A topological analysis of our results, using the program TOPOS [6], was undertaken to further investigate the geometry of the phase transition. This allows the framework to be classified as a simplified net and broken down into minimal cages by the use of graph theory. This analysis resulted in the discovery of a new net classification, "jmc1", which is a (4,4,4,4,8)-coordinated net with stoichiometry. Five corresponding cages were also identified: $[4^4]+2[4^2.6^2]+[4^2.5^4]+[4^4.7^4]+2[4^4.5^2.6^2.7^2]$. A determination of the void space volume within each cage configuration, as well as the occupancy volumes of the cages, was then performed by the calculation of Voronoi-Dirichlet polyhedra. Comparison between these volumes indicates a significant overall expansion of the framework around the transition temperature, followed by a contraction to a size that is less than that of the lower temperature frameworks.

We close with a comparison of the GdP_5O_{14} framework to that of other RP_5O_{14} frameworks.

[1] P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angewandte Chemie International Edition* **2005**, *44*, 1816-1820. [2] H.K. Chae, D.Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A.J. Matzger, M. O'Keeffe, O.M. Yaghi, *Nature* **2004**, *427*, 523-527. [3] A.L. Goodwin, K.W. Chapman, C.J. Kepert, *Journal of the American Chemical Society* **2005**, *127*, 17980-17981. [4] H.P. Weber, B.C. Tofield, P.F. Liao, *Physical Review B* **1975**, *11*, 1152-1159. [5] T. Kobayashi, T. Sawada, H. Ikeo, K. Muto, J. Kai, *Journal of the Physical Society of Japan* **1976**, *40*, 595-596. [6] V.A. Blatov, *IUCr Computing Commission Newsletter* **2006**, *7*, 4-38.

Keywords: transition, topology, gadolinium

MS81.P41

Adsorption mechanism of nitrogen oxide on hollandite surface

Kenjiro Fujimoto, Chihiro Yamakawa and Shigeru Ito, *Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science (Japan)*. E-mail: fujimoto_kenjiro@rs.tus.ac.jp

Hollandite-type compound has one-dimentional tunnel structure along c-axis. From the unique structure, hollandite-type oxides have hitherto studied as one-dimentional fast ionic conductor and nuclear waste immobilizer. Also, Sn-type hollandite oxide $K_2Ga_2Sn_6O_{16}$ (KGSO) showed higher the amount of adsorption and the selective reduction catalysis for nitrogen oxide (NO) than the other isomorphic compounds. In this study, isomorphic structure $K_xGa_xTi_{8-x}O_{16}$ (KGTO, x~1.6) single crystal was grown by flux slow cooling method and refined the structure for comparing with KGSO. Furthermore, KGSO and KGTO powder were prepared by solid state reaction for studying the correlation of NO adsorption property and crystal structure.

$K_{1.59}Ga_{1.59}Ti_{6.41}O_{16}$ single crystals were obtained under the following condition; crystal composition (C): $(K_2CO_3)_1(Ga_2O_3)_1(TiO_2)_8$, flux composition (F): $(K_2CO_3)_1(MoO_3)_1$, C/F: 20/80, melted at 1350°C for 12 hours, cooled to 950°C by 4°C/hour. Structure refinement including newly constraint condition [1] of KGTO was calculated by JANA2006 [2] program. Reliability factor was R=0.0153 and wR=0.0481 under anisotropic condition, respectively.

Table 1 shows the lattice parameter and the atomic coordinate of potassium site. The differences in the lattice parameters presumably resulted from the ionic radii of Sn and Ti at the center of the octahedral sites (Sn^{4+}: 0.690nm > Ti^{4+}: 0.605nm). And, it was thought that the difference of the atomic coordinate of K2-site is due to the site-occupancy of potassium in one-dimensional tunnels. From the site-occupancy of KGTO (75%) and KGSO (90%) and the atomic coordinate, the distances between the K2-site and hollandite surface were calculated as 0.785 nm for KGTO and 0.766 nm for KGSO,

respectively. Furthermore, from diffuse reflectance infrared fourier transformed spectrum, it was thought that there was correlation between the amount of NO adsorption and the distances between K2-site and hollandite surface.

Table 1 Lattice parameters and potassium atomic coordinates of KGTO and KGSO.

