ESRF	**Experiment title:** Investigation of the local structure of metastable multinary tungsten phosphates ($M_yP_xW_{1-x-y}O_{2.5+\delta}$ with average structures related to WO_3	**Experiment number**: CH-5162
Beamline: ID 22	**Date of experiment**: from: 04/12/17 to: 04/12/17	**Date of report**: 23/02/18
Shifts: 1	**Local contact(s)**: Catherine Dejoie	*Received at ESRF:*

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Report:

1. Introduction

A new approach to the synthesis of metastable multinary tungsten phosphates $(M_yW_{1-x-y}P_x)O_{2.5+\delta}$ leads for various compositions to the formation of phases with average structures that can be related to tetragonal [1] or cubic [2] WO_3. Although formation of such tungsten phosphates with rather small amounts of P_2O_5 by thermal decomposition of $H_3PW_{12}O_{40} \cdot 29H_2O$ [3,4,5] or $[Al(H_2O)_6]PW_{12}O_{40} \cdot 4H_2O$ [6] is known for more than three decades, no structural or crystal chemical interpretation or even an explanation for the incorporation of phosphorus into a WO_3-type lattice has been provided in literature, so far. The aim of our synchroton experiment was to provide information on the local structure of these WO_3-related phosphates by analysis of pair distribution functions. These experimental data should allow for a more comprehensive structure modelling.

2. Experimental

Four tungsten phosphates $(W_{1-x}P_x)O_{3-x/2}$ with different tungsten-phosphorus ratio (x = 0.125, 0.15, 0.2, 0.25) and four compositions with either additional silver or vanadium $\{(Ag_{0.1}W_{0.6}P_{0.3})O_{2.6}$, $(V_{0.05}W_{0.5}P_{0.45}O)_{2.5+\delta}$, $(V_{0.167}W_{0.5}P_{0.333})O_{2.5+\delta}$, $(V_{0.167}W_{0.333}P_{0.5})O_{2.5+\delta}\}$ had been prepared by *solution combustion synthesis* [7] followed by stepwise calcination up to 600 °C. Data collection has been performed on beamline ID 22 with an incident beam energy of 69.42 keV, close to the absorption edge of tungsten (69.525 keV). For each sample 300 XRPD pattern were rapidly collected (~7 sec./image) on a 2D-IP-Detector and averaged to achieve better statistics. The PDF curves were computed with the computer program *pdfgetx3* [8].

3. Results

Since the XRPD pattern show neither a superstructure nor a different pattern than the one of WO_3, the model must not allow for a long-range periodicity concerning the phosphorus incorporation. The tungsten phosphates $(W_{1-x}P_x)O_{3-x/2}$ show similar PDF curves with only small differences and no clear tendency concerning the tungsten-phosphorus-ratio (Figure 1). Small-Box simulations for the short-range structure (r < ~7 Å) of $(W_{0.75}P_{0.25})O_{2.875}$ with the program *PDFgui* [9] based on a biphasic model of γ-WO_3 (Z = 8) and $W_8P_4O_{32}$ (Z=1) (ratio 1:1) do account for most of the features in the observed PDF curve, but are still insufficient to resemble it perfectly (Figure 2). Especially the medium-range order of the structure-model, which is primarily dominated by the tungsten-tungsten-distances, fits only roughly the experimental PDF curve.

