

In the present work, we investigate the influence of crystallite size on the crystal structure, local order and Co oxidation state of LSC nanopowders synthesized by two different chemical methods: citrate-complexation method (C) and stoichiometric nitrate-glycine solution-combustion process (G) [2].

G-process yields porous and deagglomerated powders consisted of nanosized crystallites (average crystallite size,  $D = 25$  nm) that exhibit single perovskite phase after calcination at  $900^\circ\text{C}$  5 hours. Citrate complexation method produce foamy powders, but the perovskite phase is achieved at  $1100^\circ\text{C}$ . This promotes crystallite growing up to sub-micron sizes ( $D > 200$  nm). XRD patterns showed the retention in metastable form at room temperature of the high temperature cubic phase for the nanopowders synthesized by G-process, while powders with bigger crystallite size exhibit the common rhombohedral phase.

X-ray absorption spectra (XAS) of the Co K-edge ( $7709$  eV) were recorded at the D04B-XAFS1 beamline of LNLS, Brazil. Data were collected at room temperature in air. *WinXas* and *fdmnes* codes were used in the analysis. Changes seen in the 2<sup>nd</sup> derivative of the X-ray absorption near edge spectra (XANES) in the pre-edge region, may be ascribable to the differences observed in the crystal structure and also to oxygen vacancies, as shown by simulations using *fdmnes* code. Also, experimental XANES may be explained in terms of oxygen vacancies. Remarkably, Co(IV) was not needed in these analyses. Some authors claimed Co(IV) appears when Sr substitutes La in LSC [3]. This idea goes against the goal of introduce Sr(II) in the A-site to generate oxygen vacancies, based on unit cell neutrality. Accordingly, Fourier transform of EXAFS signal shows an increase of the concentration of oxygen vacancies in the nanopowdered samples.

In view of the results of this investigation, the enhanced electrochemical performance of nanostructured LSC cathode may be ascribed to a larger concentration of oxygen vacancies, induced by the small crystallite sizes, in the order of 25 nm.

[1] L.M. Acuña *et al.*, submitted to *Journal of Power Sources* **2011** [2] N.P. Bansal, Z. Zhong, *Journal of Power Sources*, **2006**, *158*, 148-153. [3] V. Sikolenko *et al.*, *Journal of Magnetism and Magnetic Materials*, **2007**, *310*, e181-e183.

**Keywords:** perovskite, nanocrystals, XAS

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### Structure of an Octahydrated Metformium Decavanadate Salt

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Decavanadate compounds have received considerable attention due to their possible application in blood glucose lowering. The current work is part of a study combining multiple therapeutic agents in the same crystal lattice for potential benefit in treatment of diabetes mellitus. Metformin is a biguanide derivative which is commonly used as an oral hypoglycemic drug to treat type 2 diabetes mellitus. In this study, we report a compound of metformium decavanadate,  $[\text{C}_4\text{H}_{12}\text{N}_5^+]_3[\text{H}_3\text{O}^+][\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}] \cdot 8\text{H}_2\text{O}$ , synthesized from  $\text{V}_2\text{O}_5$ ,  $\text{C}_4\text{H}_{11}\text{N}_5\text{HCl}$ , and  $\text{H}_2\text{O}$  in molar ratio of 1.2:1:555 (pH 5) by refluxing at  $60^\circ\text{C}$  for 15 hours, followed by crystallization at room temperature. The crystals were analyzed by X-ray diffraction, SEM/EDX, FTIR, and thermal analysis (TGA/DSC) under nitrogen and oxygen atmosphere.

The IR spectrum has a strong peak at  $961\text{ cm}^{-1}$  that can be assigned to  $\nu(\text{V}=\text{O})$ , strong bands at  $844$ ,  $743$  and  $589\text{ cm}^{-1}$  characteristic of  $\nu(\text{V}-\text{O})$  and  $\delta(\text{V}-\text{O}-\text{V})$ , and a weak band at  $836\text{ cm}^{-1}$  attributed to

$\nu(\text{V}-\text{OH})$  protonated decavanadate. The bands in the range  $3360$ - $1067\text{ cm}^{-1}$  are typical of metformium ion. The broad band at  $3517\text{ cm}^{-1}$  can be assigned to  $\text{H}_2\text{O}$  in the compound, consistent with eight water molecules corresponding to 9.49% (calc. 9.52%) weight loss observed below  $160^\circ\text{C}$  by TGA. An amorphous (by XRD) black residue with weak IR bands at  $746\text{ cm}^{-1}$  and  $539\text{ cm}^{-1}$  remaining after heating to  $700^\circ\text{C}$  was not further characterized. The solution properties of this compound were also characterized using multinuclear NMR spectroscopy.

