

favourable method due to homogenous or heterogeneous chemical reaction through a highly controlled diffusion leading to the formation of high quality nanocrystals having desired size, shape, dispersability and properties. Several approaches have been adopted by researchers to control size, shape, dispersability and in turn the properties of materials. Amongst them selective doping, precursors used, surfactants, synthesis method, etc. are important ones. Surfactants also help in modifying the surface charge of nanocrystals, such that, the material becomes either hydrophobic or hydrophilic. Experiments were carried out at 150°C with autogeneous pressure over an experimental duration of 16 hours in General Purpose autoclaves provided with Teflon liners. A variety of organic and inorganic solvents (propanol, ethanol, HCl, NaOH, HF) and also various surface modifiers (oleic acid, gluconic acid, *n*-butylamine, hexaldehyde, and benzylaldehyde) were tried. ZnO was selectively doped with molybdenum, silver, niobium, and also co-doping with silver and chromium has been carried out. The products were freeze dried and subjected to a systematic characterization using powder XRD, FTIR, UV-Vis spectroscopy, Thermal analysis, SEM, TEM, and Photoluminescence spectroscopy. The powder x-ray data shows homogeneous resultant product with high crystallinity. The FTIR spectra show the presence of various functional groups depending upon the type of surface modifier used in the *in situ* surface modification. TGA curves show the release of hydroxyl, carbonates and other organic molecules up to 500°C. UV-VIS spectroscopy study indicates the shift in the band gap depending upon the doping metal(s) and the band gap also shifts slightly accordingly. Photoluminescence spectra of pure and doped and surface modified ZnO nanocrystals show very interesting results which well correlates with the powder XRD and photocatalytic data. Higher concentration of dopants leads to structural distortion and contributes to the worsening of photocatalytic properties as well as lowering free exciton energy peaks. The application potential of products was evaluated using photocatalytic degradation of organic dyes and the ZnO nanocrystals synthesized are highly effective for the degradation of several toxic organic dyes.

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Growth of metal oxide – Organic hybrid nanocrystals and their interfaces in environmental applications

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Metal oxides, particularly TiO₂ and ZnO find extensive applications in modern technology including photocatalysis for environmental issues. Major breakthrough occurred during 1970s when Fujishima and Honda (1972) reported electrochemical photolysis of water at semiconductor electrode (TiO₂) [1]. With the discovery of quantization effect during the late 1970s, the size reduction in metal oxide semiconductors became a major objective to achieve higher efficiency in their applications. Difficulties in the growth of metal oxide nanocrystals were associated with the control of size, morphology, coagulation, reproducibility of results and dispersability. During 1990s several such attempts were made on the use of organic molecules as ligands or capping agents or surfactants. Also *ex situ* surface modification was tried with limited success. Thus an alternate route was envisaged to obtain high quality nanocrystals of TiO₂ and ZnO with controlled size, morphology,

dispersability and without any coagulation using *in situ* surface modification through Hydrothermal, Solvothermal and Supercritical hydrothermal routes [2]. The size could be reduced significantly to a few nanometers without any coagulation and the organic coating was so much uniform and thin, that did not alter the inherent properties of metal oxide core. The organics which are insoluble and exist as separate phases under ordinary conditions became homogeneous phases under hydrothermal / solvothermal conditions. The small size and high surface to volume ratio of the individual nanoparticles imparts distinct size tunable physical and electronic properties that have prompted some to refer to them as “artificial atoms” [3]. A highly controlled self-assembly of these hybrid nanocrystals when dispersed in organic solvents into two-dimensional and/ or three-dimensional ordered structures or super-lattice structures remains a relatively unexplored area. The mechanism of formation of organic-inorganic hybrid nanocrystals is very important. Here, theory of mechanism of the formation of organic-metal oxide interface has been discussed in detail with specific case studies. Another greatest advantage of such an *in situ* modification is that the nanocrystals surfaces could be made either hydrophobic or hydrophilic. The organics could be easily removed through sintering at around 500°C, such that crystals still remain as individual nanocrystals with controlled size and morphology. Experiments were carried out within the temperature range 150 – 250°C with autogeneous pressure. The run products were characterized using powder XRD, FTIR, UV-VIS, Positron annihilation lifetime and photoluminescence spectroscopy, TEM, SEM, etc. followed by a systematic evaluation of photocatalytic properties through degradation of toxic organic industrial effluents and waste. Thus the nanohybrid metal oxide crystals could be the most effective and prospective materials for environmental issues.

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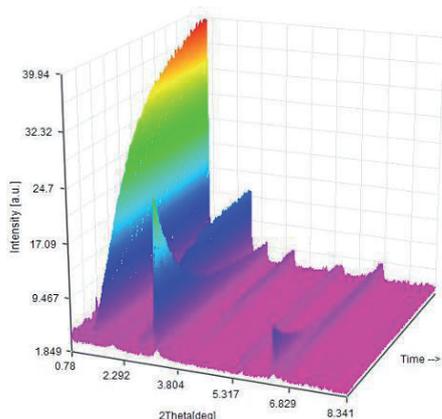
Study of the intercalation of organic molecules into Hydrotalcite by fast in situ XRPD

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A new mild and fast solid state [1] for the preparation of exchanged layered double hydroxide materials (LDH), in particular, for the intercalation of bioactive molecules was extended and adapted from the intercalation of phenylbenzimidazolsulfonic acid to two other kind of compounds. The chosen organic guest were 3-carboxy-coumarin and, given their importance, a series of non-steroidal-anti-inflammatory-drugs with different pka and steric hindrance; namely Ketoprofen, Flurbiprofen, Ibuprofen, and Tiaprofenic acid.

