Growth process of methane hydrate from D_2O ice powder was measured under pressurized CH_4 gas by in situ neutron powder diffraction. We used HRPD and HERMES [1] at JRR-3 in Japan. To avoid melting ice, the CH_4 gas was gradually applied at 240 K as an isothermal process. The diffraction peaks of methane hydrate were observed at 2 MPa. The pressure was kept at 2 MPa for several hours. After that, the pressure was increased until 6 MPa. However, the growth rate of methane hydrate did not change. Accordingly, the pressure did not affect the growth rate under the sufficient pressure for the crystal growth. Following, the temperature was changed under nearly isobaric process (6-7 MPa). When temperature was changed from 265 K to 270 K, an increase of the growth rate was observed. At 275 K, the D_2O ice was melted and the growth rate drastically increased. After 4 hours, almost all of the D_2O ice was changed to methane hydrate. As a result, temperature is more effective parameter for the crystal growth of methane hydrate. Moreover, we will discuss the size effect of ice grain.

[1] K. Ohoyama, T. Kanouchi, K. Nemoto, M. Ohashi, T. Kajitani, Y. Yamaguchi: Jpn. J. Appl. Phys. Vol37(1998)3319-3326.

Keywords: crystal growth, neutron powder diffractometry, *in situ* observations

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Abiotic growth and biological dissolution of pyrite surfaces

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The relevance of microbial pyrite oxidation processes has resulted in a large number of studies by which microbial oxidation of Bacteria and Archaea were experimentally examined. Because pyrite is a potential, nontoxic candidate for photoelectrochemical and photovoltaic applications, it is important to know how the surfaces of pyrite can be controllably altered. Natural pyrite crystals are often impure, thus, the synthesis of high quality pyrite single crystals is of interest. A potential technique to synthesize pyrite single crystals is the CVT- technique. With this technique it was possible to produce crystals with edge lengths of up to 8.5 mm and habits of up to five forms ({100}, {111}, {210}, {211}, and {221}). The composition and stoichiometry of the crystals were observed near to ideal FeS_2 (S : Fe = 1.98(8)) and studies of the topography of crystal surfaces indicated the high quality of the synthesized crystals. To enhance our understanding of effects of pyrite dissolution mediated by Archaea and various influence parameters (time, temperature, crystallographic orientation surfaces), etching experiments on synthetic pyrite crystals were performed. As biological oxidants two archaeal strains, namely Metallosphaera sedula and Sulfolobus metallicus, were employed. Studies with Scanning Electron Microscopy (SEM) showed cell attachment and etching effects during the whole time period. Surface alteration forms features up to several tens of microns in size, while the shape of the features varies with face-symmetry and edges of etch pits follow distinct directions. However, control experiments with abiotic oxidants showed, that the shapes of the euhedral etch pits are similar, but smaller in sizes, indicating a higher dissolution rate for microbial than abiotic etching.

Keywords: growth from gaseous phase, dissolution etch phenomena, biological activity

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Synthesis and structural characterization of ZnO deposited by chemical bath

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Thin films of zinc oxide (ZnO) were deposited on glass substrates by chemical bath deposition technique (CBD), varying the contents of nitrate zinc ($Zn(NO_3)_2$) and thiourea ($(NH_2)_2CS$) in the bath solution . The deposition temperature was 80 ℃ keeping constants the pH value, volume, deposit time and mechanical stirring speed. The samples were characterized by X-ray diffraction (XRD) and transmittance. By X-ray is found that the material is polycrystalline with a Wurzita type structure and with a preferential crystallographic direction (100) for smaller amounts of $Zn(NO_3)_2$, while for larger amounts of $Zn(NO_3)_2$ the material presents a preferential crystallographic direction (002), also the diffractograms show that the presence of thiourea stimulates the reaction desired between precursors. By transmittance is found that with a larger amount of Zn $(NO_3)_2$ the material presents a tendency to increase its energy band gap.

Keywords: semiconductor thin films, zinc oxide, chemical deposition of oxides

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Influence of bath composition in structure of ZnO deposited by microwave activated chemical bath

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ZnO films were deposited on glass substrates by microwave activated chemical bath deposition technique (MW-CBD), varying the composition of the bath in the relationship 1:1, 1:2, ... 1:10 of $(Zn(NO_3)_2$:$CO(NH_2)_2$, while the reagents that makes the solution become basic are maintained constant as well as the power and time deposit. Samples were characterized by X-ray diffraction (XRD), photoluminescence and transmittance; XRD diffractograms show that material is polycrystalline, hexagonal wurzite type, and the lattice constants and the unit cell volume increases as relationship is varied from 1:1 to 1:10. Furthermore, the samples show a preferential orientation along the c-axis indicated by the intensity of 002 reflection, the same was observed in the residual powder of the reaction that was not deposited on substrate. Photoluminescence spectra show a yellow-red emission of deep-levels related to defects, but there is not significant variation due to relationship of precursors.

