

## Posters



# HYDROTHERMAL CONVERSION OF CERIUM OXALATE INTO CeO<sub>2</sub>.nH<sub>2</sub>O OXIDE

N.Assi, V.Tyrpekl

Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova, 2030 Prague, Czech Republic

#### 1. Introduction

In the last few decades, various methods were applied for the synthesis of micro and nano structures of metal oxide which consist of precipitation, combustion, ionic liquid route, and sol-gel. The inconveniences presented in these methods such as pH control, the high temperature used, long reaction time and low purity, encouraged the researcher to find the suitable substitution methods. Thermal decomposition methods could be employed as an alternative approach. The utility of thermal decomposition for inorganic salts such as hydroxide, carboxylate, acetate, and oxalate has been extensively used to obtain metal oxides [1].

Oxalate hydrate could be a good precursor for the preparation of metal oxide due to its large quantity mass loss in the hydrothermal process (more than 50 wt %), low cost, easy synthesis, and low decomposition temperature in the air. Indeed, the hydrothermal decomposition of metal oxalates is a clean, flexible and powerful approach toward metal oxide with possible scale-up potential [2].

Metal oxalate hydrates can be dehydrated and decomposed by pressure and heating and finally converted to metal oxide. Ergo, metal oxalate hydrates have been exploited as a precursor to convert metal oxides with solid-state reaction methods [3].

In this study, we prepared a ceria solid solution with simple oxalate precipitation [4]. The obtain powder which consist  $Ce_2(C_2O_4)_3.10H_2O$  was used for conversion to  $CeO_2$  with hydro-thermal treatment. The impact parameters such as pH, and hydro-thermal temperature were evaluated on the physicochemical characterization of the final powder.

#### 2. Experimental and Instrumental section

All the reagents used in this work were analytical grade and all solutions were prepared with Millipore water. Briefly, appropriate amount of oxalic acid (0.1 M) add to the cerium(III) nitrate hexahydrate (0.1 M) mixed together. The white precipitation was washed 3 times with Millipore water, centrifuged and dried at 50 °C in an oven. 0.25 g of the obtained powder with 21 mL of diluted nitric acid was transferred to the Teflon-lined autoclave for hydrothermally treatment. The final product washed 3 times with Millipore water, centrifuged and Stimes with Millipore water, centrifuged and Stimes with Millipore water, centrifuged and dried at 50 °C in an oven. The final product washed 3 times with Millipore water, centrifuged and dried at 50 °C in an oven. The final powder was characterized with XRD and SEM.

#### 3. Result and Discussion

Several parameters are affected to synthesis metal oxide from metal oxalate as precursor. The pH value is the significant key factor for the nature and crystallinity [5]. Therefore, the influence of the initial pH during the  $Ce_2(C_2O_4)_3.10H_2O$  hydrothermal treatment was investigated in the 1, 2 and 3. The target pH was reached by adding different concentration of nitric acid. The XRD patterns of the final powder prepared in 220 °C at different adjusted pH for 24 h are shown in the Fig. 1.



Figure 1. Powder X-ray diffraction diagrams obtained after hydrothermal treatment of  $Ce_2(C_2O_4)_{3.1}0H_2O$  in variation initial pH



Figure 2. Powder X-ray diffraction diagrams obtained after hydrothermal treatment of  $Ce_2(C_2O_4)_3$ .10H<sub>2</sub>O with various temperatures in pH 1 during 24 h.

Other main effective parameter on the materials physicochemical properties is temperature [8]. Therefore, the effect of hydrothermal treatment for converting  $Ce_2(C_2O_4)_3.10H_2O$  to  $CeO_2$  was evaluated at 180, 200 and 220 °C with adjusted pH 1 for 24 h. As the XRDs are illustrated in the Fig. 2 with increasing hydrothermal temperature the initially precipitated of  $Ce_2(C_2O_4)_3.10H_2O$  converted to  $CeO_2$ . The optimum temperature for the conversion is 200 °C and in higher temperature it just lead to sharp peaks and consequently growing crystallise structure.





