

iodine atoms at vertex sites plus octupole-octupole interactions between the central tin sites. The simulations were performed under constant pressure and temperature conditions. Starting from the crystalline state in which the nearest molecules are in face-to-face configuration (type-I), the system was melted by heating. When melted, about the half of the molecular pairs is in vertex-to-face configuration (type-II), whose population increases with increasing pressure. Since the distance between the nearest intermolecular iodines is shorter in type-II than in type-I, polymerization is easier to occur on further compression in the liquid than in the solid in which all the molecules are in type-I. This is why the transition occurs at much lower pressure,  $\sim 1.5$  GPa, in the liquid state than in the solid state.

Keywords: liquid state, high pressure, molecular dynamics simulations

### P20.03.31

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#### Solid state reactions with photocrystallography

Stefanie Schiffers

University of Bath, Chemistry, University of Bath, Bath, Somerset, BA2 7BA, UK, E-mail: ss343@bath.ac.uk

X-ray crystallography is an important analytical method for the characterisation of molecules and array materials in the solid state, but until recently it has always been viewed as a static ground state technique. However, during the last decade, the methodology has developed so that techniques such as photocrystallography can be used to look at the structures of materials as they change. Photocrystallography is crystallography applied to photo-induced species. It combines spectroscopic and crystallographic techniques to allow the study of light-induced metastable and transient species. The technique can be used in single crystal or powder X-ray diffraction studies. Since the work of Schmidt, who established the principles for [2+2] photoreactions in the solid state, further research has commenced into the design of crystals, which then can readily undergo a reaction in the solid state. MacGillivray and coworkers have described a method for aligning alkenes in crystals with the help of a template. By developing this methodology further we have prepared a series of metal complexes with pyridylethylene derivatives as ligands. We now present an analysis of the solid state reaction of these complexes and of a series of coumarins using single crystal and powder diffraction methods. The research includes kinetic studies of the [2+2] photoreaction in solution and a comparison to that in the solid state. The effect of external changes on the systems, such as high pressure, has also been investigated. The first results that show the tolerance of systematically changing the dynamic equilibrium in these cycloaddition reactions is presented.

Keywords: high pressure crystallography, time-resolved analysis, solid state photochemistry

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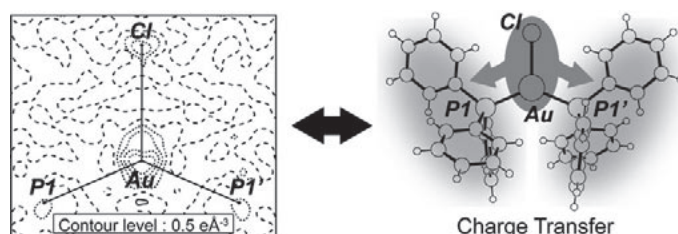
#### Different emission colors and photoexcited structures of [AuCl(PPh<sub>3</sub>)<sub>2</sub>] in two polymorphic crystals

Manabu Hoshino<sup>1</sup>, Hidehiro Uekusa<sup>1</sup>, Satoshi Ishii<sup>1</sup>, Takuhiro Otsuka<sup>1</sup>, Youkoh Kaizu<sup>1</sup>, Yoshiki Ozawa<sup>2</sup>, Koshiro Toriumi<sup>2</sup>

<sup>1</sup>Tokyo Institute of Technology, Department of Chemistry and Materials

Science, H-62, 2-12-1, O-okayama, Meguro-ku, Tokyo, 152-8551, Japan, <sup>2</sup>University of Hyogo, E-mail: mhoshino@chem.titech.ac.jp

[AuCl(PPh<sub>3</sub>)<sub>2</sub>] crystal (**1a**) shows green emission ( $\lambda = 510$  nm) by UV irradiation, which is related with shrinkage of all metal-ligand bond in photoexcited structure. However, the novel polymorphic crystal (**1b**) shows blue emission ( $\lambda = 470$  nm), indicating different photoexcited structure in **1b**. So, the photoexcited structure in **1b** was examined by X-ray structural analysis of the photo-stabled crystal. Diffraction data were collected at SPring-8 BL02B1, using the multiple-exposure IP method on the low-temperature vacuum X-ray camera. The photo-difference ( $F_{\text{on}} - F_{\text{off}}$ ) Fourier synthesis indicated that charges on Au and Cl atoms are decreased and no geometrical change occurred by photoexcitation. By comparison with the results of emission spectrum measurement and DFT calculation, these decreasing of charges around Au and Cl are due to charge transfer from the orbital around the Au-Cl bond to the electron-delocalized  $\pi^*$  orbitals in PPh<sub>3</sub> ligands. In summary, it has been revealed that the photoexcited structure of [AuCl(PPh<sub>3</sub>)<sub>2</sub>] in **1b** shows no geometrical change and has the charge-transferred nature, which leads blue emission.



