to occur, the band maximum showing a non-linear blue shift with pressure.

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Keywords: high-pressure, phase transitions, alkali sulfides

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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 ℃ [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 TlI, 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 → TlI → B2 was observed at high pressure, room temperature. The pathway of transformations in AgBr was found to be B1→ (unknown phase) → KOH → TlI 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 ℃) and found that TlI-type AgBr maintained the same structure type (TlI). 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 ℃), AgI did not transform to the B2 phase. Based on the current experimental results, we conclude that the topological transition of B1-KOH-TlI-B2 type AgCl can be achieved by applying pressure along. The occurrence of the TlI 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 KOH-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 TlI 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 ionicities 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.

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Keywords: high pressure, phase transition, silver halide

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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 $NH^{+}\cdots N$ 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 nonslovated dabcoHI crystals so far are: *P*6*m*2, *Pbcm*, *Pmc*2_1, *Pmm*2, *Cmm*2, *P*2/*c*. In all the structures determined by X-ray diffraction linear or nearly linear chains of cations are linked by $NH^{+}\cdots N$ hydrogen bonds. The main structural differences between the polymorphs are in 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 (*Pca*2_1), phase II (*Cmc*2_1) and phase III (*P*6*m*2). The $NH^{+}\cdots N$ hydrogen bonded chains, which are characteristic for all dabcoHI structures, are present only in phase III of dabcoHBr. In phases II and III they are broken and $NH^{+}\cdots Br$ ionic pairs are formed. Moreover, pressure 1.30 GPa led to N-methylation of dabco.

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Keywords: hydrogen bonding, phase transition, high pressure

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Amorphization in rare earth tungstates with modulated scheelite-type structure under pressure

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In this study we investigate the α-phases of La, Ce, Pr and Nd tri-tungstates under high pressure. These compounds showed amorphization when they are under pressure, which is partially reversible when the pressure is released, as in the α-phases of Nd, Tb and Eu molybdates [1]. High-pressure powder X-ray diffraction experiments have been performed at room temperature in the MALTA X-Ray Diffractometer (Xcalibur from Oxford Diffraction, Universidad Complutense de Madrid). The samples have been prepared by a conventional solid-state reaction of La_2O_3, $Ce_2(CO_3)_3$, Pr_6O_{11}, Nd_2O_3. In this work, we have applied a new alternative method for treating distorted structures by means of symmetry mode analysis (for the displacively distorted α-phase from the tetragonal scheelite structure) performed using the program AMPLIMODES, developed in the Bilbao Crystallographic Server [2], and the Rietveld refinement of the amplitudes of such symmetry modes using the Fullprof program [3]. The proposed studies have been complemented with theoretical *ab initio* total-energy calculations where we have obtained an anomalous expansion of the cell parameters.

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MS40.P18

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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.

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Keywords: photochromism, photochemistry, pressure,

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Investigating the Structure of $BaTiO_3$ using Pair Distribution Function Analysis of High Energy X-ray Scattering Data

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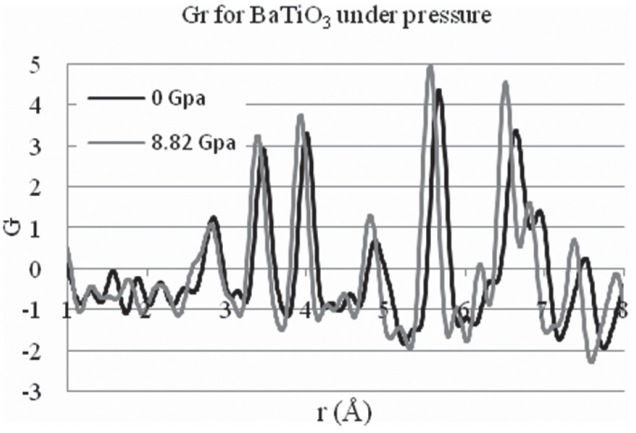
Barium titanate ($BaTiO_3$) is a perovskite ferroelectric oxide that undergoes phase transitions under changes in pressure. It has been one of the most exhaustively studied ferroelectric materials since its discovery, and many would consider it the prototype. At room temperature and pressure it possesses a tetragonal structure, which arises due to the elongation of the cubic unit cell along the [001] direction. At high pressures, $BaTiO_3$ undergoes a phase transition to what is generally believed to be a cubic structure. There is some debate on the exact structure of this high pressure phase and the exact transition pressure; this is because spectroscopic signals indicating the Ti atom is still off the ideal position persist even though no distortion can be measured in the unit cell parameters.

In this work we are using the pair distribution function (PDF) analysis method to further study these phase transitions. The PDF is obtained *via* the Fourier transform of the total scattering pattern and yields more information than standard Rietveld analysis as Bragg and diffuse scattering are analysed together without bias, revealing the short and intermediate range order of the material regardless of the degree of disorder. PDF analysis has been used to study the structure of Barium Titanate over a range of pressures around the expected phase transition from tetragonal to cubic structures.



Keywords: high-pressure, phase transition, pair distribution function.

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Modeling of disorder in $BaThF_6$: anharmonic displacement parameter from high-pressure data

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Binary and ternary fluorides with the tysonite structure are extensively studied due to their superionic conductivity [1,2] and their optical properties in the presence of rare earth elements [3]. They