

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 $M(\text{II})\text{ThF}_6$ ($M=\text{Cd}, \text{Ba}, \text{Hg}, \text{Pb}$) 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 $P6_3/mmc$ ($a = 4.296(1) \text{ \AA}$ and $c = 7.571(1) \text{ \AA}$), 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 $\sin\theta/\lambda$ 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

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High pressure structure of $\text{Mn}_2(\text{CO})_{10}$: 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 $\text{Mn}_2(\text{CO})_{10}$ 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 $\text{Co}_2(\text{CO})_6\text{L}_2$ ($\text{L}=\text{AsPh}_3, \text{PPh}_3$) [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 $\text{Mn}(\text{CO})_5$ moieties, leading to an unprecedented Mn-Mn off-axis bond (the Mn-Mn bond does not coincide with the Mn- $\text{CO}_{\text{apical}}$ 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.

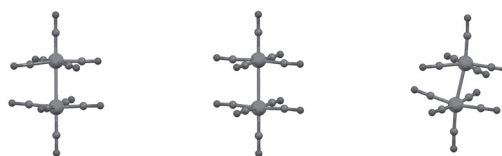


Figure 1. Left: the molecular conformation of $\text{Mn}_2(\text{CO})_{10}$ at ambient condition (*staggered*). Centre: the molecular conformation at 3GPa as hypothesized from Raman spectroscopy (*eclipsed*). Right: the conformation of $\text{Mn}_2(\text{CO})_{10}$ at 3GPa from P-DFT theoretical predictions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

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

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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.

Poster Sessions

[1] R.F.W. *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, **1990**. [2] T.A. Keith *Atomic Response Properties in The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design*; C.F. Matta, R.J. Boyd, Eds., Wiley-VCH, Weinheim, **2007**. [3] N.K. Hansen, P. Coppens, *Acta Crystallogr.* **1978**, *A34*, 909-921. [4] A. Volkov, P. Macchi, L.J. Farrugia, C. Gatti, P. Mallinson, T. Richter, T. Koritsanszky, *XD2006* **2006**.

Keywords: atomic polarizability, multipolar model, linear optic properties

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Charge-density studies of a new class of high performance NLO materials

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The current optoelectronics industry is highly motivated to finding new non-linear optical (NLO) materials since they are key to advanced display technologies, telecommunications and the laser industry. Organic NLO materials are attractive due to their large NLO response and fast response time. Despite the importance of the organic NLO chromophores, progress has been hampered by the incremental or serendipitous methods by which new classes of organic NLO materials have been discovered. Chance findings have had essentially random origins, while traditional NLO materials design methods are based on iterative chemical substitutions of an *a priori* known NLO active organic molecular framework. A new systematic approach to discover NLO materials was proposed by our group, which employs data-mining techniques combined with quantum mechanical calculations [1]. Two independent search strategies were implemented in this data-mining method, each predicting the best organic NLO materials and producing a ranked list of NLO response. Both approaches search a representative set of organic chemical space based on the Cambridge Structural Database (CSD). The CSD houses the world's repository of all published organic crystal structures. The backbone of 2,4,5,7-tetranitrofluorenes (TNFs) was one of the several promising structural motifs discovered in this prediction work and furthermore, their predicted NLO properties were among the highly-ranked. This study focuses on the experimental validation of the TNF derivatives.

TNFs are two-dimensional structures composed of *meta*-substituted strong electron-withdrawing nitro groups, connected to the fluorene backbone. Seven TNF derivatives with different electron-donating groups were studied here. Topological analysis of the molecular electronic structure and charge transfer dynamics were investigated by means of charge density studies: firstly, high resolution X-ray diffraction data were obtained from synchrotron-based diffractometer (BM01A, ESRF, France); secondly, complementary neutron diffraction was employed to locate the hydrogen positions and their hydrogen bonding network. Lastly, the neutron determined atomic positions and the scaled thermal factors for hydrogen were then used for the X-ray multipolar refinement. In order to compare the charge density analysis with the NLO response (hyperpolarizability, β), optical experiments based on hyper-Rayleigh scattering (HRS) technique [2] were carried out to characterise the absolute hyperpolarizabilities of the subject compounds.