Figure 3. SEM images of Ce<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>.10H<sub>2</sub>O conversion to CeO<sub>2</sub> in different hydrothermal treatment (a-c) and pH (c-e) during 24 h.

Final structure such as size, crystal thickness, aggregation and purity are related to the synthesis condition, as confirmed by our achievement. However, Fig. 3 shows the size and morphology of the achieved powder from hydrothermal treatment of  $Ce_2(C_2O_4)_3.10H_2O$  to the CeO<sub>2</sub>. Such modification of this conversion was correlated to increase crystallite phase with temperature and pH as already evidenced by XRD measurements. As it illustrated in Fig. 3 (a-c) with increasing the temperature from 180 to 220 C aggregation of the nano powder sticking together to formation bigger structure was occurred. Also with increasing pH from 1 to 3, gradually conversion of  $Ce_2(C_2O_4)_3.10H_2O$  to the CeO<sub>2</sub> was decreased and porous powders in the low pH change to the rods and it shown in Fig. 3 (c-e).

### 4. Conclusion

Cerium (III) precipitated with oxalic acid in the aqueous solution and the white powder of  $Ce_2(C_2O_4)_3.10H_2O$  was achieved. Entirely conversion of  $Ce_2(C_2O_4)_3.10H_2O$  to the  $CeO_2$  was done with hydrothermal treatment. This conver-

sion was profoundly related to several parameters such as pH solution and temperature in the process of hydrothermal treatment which optimized in this procedure.

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# P2

## THE INFLUENCE OF ENERGY-FILTERING ON KINEMATICAL AND DYNAMICAL STRUCTURE REFINEMENT FROM 3D ED DATA

# M. Cabaj <sup>1</sup>, L. Palatinus <sup>1</sup>, I. Andrusenko <sup>2</sup>, M. Gemmi <sup>2</sup>

<sup>1</sup>Department of Structure Analysis, Institute of Physics, Czech Academy of Sciences, Prague, Czech Rep. <sup>2</sup>Istituto Italiano di Tecnologia, Center for Materials Interfaces, Electron Crystallography, Pontedera, Italy -Pontedera (Italy) mkcabaj@fzu.cz

X-ray diffraction data is a well-established and reliable approach of solid-state structure solution and refinement. Compared to it, electron diffraction is still not as commonly used due to various reasons, one of them being higher figures of merit indicating poorer accuracy of structure refinement. There are many ways to address this problem, ranging from using more complex theoretical approach for structure refinement, to installing additional parts of equipment, which enable collection of higher quality data.

In this work we investigate the influence of energy-filtering on data refined with kinematical and dynamical approach.

Four sets of data – two filtered and two unfiltered – were collected from two crystals of metal-organic polymer containing Zn(II), water and 4,4'-biphenyldicarboxylic acid. For first crystal, the unfiltered data were collected first and the filtered – second. For the other crystal the order of data collection was reversed. This protocol ensures that the observed differences are not due to the radiation damage.

All datasets were processed with PETS2 [1], and then solved and refined with JANA2020 [2]. We processed all four data set in an identical manner to ensure a reliable and unbiased comparison. In each case we observed some differences in R-factors. For kinematical refinement the R factors were slightly lower for the unfiltered data (less than 1% of difference), with the except of R(all), which was higher for the filtered data. The situation was different for the dynamical approach – all R factors were higher for the unfiltered data, and again – the difference was usually less than 1%.

The obtained results confirm the preliminary hypothesis that the energy-filtering affects the kinematical and dynamical data refinement process in a different way. The change in all R factors is not considerable, but still measurable. Adding an energy-filter negatively affects kinematical refinement, but improves the dynamical one.