Keywords: charge density distribution, photocrystallography, polymorphism

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#### Single crystal structure analysis of photo-excited state of halogen-bridged dicopper(I) complexes

Yoshiki Ozawa<sup>1</sup>, Shingo Yoshida<sup>1</sup>, Nobuyuki Kitayama<sup>1</sup>, Minoru Mitsumi<sup>1</sup>, Koshiro Toriumi<sup>1</sup>, Kiyoshi Tsuge<sup>2</sup>, Hiromi Araki<sup>2</sup>, Yoichi Sasaki<sup>2</sup>

<sup>1</sup>University of Hyogo, Department of Material Science, Harima Science Garden City, Kamigori, Hyogo, 678-1297, Japan, <sup>2</sup>Hokkaido University, Sapporo, 060-0810, Japan, E-mail: ozawa@stkt.u-hyogo.ac.jp

Photo-luminescent halogen-bridged dicopper(I) complexes [Cu<sub>2</sub>X<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(L)]<sub>∞</sub> (L = 4,4'-bpy or pyz, X = I or Br) consist of {Cu<sub>2</sub>X<sub>2</sub>} planer units, which are bridged by diimine (L) ligands constructing infinite chain structures. The assignments of intense emission bands of these copper(I) compounds is the copper to ligand charge transfer (MLCT) states. We have tried to observe direct geometrical distortion of the complex by photo excited state crystallographic technique. We also have made the same experiments for discrete dimeric copper(I) complexes [Cu<sub>2</sub>I<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(L')<sub>2</sub>] (L' = Phpy, pyz) having similar metal-organic frameworks which show less luminescent performance. Single crystal X-ray diffraction experiments were performed by using the low temperature vacuum X-ray camera at SPring-8 BL02B1 beamline. Full intensity data of both under light irradiated by CW laser, and non-irradiated conditions were collected by multiple-exposure IP method. Photo-difference Fourier syntheses for the bipyridine complex show that a small portion of two Iodine atoms shift toward close to each other in the {Cu<sub>2</sub>I<sub>2</sub>} plane. Results of the least-square refinements of I and Cu

atom positions based on the response ratio show that there are 1.1 % excited-state species in the crystal in which the I-I distance (3.82(2) Å) is contracted from the ground states (4.41(1)Å). While in the case of the discrete dimer complex [Cu<sub>2</sub>I<sub>2</sub>(PPh<sub>3</sub>)(pyz)<sub>2</sub>], two iodine atoms tend to move out of the {Cu<sub>2</sub>I<sub>2</sub>} plane with opposite direction each other. This indicates that the {Cu<sub>2</sub>I<sub>2</sub>} rotates around an axis containing two Cu atoms. This variety of the motions of {Cu<sub>2</sub>I<sub>2</sub>} frameworks will be concerned with the geometry of the frame at the ground state and solid-state luminescent properties.

Keywords: synchrotron crystallography, photochemistry coordination compound, diffraction under non-ambient condition

## P20.07.34

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### Structural changes in YBaCo<sub>4</sub>O<sub>7+δ</sub> monitored by variable temperature neutron powder diffraction

Markus V. Valkeapää<sup>1</sup>, Stefan Norberg<sup>2,3</sup>, Sten Eriksson<sup>2</sup>, Steve Hull<sup>3</sup>, Samuli Rasanen<sup>4</sup>, Maarit Karppinen<sup>1</sup>, Hisao Yamauchi<sup>1,4</sup>

<sup>1</sup>Helsinki University of Technology, Department of Chemistry, P.O.Box 6100, TKK, Etela-Suomen laani, FI-02015, Finland, <sup>2</sup>Department of Environmental Inorganic Chemistry, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden, <sup>3</sup>ISIS Facility, Rutherford Appleton Laboratory, Didcot, Oxfordshire OX11 0QX, UK, <sup>4</sup>Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan, E-mail: markus.valkeapaa@tkk.fi

In 2006 it was reported that YBaCo<sub>4</sub>O<sub>7</sub> [1] (Y-114) is not oxygen-stoichiometric but absorbs oxygen up to  $\delta = 1.5$  and then releases it upon heating (even in O<sub>2</sub> atmosphere) in a single, sharp step below 400 °C [2]. The oxygen storage capacity of Y-114 substantially exceeds those for the known oxides; CeO<sub>2</sub>-ZrO<sub>2</sub>: 1.50 mmol-O/ g<sub>catalyst</sub> (500 °C) [3], Y-114: 1.88-2.82 mmol-O/ g<sub>catalyst</sub> (340 °C). By means of in situ X-Ray Diffraction the unit cell of the oxygen-rich phase was identified [4]. This cell (o) is a super cell of the parent cell (h) where  $a_o \approx \sqrt{3}a_h$ ,  $b_o \approx c_h$ , and  $c_o \approx a_h$ . This finding confirmed that oxygen absorption in Y-114 is, as expected, not based on a filling of crystallographic vacancies but rather an adaption of the structure to the increased temperature in presence of oxygen. These findings are confirmed in a very recent paper by Chmaissen et al. [5], where the determination and refinement of YBaCo<sub>4</sub>O<sub>8.1</sub> structure is reported for the first time. Here, we will present our results on structural changes during oxygen intake and release in YBaCo<sub>4</sub>O<sub>7+δ</sub> as monitored by variable temperature neutron powder diffraction.

