

MS81.P38*Acta Cryst.* (2011) A67, C716**3-D transition metal phosphate zeotypes: controlling dimensionality with chemical substitution**

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Materials with both magnetic and electric orders such as the magnetoelectric (ME) multiferroics have received significant attention in recent years. [1], [2] The coupling of such behaviours should give rise to technological uses but also lead to rich physics. Often, ferroelectric and magnetic phases have very different ordering temperatures, which suggest that the processes are driven by different microscopic interactions, but for a significant number of materials these coincide and ferroelectricity can be generated by long-range order. Phosphate based materials have been discovered with applications across the whole range of solid state chemistry and physics from battery materials to solid oxide fuel cells and proton conductors. The lithium orthophosphates (LO) LiMPO₄ with M = Mn, Fe, Co and Ni are a prototypical iso-structural group of antiferromagnets (AFs) that show ME below their Néel temperatures. [3],[4],[5],[6],[7].

Here we present work on materials of the type ABPO₄ with A = Rb and Cs and B = Co, Ni and Cu that show novel frameworks based on structures intermediate between that of zeolite ABW and the natural mineral olivine that have the potential to yield interesting properties. In the Cu system, polymorphic piezo-chromic behaviour is observed at RT driven by coordination changes in the Cu polyhedra. The structure can be locked into one of the polymorphs by doping with Ni and the dimensionality of the structure can be tuned by substitution of the A site cation [8].

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MS81.P39*Acta Cryst.* (2011) A67, C716**Optical properties of lanthanum – gallium tantalate crystals**

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Lanthanum – gallium tantalate crystal La₃Ta_{0.5}Ga_{5.5}O₁₄ (langatate) is a piezoelectric material with a piezoelectric constant about three times higher than that of quartz and is stable over a wide temperature range. Langatate is LGS-type crystals which have the Ca₃Ga₂Ge₄O₁₄ type structure with the P321 space group. This crystal is widely used in design of sensors based on the direct piezoelectric effect. One of the investigation issues of langatate is crystal coloration which depends on the presence of color centers. It is necessary to understand the mechanism and nature of color centers formation in crystals to have influence on formation processes. Growth conditions and heat treatment are factors of great.

In this study, we performed experiments with langatate crystals produced by the company Fomos-Materials. The crystals were grown by the Czochralski method in iridium crucibles in an Ar atmosphere

and in a mixture of argon and oxygen (Ar +(2%)O₂) and (Ar +(–0,5%) O₂). Crystals grown in Ar atmosphere are almost colorless, while those grown in (Ar+O₂) atmosphere are of bright orange color.

Presence of point defects in structure and processes of recharge have an influence on color centers formation. It leads to generation of optical active localized states. Formation processes might be activated with additional postgrowth treatment particularly with annealing.

Isothermal annealing in the air was carried out at temperature 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, each sample was held within 4 hours at only one temperature. The experiment required using the polar cut samples 2 mm thickness. All samples were investigated with methods of optical spectroscopy, optical microscopy, atomic force microscopy, X-ray photoelectron spectroscopy before and after annealing. Optical transmission and diffused reflection spectra were measured with spectrophotometer "Cary 5000 UV-VIS-NIR" in the wavelength range 230-3000 nm and attachment "DRA 2500" for diffused reflection measurements. A strong effect of the annealing temperature on the state of defects in langatate structure and crystal surfaces has been revealed. It depends on the growth atmosphere.

Increased absorption is observed on specific absorption bands at wavelengths 280 nm, 360 nm and 480 nm. Consecutive decrease of transmission coefficient is accompanied by temperature rise.

Measurement by means of optical microscopy demonstrated the fact that annealing leads to significant change of one of the crystal surfaces. Optical transmission spectra give integral characteristic measurements of diffused reflection spectra of both surfaces. Analysis of these spectra shows differences between diffused reflection coefficients of positive and negative surfaces of the samples. It might be connected with unequal structure changing of surfaces.

Results of the surface research by means of X-ray photoelectron spectrometer PHI 5500 ESCA exhibit tendency to decreasing of correlation Ga to La concentrations in samples subjected to annealing at 1000 °C.

Obtained results are evidence of isothermal annealing having a profound effect on both optical properties and surfaces states in La₃Ta_{0.5}Ga_{5.5}O₁₄ crystal. Dependence of surface state on their polarity and the growth atmosphere is observed.

Keywords: annealing, property, optics

MS81.P40*Acta Cryst.* (2011) A67, C716-C717**Temperature dependent phase transition and topological classification of GdP₅O₁₄**

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Porous materials have attracted much interest in their potential to absorb other molecules into the crystal framework for a variety of uses ranging from solar cells to gas recognition and storage [1], [2]. Relationships between temperature and structure geometry often prove to be of great importance in this regard [3].

In a multi-temperature, single-crystal X-ray diffraction study on gadolinium ultraphosphate (GdP₅O₁₄), we have investigated the second-order monoclinic to orthorhombic solid-state phase transition. Temperature measurements ranged from 125K to 480K, and the images were integrated and refined assuming both the monoclinic structural framework, and the orthorhombic framework. The results were then compared and the phase transition was found to be around 350K-400K. This result is consistent with the predictions and results reported from previous ferroelasticity studies [4], [5].

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 $\text{GdP}_5\text{O}_{14}$ framework to that of other RP_5O_{14} frameworks.

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Adsorption mechanism of nitrogen oxide on hollandite surface

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Hollandite-type compound has one-dimensional tunnel structure along c-axis. From the unique structure, hollandite-type oxides have hitherto studied as one-dimensional fast ionic conductor and nuclear waste immobilizer. Also, Sn-type hollandite oxide $\text{K}_2\text{Ga}_2\text{Sn}_6\text{O}_{16}$ (KGSO) showed higher the amount of adsorption and the selective reduction catalysis for nitrogen oxide (NO) than the other isomorphous compounds. In this study, isomorphous structure $\text{K}_x\text{Ga}_x\text{Ti}_{8-x}\text{O}_{16}$ (KGTO, $x \sim 1.6$) 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.

$\text{K}_{1.59}\text{Ga}_{1.59}\text{Ti}_{6.41}\text{O}_{16}$ single crystals were obtained under the following condition; crystal composition (C): $(\text{K}_2\text{CO}_3)_1(\text{Ga}_2\text{O}_3)_1(\text{TiO}_2)_8$, flux composition (F): $(\text{K}_2\text{CO}_3)_1(\text{MoO}_3)_1$, 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 ^[a]	
<lattice parameter>				
a / nm	1.0111(2)		1.0389(2)	
c / nm	0.29630(5)		0.3132(2)	
V / nm ³	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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Substituents effect on molecular and crystal structures of phenyl ferrocenylmethyl 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 ferrocenylmethyl 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),