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	Crystal 1			Crystal 2		
	Filter off	Filter on	Difference (off-on)	Filter on	Filter off	Difference (off-on)
Kinematical refinement						
R(obs)	24.94	25.13	-0.19	26.11	25.95	-0.16
wR(obs)	29.00	29.51	-0.51	30.02	28.91	-1.11
R(all)	32.47	30.78	1.69	29.35	31.46	2.11
wR(all)	29.91	30.35	-0.44	30.37	29.36	-1.01
Dynamical refinement						
R(obs)	10.27	9.78	0.49	12.46	12.94	0.48
wR(obs)	11.73	11.12	0.61	14.16	15.33	1.17
R(all)	16.71	16.24	0.47	15.35	16.26	0.91
wR(all)	13.34	12.78	0.56	14.82	15.94	1.12

Table 1. The differences in R-factors for each dataset.

#### Krystalografická společnost

# **P3**

## SOLUTION OF CRYSTAL AND MAGNETIC STRUCTURES IN JANA2020

## M. Henriques, C. A. Correa, V. Petříček and M. Dušek

Department of Structure Analysis, Institute of Physics, Academy of Sciences of the Czech Republic, 18221 Praha, Na Slovance 2, Czech Republic henriques@fzu.cz

The new Jana2020 is a natural successor to the previous version of the Jana2006 program [1], which was used to solve regular, modulated, and magnetic structures. The most important changes include a major improvement in the graphical interface, which allows the user full control of the individual steps of the solution and specification of crystal structures. Current changes in the structure can be monitored either in the mode of displaying the crystal structure, or by comparison of the measured and calculated profile from the powder data.

Since the formation of modulated and magnetic phases is very often associated with phase transitions, the procedure for detecting the coexistence of more independently diffracting domains has been significantly improved in the new version. In some cases, during the test of the space and superspace group, we receive incorrect information about the symmetry of the crystal, but also about its actual translational symmetry [2]. Therefore, the procedure was supplemented by an analysis of possible domain overlap.

Another significant improvement of the program is the ability to perform a series of structure refinements the system of data measured under different conditions (temperature, pressure, time). After solving and specifying the initial structure, automatic refinement takes place on all blocks of measured data. The procedure is supplemented by a graphical display of changes in advanced parameters.

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**P4** 

## CRYSTAL AND MAGNETIC STRUCTURES IN THE Nd<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub> (0.1 x 0.9) SOLID SOLUTIONS

# H. Nakatsugawa<sup>1</sup>, Y. Kamatani<sup>1</sup>, C. H. Hervoches<sup>2</sup>

<sup>1</sup>Yokohama National University, Japan <sup>2</sup>Nuclear Physics Institute, Rež, Czech Republic

Rare-earth orthoferrites  $RFeO_3$  (R = La, Nd, Dy,...) are of particular interest due to their potential multiferroicity, magnetoelectric effects, and other functional properties.

In this study, the Nd<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub> series (0.1 x 0.9) have been prepared. Magnetization measurements from 5K to 700K show weak antiferromagnetic behaviour and paramagnetism following the typical Curie-Weiss law above 600K.

To clarify the correlation between the crystal structure and magnetic structure of  $Nd_{1-x}Sr_xFeO_3$  (0.1 x 0.9), powder neutron diffraction (PND) data of the  $Nd_{1-x}Sr_xFeO_3$  (0.1 x 0.9) samples were collected at 15 K, 298 K, and 500 K with the medium resolution neutron powder diffractometer (MEREDIT), part of the CANAM infrastructure, at the Nuclear Physics Institute, Czech Republic. All Rietveld refinements were carried out using the GSAS-II suite of programs [1].

It is confirmed that the FeO<sub>6</sub> octahedron distortion is relaxed as *x* increases and approaches the crystal structure of the pseudo-cubic. Fig 1 shows the evolution of Fe-O-Fe angles with *x* in Nd<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub> (0.1 x 0.9).