The extended π -conjugation of the fluorene backbone and the donor-to-acceptor charge transfer process in these compounds were confirmed by charge density studies. The β obtained from charge density study are consistent with the HRS findings. All the subject compounds show very promising NLO responses which reflect on the success of the prediction work. In particular, the β_{HRS} of the compound,

1-methyl-2-((2,4,5,7-tetranitro-9H-fluorene-9-ylidene)methyl)pyrrolidine, is $1585 \pm 90 \times 10^{-30}$ esu, which is the largest value in this category reported to date.

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Keywords: charge density study, hyper-Rayleigh scattering, data-mining

MS41.P03

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Polytype of illite clays solved by charge flipping

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Polytypism is a common phenomenon in clay minerals. The identification of the polytype of illite clays by powder X-ray diffraction is often depended upon the diagnostic reflections, e.g. pair reflections 20-4 and 204 of $2M_2$ illite separating from 11-5, 02-5 and 023 reflections of $2M_1$ illite, pair of 114 and 11-4 of $2M_1$ differing from -112 and 112 of $1M$ illite. However, when other phase and multi polytypes present, these diagnostic reflections lose their brilliancy and the work for determining the polytype of clay sample becomes difficult. This study tries to use charge flipping [1] to reconstruct the 3-D map of the electron density for different polytypes of illite clays and from which the relative rotation ($n \times 60^\circ$) between two basic 2:1 layers could be observed and thus the polytype solution of illite clays can be made.

The Rietveld refinement is used for phase identification and quantitative evaluation. The result shows 75.4% of $2M_2$, 17.3% of $2M_1$ polytype illite and 7.4% of quartz presenting in sample HW-382 (GOF=2.84%). Le Bail fit [2] is well performed and GOF=1.73%. With the help of charge flipping algorithm [3], the 3-D electron density distributions of different illite polytypes are reconstructed. From the maximum electron densities, the corresponding coordinates of atoms in octahedral (M_1 -*trans* site and $M_{2,3}$ -*cis* site) are derived. The 60° rotation between adjacent M layers of $2M_2$ polytype illite (figure 1A) and the $2 \times 60^\circ$ rotation between adjacent M layers of $2M_1$ polytype of illite (figure 1B) can be observed. The distortional parameters $\tau=109.21^\circ$ and $\Delta z=0.378 \text{ \AA}$ indicate a little elongation and an out-of-plane tilting presenting along/in T sheet of $2M_2$ illite while $\tau=111.13^\circ$ and $\Delta z=0.236 \text{ \AA}$ render the thickening and tilting in T sheet of $2M_1$ illite.

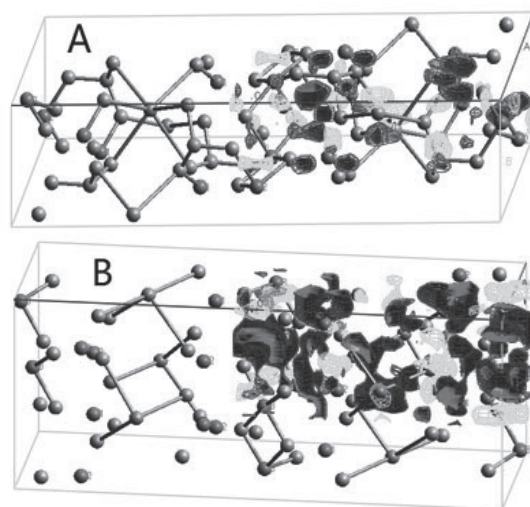


Fig. 1 Crystal structure of illite with 1/8 part overlapped with 3-D electron density distribution. A: $2M_2$ polytype; B: $2M_1$ polytype.