eu₂(MoO₄)₃ and fluorides LuF₃ and Na₃Lu₉F₃₂ were produced by different methods.

X-ray investigations have shown that independently of synthesis method the first stages of crystallisation of such compounds are characterized by new three phenomena.

First phenomenon is the formation of very unusual two-phase state of simple rare earth oxides Eu₂O₃, Lu₂O₃, La₂O₃, Gd₂O₃, garnet Y₃Ga₅O₁₂ and Na₃Lu₉F₃₂ at early stages of the nanocrystallites formation. These phases are isomorphous and have different lattice parameters. Detailed x-ray investigations have shown that both phases are realized in the same crystallite. This two-phase state transforms then into one-phase state in process of growth of the dimensions of the crystallites. It permits us to conclude that along the early stages of nanocrystallization the nano-grains consist of surface and core phases. The surface phase has enlarged lattice parameters with

respect to core phase parameters. We pay your attention that the all listed compounds have cubic unit cells.

It is worthwhile to stress that we did not record the two-phase states in LuBO_3 and $\text{Eu}_2(\text{MoO}_4)_3$ in nano-dispersed state. We have realized such two-phase states in these compounds after a long grinding of micro-dispersed powders only.

The second phenomenon is phase reversibility. It means that the phase sequence known for macro-sized powders at increasing temperature is reversible for nano-sized grains. For example, for macro-sized powders of $\text{Eu}_2(\text{MoO}_4)_3$ low temperature phase is α -phase. It undergoes phase transition into β -phase at 800 C. In process of annealing of the precursor of $\text{Eu}_2(\text{MoO}_4)_3$ the phase sequence is as follows: β -phase \rightarrow α -phase \rightarrow β -phase again. The same is observed for LuBO_3 in process of annealing of the precursor: high vaterite phase \rightarrow calcite phase \leftrightarrow high vaterite phase again instead of the previously known sequence: calcite phase \leftrightarrow high vaterite phase.

The third phenomenon is the effect of acceleration of phase formation at lower temperature and for shorter time if temperature of the sample under synthesis is increased continuously. Such effect was observed in process of borates ReBO_3 and garnets $\text{Re}_3\text{M}_5\text{O}_{12}$ synthesis. It was established that the initiating effect of the continuous heating on synthesis of the garnets (which have only cubic structure for all Re-atoms) from amorphous precursor state is realized in acceleration of the synthesis of the compounds and fast growth of the dimensions of the formed crystallites from nano- to micro-sizes. For the borates which have a few different phases in dependence of the Re-atom used the continuous heating brings to formation together with equilibrium phase of the new phases known for other rare earth elements.

Keywords: rare-earth compounds, nanostructures, X-ray diffraction