Pressure-induced B1-B2 phase transition in AgX: revisited
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A large number of known AB compounds adopt the B1 (NaCl) structure. Under pressure, most of them transform to the B2 (CsCl) structure directly or via intermediate phase(s). The computational investigations suggest that the dense B2 phase is favored at high pressure for silver halides with the B1-structure (AgX; X=Cl, Br and I). The experimental studies have shown that AgCl transforms from B1 to B2 at 17 GPa, 200 °C [1]. In-situ X-ray work [1] showed two intermediate phases existing between the B1 - B2 phase transition in AgCl, with the structure of KOH and TII, respectively. As for AgBr and AgI, both are known to undergo B1- KOH-type structural transitions [2] in the pressure range between 13 - 16 GPa. In this study, we extended the experimental conditions to higher pressure to investigate the phase transitions in AgBr and AgI and to find out if they share the same topological transition as AgCl under high pressure.

The silver halides were studied in the diamond anvil cell (DAC) by angular dispersive X-ray powder diffraction technique. The high-pressure phase transformations of AgCl, AgBr and AgI were investigated up to 28, 41 and 56 GPa, respectively. In AgCl, a phase transition sequence B1 → KOH → TII → B2 was observed at high pressure, room temperature. The pathway of transformations in AgBr was found to be B1→ (unknown phase) → KOH → TII at high pressure. The “unknown phase” observed in AgBr was found for the first time and has been detected in three consecutive runs carried out in this study. At 35.5 GPa, we applied the laser heating (estimated temperature ~ 500 °C) and found that TII-phase AgBr maintained the same structure type (TII). For AgI, the KOH-type high-pressure phase was observed up to 27 GPa. Upon further compression to the pressure of 56 GPa, and after annealing by laser heating (estimated temperature ~ 500 °C), AgI did not transform to the B2 phase. Based on the current experimental results, we conclude that the topological transition of B1-KOH-TII-B2 type AgCl can be achieved by applying pressure along. The occurrence of the TII phase in AgBr at high pressures, shows that the structural transition sequence of B1-B2 in AgBr is similar to the one found in AgCl. Yet, an additional new low-pressure phase is found to exist in AgBr between the B1 and KOH phase.

Computational studies confirm the same transition sequence for the B1-B2 transition of AgI [3]. Within the experimental data resolution, KOH-type AgI is identified to be stable up to 27 GPa, at least. Compared with AgCl and AgBr, the stability range of the KOHI-type AgI is surprisingly wide, an effect which has also been noted in the computational study [3]. However, our X-ray diffraction data of AgI above 40 GPa do not confirm the TII structure type, which was predicted to be the stable polymorph in the computational studies [3].

In general, the transition pressures of this multiple series of solid-solid phase transformation are increasing with decreasing ionicity of this series of AgX compounds. The ionicties for AgCl, AgBr and AgI are 0.869, 0.847 and 0.775, respectively. The predicted pressures to reach the stability region of the B2-type structures for AgBr and AgI are above 35 GPa [4] and 105 GPa [5], respectively.

Keywords: high-pressure, phase transitions, alkali sulfides

Polymorphism of 1,4-diazabicyclo[2.2.2]octane complexes with HI and HBr
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Materials with dielectric constant exceeding 1000 are most coveted for electronic applications in miniature devices. Such properties are exhibited by ferroelectric relaxors, which are mainly the doped lead-containing perovskite ceramics. Therefore organic relaxors are sought, which would be easier in production and more environment friendly: less energy is required for their production and deposition on substrates and they are easier for disposal. Most recently the giant dielectric response was found in NH2–N bonded 1,4-diazabicyclo[2.2.2]octane hydroiodide (dabcoHI) and hydrobromide (dabcoHBr) [1, 2].

A multitude of new polymorphs of dabcoHI has been obtained at elevated pressure and temperature [3]. The crystal symmetries identified for the nonsolvated dabcoHI crystals so far are: P6n2, Pbcn, Pmcn2, Pnn2, Cmnn2, P2c. In all the structures determined by X-ray diffraction, the arrangement of the poly-cationic chains and iodide anions, and in the conformation of dabco cations. When crystallized from methanol, up to 1.70(5) GPa dabcoHI forms unsolvated crystals, and at higher pressure solvates could be obtained only.

Only three phases of dabcoHBr could be obtained: phase I (Pca21), phase II (Cmc21), and phase III (Pbn2). The NH2–N hydrogen bonded chains, which are characteristic for all dabcoHI structures, are present only in phase II of dabcoHBr. In phases II and III they are broken and NH2–Br ionic pairs are formed. Moreover, pressure 1.30 GPa led to N-methylation of dabco.

Keywords: hydrogen bonding, phase transition, high pressure

Amorphization in rare earth tungstates with modulated scheelite-type structure under pressure
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**MS40.P15**


**MS40.P16**


**MS40.P17**

MS40.P18  
Non ambient crystallographic studies of dithienylethene optical molecular switches  
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Dithienylethene compounds are of significant interest due to their photochromic properties. These compounds undergo electrocyclic ring closure and opening reactions when irradiated and are stable to thermal reversion and fatigue, making them ideal for applications within the area of the molecular memories and switches [1]. More recently interest has developed with regards to their solid state properties, demonstrating interesting and unique behaviour for photochromic compounds such as capacity for single crystal transformations between the open and closed form and the ability to exert mechanical force upon an object upon irradiation [2-3].

Therefore we report the structures of a series of new dithienylethene based systems and report on their solid state behaviour, demonstrating several reversible single crystal to single crystal transformations to high levels of conversion. We also report an investigation into the behaviour of four dithienylethenes under elevated pressure, ranging from 0 to 10 GPa in the single crystal and report interesting changes in conformation and intermolecular packing forces.


Keywords: photochromism, photochemistry, pressure,