Figure 1. Evolution of Fe-O-Fe angles vs x.

At room temperature, the materials present antiferromagnetic order, with magnetic moment of Fe decreasing from ~ 3.2  $\mu$ B for x = 0.1 to ~1.0  $\mu$ B for x = 0.6 and magnetic spins oriented in the *a*- or *c*-axis (BNS Magnetic Space Group: P21'/m', Pn'ma', or Pnma).

#### Krystalografická společnost



Figure 2. Magnetic structure of  $Nd_{0.9}Sr_{0.1}FeO_3$  (x = 0.1) at room temperature and 15K.

At 15 K, in the range x = 0.1 - 0.4, the magnetic spins order in the *b*-axis direction (BNS Magnetic Space Group: P21'/m' or Pn'ma'); A more complex magnetic structure is observed for x 0.5.

The magnetic structures for  $Nd_{0.9}Sr_{0.1}FeO_3$  at RT and 10K are shown in fig 2. Crystal and magnetic structures were drawn using VESTA [2].

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P5

## CRYSTAL STRUCTURE STUDY OF XENON COMPOUNDS USING 3D ELECTRON DIFFRACTION

public.

## Kshitij Gurung

Institute of Physics, Czech Academy of Sciences, Prague

The low stability of the xenon compounds in the atmosphere and under the electron beam makes it quite a challenge for their crystal-structure studies using electron diffraction. At the same time, some of these compounds are difficult to crystallize in large crystals, and electron diffraction is the only way to elucidate their structure. Recent progress in 3D electron diffraction (3D ED) makes it a promising technique for studying the crystal structures of these largely unexplored compounds. To verify the feasibility of the application of 3D ED to these compounds, we investigated XeF<sub>2</sub> and [XeF][TaF<sub>6</sub>]. Sample loading was achieved by the use of a glovebox and a homemade construct that utilized liquid nitrogen, preventing the exposure of the sample to moisture. Energy-dispersive X-ray spectroscopy (EDS) confirmed the presence of xenon and fluorine in the loaded sample. The electron diffraction on XeF<sub>2</sub> confirmed the presence of this phase. However, the crystal quality was not sufficient to obtain a full single crystal 3D ED data set. However, the compound turned out to be sufficiently stable under the electron beam to potentially permit a 3D ED data collection. These results, albeit preliminary, demonstrate that it is possible to investigate nanocrystalline xenon-containing compounds as well as other air-sensitive and reactive materials by 3D ED.

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## **P6**

# X-RAY DIFFRACTION AND NEUTRON DIFFRACTION OF THE SKIN BARRIER MODEL

# P. Pullmannová<sup>1</sup>, N. Kučerka<sup>2,3</sup>, R. Georgii<sup>4</sup>, B. Demé<sup>5</sup>, J. Maixner<sup>6</sup>, B. Čuříková-Kindlová<sup>6</sup>, K. Dvořáková<sup>6</sup>, V. Ondrejčeková<sup>1</sup>, J. Zbytovská<sup>1,6</sup>, K. Vávrová<sup>1</sup>

<sup>1</sup>Skin Barrier Research Group, Charles University, Faculty of Pharmacy, Hradec Králové, Czechia <sup>2</sup>Faculty of Pharmacy, Comenius University, Bratislava, Slovakia

<sup>3</sup>Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia

<sup>4</sup>Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Garching, Germany

<sup>5</sup>Institut Laue-Langevin - 71 avenue des Martyrs, CS 20156, 38042 Grenoble Cedex 9 – France

