with others indicating larger spacing. Samples reach in PCL (% ≥ 80) exhibit also smaller spacings. Examination of SAXS curve for clay intercalated PHB suggests the existence of thin platelets, constituted by single layers or a stacking of few layers. No evidence of similar behavior has been observed in NC prepared with other polymers proportions, in spite of the observed improvement of their characteristics.

[1] A. Botana et al. *Applied Clay Science* **2010***, 47,* 263–270. [2] S. S. Ray & M. Bousmina, *Progress in Materials Science* **2005***, 50,* 962–1079.

Keywords: Biodegradable polymers, Polimers Clay Nanocomposites

MS74.P31

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MEM electron density study of $NaGaH_4$

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The search for hydrogen storage materials has received massive attention during the past decade in hope that hydrogen, in the future, may replace fossil fuels as energy carrier. Among the considered compound, it is worth mentioning $NaGaH_4$ that is formed of almost isolated GaH_4^- anions and spherical Na^+ moieties. It has about 4.2 wt% hydrogen, therefore not fulfilling the requirements for being a candidate hydrogen storage material for mobile applications. However, the compound reveals peculiar structural features that deserve further examination. In particular, a phase transition around 280 K has been pointed out by an anomaly in heat capacity measurements. [1] XRPD analysis likewise revealed a discontinuity in atomic displacement parameters when going from low to high temperatures. [2] V. P. Tarasov et al., on the basis of NMR data, implied that the phase transition can be attributed to changes in the orientation state of the distorted $Ga(H,D)_4^-$ anion. [3] Despite all the hints of a phase transition, structural knowledge is still lacking.

We studied $NaGaH_4$ in the temperature range 90 K – 390 K by synchrotron X-ray powder diffraction data collected at SPring8, Japan. Complementary synchrotron neutron powder data were collected at PSI, Switzerland, on the deuterated sample, $NaGaD_4$. For each of the considered temperatures, the Maximum Entropy Method (MEM) is utilised to maximise the information contained in the extracted structure factors and to determine the corresponding electron density. The MEM charge density at 90 K (fig. 1) is analysed within the quantum theory of atoms in molecules, [4], and compared to theoretical charge density obtained from periodic ab initio DFT calculations.

The Rietveld refinements and MEM densities of $NaGaH_4$ and $NaGaD_4$ do not show any apparent, structural indication of the expected phase transition. A possible explanation is provided by Raman scattering studies which imply a symmetry reduction with increasing temperature. [5] This is supported by structural NMR results which up to the phase transition demonstrate a temperature movement towards axial symmetry for the GaH_4 tetrahedron. [3] Therefore, starting from the *Cmcm* space group (63) of $NaGaH_4$, we explored its maximal non-isomorphic subgroups through Rietveld refinements of the 300 K neutron and X-ray data. Of the symmetry reduced space groups, $P2_1/m$ (11) is the only one capable of describing the structural NMR results.

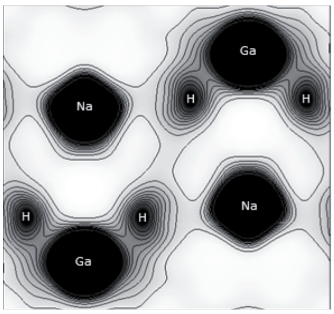

Figure 1 (200) contour plot of the MEM charge density of $NaGaH_4$ at 90 K. The density starts at 0.4 eÅ^{-3} and has contour level 0.1 eÅ^{-3}.

[1] V.E. Gorbunov et al., *Zh. Neorg. Khim.* **1982**, *27*, 1915-1920. [2] A.V. Irodova et al., *Zeitschrift Fur Physikalische Chemie Neue Folge* **1989**, *163*, 239-242. [3] V.P. Tarasov et al., *Russ J Phys Chem B* **2007**, *1*, 653 – 660. [4] R.F.W. Bader. *Atoms in Molecules: An Quantum Theory.* **1990**, Oxford University Press. [5] K.S Gavrichev, *Inorg Mater* **2003**, *39*, 89-112.

