MS16 Understanding of functional materials

Chairs: Dr. Oleg Siidra, Dr. Claire Colin

MS16-O1

Novel structures of U minerals and compounds: from natural to synthetic crystals

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In Nature, uranyl minerals occur as important alteration products formed during weathering of uraninite, UO_{2+x}, also referred to as oxidation–hydration weathering; it is of interest because of its analogy to the alteration of UO_{2+x} in the spent nuclear fuel [1]. Crystal structures of uranyl minerals are known for their remarkable compositional diversity and topological variability. In past few years, our knowledge of the uranyl crystal-chemistry has increased a lot; nevertheless, since the most recent overview summarizing 610 inorganic and 117 mineral structures [2] substantial discoveries have been made. Among them, it should be mentioned a discovery of the first natural uranyl mineral that contains nano-scale clusters in the mineral ewingite, $Mg_8Ca_8(UO_2)_{24}(CO_3)_{30}O_4(OH)_{12}(H_2O)_{138}$, which is nowadays considered as the most complex mineral structure in Nature [3]. Some novel structure topologies are growing every year along with finds of new minerals and efforts to synthesize novel materials in laboratories.

References:

[1] Plášil, J. (2014). J. Geosci. 59, 99-114.
[2] Lussier, A.J. et al. (2016), Can. Mineral. 54, 177-283.
[3] Olds, T.A. et al. (2017). Geology, 45, 1007-1010.

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MS16-O2

New functional ferroics through crystallography

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A large fraction of functional materials used today are based on ferroic materials, in which the modulation or switching of the ferroic order parameter by temperature, pressure, electric or magnetic field, produces the functional property (*e.g.,* permittivity, piezoelectricity, magnetoresistance) as used in devices. As most functional coefficients are highly sensitive to lattice softening at ferroic phase transitions, one of the main tools to engineer these materials for optimal performance is formation of solid solutions, where phase transition temperatures can be tuned to lie within or without the device's operating range. This strategy is widespread in oxide perovskites *e.g.,* $PbZrO_3$-$PbTiO_3$ (PZT), where the Zr/Ti ratio is adjusted to coincide with a morphotropic phase boundary (MPB) between the rhombohedral (R, polarisation P along $[111]_p$) and tetragonal (T, P along $[100]_p$) symmetries, at which the piezoelectric charge coefficient and other performance characteristics maximize. However, the science controlling the properties of solid solutions is complex and insufficiently understood to enable accurate prediction of the success of such strategies, thus frustrating materials design. By consideration of the chemical control of this relationship between local and average structure, significant progress has been made in materials design. We utilised a design approach exploiting the nanoscale information available from Reverse Monte Carlo analysis of pair distribution function (pdf) data from total scattering experiments that treats Bragg and non-long-range-order derived scattering equally. The Liverpool and Leeds team used this total structure approach to identify a new lead-free MPB family. Neutron pdf analysis of the lead-free polar R phase $BiTi_{3/8}Fe_{2/8}Mg_{3/8}O_3$ (BTFM)[1] revealed two key features that were exploited to isolate a T symmetry Bi-rich perovskite. This T phase was then used to construct an MPB with R BTFM. Further, this new T phase forms a complete solid solution with R BTFM that affords a complex structure not purely due to either end-member with a maximum in d_{33} *i.e.,* an R-T MPB with a Curie temperature of over 600 °C.[2] This MPB is sufficiently robust to permit an increase of Fe content to 68% that generates room temperature weak ferromagnetism while retaining switchable polarisation:[3] a room temperature magnetoelectric ferromagnetic ferroelectric by incorporation of magnetic percolation into the original pdf-inspired MPB.

References:

[1] Chong, S. Y., et al. (2012). J. Am. Chem. Soc., 134(13), 5836–5849.
[2] Mandal, P., et al (2015). Adv. Mater., 27(18), 2883–2889.
[3] Mandal, P., et al. (2015) Nature, 525(7569), 363–366.

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