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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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Keywords: hHigh pressure amorphization, rare earth tungstates

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,

MS40.P19

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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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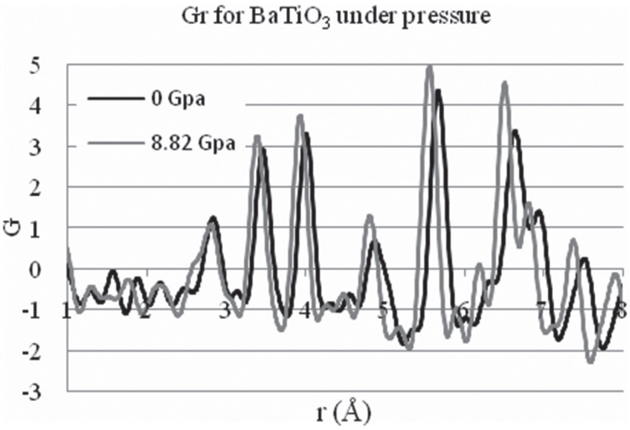
Barium titanate ($BaTiO_3$) is a perovskite ferroelectric oxide that undergoes phase transitions under changes in pressure. It has been one of the most exhaustively studied ferroelectric materials since its discovery, and many would consider it the prototype. At room temperature and pressure it possesses 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.

MS40.P20

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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 are used as solid electrolytes in chemical sensors, fluorine sources and batteries [4]. In particular, it has been shown that Ce-activated scintillators, show very good combinations of stopping power, speed, and luminosity and as a consequence there is a continued search for improved host crystals for the Ce activation [5]. Ternary fluorides M(II)ThF$_6$ (M=Cd, Ba, Hg, Pb) have been identified to be good candidates for such applications [6].

We have investigated the structure of BaThF$_6$ as a function of temperature and pressure with single-crystal x-ray diffraction using synchrotron radiation [7]. The compound crystallizes in the tysonite structure, space group P6$_3$/mmc (a = 4.296(1) Å and c = 7.571(1) Å), at ambient conditions. It is stable at least down to 150 K and up to 4 GPa. In this range of pressures and temperatures, the fluoride is characterized by a high degree of disorder, both on the cationic and anionic positions. Despite the different valence states and sizes, both cations, Ba^{2+} and Th^{4+} occupy the same crystallographic site in the ideal tysonite structure.

The cationic disorder is described by two alternative approaches. The first model corresponds to a split-atom position model in which Ba^{2+} is maintained on a special position with site symmetry -6m2, while Th^{4+} is slightly displaced from the respective position. In the second model, both cations are maintained on the ideal position and anharmonic displacement parameters using a tensor of third order are introduced. Anharmonic displacement parameters could be refined not only from low temperature data, but also from high-pressure single-crystal x-ray data measured *in situ* in a diamond anvil cell. Our results have shown that the sinθ/λ diffraction limit reached in high-pressure experiments is crucial for the successful application of the anharmonic approach. The feasibility and general problems of anharmonic refinements of high-pressure x-ray data will be further commented.

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Keywords: anharmonicity, pressure, fluoride

MS40.P21

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High pressure structure of Mn$_2$(CO)$_{10}$: an *off-axis* M-M bond

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The bond between transition metals has always attracted structural chemists, because of the intriguing features that characterize this interaction. In particular, Mn-Mn bond in Mn$_2$(CO)$_{10}$ is one of the most characterized, because of the historical importance of this molecule [1]. Spectroscopic characterizations at high pressure have also been reported, suggesting the occurrence of a phase transition above 0.8 GPa producing a conformational change (from *staggered* to *eclipsed*) [2]. This transformation would be very similar to that we observed on species like Co$_2$(CO)$_6$L$_2$ (L=AsPh$_3$, PPh$_3$) [3].

However, periodic DFT calculations and X-ray powder diffraction are not in agreement with the reported interpretation of the Raman spectra. Indeed, no conformational change is observed on increasing the pressure, but a curious rotation of the two Mn(CO)$_5$ moieties, leading to an unprecedented Mn-Mn off-axis bond (the Mn-Mn bond does not coincide with the Mn-CO$_{\text{apical}}$ axis, as in the gas phase molecular structure, see the Figure). Interestingly, this molecular geometry can be anticipated also from diffraction at ambient pressure, because the molecule shows an incipient distortion. Single crystal data at high pressure are not possible, because the samples easily break upon application of the pressure.

Theoretical calculations within the interacting quantum atom approach are also used to discuss the new geometry.

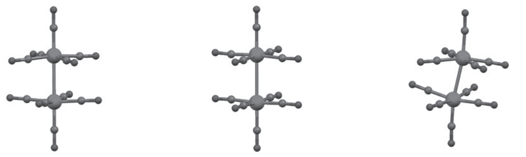

Figure 1. Left: the molecular conformation of Mn$_2$(CO)$_{10}$ at ambient condition (*staggered*). Centre: the molecular conformation at 3GPa as hypothesized from Raman spectroscopy (*eclipsed*). Right: the conformation of Mn$_2$(CO)$_{10}$ at 3GPa from P-DFT theoretical predictions and XRPD experiments.

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Keywords: metal-metal bond; high pressure; X-ray diffraction

MS41.P01

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Atomic polarization and multipolar model

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When a molecule is placed in an external electric field, its electron distribution changes in response. A useful measure of this effect is the molecular dipole moment together with its first and second derivatives (polarizability, hyperpolarizability). Using the QTAIM theory [1] it is possible to decompose the dipole moments and the polarizabilities into the atomic components. It was previously discussed [2] that each atomic contribution can be expressed as the sum of "atomic polarization" and "charge transfer" contributions. The transfer contribution is given by the weighted translation vector from atom's nucleus to the corresponding BCP, its sign and value strongly depend on the nature and number of bonded groups to the selected atom.

Here we present the relationship between the charge density distribution, obtained with the use of multipole model of Hansen and Coppens [3], and electric properties such as electric dipole moment, as well as the response of a molecule to the external electric field in simple organic molecules. It is well established that the multipolar reconstructed electron density (XD2006 [4]) can provide sufficiently accurate electric moments of a molecule in the crystal, however our preliminary results show that this does not hold for derivatives of the electric moments. In particular, while the bond polarity term is sufficiently well reconstructed (at least at zero field), the atomic polarization term is more problematic, even without the application of an external electric field. Empirical methods to estimate the polarizability based on the zero field electron density distribution will be tested, in order to allow estimation of linear optic properties from a multipolar model.