**Keywords:** metformium, decavanadate compound, diabetes mellitus

## MS56.P08

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### Ferroelectricity and XANES spectra in $\text{PbTiO}_3$ , $\text{BaTiO}_3$ and $\text{SrTiO}_3$

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$\text{PbTiO}_3$  and  $\text{BaTiO}_3$  perovskites have been intensively studied for a long time, because of having ferroelectric (FE) properties at ambient condition and being very useful as functional materials. In particular, some X-ray absorption fine structure (XAFS) studies were carried out to investigate the mechanism of ferroelectric-paraelectric phase transition for these materials [1].  $\text{SrTiO}_3$  has the same perovskite type structure and phase transitions as  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$ . There is little research of comparing them on detailed temperature dependence and phase transitions. The temperature dependence of Ti-K edge XANES spectrum of  $\text{PbTiO}_3$ ,  $\text{BaTiO}_3$ , and  $\text{SrTiO}_3$  perovskite has been investigated. We have investigated the temperature dependence of XANES spectra in order to detail information of local structure on ferroelectric mechanism and distortion of local environments. We performed the synchrotron radiation experiment in the photon factory of KEK in a wide temperature range.

The previous study revealed that [1], in the tetragonal  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$  phase, a pre-edge absorption has quite large at room temperature. This peak caused by the electronic transition from  $1s$  to  $3d$  in the Ti atom. The quadrupole transition is enhanced by the addition of a dipole transition from the mixture of p character into the  $3d$  final state due to the broken centrosymmetry of the crystal. In the undistorted cubic  $\text{SrTiO}_3$  at room temperature, where the structure distortion is minuscule, the feature of pre-edge peaks becomes much smaller but exists. The pre-edge feature is appropriate for obtaining mixture information in  $3d \cdot 4p$  orbit of the Ti atom. The feature of the peak of dipole transition and physical properties depend on local structure change in perovskite. In the results obtained in this experiment, the pre-edge feature of ferroelectric perovskite tends to decrease toward Curie point ( $T_c$ ) with temperature rise. This decrease of this peak is due to the shift from the off-center position of the Ti atom with respect to the oxygen octahedron to center position. The ferroelectric perovskite undergoes phase transition above  $T_c$ , and it becomes dielectric cubic perovskite. The strong pre-edge absorption has existed and the local distortion remains in cubic phases. The height of pre-edge for dielectric perovskite increases with temperature rise and also from the lowest temperature phase to the highest temperature phase. This increase is not influenced by anharmonic thermal vibration and is thought to be influenced by local distortions by harmonic lattice vibration. It is thought that the tendency that pre-edge absorption of perovskite decreases with temperature rise is only a feature of ferroelectric tetragonal perovskite. By the comparison of XANES

spectra we will discuss the electric structure, distortion of polyhedra related to ferroelectricity and thermal vibration.

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**Keywords:** ferroelectric, XANES, phase transition

## MS56.P09

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### Temperature dependence of pre-edge feature in Ti K-edge XANES spectra for $\text{ATiO}_3$ , $\text{A}_2\text{TiO}_4$ (A=Mg, Ca, Fe, Sr and Ba) and $\text{TiO}_2$ compounds