Likewise, the results of the transmittance indicate that the optical energy bandgap is constant for all reactions with a value about 3.29 eV.

Keywords: chemical bath deposition, ZnO, semiconducting materials

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Hydrothermal synthesis of doped ZnO and its application in photodegradation of toxic amaranth dye

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The semiconductors like TiO_2 and ZnO when illuminated under UV or sunlight produce electrons and holes. At the surface these electrons reduce adsorbed oxygen and the holes oxidize organic compounds or adsorbed water molecules. This property can be used to disintegrate toxic organic compounds and treat industrial effluents efficiently for environmental issues. Here, the author reports the synthesis of ZnO under mild hydrothermal conditions (Temperature =150℃, Pressure = Autogenous, Duration = 24 hrs). Several active metals like tungsten, molybdenum, chromium, manganese, etc., was doped in a ratio 1, 3, 5 and 10 %. The compounds synthesized were characterized using powder X-ray diffraction (XRD), Fourier infrared spectroscopy (FTIR), photoluminescence and scanning electron microscopy (SEM). The photodegradation property of these compounds was testified by the degradation of Amaranth Dye of different concentration under both sunlight and UV light. The effect of various parameters such as initial dye concentration, catalyst loading, pH of the medium, source and intensity of illumination on the photocatalytic degradation of Amaranth dye using ZnO doped with various metals were investigated. The photodegradation efficiency of these compounds was calculated by percent transmission (%T) and chemical oxygen demand (COD). The reduction in the COD values and the increase in the %T of the treated dye revealed the complete destruction of the organic molecules present in the Dye. The results obtained are highly encouraging and further work is being carried out for the use of these photocatalytic compounds for other toxic organic decomposition.

Keywords: mild hydrothermal synthesis, toxic organic compounds disintegration, photocatalysis

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Structural characterization of nanostructures hierarchical rare earth doped ZnO colloids

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In the last years, rare earth doped nanometric semiconductors have shown a increased interest in the field of optical communication, phosphors, photonic crystals, displays, etc. In materials science, the properties of the obtained material strongly depends on the synthesis method, requiring a strictly characterization of the obtained material in order to understand the relevant condition that leads to the optimal properties desired. Rare earth doped ZnO was obtained by hydrothermal process and the resulting structures were characterized by X-Ray Diffraction (XRD), Low Angle X-Ray Diffraction (LAXRD), Field Effect Scanning Electron Microscopy (FE-SEM) and Extended X-ray Absorption Fine Structure (EXAFS). The results show an complex hierarchical structure composed by nanobuilding blocks of doped ZnO without phase segregation. The self assembly of this nanocrystals generates a monodisperse colloids that orders in colloidal crystals. A deeper discussion of the results will be show.

Keywords: colloidal crystals, nanoestructured, hierarchical

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Crystal growth peculiarities of new oxide conductor $La_2Mo_2O_9$ in the system La_2O_3 - MoO_3

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$La_2Mo_2O_9$ (LM) is known as a new oxide conductor owing to the potential application as the solid electrolytes. At the phase transition at 580°C cubic phase $P2_13$ turns into monoclinic polar phase $P2_1$ at room temperature. This allows to suppose that the nature of this transition may be ferroelectric-ferroelastic. For study of such properties reasonably large crystals could be obtained. The main goal of this research was the growth of LM crystals in the system La_2O_3 - MoO_3. This task was difficult due to high liquidus temperatures, incongruent melting, and instable growth. As LM melts incongruently, the flux method with spontaneous crystallization in alumina crucible was used. The reagents (La_2O_3 annealed obligatory at 1000°C, MoO_3) were extra pure grade. For each crystal growth run the melt content, eutectic and liquidus temperatures, cooling rate, temperature gradient, the temperature of the crystal nucleation and the morphology of the obtained crystals have been determined. Cooling rates were in the range 0.3-3.0 grad/h at the maximum temperature 1350°C.The known diagram La_2O_3 - MoO_3 have been refined by the crystal growth experiments. The LM crystals have morphologic peculiarities connected with the significant supercooling of the melts. Polycrystalline plates at the melt surface and dendrite-like crystals in the volume of the melt are observed. Attempts to modify the melt by doping (Nd, Zn, B, Ca) were ineffective. Plates consisted of several single crystal grains with sizes near 5x5x3 mm. LM single crystals of such size were obtained for the first time. The work was supported of the grant RFBR No 07-02-00180.

Keywords: crystal growth from solution, $La_2Mo_2O_9$, phase diagrams