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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.

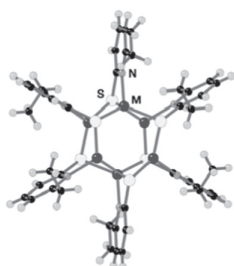


Fig.1

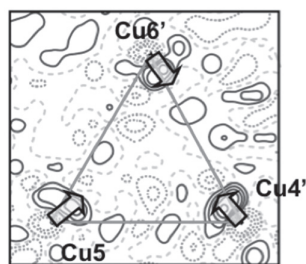


Fig.2

[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

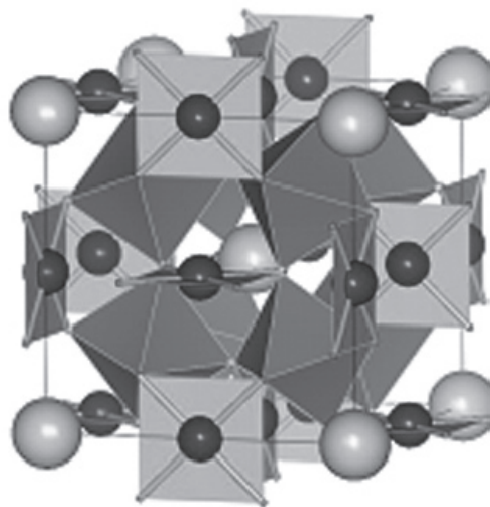
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A very unusual ordered arrangement of the A-site ions in the simple ABO_3 perovskite produces $\text{AA}'_3\text{B}_4\text{O}_{12}$ A-site ordered perovskites. The A site accommodates alkaline metals, alkaline-earth metals, and

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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