Keywords: maximum entropy, hydrogen storage, powder diffraction

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Controlled annealing of nanocrystalline Y_2O_3

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Well crystallized cubic Y_2O_3 turns out to be an excellent material for calibration purposes in powder diffraction. In various respects it clearly supersedes the well established standard materials Silicon (SRM 640d) [1] or Lanthanum hexaboride (SRM 660b) [2]. On the other hand Y_2O_3 is a well known and commercially available nanomaterial. We have studied two different batches (30 – 50 nm and <50 nm nominal particle sizes) with respect to time- as well as temperature dependence of annealing process. Heat treatment was performed in platinum crucibles in air. Special care was taken to keep conditions for both samples most consistent. Powder diffraction patterns were taken in transmission mode using a Huber G670 Guinier camera applying Cu-$K_{\alpha 1}$ radiation. Modelling of peak shapes along with derived lattice parameters are critically evaluated. Clearly such evaluation needs to keep in mind that applicability of standard powder diffraction methods on nanocrystalline materials is controversially debated [3].

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[1] SRM 640d; *Silicon Powder Line Position and Line Shape Standard for Powder Diffraction*; National Institute of Standards and Technology; Gaithersburg, MD **2010**. [2] SRM 660b; *Lanthanum Hexaboride Powder Line Position and Line Shape Standard for Powder Diffraction*; National Institute of Standards and Technology; Gaithersburg, MD **2010**. [3] B. Palosz, E. Grzanka, St. Gierlotka, S. Stelmakh, *Z. Kristallogr.* **2010,** *225,* 588–598.

Keywords: nanocrystal, yttrium oxide

MS74.P33

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Preparation and structural characterization of HFMOD-WO_3 thin films

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Tungsten oxide films have been successfully deposited by hot-filament metal oxide deposition (HFMOD) technique under atmospheric pressure and an oxygen atmosphere. Although several techniques were used to characterize the WO_3 layers, this work emphasizes the results obtained by X-ray diffraction and Raman spectroscopy. The chemical stoichiometry was determined by X-ray photoelectron spectroscopy (XPS), obtaining WO_3. By X-ray diffraction obtained that the as-grown WO_3 films present mainly the crystalline phase monoclinic, whose lattice parameters values: *a*= 3.8465 Å, *b*= 7.5449 Å, *c*= 7.3066 Å, β= 90.924°. The Raman spectrum of the as-deposited film shows intense peaks at 801, 710, 262 and 61 cm^{-1}, which are typical Raman peaks of crystalline WO_3 (m-phase) that correspond to the stretching vibrations of the bridging oxygen, which are assigned to W-O stretching (ν) and W-O bending (δ) modes respectively. Annealing WO_3 thin films at the temperatures range from 100 to 500ºC during 10 min in a nitrogen atmosphere; they changed of crystalline phase about 300ºC of monoclinic to orthorhombic, which was corroborated by X-ray diffraction and Raman spectroscopy

Keywords: vibrational, dispersion, X-ray

MS75.P01

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Atomic diffusion in liquid B_2O_3 under pressure from *ab initio* molecular dynamics

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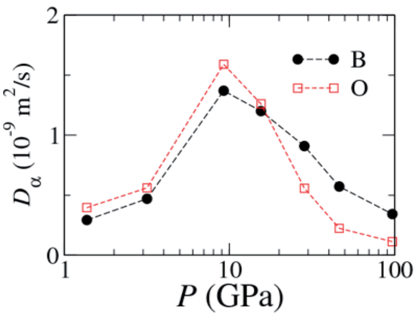
Transport properties of covalent liquids under pressure are very interesting in the sense that they show unexpected pressure dependence. For a number of covalent liquids, such as SiO_2 and GeO_2 the diffusivity of atoms was shown to increase with pressure. It is, however, unclear how the rearrangement process of the covalent bonds is affected by compression.

