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MEM electron density study of NaGaH₄
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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 NaGaH₄ that is formed of almost isolated GaH₄ 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 NaGaH₄ 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, NaGaD₄. 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 of NaGaH₄ 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 refinement and MEM densities of NaGaH₄ and NaGaD₄ 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.

Keywords: Biodegradable polymers, Polymers Clay Nanocomposites

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Controlled annealing of nanocrystalline Y₂O₃
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Well crystallized cubic Y₂O₃ 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 Y₂O₃ 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-Kα 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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Keywords: nanocrystal, yttrium oxide

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Preparation and structural characterization of HFMOD-WO₃ thin films

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 WO₃ layers, this work emphasizes the results
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Atomic diffusion in liquid $\text{B}_2\text{O}_3$ 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 $\text{SiO}_2$ and $\text{GeO}_2$, 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 $\text{B}_2\text{O}_3$, which is a typical covalent liquid.

Figure shows the calculated diffusion coefficients $D_i$ for $i=\text{B}$ and $O$ atoms as a function of pressure. Clearly, liquid $\text{B}_2\text{O}_3$ 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 pressure. 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 asymmetric 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 $\text{SiO}_2$.

Keywords: vibrational, dispersion, X-ray

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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 pressure 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.


Keywords: phase, liquid, pressure

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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