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Photoexcited state crystallography of luminescent hexanuclear d¹⁰ metal complexes

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Hexanuclear metal complexes of Cu(I) or Ag(I) [$M_6(R\text{-pyt})_6$] ($M = \text{Cu, Ag}$; $\text{pyt}^- = \text{pyridinethiolato}$) (Fig. 1) give intense luminescence under UV illumination in the solid-state. The nature of the emission has been assigned to a triplet multi-metal cluster-centered (^3CC) transition state like as in the halogen bridged Cu(I) tetranuclear cubane-like cluster complexes. [1,2] On the photo-excited states, the metal-cluster core is expected to be shrunk because of an electron migration to the CC orbital, that has a bonding-character. To figure out the photo-emission process by direct observation of the molecular distortion, we have performed single crystal X-ray structure analyses at the photo-excitation states.

X-ray diffraction experiments under photo-irradiation were performed at the SPring-8 BL02B1 station. A single crystal of the copper(I) complex with ethyl-pyridinethiole ligands [$\text{Cu}_6(\text{Et-pyt})_6$] ($\text{Et-pytH} = 6\text{-ethylpyridine-2-thione}$) was mounted on the vacuum camera at 25 K was used for X-ray diffraction data collection under UV laser (325/442 nm, 0.03/0.1 W) irradiation. Photo-difference Fourier syntheses at the section of the triangle Cu_3 plane perpendicular to the virtual 3-fold axis of the molecule show that two of three Cu atoms move toward to the remaining Cu atom (Fig. 2). This indicates that the contraction of Cu-Cu atomic distance will occur at the photo-excitation state resulting in shrinkage of the metal cluster core. We have also performed the same experiments for the silver complex [$\text{Ag}_6(\text{Et-pyt})_6$]. The observed peaks and holes of charge densities in the photo-difference Fourier maps are similar to that in the Cu crystal, although their amplitude is below the significant levels.

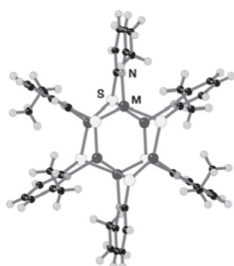


Fig.1

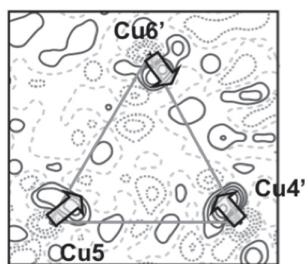


Fig.2

[1] H. Xie, I. Kinoshita, T. Karasawa, K. Kimura, T. Nishioka, I. Akai, K. Kanemoto, *J. Phys. Chem. B*, **2005**, *109*, 9339-9345. [2] P.C. Ford, A. Vogler, *Acc. Chem. Res.* **1993**, *26*, 220-226.

Keywords: photochemistry, accurate measurement, synchrotron radiation

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A-site ordered perovskite-structure oxides with functional properties

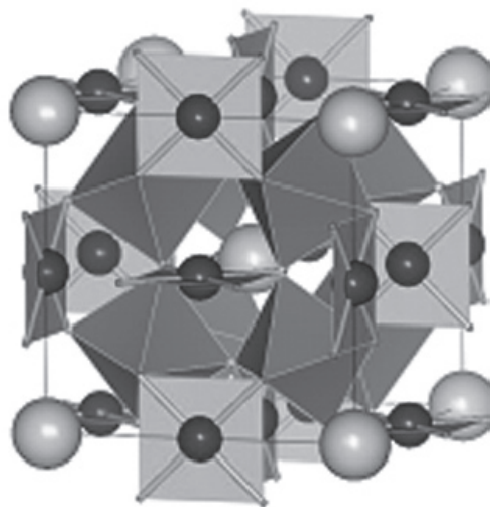
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A very unusual ordered arrangement of the A-site ions in the simple ABO_3 perovskite produces $\text{AA}'_3\text{B}_4\text{O}_{12}$ A-site ordered perovskites. The A site accommodates alkaline metals, alkaline-earth metals, and

lanthanides like those in the simple perovskites. At the originally 12-fold coordinated A' site, transition-metal ions such as Cu^{2+} and Mn^{3+} form square coordinated units that align perpendicular to each other. The presence of the transition-metal ions at both A' and B sites produces A'-A' and and/or A'-B interactions in addition to B-B interaction usually seen in the simple perovskite materials. Competitive and/or cooperative interplay of these interactions gives rise to diverse and intriguing physical properties [1].