<sup>6</sup>University of Chemistry and Technology Prague, Faculty of Chemical Technology, Prague, Czechia

pullmanp@faf.cuni.cz

The physical barrier of the skin is located in its outermost layer – the stratum corneum (SC). SC consists of cornified cells embedded in the highly organized extracellular lipid matrix containing mainly ceramides (Cer), free fatty acids (FFA), and cholesterol (Chol). The skin lipids behaviour is studied in models of various complexity. We have studied the simple model based on Cer with C24 acyl chain (type NS or NH), FFA (C16 – C24 chains), and Chol at the equimolar ratio and a complex model prepared from isolated and purified human skin lipids (but still missing cornified cells). The models were prepared in the form of thin layers applied onto supporting wafers. They were annealed at the temperature above the melting point at low or high humidity. The regular structure was evaluated by the following methods:

- 1. X-ray diffraction measured with an X'pert PRO powder diffractometer with the Bragg-Brentano geometry (PANalytical B.V., Netherlands)
- 2. Neutron diffraction using a cold-neutron three-axis spectrometer MIRA located at the neutron source in Heinz Maier-Leibnitz Zentrum (Garching, Germany) (a simple model)
- 3. Neutron diffraction using a D16 small-q diffractometer (Institut Laue-Langevin, Grenoble, France) (the human skin lipids)

The simple model based on Cer C24/FFA/Chol showed immense structural variability dependent on the annealing conditions. Bragg peaks at small angles provided a repeat distance (d) of 5.3 nm (Fig. 1A a), which is known from the literature [1], but also the repeat distances of 10.6 nm (Fig.1A b), 15.9 nm (Fig.1A c), and 21.2 nm (Fig. 1A d) were found [2]. All the peaks belong to the one-dimensional lamellar structures with an orthorhombic lipid chain sublattice (peaks at wide angles). The separated Chol (\*) was also found. The repeat distance of 10.6 nm is double the theoretical maximal length of a two-chain Cer molecule in the splayed-chain conformation. The composition of the simple model with d = 10.6 nm was adjusted for the neutron diffraction experiment at different contrast conditions  $(D_2O/H_2O \text{ ratio})$ . The relative neutron scattering length density (z) was calculated according to the equation (1):

$$\rho(z) = \sum_{h=1}^{h \max} F_h \cos\left(\frac{2\pi hz}{d}\right) \tag{1}$$

 $F_h$  is the scattering form factor for the order h and z is the distance from the lamellar centre. The phase angles for a centrosymmetric structure attain the values of +1 or -1. We calculated 57 (z) profiles at 100% D<sub>2</sub>O based on different combinations of the phase angles in two subsequent steps. The most plausible  $\rho$  (z) profiles (Fig. 1B) were selected to be consistent with the molecular composition of the sample and to provide feasible water distribution profile. The plausible r(z) profiles rely on a splayed-chain conformation of Cer [3] leading to the asymmetric distribution of hydrocarbon chains in leaflets. The isolated human skin lipids formed a lamellar phase with a longer d of 13.4 nm due to the presence of ultra-long skin Cer. This long periodicity phase (LPP) [1] has a feature common with the structure with d = 10.6 nm – low intensity of the 1<sup>st</sup> order peak. The human skin lipids were measured by neutron diffraction at different contrast conditions (D<sub>2</sub>O/H<sub>2</sub>O ratio). The (z) profile of LPP based on one combination of the phase angles for  $6 F_h$  is shown in Fig. 1C. We suppose that the molecular arrangement of the LPP is also based on the splayed-chain conformation of Cer. The (z) profiles of LPP need to be corroborated with electron density profiles and other experiment to verify the plausibility of our model.

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**Figure 1.** X-ray diffraction patterns of the simple models based on the Cer NS24/FFA/Chol mixture prepared at various annealing conditions. Asterisks indicate the peaks of separated crystalline Chol. Full grid lines predict the peaks at d = 5.3 nm, dashed grid lines predict the odd orders of peaks at d = 10.6 nm. The peaks of the orthorhombic chain sublattice are apparent in the wide-angle region (panel A). Neutron diffraction patterns and (z) profiles of the simple model based on the Cer NH24/Cer NS24/FFA/Chol (panel B) and human skin lipids (panel C).