Interpreting and modelling trace element data requires quantitative information on how elements partition between coexisting mineral and melt phases, which in turn requires understanding of the mechanisms of trace-element incorporation. This goal can be achieved combining various experimental (X-ray diffraction, spectroscopic methods, microbeam analysis) and computational techniques. This combined multidisciplinary approach allows integration of structural information at both short- and long-range scale, and provides greatly enhanced interpretative and modelling tools for geochemistry and, in general, for material sciences. In fact, a correct model of the incorporation and local environment of dopants is crucial to interpret many technological properties and to design innovative materials. A number of case studies (mainly based on electron microprobe analyses, single-crystal and powder X-ray diffraction, XANES and EXAFS spectroscopy applied to natural and synthetic garnets) will be discussed. They mainly concern: i) changes in the local environment of cations along solid solutions; ii) multiple mechanisms of incorporation and partitioning of minor and trace elements in mineral structures with multiple sites with different coordination geometries.

Keywords: XRD, absorption spectroscopy, trace elements

MS10 INTEGRATED CRYSTALLOGRAPHIC, SPECTROSCOPIC, AND COMPUTATIONAL APPROACHES

Chairpersons: Andreas Roodt, Santiago Alvarez

MS10.24.1

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Time-resolved Photocrystallography of Short-lived Molecular Excited States

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Time-resolved photocrystallography is capable of providing atomic-resolution information on the nature of very short-lived transient species [1]. In its comprehensive application diffraction studies are combined with absorption and emission spectroscopy and parallel theory calculations. Several recent single-crystal results on triplet excited states, including large contractions up to 0.85Å in a binuclear Rh-Rh complex and in a Cu(I) pyrazolate crystal, the latter leading to excimer formation through transient intermolecular Cu···Cu bonding, will be presented. Parallel theoretical calculations give insight into the electronic nature of the excitations. It is evident from the completed studies that the effect of the crystalline environment has a constraining influence when large shape changes are predicted, but is much less severe when intramolecular contractions occur. As may be expected, the crystal structure becomes the determining factor when intermolecular excitations are taking place.

The field is to be extended to include study of excited singlet states with nanosecond lifetimes and monitoring of irreversible chemical reactions in crystalline materials. Modifications in the techniques needed to accomplish such studies will be discussed.

[1] Coppens P., *Chem. Commun.* 2003, 1317. [2] Coppens P., Gerlits O., Vorontsov I. I., Kovalevsky A. Yu., Chen Y.-S., Graber T., Novozhilova I. V., *Chem. Commun.*, 2004, 2144. [3] Coppens P., Vorontsov I. I., Graber T, Milan Gembicky M., Kovalevsky A. Yu., *Acta Cryst.*, 2005, A**61**, 162-172.

Keywords: time-resolved diffraction, photochemistry, theoretical chemistry

MS10.24.2

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Crystal Structure Prediction with WIEN2k

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The ground state properties of solids are calculated within density functional theory (DFT) using the WIEN2k code [1] that is based on the full-potential augmented plane wave (APW) method. From the total energy the relative stability of different structures can be compared. By minimizing the forces acting on the atoms we can optimize the atomic positions. For the relaxed geometry the electronic structure is known, from which properties and spectra can be calculated. Phonons can be obtained with a direct method, in which the dynamical matrix is derived from a set of forces that are created when a single atom is displaced along a symmetry-adapted direction in a supercell containing 60-100 atoms. From a limited number of such displacements the complete phonon spectrum can be derived.

Such calculations will be illustrated for $Y_2Nb_2O_7$ that (based on powder diffraction) was proposed to crystallize in the pyrochlore structure and experimentally was found to be an insulator [2]. DFT calculations would make it metallic but the phonons indicate an instability that leads to a significant distortion of the structure, in which it is an insulator. Another example is the ferroelectric phase transition that occurs in the Aurivillius compound $SrBi_2Ta_2O_9$. In this case three phonons, a combination of 1 hard and 2 soft phonon modes, are needed to describe this unconventional ferroelectric phase transition.

[1] Schwarz K., Blaha P., Madsen G.H.K., *Comp. Phys. Commun.*, 2002, **147**, 71. [2] Blaha P., Singh D.J., Schwarz K., *Phys. Rev. Lett.*, 2004, **93**, 216403.

Keywords: DFT, computation, band structure

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Correlation of Structures and Reactivity of Bispidine Coordination Compounds

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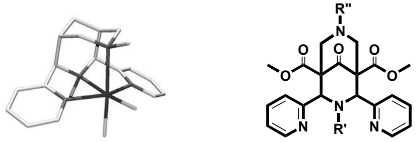
Bispidine-type ligands are relatively easy to synthesize, and a large number of tetra-, penta- and hexadentate ligands, including chiral and dinucleating ligands with a variety of donor groups are available (shown in the Figure is a tetradentate ligand and the simplified structure of the corresponding metal complex with two monodentate co-ligands).



The very rigid ligand structures and the elasticity of the coordination sphere, as well as the enforced octahedral geometry with two electronically and structurally distinct sites for substrate coordination lead interesting molecular properties: μ-peroxodicopper(II) complexes with dinucleating bispidine ligands are among the most stable examples known today, four coordination modes of catechol to copper(II) have been observed, structurally characterized and found to exhibit catechol oxidase activity, "Jahn-Teller isomers" have been observed and analyzed in detail, the iron(II)/H_2O_2 system is an efficient oxidation catalyst and various mechanistic pathways have been found and analyzed in detail. These and other properties are interpreted on the basis of X-ray data, DFT, MM and ligand field calculations, and the molecular properties are found to strongly correlate with specific structural parameters.

Keywords: catalysis, oxygen activation, structure correlation

MS10.24.4

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Structure of Halofullerenes Using Experimental and Theoretical Approaches

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Halogenated fullerenes are compounds of profound fundamental and practical importance. Investigation of these fullerene derivatives is complicated by the formation of compound and/or isomer mixtures. Theoretical calculations at the DFT level of theory allow a reliable prediction of relative energy, geometry, and spectroscopic properties of halofullerene molecules containing more than 100 atoms.

In the absence of experimental crystallographic data, a comparison of experimental and calculated IR spectra was indicative for a choice