		KGTO		KGSO[4]
<lattice parameter>				
a / nm		1.0111(2)		1.0389(2)
c / nm		0.29630(5)		0.3132(2)
V / nm³		0.3028(1)		0.33380(2)
<K site>				
K1/K2	x	0	x	0
	y	0	y	0
	z	0.5/0.725(6)	z	0.5/0.748(18)

[1] Y. Michiue, *J. Solid State Chem.* **2007**, *180*, 184. [2] V. Petricek, M. Dusek and L. Palatinus, *The Crystallographic Computing System JANA2006*, Institute de Physics, Praha, Czech Republic, **2006**. [3] K. Fujimoto, C. Yamakawa and S. Ito, *Solid State Ionics* **2010**, *184*, 74-77. [4] K. Fujimoto, private communication.

Keywords: hollandite, catalyst, adsorption

MS81.P42

Substituents effect on molecular and crystal structures of phenyl ferrocenoylmethyl thioethers

J.L Ferreira da Silva, M.T. Duarte, S.G. Harjivan, M.M. Marques, A.P.Ferreira, *Centro de Química Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa, 1049-001 Lisboa (Portugal)*. E-mail: joao.luis@ist.utl.pt

It is well known that intermolecular interactions (from strong O-H···O to weaker C-H···π hydrogen bonds) can affect significantly both the molecular and the crystal structure of compounds [1], [2]. This work analyses the effect of various phenyl ring substituents (H, NO₂, etc) on both these features by comparing a series of *para*-substituted phenyl ferrocenoylmethyl thioethers.

All the compounds studied show as main intermolecular interactions C-H···O(carbonyl) hydrogen bonds, that lead to the formation of linear chains. The secondary interactions observed will determine their molecular structure and overall supramolecular arrangements.

In the non-substituted compound the absence of donors stronger than the C-H cyclopentadienyl (Cp) bonds forces the phenyl-containing moiety to rotate around a CH_2-S bond in order to leave this ring facing one C-H bond of the upper Cp ring, thus forming a C-H···π intramolecular bond and, concomitantly, adopting a more compact structure (Fig 1).

If *para* substituents with the ability to get involved in intermolecular contacts (like chlorine or methoxy) are used, the tendency is for the rotation to occur in the exact opposite direction, placing the phenyl ring as far as possible from the ferrocenyl group, providing enough room for Cl···Cl halogen bonding or C-H···O hydrogen bonds.

When a group like nitro is used, it allows the establishment of an extended conjugated π-system. Therefore, the whole molecular moiety containing the phenyl ring will adopt a quasi planar geometry (Fig 2),

contributing to the stability of the molecule and promoting the packing of molecules in dimers formed by C(Cp)-H⋯O(nitro) hydrogen bonds.
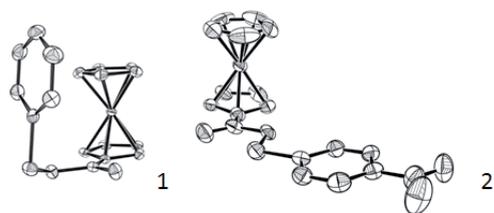
[1] G.R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in structural chemistry and biology,* ed. IUCR, Oxford University Press, Oxford, **1999**. [2] M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyama, H. Suezawa, *CrystEngComm.* **2009**, *11*, 1757-1788.

Keywords: structure, supramolecular, substituent

MS81.P43

A transmission electron microscopy study of the atomic structure of $Na_{1/2}Bi_{1/2}TiO_3$ (NBT)

Yingyi Zhang,[a] Laure Bourgeois,[a,b] Ray Withers,[c] Joanne Etheridge,[a,b] *aDepartment of Materials Engineering, Monash University, VIC. 3800, (Australia). bMonash Centre for Electron Microscopy, Monash University, VIC. 3800, (Australia). cResearch School of Chemistry, Australian National University, Canberra, ACT 0200, (Australia).* Email: yingyi.zhang@monash.edu.au

Piezoelectric and ferroelectric, perovskite ceramics (chemical formula, ABO_3) are widely used in electromechanical devices such as transducers, sensors and so forth for a variety of applications ranging from smart car shock absorbers to pressure sensors. $PbZr_{1-x}Ti_xO_3$, (abbreviated as PZT) is currently the most important and commonly used perovskite in this field. However, from the perspective of environmental protection, the presence of lead makes the use of PZT undesirable. Therefore, in an attempt to replace PZT and other lead-containing perovskites, much effort has been devoted to developing a lead-free perovskite with attractive electromechanical properties. The compound $Na_{1/2}Bi_{1/2}TiO_3$, (abbreviated as NBT) is one of the most promising such candidates.

