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.

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MS81.P41

Adsorption mechanism of nitrogen oxide on hollandite surface

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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)

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MS81.P42

Substituents effect on molecular and crystal structures of phenyl ferrocenoylmethyl thioethers

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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 CH₂-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),