In order to clarify the microscopic mechanism of atomic diffusion in covalent liquids under pressure, we performed *ab initio* molecular dynamics simulations for liquid B_2O_3 which is a typical covalent liquid.

Figure shows the calculated diffusion coefficients D_α for α=B and O atoms as a function of pressure. Clearly, liquid B_2O_3 has a diffusion maximum around 10 GPa. The decrease in the diffusivity above a certain pressure is not surprising but quite natural. It is, however, unusual that the diffusivity of O atoms is reduced more quickly than that of B atoms with compression above 10 GPa.



We discuss the microscopic origin of this anomalous pressure dependence of the diffusivity. Around 10 GPa, covalent bonds are always exchanged by concerted reaction while the non-bridging oxygens (NBO) are needed for atomic diffusion at ambient perssure. These facts suggest that the atomic diffusion with concerted reaction gives the diffusion maximum. At about 100 GPa, almost all B atoms are overcoordinated to O atoms while only 2/3 O atoms are overcoordinated to B atoms. This asymmetry property gives rise to difference in the pressure dependence of the diffusivity. These dynamic properties under pressure will be commonly observed in other covalent liquids, such as SiO_2.

Keywords: ab initio molecular dynamics, high-pressure physics, covalent liquids

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Is there a phase transition between the two liquid states in tin tetraiodide?

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We have reported that in tin tetraiodide there are two liquid states, which are two thermodynamically stable counterparts of the metastable amorphous solid states [1]. This finding was established by in-situ synchrotron x-ray diffraction measurements, which were carried out under high pressures up to about 4 GPa.

However, no clear-cut experimental evidence has been obtained as to the existence of phase transition between the two liquid states, although the mean-field theoretical analyses of the experimental findings based on both Son-Patashinski's [2] and Franzese-Stanley's [3] models support the existence of a first-order transition [4].

In order to clarify the point, a close examination was made around the region in question in the temperature-pressure phase diagram. This includes in-situ measurements of structure and density using synchrotron x-ray diffraction and absorption. Variation of the local structure, which is characterized by a suitably defined local order parameter, showed a smooth behavior with pressure, implying a gradual change in the *local* structure. However, a jump, though very subtle, in the density variation on compression was detected at around 970 K and 1.5 GPa, just above the break point in the melting curve of the low-pressure crystalline state. The result is to be reconfirmed in the near future.

We have also examined on the theoretical side the Son-Patashinski model in some detail. To go beyond the mean-field calculations, the effects of fluctuations on the stability of the phases were investigated using a lattice version of the model. The transition between the two liquid phases was, unlike mean-field's prediction, found to be smeared out partially by the finite size effects of the system. To extract the exact nature of the transition, which the model possesses, the multicanonical ensemble simulations are currently in progress.

In conclusion, there is a phase transition between the two liquid states in tin tetraiodide, but the transition is of weak first order.

[1] K. Fuchizaki, T. Hase, A. Yamada, N. Hamaya, Y. Katayama, K. Funakoshi *J. Phys. Chem.* **2009**, *130*, 121101. [2] L. Son, G. Rusakov *J. Phys.: Condens. Matter* **2008,** *20*, 114108. [3] G. Franzese, H.E. Stanley *J. Phys.: Condens. Matter* **2007,** *19*, 205126. [4] K. Fuchizaki, T. Hase, N. Hamaya, Y. Katayama to be published.

Keywords: phase, liquid, pressure

MS75.P03

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Structure of liquid transition metal hydrogen alloys under high pressure

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Hydrogen reacts with many metals and form metal hydrides. In transition metal hydrides, hydrogen atoms usually occupy interstitial sites and the crystalline lattice expands. Though there are many studies on crystalline metal hydrides, almost nothing is known about liquid