NBT is one of the rare lead-free perovskites with *A*-site substitution. Neutron powder diffraction has shown that NBT undergoes (at least) two structural phase transitions on cooling. This study has confirmed that the room temperature phase of NBT belongs to the polar *R3c* space group. However, many experiments (in-situ neutron scattering of NBT single crystal and transmission electron microscopy (TEM) studies) have revealed deviations from the ideal R3c structure. Since these local structural deviations are critical in understanding NBT's ferroelectric properties, studying the local microstructure of NBT is essential. Detecting and characterising subtle changes in structure at the nano-scale requires the use of transmission electron microscopy.

Results will be presented of a detailed TEM study of NBT and NBT-doped with barium titanate using a combination of high resolution imaging and electron diffraction in order to investigate and understand the local structure of the rhombohedral phase at room temperature. A sequence of electron diffraction patterns obtained at different crystal orientations shows weak streaks of structured diffuse scattering, suggesting local structural modulation. This reciprocal space feature appears to be associated with "striped contrast" in TEM bright field images. The geometry of the structured diffuse scattering and the associated structural modulation will be described and its relationship with features observed in the images will be discussed.

MS81.P44

Structural phase transitions in the $Pb_2MnW_{1-x}Re_xO_6$ perovskites.

Sara Lafuerza, Joaquín García, Javier Blasco, Gloria Subías, M. C. Sánchez, V. Cuartero, *Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Universidad de Zaragoza, Departamento de Física de la Materia Condensada, C/ Pedro Cerbuna 12, 50009 Zaragoza (Spain).* E-mail: lafuerza@unizar.es

We here report on the structural properties of a new series of double perovskites, $Pb_2MnW_{1-x}Re_xO_6$. The edges of the series have been studied previously. Pb_2MnWO_6 is orthorhombic at room temperature, space group *Pnma* [1]. It is isostructural with Pb_2CoWO_6. The Pb atoms adopt distorted environments which arise from displacements out from the center of the oxygen polyhedron along the [100] cubic direction. On warming, this compound undergoes a crystal phase transition from orthorhombic to cubic. This structural modification is coupled to a change in the dielectric permittivity suggesting an antiferroelectric ground state. X-ray absorption spectroscopy revealed that this is an order-disorder transition as the local structure around Pb atoms show similar distortion degree in both cubic and orthorhombic phases. In this way, dynamic distortions in the cubic phase are frozen in the orthorhombic one [2]. Pb_2MnReO_6 is monoclinic at room temperature (space group *C2/m*) and it also transforms into a cubic phase at 410 K. The transition can be understood as the condensation of two primary modes, Γ_4^+ associated to the anti-phase tilting of ReO_6 and MnO_6 octahedra and Σ_2 associated to the collinear movement in opposite directions of, mainly, 2/3 of the Pb^{2+} cations [3]. The entropy content for this transition is smaller than the one expected for an order-disorder transition suggesting the presence of significant disorder in the low temperature phase.

The x-ray diffraction patterns of $Pb_2MnW_{1-x}Re_xO_6$ samples ($0 \leq x \leq 1$) were measured in the temperature range between 123 and 523 K. These measurements have allowed us to obtain the structural phase diagram for the whole series. All samples are cubic at high temperature and undergo a structural phase transition on cooling from cubic phase to either orthorhombic or monoclinic phases. The transition temperature (T_c) slightly decreases as the Re content increases. Below T_c, the Rietveld analysis confirms that the orthorhombic cell is maintained for $x \leq 0.2$ whereas the samples adopt the monoclinic structure for the composition range $x \geq 0.5$. Solid solution between W and Re atoms exists in the abovementioned ranges of the phase diagram. Samples included in the $0.25 \leq x \leq 0.45$ range show the coexistence of both orthorhombic and monoclinic phases. The weight fractions of each phase vary almost linearly in opposite ways in this concentration range. These features agree with the presence of a miscibility gap in the phase diagram for $0.25 \leq x \leq 0.45$.

The structural study was completed measuring EXAFS spectra at the Pb L_3, Re L_3, W L_3 and Mn K edges. In the low temperature phase, all samples show similar local structure for each atom independently of the chemical composition. This result indicates a similar degree of local distortion for these atoms in the whole series in spite of the differences in the crystal structure. The local structure has been also monitored in function of the temperature for x = 0, x = 0.5 and x = 1 samples. No changes with temperature are appreciated at all in any of these samples. This result reveals that dynamic distortions are still present in the cubic phase for the whole composition range.

[1] J. Blasco, R.I. Merino, J. García, M.C. Sánchez, *J. Phys.:Condens Matter* **2006**, *18*, 2261-2271. [2] G. Subías, J. Blasco, J. García, J. Herrero-Martín, M. C. Sánchez, *J. Phys.: Condens. Matter* **2009**, *21*, 075903. [3] J. Blasco,