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X-ray absorption near edge structure (XANES) provides important information on the electronic structure and local symmetry around X-ray absorption atom. There are three distinct pre-edge peaks correspond to electronic transitions in Ti K-edge XANES spectra. The composition, structure and temperature dependence of XANES spectra on three peaks was investigated. We measured Ti K-edge XANES spectra of various titanates,  $\text{MgTiO}_3$ ,  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{Mg}_2\text{TiO}_4$ ,  $\text{Fe}_2\text{TiO}_4$ ,  $\text{TiO}_2$  rutile and anatase, in the temperature range from 20K to 800K. Ti atoms are placed in  $\text{TiO}_6$  octahedral and  $\text{TiO}_4$  tetrahedral sites in crystal structures. The measurements of Ti k-edge XANES spectra were carried out in transmission mode at beam line BL-7C and BL-9A of the Photon Factory in KEK, Tsukuba. High temperature X-ray absorption measurements were made under a helium atmosphere. XANES spectra of all sample on each peaks is increasing as the temperature increases except for tetragonal  $\text{BaTiO}_3$  and tetragonal  $\text{SrTiO}_3$  phases.  $\text{TiO}_2$  rutile and anatase have largely different rate of rising pre-edge absorption to the temperature. The XANES spectra in the high temperature region were strongly affected by the harmonic thermal vibration of the atoms. There is an interesting relation between electronic transition and local distortion of coordination environment coming from the harmonic thermal vibration. We will discuss harmonic and anharmonic thermal vibration models by XAFS method.

**Keywords:** XANES, pre-edge peak, titanate

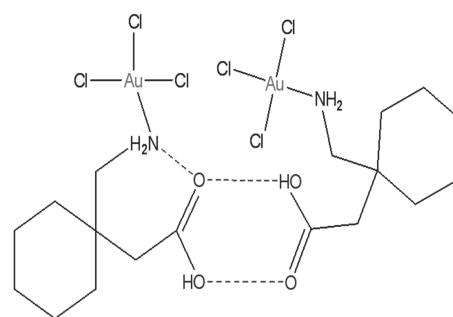
## MS56.P10

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### A gold(III) complex of the neuroepileptic drug gabapentin

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Gabapentin, a neuro-epileptic drug, has been the subject of interest lately as new polymorphs, [1] salts and hydrates have been reported, as well as the high pressure crystallisation of a novel heptahydrate [2]. The first complexes with transition metal complexes, Cu(II) and Zn(II) were reported recently by Braga and co-workers [3]. Since gold is known to have pharmaceutical applications [4] we were interested to see if we could prepare a Au(III)-Gp complex.



Auric acid was reacted with gabapentin in an aqueous solution. Two distinct types of crystals precipitated from this solution: pale yellow needle shaped crystals (**I**) and dark yellow blocks (**II**, not shown here). Their structures were determined by single crystal structure analysis. The MeOD solution  $^1\text{H}$  and  $^{15}\text{N}$ -NMR were then recorded to confirm that the gold remains coordinated to the nitrogen of the amino group in solution (**I**).

The crystal structure of (**I**) clearly shows the Au-N coordination (Au-N bond 2.043(2) Å) in the hydrogen bonded dimer. The cyclohexane is disordered over two positions, both having a chair conformation. The  $^1\text{H}$ -NMR shows peaks at  $\delta = 2.45, 2.88$  ppm for the free gabapentin  $-\text{CH}_2-$  groups ( $-\text{CH}_2-\text{COOH}$  and  $-\text{CH}_2-\text{NH}_3^+$  respectively). On dissolving (**I**) in MeOD four peaks are apparent in the  $^1\text{H}$ -NMR; at 2.45, 2.51, 3.05 and 3.12 ppm. Our current interpretation of this is that (**I**) exists as two different isomers in solution and that on crystallisation these persist in the solid state.

In conclusion, auric acid reacts with gabapentin in aqueous solution to form a Au(III)-gabapentin complex in which the Au(III) is coordinated to the amino nitrogen [5]. It appears that in this reaction an intermediate complex has been trapped given that Au(III) is known to oxidise amino acids.

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### Crystal structure of Zn complex with chelidamic acid and acridine

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4-Hydroxypyridine-2,6-dicarboxylic acid as carboxylate derivative has drawn extensive attention in coordination chemistry. This ligand could potentially provide various coordination motifs to form both discrete and consecutive metal complexes under appropriate synthesis condition [1,2]. We prepared new mononuclear complex of Zn(II) containing 4-hydroxypyridine-2,6-dicarboxylic