Two new A-site ordered perovskite-structure oxides, $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ [2] and $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ [3], are highlighted. They were synthesized under high-pressure and high-temperature conditions. The compounds contain unusually high valence states of iron: Fe^{4+} in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{Fe}^{3.75+}$ in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. Instabilities of the high oxidation states at low temperatures are resolved in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ by charge disproportionation from Fe^{4+} to Fe^{3+} and Fe^{5+} , and in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ by charge transfer between A-site Cu and B-site Fe ions. The charge disproportionation and the charge transfer are accompanied by significant changes in structural, transport, and magnetic properties.

We also show a few examples of new A-site ordered perovskites with intriguing physical properties. $\text{BiCu}_3\text{Mn}_4\text{O}_{12}$ [4] is a ferrimagnetic metal. The half metallic nature of the material produces spin-polarized conduction electrons leading to large magnetoresistance under a low applied field. In $\text{CaCu}_3\text{Ge}_4\text{O}_{12}$ - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ - $\text{CaCu}_3\text{Sn}_4\text{O}_{12}$ system [5], we can see very unusual A'-site magnetism, in which either ferromagnetic or antiferromagnetic behavior of A'-site Cu^{2+} ($S = 1/2$) spins can appear within the same structural framework.



Crystal structure of A-site ordered perovskite

[1] Y. Shimakawa, *Inorg. Chem.* **2008**, *47*, 8562. [2] I. Yamada, *et al.*, *Angew. Chem. Int. Ed.* **2008**, *47*, 7032. [3] Y.W. Long, *et al.*, *Nature* **2009**, *458*, 60. [4] K. Takata, *et al.*, *Phys. Rev. B* **2007**, *76*, 024429. [5] Y. Shimakawa, *et al.*, *J. Phys. Soc. Jpn.* **2008**, *77*, 113702.

Keywords: A-site ordered perovskite-structure oxides, crystal structure, physical property

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Electron crystallography for li-based battery materials

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Knowledge of the structural behavior of Li-based battery materials at different stages of the charge/discharge cycle can be the key to understanding their performance. Unfortunately, often these materials are only available in nanoparticle form from electrochemical experiments, as polyphasic mixtures or they are only available in small quantities coming from electrochemical cells. This hinders the use of conventional powder X-ray or neutron diffraction, but not of transmission electron microscopy, which can be performed on nanoscale crystallites of the material. However, the conventional imaging techniques such as high resolution transmission electron microscopy and high angle annular dark field scanning transmission electron microscopy can rarely be applied to Li-containing compounds due to their high sensitivity to electron beam damage.

In this lecture, it will be demonstrated that precession electron diffraction can be successfully applied for the solution and refinement of the crystal structure of Li-based battery materials. As an example, the complete structural characterization of $\text{Li}_2\text{CoPO}_4\text{F}$ high voltage cathode will be shown, including the location of all Li atoms and the determination of their coordination environment.

Keywords: lithium batteries, precession, TEM

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Oxygen tilts against polar shifts in the multiferroic BiFeO_3

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Multiferroics which simultaneously display magnetic, dipolar and structural order parameters, are currently gaining more and more attention. Among them, BiFeO_3 (BFO) is the most promising for technology applications and fundamental interest since the polar and magnetic ordering coexist at room temperature.

In this talk after describing the complex situation for bulk BFO, we will focus on our recent results obtained on BFO thin films by combining experimental and theoretical approaches. Our BFO samples were synthesized on different [001]-oriented substrates like SrTiO_3 , DyScO_3 , LaAlO_3 , MgO , etc., allowing different mismatch and/or misfit strains. These samples were studied using advanced experimental techniques including high-temperature synchrotron and neutron diffraction, piezoforce microscopy, electron microscopy, hysteresis loop, Raman spectroscopy, ... In addition and for comparison, we also used first-principles approaches, including *ab initio* (LDA, GGA, +U) and effective Hamiltonian to study the impact of the misfit strain on the multiferroic properties and more precisely the consequences on the structure and the phase transitions.