The mechanical mixture of the LDH-NO₃ and the guest compound was put in a capillary and then dampened with a drop of NaOH solution causing the intercalation to take place. The characterization of the

nanocomposites, carried out by crystallographic and thermogravimetric techniques, revealed that this synthesis yield is comparable to that of standard methods but with time, solvent, and energy saving advantages. Moreover, the in situ diffraction experiments allowed us to shed some light on the kinetics of the intercalation process with sub-second resolution and the parameters affecting the reaction.



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Crystallogenic Grounds of Isomorphism

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Crystallogeny of solid solutions (mixed crystals) should be singled out as a special field due to a complex of phenomena beyond the scope of an ordinary growth process and due to some problematic aspects like controlling isomorphous composition [1]. The principal specificity of mixed crystal formation (in contrast to that for crystals of a fixed composition) is a permanent exchange of isomorphous components between a crystal and solution, which accompanies any process. The mechanism is a combination of dissolution of unstable surface configurations with autoepitaxial overgrowth of stable ones; the appropriate surface spots spread on the surface in a manner of chaotic micro-mosaic. The monocrystallinity is kept due to the autoepitaxial overgrowth. Survival of stable surface configurations is the main factor of controlling crystal composition ("ensemble mechanism").

Such a process runs in two the ways dependently on the substance solubilities. A volume-deficit exchange runs when the crystal substance solubility is higher than the dissolved substance solubility. It is fast and causes implanting inclusions into a continuous crystal matrix (these are either inclusions of the medium solution in ternary systems or of solid phases in quaternary and more complex systems). A volume-excess exchange runs when the crystal substance solubility is lower than the dissolved substance solubility. It is slow and causes excrescences onto the crystal surface. The reaction runs by itself at isothermal conditions as well as in a combination with direct crystal growth at supercooling and with dissolution at overheating.

A metastable heterogeneous equilibrium between a crystal and compositionally foreign solution becomes settled at a supercooling of the value determined by the phase compositions (it should be noted that the quantitative indication of supersaturation is not available for such systems and using supercooling is needed). This is important factor for the component selection causing a tendency of a bimodal distribution

of precipitated units of nano- and micro-scales in composition, but the distributions are blurred due to a dispersion of local conditions. Different habits of overgrowing spots indicate a variation of their composition. Such spots are buried under new layers causing a chaotic isomorphous inhomogeneity of the bulk that is typical for such crystals.

Compositions of spontaneously precipitated crystals are also of a bimodal distribution, which character depends on supercooling in spite of supercooling does not effect on the total composition. Substantially, the bimodality is related to that of the precipitate distribution in grain sizes. This shows a complicated connection between crystal composition, supercooling and growth kinetics caused probably by an interaction of growth and isomorphous exchange as well as a solution inhomogeneity.

The described behavior of crystals was observed in situ and ex situ in numerous soluble ternary systems like $(\text{Pb,Ba})(\text{NO}_3)_2\text{-H}_2\text{O}$, $(\text{Co,Ni})(\text{NH}_4)_2(\text{SO}_4)_2\text{-6H}_2\text{O-H}_2\text{O}$, $(\text{K,Rb})\text{HC}_8\text{H}_4\text{O}_4\text{-H}_2\text{O}$, $(\text{Mg,Ni})\text{SO}_4\text{-7H}_2\text{O-H}_2\text{O}$, $\text{K}_2(\text{Cr,S})\text{O}_4\text{-H}_2\text{O}$, and $\text{K}(\text{Cl,Br})\text{-H}_2\text{O}$, as well as in quaternary ones $(\text{Co,Fe})\text{SO}_4\text{-7H}_2\text{O-NH}_4\text{SO}_4\text{-H}_2\text{O}$ and $\text{K}_2(\text{Cr,S})\text{O}_4\text{-KCl-H}_2\text{O}$. Methods of optical microscopy, atomic force microscopy, X-ray microtomography, X-ray diffractometry, microprobe analysis were used. Concentration phase diagrams were modified into nomograms for the interpreting basis.

To a conclusion, the presented concept is a substantial part of the crystal growth generalization for polyphase systems [1].

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Anomalous structure and structure reconstructions 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 Lu_2O_3 , Gd_2O_3 , Y_2O_3 , La_2O_3 and Eu_2O_3 , garnets $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Y}_3\text{Ga}_5\text{O}_{12}$, perovskites YAlO_3 and LaAlO_3 , borates LuBO_3 , GdBO_3 , LaBO_3 and YBO_3 , molybdates $\text{Eu}_2(\text{MoO}_4)_3$ and $\text{Gd}_2(\text{MoO}_4)_3$ and fluorides LuF_3 and $\text{Na}_5\text{Lu}_9\text{F}_{32}$ were produced from amorphous precursors. X-ray investigations have shown that independently of precursor method synthesis the first stages of crystallisation of such compounds are characterized by new four phenomena.

First phenomenon consists in formation of very unusual two-phase state in simple rare earth oxides R_2O_3 , garnet $\text{Y}_3\text{Ga}_5\text{O}_{12}$ and $\text{Na}_5\text{Lu}_9\text{F}_{32}$ at early stages of the nano-crystallites formation. These phases are isomorphous and have different lattice parameters. Detailed x-ray and high resolution electron microscopy investigations have shown that both phases are realized in the same crystallite and correspond to surface and core phases. The surface phase has enlarged lattice parameters with respect to core phase parameters. This two-phase state transforms then into one-phase state in process of crystallites growth. Such two-phase states was also produced in micro-dispersed LuBO_3 and $\text{Eu}_2(\text{MoO}_4)_3$ after a long milling of the powders.

The second phenomenon is phase reversibility. It means that the phase sequence known for macro-sized powders at temperature increasing 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