新学術「複合アニオン」レクチャーツアー
Lecture tour on mixed anion compounds

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2019. 01. 15(Tue) 10:00～12:00

NIMS 並木地区共同研究棟 409-410 号室

Rooms 409-410, Collaborative Research Building, Namiki site, NIMS

“Unconventional perovskites.”

Perovskite-based oxides have inspired a series of amazing discoveries in material science, and still remain a playground for solid state chemistry and condensed matter physics. Extensive research during last few decades revealed rich crystallography and crystal chemistry of perovskite-based structures with distortions of different origins – cooperative octahedral tilting distortion, charge/orbital ordering, (anti)polar displacements, cation/anion ordering – and their combinations. However, highly unusual and amazingly complex perovskite structures can still be found beyond the commonly accepted picture. Relaxing the rigid unit mode for the BX_6 octahedra may lead to broken corner-sharing connectivity of the octahedral framework and non-cooperative tilting distortion modes, realized in some double perovskites and elpasolites. Competing off-center displacements due to second-order Jahn-Teller effect and octahedral rotations/tilts lead to incommensurately modulated structures with frustrated octahedral tilting distortion in layered A-site ordered perovskites, such as $Li_{3x}Nd_{2/3-x}TiO_3$ and many others. Coupling of octahedral tilting distortion, octahedral deformation and strongly covalent Bi-O bonding results in antiferrodistortive modulated structures in isovalent A- and B-site substituted $BiFeO_3$. Finally, anion deficiency in the perovskites with lone-pair A-cations can be realized through the crystallographic shear plane mechanism, previously unforeseen for perovskites with occupied A-positions, as demonstrated by heterovalent substitutions in $BiFeO_3$ and $PbTiO_3$ and new perovskite-based $A_nB_nO_{3n-2}$ homologous series.

2019. 01. 17(Thu) 16:00～17:30

東京大学工学部総合研究機構 9 号館1階 大会議室

Main meeting room at Institute of Engineering Innovation, UT

“How advanced transmission electron microscopy can contribute to battery research?”

The design and improvement of the cathode materials for Li-ion batteries requires detailed knowledge on the crystal structure at different charge/discharge states and comprehensive understanding of the processes occurring at the nanoscale or even atomic scale level, as many electrode materials demonstrate highly inhomogeneous non-equilibrium behavior. Advanced transmission electron microscopy (TEM) is by far the most suitable and direct tool to look at the materials down to atomic scale. Recent progress in the quantitative electron diffraction methods and aberration-corrected scanning TEM imaging will be illustrated here with the examples of atomic structure investigation of various cathode materials. Electron diffraction tomography provides quantitative diffraction data enabling reliable structure solution and refinement from extremely small crystallites, typically smaller than 1 mm^3. Electron diffraction data can be acquired at very low electron dose, enabling investigation of the materials sensitive to the electron beam irradiation damage, such as polyanion and mixed-anion Li-ion battery cathodes, particularly in their charged state. The capabilities of quantitative electron diffraction in locating Li atoms and refining the occupancy of the Li positions will be demonstrated. Aberration-corrected scanning transmission electron microscopy (STEM) techniques deliver the information on the local structure with sub-Å resolution. High angle annular dark field

STEM (HAADF-STEM) imaging provides clear visualization of the cation positions, whereas annular bright field STEM (ABF-STEM) shows the location of the “light” elements, such as O and Li.

2019. 01. 18(Fri) 10:30～12:00
東京理科大学理学部 10 号館別館　1012 室
“How advanced transmission electron microscopy can contribute to battery research?”
Abstract: Same as above.

2019. 01. 21(Mon) 14:00～16:00
京大桂キャンパス　A2 棟 302 号室
Room 302, A2 Bldg., Katsura Campus, Kyoto University
“Electron diffraction tomography for solving complex structures.”
For many years electron diffraction has generally been considered as a qualitative structure characterization technique complementary to well-established X-ray and neutron diffraction methods. Dynamical diffraction effects strongly impede the use of the electron diffraction intensities for structure solution and refinement. Invention of electron diffraction tomography (EDT) provided a possibility to collect quasi-kinematical electron diffraction intensities thus opening an avenue towards broader implication of electron diffraction for quantitative structural characterization of crystalline solids. The EDT method offers unique possibilities for gathering reliable structural information from nanomaterials. Electron diffraction patterns can be taken at very low incoming electron dose, enabling investigation of the materials particularly sensitive to the electron beam irradiation damage, such as Li-based battery cathodes. Applicability of EDT to the polyanion Li-ion battery materials and other inorganic substances will be discussed based on comparison between the crystal structures provided by EDT and powder X-ray diffraction.

2019. 01. 24(Thu) 14:00～16:00
京大桂キャンパス　A2 棟 302 号室
Room 302, A2 Bldg., Katsura Campus, Kyoto University
“Interfaces as “chemical scissors” for oxide structures.”
Easily polarizable lone-pair cations can act as “chemical scissors” and can be employed for engineering non-conservative interfaces between the structural modules in oxides resulting in new intricate modular structures. Due to presence of stereoactive lone electron pair such cations as Pb^{2+} and Bi^{3+} tend to adopt incomplete and asymmetric oxygen coordination environment helping to relieve configurational strain at the interfaces and stabilize long range ordered structures. This approach will be illustrated by the examples of Pb, Bi-containing anion-deficient perovskites with crystallographic shear planes, new perovskite-based homologous series and the close-packed binary oxide superstructures. Aberration-corrected scanning transmission electron microscopy enabled the solution of these complex structures providing the necessary input for further refinement from powder X-ray and/or neutron diffraction data and revealing various modes of violating perfect arrangement of the interfaces.

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Mixed Anion