Interestingly, our data demonstrate the key role played by the oxygen octahedra tilts, which are usually neglected, while this structural degree of freedom is very common to perovskite structure. Under strain, both the polar displacements and the oxygen tilts compete and we found that tilts fight against the polarization. This original finding allows explaining the weak experimental enhancement of the polarization reported in the literature. More surprisingly, our results show that the ferroelectric temperature T_C decreases dramatically with strain while Néel temperature T_N remains virtually constant. This is in contrast with the behaviour of standard ferroelectrics where strain increases the polar cation shifts and thus T_C . We argue that the anomalous strain effect on T_C is caused by an interplay of polar and oxygen tilting instabilities. Therefore, our findings reveal novel and original results bringing a comprehensive view which should be taken into account in a larger manner in multiferroic compounds as they

usually present oxygen tilts and also in any compound displaying the perovskite structure.

Keywords: multiferroic, BiFeO_3 , oxygen tilts

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Photorefractivity via linkage isomerism: from detecting small responses to engineering large ones

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Materials that exhibit photoinduced linkage isomerism have recently attracted considerable interest for their potential applications as holographic data storage media [1]. When these compounds are exposed to light, a ligand bound to the central metal ion responds by rotating to attach itself in a different coordination mode. The resulting photorefractivity, based on isomerisation rather than the Pockels effect, demonstrates unusual and potentially useful recording kinetics [2]. An important factor inhibiting further exploitation of these materials, however, is the limited amount of photoconversion generally achieved, with less than 20% conversion to the linkage isomer typical in many materials. Here we present recent developments in the detection of small photogenerated populations alongside results suggesting that steric hindrance from the crystal surroundings is an important reason for these limited photoconversion yields.

We focus on the $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{X}]\text{Y}$ family, where the *trans* ligand **X** and counterion(s) **Y** vary. At low temperatures, several members of this family exhibit photoinduced linkage isomerism of the SO_2 ligand to side- or *O*-bound geometries [3].

We present several new ways of probing the photoinduced structural changes in these compounds. First, when analysing single-crystal photocrystallographic data, model comparison using Bayesian statistical techniques can confirm the presence of small minority metastable state populations. As an example, it provides evidence for the *O*-bound MS1 state at 100 K, newly reported elsewhere, in the compound $\text{X} = \text{H}_2\text{O}$, $\text{Y} = (\pm)\text{-camphorsulfonate}_2$ [4]. Second, XANES experiments at the Ru $L_{2,3}$ edges provide clear evidence of photoexcitation even in a material ($\text{X} = \text{pyridine}$, $\text{Y} = \text{chloride}_2$) of which single crystals were not available, and in samples of dubious crystallinity.

Finally, we show that DFT models of steric hindrance can help to rationalise the relative populations of different metastable geometries achieved at a given site. These calculations corroborate the differences observed between the Ru sites in a material with $Z' = 2$ ($\text{X} = \text{isonicotinamide}$, $\text{Y} = \text{tosylate}_2$) [5].

[1] J.M. Cole, *Z. Kristallogr.* **2008**, 223, 363–369. [2] M. Fally, M. Imlau, R. A. Rupp, M.A. Ellabban, T. Woike, *Phys. Rev. Lett.* **2004**, 93, 243903. [3] A.Y. Kovalevsky, K.A. Bagley, P.J. Coppens, *J. Am. Chem. Soc.* **2002**, 124, 9241–9248; A.Y. Kovalevsky, K.A. Bagley, J.M. Cole, P.J. Coppens, *Inorg. Chem.* **2003**, 42, 140–147; K.F. Bowes, J.M. Cole, S.L.G. Husheer, P.R. Raithby, T.L. Savarese, H.A. Sparkes, S.J. Teat, J.E. Warren, *Chem. Comm.* **2006**, 2448–2450. [4] A.E. Phillips, J.M. Cole, T. d'Almeida, K.S. Low, *J. Am. Chem. Soc.* **2011** (in preparation). [5] A.E. Phillips, J.M. Cole, T. d'Almeida, K.S. Low, *Phys. Rev. B* **2010**, 82, 155118.

Keywords: photorefractivity, linkage isomerism, detectability