

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

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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 of 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 undergo phase transition above  $T_c$ , and it become dielectric cubic perovskite. The strong pre-edge absorption has existed and the local distortion remain 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 influence of anharmonic thermal vibration and is thought to be influence of 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