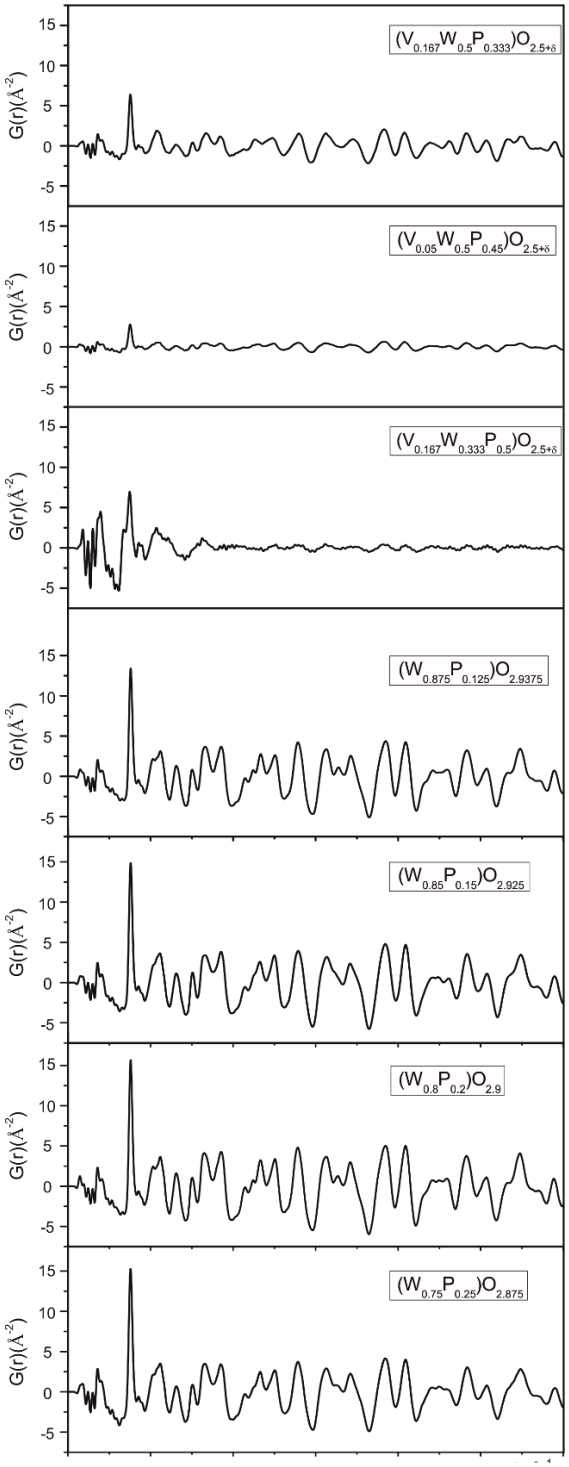

Figure 1 Experimental functions $G(r)$ of $(W_{1-x}P_x)O_{3-x/2}$ (x = 0.25, 0.2, 0.15, 0.125), $(V_{0.167}W_{0.5}P_{0.333})O_{2.5+\delta}$ $(V_{0.167}W_{0.333}P_{0.5})O_{2.5+\delta}$ and $(V_{0.05}W_{0.5}P_{0.45}O)_{2.5+\delta}$.

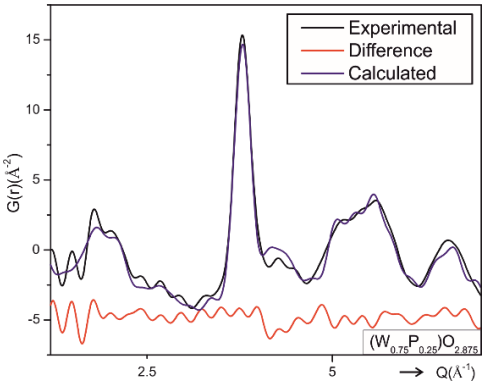

Figure 2 Experimental function $G(r)$ of $(W_{0.75}P_{0.25})O_{2.875}$ and calculated $G(r)$ for a biphasic-model of γ-WO_3 $(Z = 8)$ and $W_8P_4O_{32}$ $(Z=1)$ (ratio 1:1).

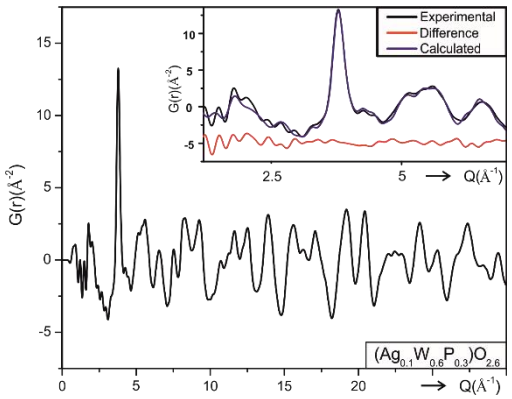

Figure 3 Experimental function $G(r)$ of $(Ag_{0.1}W_{0.6}P_{0.3})O_{2.6}$ and calculated $G(r)$ for a triphasic-model of "$AgWO_3$" (Z = 8), of γ-WO_3 (Z = 8) and $W_8P_4O_{32}$ (Z = 1) (ratio 1:12:12).

The experimental PDF curve of $(Ag_{0.1}W_{0.6}P_{0.3})O_{2.6}$ differs slightly from those of the tungsten phosphates $(W_{1-x}P_x)O_{3-x/2}$ and shows a peak at 3.3 Å with slightly higher intensity. This distance matches the distance between silver and tungsten expected for a perovskite like structure (ABO_3), with silver occupying the central A position (Figure 3). The small-box simulation based on a triphasic-model with "$AgWO_3$" (Z = 8), γ-WO_3 (Z = 8) and $W_8P_4O_{32}$ (Z = 1) (ratio 1:12:12) confirms this assumption.

The vanadium containing compounds $(V_{0.167}W_{0.333}P_{0.5})O_{2.5+\delta}$, $(V_{0.05}W_{0.5}P_{0.45}O)_{2.5+\delta}$, $(V_{0.167}W_{0.5}P_{0.333})O_{2.5+\delta}$ show significantly lower intensity for the peak at ~ 3.79 Å which originates from the tungsten-tungsten distance (respectively vanadium-tungsten/ vanadium distance). This is in good agreement with the assumption of vanadium substituting tungsten (Figure 1).

All PDF curves show distances, that can be correlated to the incorporation of phosphorus. The synchrotron experiment shows that despite the similar XRPD's the local environment differs for slightly different compositions. The development of a monophasic model and big-box-simulations are part of ongoing efforts.

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