[1] M. Valldor and M. Andersson, *Solid State Sci.* 4 (2002) 923.

[2] M. Karppinen, H. Yamauchi, S. Otani, T. Fujita, T. Motohashi, Y.-H. Huang, M. Valkeapää, and H. Fjellvåg, *Chem. Mater.* 18 (2006) 490.

[3] Y. Nagai et al., *Catalysis Today* 74, (2002) 225.

[4] M. Valkeapää, M. Karppinen, T. Motohashi, R.-S. Liu, J.-M. Chen, and H. Yamauchi, *Chemistry Letters*, 36 (2007) 1386.

[5] O. Chmaissen, H. Zheng, A. Huq, P.W. Stephens, and J. F. Mitchell, *J. Solid State Chem.*, 181 (2008) 664.

Keywords: neutron powder diffraction, variable temperature, oxygen absorption

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### Lattice parameter of microcrystalline gold in a broad temperature range

Wojciech Paszkowicz<sup>1</sup>, Roman Minikayev<sup>1</sup>, Pawel Piszora<sup>2</sup>, Michael Knapp<sup>3,4</sup>, Carsten Bähz<sup>5,6</sup>

<sup>1</sup>Institute of Physics, Dept of X-ray Studies, Lotnikow 32, Warsaw, Warsaw District, 02-668, Poland, <sup>2</sup>A. Mickiewicz University, Faculty of Chemistry, ul. Grunwaldzka 6, PL-60780 Poznań, Poland, <sup>3</sup>Institute for Materials Science, Darmstadt University of Technology, Petersenstr. 23, D-64287 Darmstadt, Germany, <sup>4</sup>CELLS-ALBA, Apartado de correos 68, E-08193 Bellaterra, Spain, <sup>5</sup>Forschungszentrum Dresden-Rossendorf, Postfach 51 01 19, D-01314 Dresden, <sup>6</sup>Hasylab at DESY, Notkestr. 85, D-22603 Hamburg, Germany, E-mail: paszk@ifpan.edu.pl

The physicochemical properties of gold make that, despite its low abundance and high price, this precious metal has a number of important applications in technology. Moreover, It is one of standards used in X-ray diffraction for pressure and temperature calibration. The accuracy of temperature calibration depends on the knowledge of temperature variation of lattice parameter. Accurate knowledge of lattice-parameter temperature dependence leads to determination of thermal expansion behaviour. Up to now there was no detailed study of the gold lattice parameter covering the low and high temperature range. In the present study, the lattice parameter and the thermal expansion coefficient for the microcrystalline gold polycrystals were studied in detail in the broad temperature range, 10 - 1050 K, using a powder diffractometer at the B2 beamline (DORIS III Synchrotron Ring, Hasylab, DESY). The apparatus configuration allowed for collection of data with high resolution and low background. The wavelength was calibrated in situ, using a diamond standard. A commercial micrometer-size gold powder was mounted within thin-wall capillaries. The experimental value of the measured lattice parameter at 300 K is 4.07818 Å. The study provides reliable data on lattice-parameter temperature dependence, as supported by the close agreement of the derived thermal-expansion data, and of the resulting value of Debye temperature, with those reported in literature.

Keywords: lattice parameter, thermal expansion, gold

## P20.10.36

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### Magnetic ordering in Dy<sub>1-x</sub>Ca<sub>x</sub>BaCo<sub>2</sub>O<sub>5.5</sub> for x = 0.0 and 0.1

Jens-Erik Jørgensen

University of Aarhus, Chemistry, Langelandsgade 140, Aarhus, Denmark, DK-8000, Denmark, E-mail: jens Erik@chem.au.dk

The crystal and magnetic structures of Dy<sub>1-x</sub>Ca<sub>x</sub>BaCo<sub>2</sub>O<sub>5.5</sub> for x = 0.0 and 0.1 have been studied by neutron powder diffraction in the temperature range from 20 to 365 K. The crystal structures of both compounds were found to be best described in space group *Pm3m* on a  $2a_p \times 2a_p \times 2a_p$  unit cells where  $a_p$  refers to the lattice parameter of the cubic perovskite unit cell. The *a*- and *b*-axes were found to decrease and increase abruptly between 315 and 350 K as the temperature increases and the unit cell volumes exhibit signs of excess thermal expansion in the temperature range from 260 to 315 K. Dy<sub>0.9</sub>Ca<sub>0.1</sub>BaCo<sub>2</sub>O<sub>5.5</sub> orders antiferromagnetically for  $T \leq 305$  K into a G-type magnetic structure with a  $2a_p \times 2a_p \times 2a_p$  magnetic unit cell. The magnetic behaviour of DyBaCo<sub>2</sub>O<sub>5.5</sub> was found to be more complex as it exhibits two magnetically ordered phases. DyBaCo<sub>2</sub>O<sub>5.5</sub> orders into a G-type magnetic structure at 260 and 290 K. A  $2a_p \times 2a_p \times 4a_p$  magnetic unit cell was needed for indexing of the magnetic